

Exploring the effect of nitrogen incorporation in modulating the catalytic properties of chitosan derived carbon supported metal catalysts for electrochemical HER, OER, ORR and biomass hydrogenation

by
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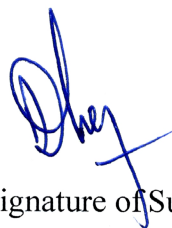
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Synopsis of the thesis

 Synopsis of the thesis to be submitted to the Academy of Scientific and Innovative Research for award of the degree of Doctor of Philosophy in Science	
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Introduction

Carbon materials have emerged as versatile materials in catalysis, widely used as catalysts and catalyst supports due to their unique and tunable properties.¹ Among the different types of carbon materials, graphite, activated carbon, carbon nanotubes (CNTs), and graphene stand out for their applications in catalysis. However, among them, activated carbon stands out as the preferred support material because of its high surface area, porosity, bulk availability, and low cost. These materials are typically synthesized by the high temperature carbonization of coal, organic precursors, or polymers. However, these sources are non-renewable in nature. Biomass is a renewable, sustainable, and cheap resource that can be used for the synthesis of value-added chemicals and carbon materials. Since biomass can be obtained from various sources, carbon materials with varying structures, morphologies, and other properties can be synthesized.² Biomass-derived carbon materials are used in various catalytic, separation, filtration, and electrochemical applications.³ However, in order to improve the properties of carbon materials, hetero-atom doping, and the introduction of surface functionalities are employed. Nitrogen (N)

doping is a common method of heteroatom doping, and it can introduce various N-functionalities in the carbon matrix.⁴ The incorporation of various nitrogen functionalities and associated structural changes enhances the electronic properties of the material, electron-donation ability, and helps in tuning the surface polarity. Typically, N-doping is done either by treating the pre-synthesized carbon material with N-containing precursors or by carbonizing the N-containing precursors alone or along with the carbon precursors.⁵ But these methods use non-renewable, expensive, and toxic N-containing chemicals such as pyrrole, aniline, melamine, dicyandiamide, pyridine, ammonia, urea, acetonitrile, N-containing ionic liquids, N-containing polymers, MOFs, etc. In many cases, to tune the pore size of the material, external templates are used. Hence, the synthesis of N-containing carbon materials is tedious, which makes them very expensive. In this regard, using a sustainable and cheap alternative to conventional N-containing precursors will be promising.

Chitin is the second most abundant natural biopolymer on earth after cellulose, and it is widely found in crustacean shells (crab, shrimp, lobster, and prawn), the exoskeletons of insects, fungi, and plankton. Chitosan can be made from chitin by deacetylation using a base. Both chitin and chitosan contain ~7% biologically fixed nitrogen in their structures, and they represent a cheap and potentially sustainable resource for the synthesis of nitrogen-containing carbon materials.⁶ In most catalytic reactions, metals play a crucial role in the activation of reactants. The amino groups together with the hydroxyl groups in chitosan are good ligands to coordinate with transition metal ions to form a chitosan-metal complex.⁷ In literature, carbon-supported single metal atom catalysts are prepared by the adsorption of metal complexes with N-donor ligands onto porous carbon support followed by a pyrolysis step, or the pyrolysis of metal coordination polymers or metal-organic frameworks rich in nitrogen and carbon, such as zeolitic imidazolate frameworks.⁸ In this context, pyrolysis of metal complexes prepared from chitosan will be a cheaper alternative, as well as reduce the multiple steps involved in the preparation of such catalysts. The aim of my PhD work is to synthesize supported metal catalysts on chitosan-derived nitrogen containing carbon and explore the effect of nitrogen doping on their catalytic applications in electrochemical hydrogen evolution reactions (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR) and thermo-catalytic Levulinic acid (LA) hydrogenation to Gamma valerolactone (GVL).

Statement of the problem

N-containing carbon materials are typically synthesized using non-renewable and expensive molecular nitrogen precursors using tedious synthetic procedures. The current research aims to

use marine biomass derived chitosan as the nitrogen and carbon source for the synthesis of N-containing carbon materials. The objectives of the thesis are briefed below,

- Exploitation of the coordinating properties of amino and hydroxyl groups of chitosan to synthesize metal chitosan complexes and its direct pyrolysis to obtain supported metal catalysts in a single step.
- Understand the role of nitrogen in the modulation of electronic structure of supported metal catalysts synthesized from chitosan and its consequences in electrochemical HER, OER, ORR and thermo catalytic hydrogenation of Levulinic acid.

Methodology

- Synthesis of ruthenium-chitosan complex and its pyrolysis to obtain ruthenium-chitosan complex pyrolyzed (Ru-CCP) materials at different pyrolysis temperatures.
- Studying the electrochemical HER performance of the Ru-CCP materials in alkaline medium.
- Elucidate the role of nitrogen in modulating the electronic properties of Ru-CCP materials by using analytical and spectroscopic characterization techniques.
- Synthesis of bimetallic FeNi-CCP catalysts at different pyrolysis temperatures.
- Studying the electrochemical OER and ORR performance of the FeNi-CCP materials in an alkaline medium.
- Comparison of activity with non-nitrogen-containing (from cellulose and activated carbon) catalysts to understand the role of nitrogen in controlling the reaction outcomes.
- Exploring the effect of nitrogen in tuning the electronic properties of FeNi-CCP materials by using analytical and spectroscopic methods.
- Synthesis of supported ruthenium catalysts via wetness impregnation on activated carbon, nitrogen-containing carbon from chitosan, and Ru-CCP catalysts by Ru-chitosan complex pyrolysis.
- Perform the LA hydrogenation reaction using the synthesized catalysts in a high-pressure batch reactor.
- Study the effect of the synthesis method and nitrogen doping on modifying the catalytic properties.

Results and their interpretation

1. Tailoring ruthenium nanocatalyst via nitrogen doping for enhanced electrochemical HER in alkaline medium

The HER is crucial for electrochemical water splitting to produce clean and sustainable hydrogen energy. This process can occur at room temperature in both acidic and alkaline electrolytes, typically using platinum-based nanoparticles as the state-of-the-art catalyst.⁹ However, the high cost of proton exchange membranes and the slow electron-transfer kinetics of the oxygen evolution reaction (OER) in acidic media limit the use of acid electrolyzers. These challenges can be mitigated by using an alkaline medium, although the HER electron-transfer kinetics with platinum catalysts are significantly slower in alkaline conditions compared to acidic ones. Consequently, ongoing research aims to enhance the activity of platinum catalysts and develop cost-effective alternatives. Notably, ruthenium catalysts have shown HER activities in alkaline media comparable to platinum catalysts.¹⁰ In this work, the Ru-based catalyst was synthesized by Ru-chitosan metal complex pyrolysis at temperatures ranging from 500 to 700 °C, and their electrochemical HER performance was evaluated in alkaline medium by linear sweep voltammetry in a 3-electrode system against Hg/HgO reference electrode. The Ru-CCP catalyst synthesized at 500 °C exhibited outstanding performance compared to the commercial 20 wt% Pt/C catalyst with very low overpotential. This remarkable performance is attributed to the unique structural and electronic properties of Ru-CCP catalysts, characterized by the formation of ultrasmall ruthenium nanoparticles with significant Ru-N interaction, as revealed by HR-TEM, XPS, and XAS studies. Nitrogen doping stabilized the ruthenium nanoparticles, created active sites within the carbon framework, and thus enhanced the HER activity. The optimal synthesis temperature was identified as 500 °C, balancing graphitization, and nitrogen content to achieve the desired ratio of charged and reduced ruthenium species. This study highlights a sustainable approach for synthesizing Ru/N-cooped carbon catalysts, leveraging the strong metal-support interaction facilitated by nitrogen doping.¹¹

2. Nitrogen-containing carbon-supported Fe-Ni bimetallic catalyst for electrochemical OER and ORR

Electrochemical ORR and OER are essential in energy conversion technologies like fuel cells and metal-air batteries. ORR reduces oxygen to water or hydroxide ions, while OER oxidizes water to oxygen. Both reactions require efficient catalysts due to their slow kinetics. Platinum is commonly used for ORR, and iridium or ruthenium oxides for OER, but their high costs drive the search for alternatives. FeNi bimetallic catalysts have emerged as promising options,

offering enhanced activity and stability through synergistic effects.^{12,13} They improve electron transfer kinetics and corrosion resistance, making them cost-effective and sustainable for electrochemical applications. Pure multi-metallic compounds often suffer from strong agglomeration, limiting their catalytic efficiency. Coupling metal alloys with a conductive carbon support, particularly heteroatom-doped carbon, can enhance electron/mass transfer, disperse metallic species, and improve chemical stability.¹⁴ The doped heteroatoms also boost catalytic activities by introducing active configurations. The FeNi catalysts supported on N-doped carbon materials use non-renewable and expensive N-precursors, and the synthetic procedures are often cumbersome. Here, the FeNi-CCP catalyst was synthesized by the pyrolysis of the FeNi-chitosan complex at a pyrolysis temperature of 800 °C. To understand the effect of N-doping, the catalysts were prepared from cellulose as well as activated carbon and pyrolyzed at the same temperature. The FeNi-CCP catalyst showed a remarkable lower overpotential compared to the control samples as well as commercial RuO₂ toward OER in alkaline medium. However, the catalyst did not show comparable performance to that of Pt/C in ORR. The characterization of the catalyst showed the formation of a Fe-Ni alloy along with smaller particles compared to the control samples. The XPS analysis revealed that in the absence of N-doping, the surface of the alloy species shows more oxidized species of Fe, and in the presence of N and Ni, the Fe become electronically rich and aid in the formation of stable surface alloy species, which cause the enhanced OER activity of the catalyst.

3. The effect of nitrogen doping in ruthenium-supported carbon catalyst and its activity towards Levulinic acid hydrogenation

Levulinic acid is a platform chemical derived from cellulosic biomass. The hydrogenation of LA to GVL is highly valued because GVL is a renewable, stable product that is used as a solvent, fuel additive, and intermediate for fine chemicals.¹⁵ Ruthenium based catalysts are reported to be very selective and efficient for the hydrogenation of carbonyl group in LA. Among them, Ru supported carbon catalyst (Ru(5)/C) is widely used for this transformation. However, commercial Ru/C catalysts suffer from leaching of the metal and sintering at elevated temperatures, causing the deactivation of the catalysts and poor reusability.¹⁶ In the literature, the use of N-doped carbon supports has been found to be efficient in improving the metal-support interaction of the catalyst, which in turn increases the stability and activity of the catalyst.^{16–18} In this work, three different carbon-supported Ru catalysts were synthesized with a metal loading of 1 wt%. The catalysts Ru/C and Ru/NC were synthesized by the wetness impregnation method on commercial activated carbon and N-containing carbon synthesized by

pyrolysis of chitosan, respectively. The Ru-CCP catalyst was synthesized by the pyrolysis of the Ru-chitosan complex. All the catalysts were reduced under hydrogen at 400 °C before using in the reaction. Initially, LA hydrogenation was conducted in a batch reactor using hydrogen in water with Ru/C catalyst to optimize the reaction conditions. At 100°C and 10 bar H₂ pressure, 97.6% of LA was converted to 89% GVL in 3 hours. At the optimized conditions, the LA hydrogenation activity of the Ru/NC and Ru-CCP catalysts was studied. The results showed comparable performance of both Ru/C and Ru/NC catalysts, and the Ru-CCP catalyst showed poor performance. When the activity of the Ru/C and Ru/NC catalysts was compared based on the surface area normalized TOF (turn over frequency), the Ru/NC catalyst showed a 1.4-time higher value, suggesting improved kinetics of hydrogenation of LA using the Ru/NC catalyst. Also, the TOF of the Ru/NC catalyst was higher compared to the Ru catalyst on N-doped carbon reported in the literature. Hence, the Ru/NC catalyst proved to be superior in terms synthetic viability and performance. Based on the observation from the XPS, the presence of oxidized ruthenium could be because of the presence of N, and which can enhance the carbonyl group activation and dehydration step to form GVL and improve the performance of the overall reaction.

Conclusions

In this work chitosan was effectively utilized to synthesize nitrogen-containing carbon support as well as supported metal catalyst in a single step pyrolysis method. In the first work the Ru-CCP catalyst synthesized showed efficient stable performance towards electrochemical HER, where the N-doping influence the formation of small and stable ruthenium particles as well as control the ratio of oxidized to metallic ruthenium to vary the activity significantly. In the second working chapter N-incorporation aids the formation of electronically rich Fe species and causes the formation of small FeNi alloy nano particles in FeNi-CCP catalyst. The catalyst outperformed the RuO₂ and control samples for electrochemical OER. Ru/NC catalyst synthesized via wetness impregnation using the N-containing carbon support derived from chitosan showed higher activity in terms of TOF and offered a viable and cheap synthesis procedure than the similar reported catalysts. In all three works the chitosan-based carbon offers a viable and sustainable way of synthesizing the catalysts. The role of nitrogen doping was understood by the analysis of catalysts via various characterization methods. The electronic structure modulation of the Ru catalysts was found to be caused by the Ru to N electron transfer, meanwhile, in the FeNi catalysts, the N to metal electron transfer was seen. Also, the presence

of nitrogen in the catalyst aids in the formation of small and stable metal particles and causes the overall enhancement of the catalytic performance.

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List of abbreviations

AC:	Activated carbon
CNTs:	Carbon nanotubes
CNFs:	carbon nanofibers
LIBs:	Lithium-ion batteries
NDC:	Nitrogen doped carbon
HER:	Hydrogen evolution reaction
OER:	Oxygen evolution reaction
ORR:	Oxygen reduction reaction
PDC:	Phosphorous doped carbon
CVD:	Chemical vapor deposition
g-C ₃ N ₄ :	graphitic carbon nitride
M-CCP:	Metal chitosan complex pyrolyzed material
LA:	Levulinic acid
GVL:	Gamma valerolactone
XRD:	X-ray diffraction
XPS:	X-ray photoelectron spectroscopy
XAS:	X-ray absorption spectroscopy
XANES:	X-ray absorption near edge spectra
EXAFS:	Extended X-ray absorption fine structure
LSV:	Linear sweep voltammetry
RDE:	Rotating disk electrode
ECSA:	Electrochemically active surface area
TGA:	Thermal gravimetric analysis
CV:	Cyclic voltammetry
ICP-OES:	Inductively couple plasma-Optical emission spectroscopy

HR-TEM: High-resolution transmission electron microscopy

HAADF-STEM: High-angle annular dark-field scanning transmission electron microscopy

CNC: Chitin derived nitrogen containing carbon

Py-N: pyridinic nitrogen

Pr-N: Pyrrolic nitrogen

G-N: Graphitic nitrogen

O-N: Oxidized nitrogen

MP-AES: Microwave plasma -Atomic emission Spectroscopy

NC: Nitrogen containing carbon

ADT: Accelerated durability test

TOF: Turn over frequency

TPD: Temperature programmed desorption

RID: Refractive index detector

MB: Mass balance

BE: Binding energy

SNTOF: Surface area normalized turn over frequency

HPA: 4-hydroxypentanoic acid

1. General Introduction and Literature Survey

1.1. Carbon materials in catalysis and energy related research

Carbon materials have emerged as versatile and highly efficient catalysts or catalyst supports in a broad range of thermo and electrocatalytic reactions due to their unique physical and chemical properties like large specific surface area, high porosity, relative chemical inertness, hydrothermal stability, high electrical conductivity etc. The diversity of carbon materials, which includes graphite, graphene, activated carbon (AC), carbon nanotubes (CNTs), fullerenes, and activated carbons, allows for a wide array of applications in catalysis. The structure of different types of carbon is shown in Figure 1.1. Graphite has layers of hexagonally arranged carbon atoms that stack over each other with Van der Waals forces, whereas graphene consists of a single layer of carbon atoms arranged in a honeycomb lattice. Carbon nanotubes are cylindrical structures made from rolled graphene sheets, and fullerenes are spherical or tubular molecules of carbon atoms. Activated carbon is highly porous, and amorphous carbon has a disordered structure, all contributing to diverse applications across industries.

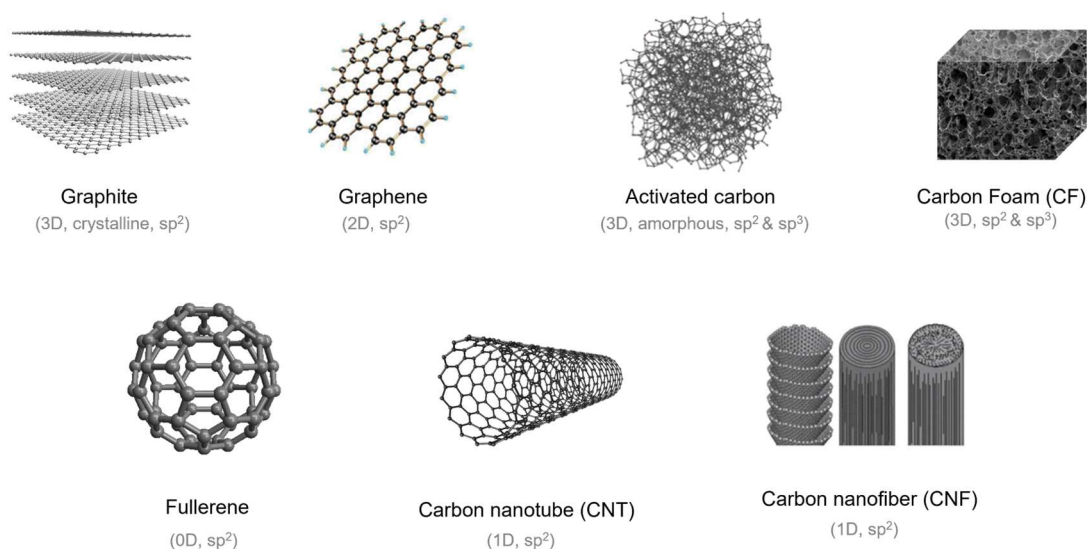


Figure 1.1. Structure and nature of different kind of carbon materials in catalysis.

Excellent hydrothermal stability in hot pressurized water makes carbon materials a suitable support in biomass conversion reactions in comparison to other common supports like oxides, mesoporous silica materials, zeolites, layered double hydroxides.^{1,2} Activated carbon itself without any modification have been reported to catalyze certain reactions.^{3–7} Recently, air oxidized carbon materials have been reported to mechanochemically break cellulose to smaller oligosaccharides.^{8–10}

Carbon materials play a crucial role in electrocatalytic reactions due to large surface area and high electrical conductivity, particularly the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).¹¹ Carbon itself is inert toward most of the electrochemical reactions. It is used as support for Pt based catalysts for HER reaction. As platinum-based catalysts are expensive, alternative catalysts must be sought after for large scale commercial application. In this regard, doping of heteroatoms such as nitrogen, sulphur, phosphorus, boron or transition metals to the carbon have been tried to improve HER activity of carbon itself, albeit of less success.^{12–16} Owing to similar valence band structure transition metal carbides, nitrides, phosphides etc. have shown good activity in HER reaction, however they possess limited stability in solution phase. Encapsulation of these materials in carbon is used as one of successful strategies to counter this problem.^{17–21} Similar heteroatom doping strategies to use carbon materials as metal free electrocatalyst for OER reaction is relatively more successful compared to HER reaction.^{22–27} Among these catalysts a metal free mesoporous nitrogen doped carbon and carbon nanotube hybrid have shown even better activity compared to IrO₂.²⁶

Carbon materials are viewed as highly promising candidates in the energy storage due to their affordability, excellent physicochemical stability, superior electrolyte infiltration capabilities and higher surface area.^{28–31} Currently, lithium-ion batteries (LIBs) and supercapacitors are the two primary types of complementary electrochemical energy storage systems dominating the market, particularly in applications like electric vehicles and portable electronic devices.^{32,33} Carbon materials such as graphite, hard carbon, carbon nanotubes etc. are used as anode materials for LIBs due to their high abundance, non-toxicity, stability and durability.^{34–36} Carbon is also used as conductive coating on cathodes with poor conductivity.³⁷ Li-ion capacitors (LICs), which combines the merits of high energy density of the batteries and high power density of the capacitors,^{38–40} works with battery type anodes (ion intercalation/deintercalation) and capacitor type cathode (adsorption desorption).^{41,42} Carbon materials such as graphene can serve both as anode as cathode materials when utilized in LICs.^{43,44}

The above discussions establish that carbon materials are indispensable in catalysis and energy related materials. Activated carbon, graphene or advanced carbon materials like CNTs, CNFs, carbon foams etc. have often shown remarkable performances in catalysis and energy related applications due to their unique structures. However, they are conventionally prepared from petroleum or coal derived feedstocks, often in energy intensive synthetic procedures like arc discharge,⁴⁵ laser ablation,⁴⁶ chemical vapor deposition,⁴⁷ which is concerning in sustainability

and environmental regards. Therefore, synthesis of carbon materials from renewable resources is of utmost importance.

1.2. Biomass derived carbon as catalysts and catalyst supports

Biomass is animal or plant residue, which can be a sustainable alternative as a feedstock for preparation of carbon materials. The lower cost, renewable nature of the biomass along with its carbon neutrality has spurred scientific interest in the past few decades. In addition, biomass has a wide range of feedstock to start with for the preparation of carbon containing materials. Table 1.1 lists some of the carbon catalysts and catalyst supports derived from biomass, which showcases the multitude of types of biomasses sources that are used. For example, lignocellulosic biomass like rice husk,⁴⁸ monkey pod plant,⁴⁹ absorbent cotton,⁵⁰ pine needle⁵¹ etc. has been used to produce carbon materials. These carbon materials are usually prepared via a one-step pyrolysis method and prepared catalysts often showed advantages over the carbon materials prepared from non-renewable sources. For example, the Pd/Graphitic mesoporous carbon prepared from rice husk showed remarkable activity and stability on C-C bond forming reactions under ligand free conditions compared to other Pd/Carbon catalysts.⁴⁸ Ni/Carbon prepared from absorbent cotton catalyzed nitro compounds hydrogenation reaction at room temperature and showed a remarkable functional group tolerance.⁵⁰

Table 1.1. Biomass derived carbon materials and their application.

Materials	Biomass source ^a	Application	Reference
Pd/Graphitic mesoporous carbon	Rice husk	Exceptional catalyst stability in C-C coupling reactions	48
MnO ₂ /Poros carbon nanosphere	Monkey pod plant	Electrocatalytic oxidation reaction	49
Ni/Carbon	Absorbent cotton	Nitro compounds hydrogenation	50
Pd/Carbon	Pine needle	High catalyst stability in Sonogashira coupling	51
N-doped carbon	Silk cocoon	CO ₂ electroreduction	52
N-doped porous carbon	Plum blossom (Melamine)	Good stability in ORR reaction	53
N-doped porous carbon	Radish (Urea)	Styrene oxidation, nitrophenol reduction	54
N-doped mesoporous carbon	Chitosan (1,10-phenantroline)	ORR reaction	55
N-doped carbon	Bio oil (Urea)	Nitrobenzene reduction	56
Porous N-nitrogen doped porous carbon	Onion peel	Reductive cleavage of azo bonds	57

Materials	Biomass source ^a	Application	Reference
Co/N-doped carbon	Chitosan	Hydrogenation of terminal olefins at incredibly mild conditions	58
Co@N-doped carbon nanotubes	Chitosan (Urea)	ORR reaction	59
N-doped carbon nanotubes	Chicken feather	HER reaction4-nitrophenol reduction	60
β -Mo ₂ C/Mo ₂ N	Soybean	Comparable Overpotential to noble metals in HER reaction	61
P-doped carbon	Starch (Phosphoric acid)	Selective aerobic oxidation of alcohols	62
P-doped carbon	Corn stover (Phosphorus acid)	Cellulose pyrolysis to phenol	63
Multielement doped carbon	Spinach (melamine as co-source)	ORR reaction	64
N, P, S doped carbon	Fish waste	Pt free counter electrode in dye sensitized solar cells	65
N,P-doped carbon	Peanut shells (Phosphoric acid)	Oxidation of benzyl alcohol to benzaldehyde	66

^aThe text in the bracket is an external hetero atom source.

Heteroatom doped carbon materials have been prepared from biomass sources owing to the natural presence of heteroatoms like nitrogen, phosphorus, sulfur etc. in some of the biomass materials. Biomass sources like silk cocoon, plum blossom, radish, chitosan, bio-oil, onion peel etc. have been used for the synthesis of N-doped carbon materials in various forms. Silk cocoon consists of 75-83 % of fibroin protein and 17-25 % of sericin protein.⁶⁷ Hence, nitrogen rich silk cocoon was pyrolyzed to create N-doped carbon, which was then activated using ZnCl₂ treatment to create pentagon defects to host CO₂ molecules, which showed excellent CO₂ electroreduction activity.⁵² N-doped porous carbon prepared from plum blossom in two steps where the plum blossom was pre-carbonized with KOH and then mixed with melamine and carbonized again.⁵³ These N-doped porous carbon materials showed a unique honeycomb like structure and a high surface area of 2118.9 m²g⁻¹. The authors suggested the porous structure of the thus prepared catalyst was a key factor in excellent ORR activity and methanol resistance in alkaline media. N-doped porous carbon prepared from radish with melamine as nitrogen source and KOH for activation showed good activity in styrene oxidation reaction and 4-nitrophenol reduction reaction.⁵⁴ Although, the surface area of the catalysts reached up to 3062 m²g⁻¹, there was no positive effect of surface area in the reactions. The reaction results were rather correlated with graphitic nitrogen percentage of the materials. Chitosan hydrogel formation in presence of 1,10- phenanthroline, by dissolution in acetic acid solution followed

by precipitation with base, followed by multistep pyrolysis led to formation of highly active catalyst for ORR reaction.⁵⁵ In this study, 1,10-phenantroline served as both nitrogen source and pore forming agent. Nitrogen doped carbon was also successfully synthesized from bio-oil polymerization with HNO_3 . The HNO_3 treatment created huge amounts of defects (characterized by Raman spectroscopy) to catalyze nitrobenzene reduction reaction.⁵⁶ Nitrogen doped carbon prepared from direct pyrolysis of onion peel, without any external nitrogen source showed good activity in breaking azo bonds under microwave conditions, although the percentage of nitrogen in the catalysts was $< 0.1\%$.⁵⁷ Co containing N-doped carbons have been reported either from chitosan alone⁵⁸ or with urea as external nitrogen source.⁵⁹ These catalyst are active for ORR reaction and selective reduction of terminal alkene groups in presence of other functional groups, which is an important reaction in pharmaceuticals.

Apart from the thermo and electrocatalysis, biomass derived nitrogen doped carbon had been used as a visible light photocatalysts for a variety of oxidation reactions.⁶⁸ This is possible because nitrogen doping can introduce band gap in graphene structure to absorb visible light, which otherwise have a zero bandgap.

Co containing carbon nanotubes could be prepared by simple mixing of Co(II)acetate, chitosan and urea followed by pyrolysis.⁵⁹ The authors reported Co(II)acetate had catalytic effect in formation of the nanotube structure. Chicken feather due to its protein rich structure consists of 65 % carbon, 10 % nitrogen, 22 % oxygen and 3 % sulphur.⁶⁹ Nitrogen doped carbon nanotubes were reported by pyrolysis of chicken feather in presence of Ni(II)acetate.⁶⁰ The catalyst was active for nitro group reduction to amino group. The authors reported that carbonization of only chicken feathers produced defective amorphous carbon, which suggested that Ni(II)acetate had structure directing effect in producing nitrogen doped carbon nanotubes. XRD and FESEM images of these samples showed formation of Ni_3S_2 nanorods with N-doped carbon wrapped around them. Removal of the Ni_3S_2 formed N-doped carbon nanotubes. N-doped carbon nanotubes synthesis in this method is not only an alternative to conventional carbon nanotube materials, but also a lower energy consuming process like arc discharge, laser ablation and chemical vapor deposition methods.

Like nitrogen doped carbon materials phosphorus doped carbon materials are also interesting in catalysis. Biomass derived phosphorous doped carbons (PDC) are prepared using starch⁶² or cellulose containing corn stover⁶³ as carbon source and phosphoric acid as phosphorus source. Phosphorus doped catalysts thus prepared contain a higher degree of defect sites compared to only carbon prepared from starch or cellulose along with -O-P, O=P, and -O-P-O- functional

groups. PDC has shown remarkable selectivity ($> 99\%$) towards phenol from catalytic pyrolysis of cellulose.⁶³ PDC catalyst also showed a higher turnover frequency in alcohol oxidation reactions compared to any other reported heteroatom doped carbon materials.

Multielement doped carbon materials are very exciting materials not only in catalysis, but also in energy storage devices like batteries and capacitors. Several types of biomass sources consist of proteins and enzymes which contain elements like nitrogen, phosphorus and sulfur in the molecular structure along with minerals. This provides an opportunity to prepare multielement doped carbon materials from biomass. For example, spinach have been reported to serve as source of carbon, nitrogen and iron for preparation of Fe-N_x moieties on carbon which showed better ORR activity compared to commercial Pt/C.⁶⁴ Carbonization of fish waste have reported to produce nitrogen, phosphorus and sulfur doped carbon without use of any external source, which showed better activity in triiodide reduction compared to Pt catalyst.⁶⁵ The catalyst possessed surface area as high as 2933 m²g⁻¹ with a porous structure. Carbonization of peanut shells along with phosphoric acid produced phosphorus and nitrogen doped carbon, which showed excellent activity (100 conversion, 99.7 % selectivity at just 90 °C and 1 bar O₂ pressure) in aerobic oxidation of benzyl alcohol.⁶⁶

In summary, synthesis of carbon compounds from biomass sources is an effective and sustainable way to create innovative materials for energy storage and catalysis. Important heteroatoms including nitrogen, phosphorus, and sulfur are found naturally in biomass sources like silk cocoon, plum blossom, radish, chitosan, bio-oil, onion peel, and more. These components play a crucial role in improving the efficiency of carbon-based materials in a variety of catalytic processes.

1.3. A closer look at nitrogen doped carbon materials from biomass

The discussion in the previous section makes it evident that doping nitrogen onto carbon is one of the most studied among heteroatoms. In fact, interest in nitrogen doped carbon materials was triggered as early as 1964 by Jasinski's finding of metal phthalocyanines as ORR catalysts.⁷⁰ Numerous factors can be used to explain the fundamental cause of the popularity of nitrogen-doped carbon materials. In order to explore them one by one first it is important to understand the nature of nitrogen in NDC materials. There are four common types of nitrogen in NDC materials, which are pyridinic (Py-N), pyrrolic (Pr-N), quaternary graphitic (G-N) and pyridinic N-oxide (O-N) as shown in Figure 1.2. Apart from G-N all other nitrogen species makes three bonds with carbon, hence their presence creates defects in carbon structure. These defective sites are proposed to serve as active sites for nucleation and growth of metal nanoparticles

during the synthesis supported metal catalysts on NDC.⁷¹ It is proposed that π orbitals of nitrogen can hybridize with d orbitals of transition metals to provide stronger metal support interactions, thus inducing strong binding of metals to support, which leads to higher catalyst stability.^{72–74} NDC materials can stabilize extremely small metal clusters and single atoms.^{75,76} Metal single atoms on nitrogen doped carbon is proposed to mimic organometallic catalysts or even enzymes, where NDC materials can be considered as ligands.⁷⁷ Interfacial charge transfer between NDC and metal nanoparticles can lead to favourable metal electronic states for catalysis.⁷⁸

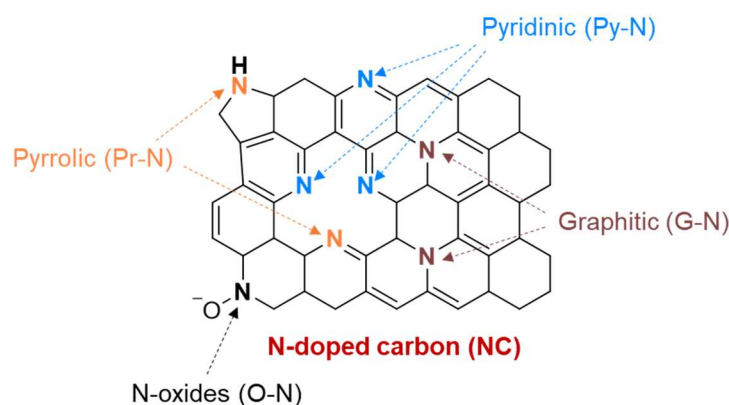


Figure 1.2. Structure of nitrogen doped carbon showing the presence of four different type of nitrogen species.

In summary, nitrogen-doped carbon (NDC) materials are highly valued in catalysis due to their unique nitrogen types, which create structural defects that enhance catalytic activity. These defects support the growth of stable metal nanoparticles and single atoms, mimicking organometallic catalysts and enzymes. Strong metal-support interactions and favorable electronic states further boost their effectiveness, explaining the sustained interest and research in NDC materials.

1.4. Chitin and chitosan as a sustainable resource for nitrogen containing carbon

From the discussion in section 1.2. it is clear that among the multitude of biomass resources used for synthesis of NDC chitin or its deacetylated product chitosan is used the most. The underlying reason being its abundance in nature⁷⁹ and chitin is the second most abundant biopolymer in the world after cellulose. Chitin constitutes 14-50 % of exoskeletons of crustaceans like crab, shrimp, lobster etc. and shells of mollusks, fish scales, squid pen exoskeleton of certain arthropods.⁸⁰ A statistics by FAO shows annual production of capture fisheries and aquaculture reached 179 million tons in 2020 and have seen a rapid growth in last

decade.⁸⁰ Additionally, fungi like mushrooms, and cell walls of microalgae also contains chitin.^{81,82} Hence, chitin is cheaply available for utilization to produce valuable nitrogen containing chemicals, materials or NDCs.

Chitin is obtained majorly by the fractionation of crustacean shell waste. Since the shell waste contains minerals like CaCO_3 and proteins as major components along with chitin, In the industrial method of fractionation, the cleaned and dried shell waste is demineralized using acids and deproteinized using bases. The final step involves a decolouration procedure to obtain chitin. There are several other methods such as biological methods and solvent extraction methods for the isolation of chitin.⁸³

Structurally, chitin is a linear homopolymer of *N*-acetyl-D-glucosamine (NAG) linked via β -(1 $\rightarrow$ 4) glycosidic bonds to form chitin chains as shown in Figure 1.3a. The chitin chains are then stacked in different orientations to give rise to three different polymorphs of chitin. In α -chitin, alternative chains are stacked in opposite directions, whereas in β -chitin all the chains are stacked in the same direction. On the other hand, γ -chitin two parallel chains are stacked over one chain in opposite direction. Interchain hydrogen bonding holds the chitin chains together. Thermodynamically, α -chitin is the most stable configuration of chitin. The crystallinity of α -chitin is due to the presence of intra-chain (C3'-OH to O5, C6'-OH to acetamido carbonyl O7 and C6-OH to O6') and interchain (between NH and the acetamido carbonyl O7' and C6'-OH to O6) hydrogen bonding between the polymeric chains of the chitin as shown in Figure 1.3b.

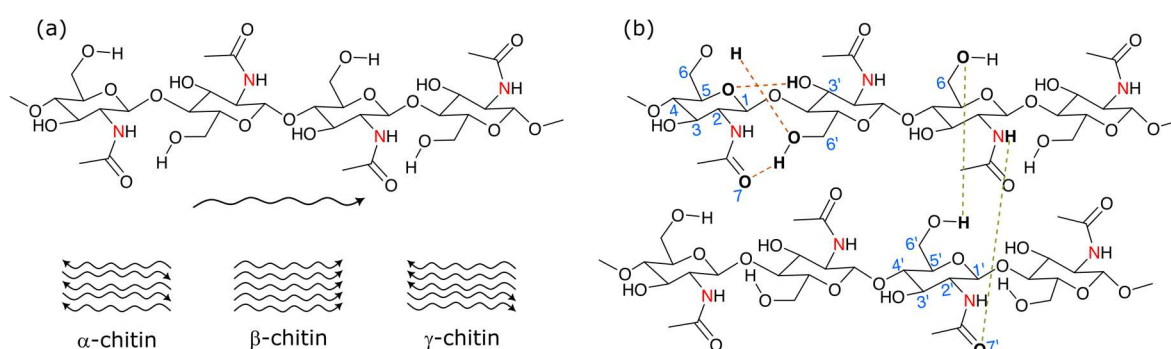


Figure 1.3. (a) Stacking of chains in different polymorphs in chitin, (b) Intra and interchain hydrogen bonding in chitin. (Reproduced and adapted from Ref. 84)

Chitin contains an acetamido group at the C-2 position of its monomer structure. Deacetylating this group with a base form an amino group, resulting in chitosan. The extent of deacetylation determines the ratio of D-glucosamine and *N*-acetyl-D-glucosamine units in chitosan, making it a heteropolymer. Typically, chitosan possesses a degree of deacetylation $> 50\%$. Chitin and chitosan have about 7% biologically fixed nitrogen due to the acetamido and amino groups,

making them valuable nitrogen sources. The transformation of shell waste derived chitin to chitosan is represented in Figure 1.4. Moreover, chitin is a non-edible biomass possessing no conflict with food, which makes it an ideal resource for preparation of NDCs. Chitin is highly crystalline and inert in nature due to the inter and intramolecular hydrogen bonding network. However, chitosan is relatively less crystalline depending on the degree of deacetylation, making it a more suitable alternative for the preparation of NDCs because of its enhanced solubility and presence of chelating efficient amino groups.

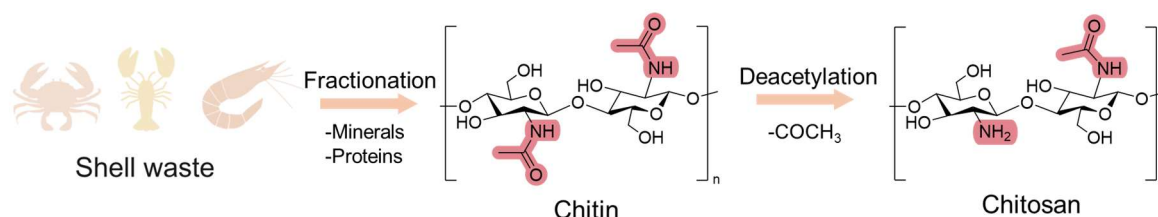


Figure 1.4. Schematic representation of shell waste fractionation to form chitin, followed by deacetylation to obtain chitosan.

1.5. Methods of preparation of nitrogen doped carbon from chitin biomass

NDC formation from chitin is a complex process involving elementary reactions like hydrolysis, dehydration, aromatization, condensation etc. to lower the oxygen content. Generally, NDCs are prepared from chitosan in three different ways, namely, chemical vapor deposition method, hydrothermal or solvothermal method, and pyrolysis under inert atmosphere.

1.5.1. Chemical vapor deposition method

The chemical vapor deposition (CVD) method involves deposition of vapors of precursor materials on a substrate at elevated temperatures. Kumar et al. reported nitrogen can be doped to graphene substrate at 300 °C via decomposition of chitosan.⁸⁴ The synthesis process was carried out at 300 °C in a tubular furnace with a flow of Ar. The resulting material contained 4.5 % nitrogen. They further reported the synthesis of nitrogen containing graphene quantum dots, using chitosan as only source.⁸⁵ The resulting material is 2.5 nm thick and contains 4.2 % nitrogen via a low temperature atmospheric pressure CVD process on a copper foil as substrate. The synthesis was proposed to proceed via three steps, namely, 1. Decomposition of chitosan into nitrogen containing chemicals, 2. Adsorption of the reactive species on to copper surface, 3. Nucleation to form N-doped graphene quantum dots. The volatile chemicals formed from decomposition of chitin involved nitrogen containing heterocyclic compounds like pyrazines, pyridines, pyrroles.⁸⁶ The use of only chitosan, low temperature, and atmospheric pressure

render this approach appealing for the large-scale manufacturing of N-containing graphene quantum dots.

1.5.2. Hydrothermal or solvothermal treatment

This method generally involves solvothermal treatment under autogenous pressure sometimes in combination with high temperature pyrolysis under inert atmospheres. The solvothermal treatment is generally carried out at temperatures between 100 to 350 °C. Generally, the carbonization temperature has a profound effect on the final structure and properties of the carbon. For example, hydrothermally treated chitosan at 180 °C produces NDC with good chemical stability and porosity, however increasing the carbonization temperature leads to decrease in oxygen and nitrogen content of the NDC.⁸⁷ Albeit of the low temperature conditions, the NDC produced by this technique still possesses a greater surface oxygen content, necessitating further pyrolysis in most cases.

1.5.3. Pyrolysis

In contrast to solvothermal methods, pyrolysis methods operate at high temperatures ranging from 500 °C to 1000 °C under an inert atmosphere of Ar or N₂. At lower temperatures, amorphous porous NDCs are formed, while at higher temperatures more graphitic NDCs are formed at the expense of pores and sometimes nitrogen content. However, from the catalysis point of view often a balance between both phenomena is required. Post synthetic or in-situ chemical activation with additives like KOH, NaOH, ZnCl₂, K₂CO₃, K₂FeO₄ is often used for this. In case of post synthetic activation of carbon materials, at first NDCs are formed by pyrolysis, the resulting materials are mixed with activating agents, which is then followed by a high temperature treatment at 700- 900 °C. In case of in-situ activation, the chitosan is first mixed with an activating agent followed by pyrolysis.⁸⁸⁻⁹⁰ During the activation process, chemical reaction between the activator and relatively amorphous region of the carbon framework forms soluble salts, which can be washed out to generate porous structure. The activating agents are removed from the material by washing them with inorganic acids. Use of an optimized amount of activator is key as higher amounts leads to collapse of adjacent micropores and sometimes pore clogging by formation of insoluble metallic species on the carbon matrix. Use of KOH, NaOH etc. for chemical activation of NDCs is hazardous and produces a huge amount of soluble waste. Hence, activators like ZnCl₂, K₂CO₃ etc. are explored as alternatives, where the biproducts are volatile and do not generate huge amount of waste. Singh et al showed that use of an optimum amount of ZnCl₂ as activator could lead to formation of NDC containing meso and micropores with a surface area of 1863 m²g⁻¹.⁹¹ The authors

proposed ZnCl_2 penetrates deep into the biomass structure during carbonization, which then forms volatile species possibly ZnCO_3 at higher temperature and their escape leads to formation of micro/meso pores. Similarly, use of K_2CO_3 as activating agent leads to formation of microporous nitrogen doped carbon nanospheres with surface area of $2569 \text{ m}^2\text{g}^{-1}$.⁹²

Another common strategy to synthesize NDCs is to use additives like urea,⁹³ melamine,⁹⁴ hexaketocyclohexane,⁹⁵ acetic acid,⁹⁶ polyethylene glycol⁹⁷ and ionic liquids.^{98,99} Most often these additives function as templates to regulate pore structure. One of the advantages of using these additives is avoidance of inorganic activators and increased nitrogen content in case of urea and nitrogen containing ionic liquids. Liu et al. reported synthesis of N containing carbon nanosheets from the pyrolysis of urea and chitosan.¹⁰⁰ Urea is proposed to form graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) at lower temperature which then acts as additional source of nitrogen and structure directing agent during the formation of carbon, resulting in higher surface area of $1510 \text{ m}^2\text{g}^{-1}$. Melamine, another nitrogen source, which have a monolithic structure comparable to that of $\text{g-C}_3\text{N}_4$ is also used in preparation of nitrogen containing carbon from chitosan.⁹⁴ Controlled freeze drying of mixture of acetic acid solubilized chitosan and melamine followed by a two-step pyrolysis and KOH activation led to crystallized graphitic nitrogen containing carbon materials, which showed excellent activity in alkaline ORR reactions as metal free catalysts. However, use of these organic additives for the formation of porous carbon does not strictly adhere to the sustainability goal of using chitosan as the source of carbon and nitrogen. The synthesis of NDC from chitosan via different synthesis methods are summarized in Table 1.2.

Table 1.2 Summary of synthesis of NDC from chitosan

Synthesis method	Conditions	Product	Remarks	Ref.
CVD	300 °C in tubular furnace with Ar/H ₂ gas flow on Cu	Nitrogen doped graphene	Mild conditions, Single step	84,85
Hydrothermal method	180 °C under autogenous pressure	N containing amorphous carbon	Higher oxygen content in the resulting material	87
Pyrolysis	Chitosan and activator (KOH, NaOH etc.) mixture heated at 500 – 1000 °C under inert gas (N ₂ , Ar, He) flow	N-containing porous carbon	Higher surface area Generation of huge amount of waste	88–90

Synthesis method	Conditions	Product	Remarks	Ref.
Pyrolysis	Chitosan ZnCl ₂ (or K ₂ CO ₃) mixture heated at 600-700 °C under inert atmosphere.	N-Containing porous carbon	High surface area Greener compared to KOH, NaOH activation	91, 92
Pyrolysis	Mixture of chitosan and organic additives heated at 600-900 °C under inert atmosphere	N-containing porous carbon	High surface area and porosity, Use of organic additives not sustainable	94-100

1.6. Synthesis of supported metal catalysts from chitin

Metal containing catalysts from chitin can be synthesized by two methods, a. introduction of metal to pre-formed NDCs, b. In-situ formation of metal phase from metal-chitin composite materials. The details of each of the methods are described below.

1.6.1. Introduction of metal on pre-synthesized NDCs

In this method, NDC is synthesized first in one of the methods described above. The metal precursor is deposited by conventional wetness impregnation method or incipient wetness impregnation method followed by a thermal or chemical reduction treatment. Zhao et al. prepared Pt/NDC via polyol reduction of H₂PtCl₆ in NDC containing solution.¹⁰¹ Pt dispersion was uniform in the resulting catalyst, which showed better performance in electrochemical methanol reduction reaction compared to that of commercial Pt/Carbon catalyst. Lee et al. used a chitosan derived hierarchically porous NDC as support for a Pd containing catalyst for formic acid dehydrogenation reaction.¹⁰² They observed the porous structure and nature of nitrogen species in the support was crucial factor in determining the catalytic activity. Xin Xiao et al. prepared a Ru/NDC by wetness impregnation of ruthenium on chitosan derived NDC followed by thermal reduction with molecular H₂.¹⁰³ The resulting catalyst showed promising activity in hydrogenation of cellobiose to hexitols as result of higher dispersion of ruthenium nanoparticles. Although, this method is quite straightforward and can lead to highly dispersed metal nanoparticles due to metal nitrogen interactions, it still uses the NDC synthesis with external additives or activators. Hence alternative methods should be looked at.

1.6.2. In-situ formation of metal phase form metal-chitosan composite

In-situ formation of metal nanoparticles from composite of metal precursors and chitosan can solve these problems as metal precursor itself can act as structure directing agent or activating agent many times. Reduction of metal precursors to metal nanoparticles in most cases does not

need the use of external H_2 source as under pyrolysis conditions chitosan degradation itself produces hydrogen. This method involves formation of a composite material of metal precursor with either only chitosan or sometimes with an additional nitrogen containing chemical.

1.6.2.1. Metal@NDC from chitosan with external additives

Fe, Ni precursor, NaCl and chitosan was ground together for a homogeneous mixing, which was then added to aqueous acetic acid solution for complexation followed by high temperature treatment under NH_3 atmosphere to produce FeNi/NDC material.¹⁰⁴ Addition of external NH_3 increased pyridinic nitrogen content of the final material. Mesoporous SBA-15 was added to $RuCl_2$ solution to which a glucosamine hydrochloride solution in H_2SO_4 was added, after drying and pyrolyzing the mixture and etching with HF porous Ru/NDC was formed.¹⁰⁵ Many reports in the literature utilize glucosamine as a precursor for synthesizing NDC material, often with external additives like urea and melamine. However, from an energy efficiency perspective, the use of such external additives or chitosan monomers is undesirable. Therefore, synthesis methods that avoid external additives and use biopolymer chitosan directly are more extensively studied.

1.6.2.2. Metal@NDC from chitosan without external additives

Chitosan is long known for its metal sorption properties in solutions, because of the presence of the amine group in the glucosamine unit.¹⁰⁶ The metal sorption in chitosan is either due to chelation of metal cations to amine groups or due to electrostatic attraction of anionic metal complexes to protonated form of the amine group. Which interaction takes part is dictated by the nature of the metal precursor and pH of the solution. Generally, at pH above 4 the amine groups remain as amine groups, while at pH below 4, they are protonated. Hence, at pH below 4 and with a metal precursor that can form anionic species electrostatic attraction is the preferred mode of interaction, whereas at pH above 4 and with a metal precursor which contains cationic form of metal precursor would result in chelation of metal cations.

1.6.2.2.1. Synthesis of metal containing catalysts with electrostatic interactions

Molybdate species showed electrostatic interactions with protonated amine groups of chitosan in acetic acid solution, which was then freeze dried and pyrolyzed under Ar atmosphere at 750 °C to form $MoC_2@NDC$ materials (Figure 1.5).¹⁰⁷ In a similar manner, using $[PW_{12}O_{40}]^{3-}$ as metal precursor WC/NDC has been synthesized.¹⁰⁸ Pd@NDC was prepared from chitosan solution in aqueous HCl containing Na_2PdCl_4 (Pd^{2+}).¹⁰⁹ Chitosan thin films, prepared by spin coating of chitosan in aqueous acetic acid solution on to quartz plates, were immersed onto

AuCl₄ solutions, which was then dried and pyrolyzed at 900 °C to produce (111) oriented Au nanoparticles, which is interesting given the applications of oriented metal nanoparticles.¹¹⁰ This procedure has been exploited for the synthesis of Pt nanoparticles with orientation in particular crystallographic direction.⁹³



Figure 1.5. Molybdate-chitosan interaction as a representative example of exploitation of the interaction between anionic metal complex and protonated amine group in chitosan for the synthesis of metal containing NDCs. Reproduced from Ref. ¹⁰⁷ under the terms of the Creative Commons CC BY license.

Despite the promising prospects of this method, the synthesis methods are often complicated. Most importantly, this method is only limited to use of anionic metal precursors. However, most of the easily available metal are metal chlorides, nitrates or acetates. Hence, exploring methods which use chelation interactions with metal cation and chitosan amino group would bring versatility to the use of chitosan in synthesis of supported metal catalysts.

1.6.2.2.2. Synthesis of metal containing NDCs with chelation interactions

Freeze drying of aqueous solution of CuCl₂ and chitosan followed by thermal reduction at 500 °C with 5 % H₂ in Ar lead to formation of Cu@NDC.¹¹² The uniform dispersion of the Cu was suggested to stem from the Cu²⁺ → NH₃ chelation. Pd@NDC was obtained by chelation interaction via pyrolysis of a blend of chitosan and PdCl₂.¹¹³ A Co-Co₃O₄@NDC was prepared by complexing Co(OAc)₂ with chitosan dispersed in ethanol, followed by pyrolysis of the resulting complex.^{114,115} This also used the concept of chelation of Co²⁺ with NH₃ and OH groups in chitosan (Figure 1.6). Despite the potential, this method is only applied to a few systems and intricate details about supported metals thus prepared are not fully explored. A summary of synthesis of Metal@NDC from chitosan given in Table 1.3.

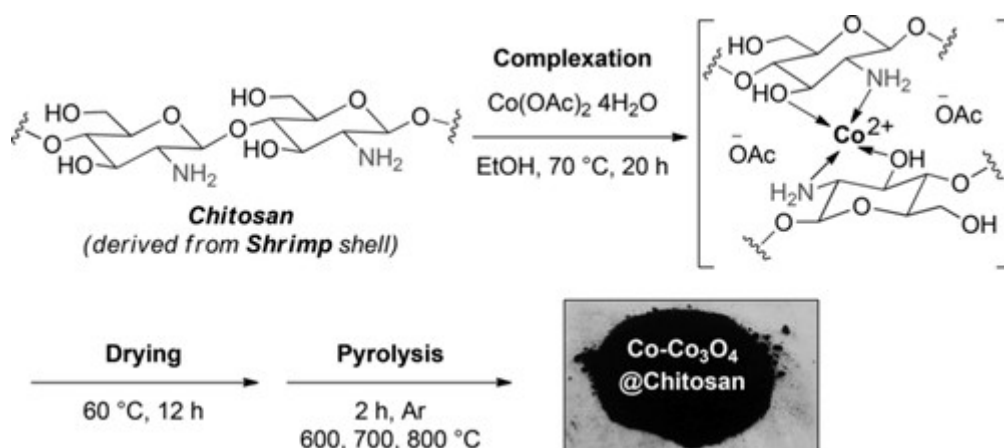


Figure 1.6. Co²⁺-chitosan interaction as a representative example of metal cation chelation with chitosan amino groups. Reproduced with permission from Ref. ¹¹⁴ Licence number: 5820660443804.

Table 1.3 Summary of synthesis of Metal@NDC from chitosan

Conditions	Remarks	Ref.
Polyol reduction of H ₂ PtCl ₆ in NDC containing solution or wetness impregnation of Ru or Pd precursor followed by thermal reduction	Uniform metal dispersion, NDC synthesis not sustainable	101 - 103
Pyrolysis of mixture of Fe, Ni precursor along with NaCl in an NH ₃ atmosphere	Use of NH ₃ as external nitrogen source is unsustainable	104
Metal chitosan composite formation by using electrostatic interaction of NH ₄ ⁺ groups of chitosan under acidic conditions and anionic metal precursors followed by pyrolysis	No use of external additives, Complicated procedure, Limited to only anionic metal precursors	107-110
Chitosan metal precursor chelation followed by pyrolysis	No use of external additives, Simple procedure, Only a few metal systems reported till date	112-115

1.7. Scope and objectives of this study

Although the synthesis of metal@NDC has gained attention recently, the potential of metal-chitosan interactions remains largely untapped. While some research has focused on electrostatic interactions between protonated chitosan and anionic metal complexes to produce faceted metal nanoparticles on NDC, the chelation ability of chitosan to produce metal@NDC has been explored in only a few studies. Given that commonly available metal precursors are typically in cationic form, investigating the preparation of metal@NDC through the chelation ability of chitosan and metal cations is of great significance. Additionally, there is a lack of

structure-activity relationship studies in catalysis using these materials and direct comparisons with conventional nitrogen-doped carbon. Moreover, the nature of active sites, as determined by advanced characterizations, remains unclear in the literature.

In this work, a synthesis method for preparing Metal@NDC by exploiting the chelation ability of chitosan with cationic metal precursors is studied. The procedure involves forming a complex of metal cations with chitosan in a 1% acetic acid solution, which is then precipitated with acetone to form a metal-chitosan complex gel network. This gel is subsequently pyrolyzed to produce the final material, termed M-CCP (metal chitosan complex pyrolyzed material). Advanced characterizations demonstrate that the catalysts formed via this method can stabilize small metal nanoparticles. The electronic properties of the metal can be adjusted by varying the nitrogen content, which is dependent on the pyrolysis temperature, thereby tuning the catalytic activities of the samples. Additionally, we studied metal impregnated on NDC (M/NDC) prepared via wetness impregnation, followed by the reduction of metal precursors supported on pre-synthesized NDC from chitosan. These materials are explored as electrocatalysts in HER, OER, ORR reactions and catalyst in biomass derived Levulinic acid hydrogenation reactions. The subsections below briefly describe chapter wise objectives of the thesis.

1.7.1. Tailoring ruthenium nanocatalyst via nitrogen doping for enhanced electrochemical HER in alkaline medium

The Hydrogen Evolution Reaction (HER) is an elementary reaction in electrochemical water splitting, producing clean hydrogen energy.^{116,117} This process occurs at the cathode, in both acidic and alkaline electrolytes at room temperature, typically using platinum-based nanoparticles as catalysts. However, the high cost of proton exchange membranes and slow electron-transfer kinetics of the Oxygen Evolution Reaction (OER) in acidic media limit the use of acid electrolyzers.¹¹⁸ These challenges can be mitigated in alkaline media, although HER kinetics with platinum are slower than in acidic conditions. Consequently, recent research focuses on enhancing platinum catalysts and developing cost-effective alternatives for platinum.^{119–121}

Recent studies on ruthenium catalysts have shown promising HER activities in alkaline medium, mainly Ru catalysts supported on carbon materials have been a choice of research.^{122,123} Nitrogen doped carbon materials (NDC) have been effective in enhancing the metal support interaction and thereby improving the catalyst performance.^{124–126} However, the conventional synthesis of the Ru/NDC uses molecular nitrogen precursors which are non-renewable and expensive.^{127–129} Also, controlling the particle size and the electronic environment of Ru is vital

in achieving improved catalytic performance. The detailed literature on this work is given chapter 2. Chitin or its derivatives has been identified as a promising N-containing source for NDC. There are couple of literature on HER which uses the chitin/chitin derivatives along with additional N-precursors and additives.

- The objective of this work is to synthesis a ruthenium supported NDC catalyst termed Ru-CCP, using Ruthenium-chitosan complex pyrolysis strategy without using additional N-dopants or additives
- Study the catalytic activity towards electrochemical HER and carry out catalyst synthesis at different pyrolysis to study the effect of N content and species of nitrogen involved in controlling the catalytic properties
- Study the electronic and structural properties of ruthenium catalyst influenced by the N-doping and derive the structure activity correlation using advanced characterization tools.

1.7.2. Nitrogen containing carbon-supported Fe-Ni bimetallic catalyst for electrochemical OER and ORR

The electrochemical OER and ORR are vital for energy conversion technologies such as fuel cells and metal-air batteries. ORR reduces oxygen to water or hydroxide ions, while OER oxidizes water to oxygen, both requiring efficient catalysts due to their slow kinetics. Platinum is commonly used for ORR, and iridium or ruthenium oxides for OER, but their high costs necessitate finding alternatives. FeNi bimetallic catalysts have emerged as promising options, offering enhanced activity and stability through synergistic effects.^{130–132} They improve electron transfer kinetics and corrosion resistance, making them cost-effective and sustainable for electrochemical applications. However, pure multi-metallic compounds often suffer from strong agglomeration, which limits their catalytic efficiency. Coupling metal alloys with conductive carbon support, particularly heteroatom-doped carbon, can enhance electron and mass transfer, disperse metallic species, and improve chemical stability.¹³³ The doped heteroatoms also boost catalytic activities by introducing active configurations. The extended literature on this work is presented in chapter 3. FeNi catalysts supported on N-doped carbon materials traditionally use non-renewable and expensive nitrogen precursors, and the synthesis procedures are often tedious.

- The objectives in this study were to use CCP process to synthesize a bimetallic combination of Fe and Ni catalyst, i.e., FeNi-CCP using only chitosan as the source of carbon and nitrogen.
- The catalysts prepared at different pyrolysis temperatures to study the effect of nitrogen content and nature of different nitrogen species in modulating the catalytic activity towards OER and ORR.
- Studying the material properties using various characterization techniques to understand the catalytic activity.

1.7.3. The effect of nitrogen doping in ruthenium supported carbon catalyst and its activity towards Levulinic acid hydrogenation

Levulinic acid (LA) is a key platform chemical derived from cellulosic biomass. The hydrogenation of LA to gamma-valerolactone (GVL) is highly valued because GVL is a renewable and stable product used as a solvent, fuel additive, and intermediate for fine chemicals.¹³⁴ Ruthenium-based catalysts are known for their selectivity and efficiency in hydrogenating the carbonyl group in LA. Among these, Ru supported on carbon is widely used for this transformation. However, commercial Ru/C catalysts often suffer from metal leaching and sintering at high temperatures, leading to deactivation and poor reusability. Studies have shown that using N-doped carbon supports can enhance metal-support interactions, thereby increasing the stability and activity of the catalyst.^{135–137} However, the literature on Ru/NDC catalysts used for Levulinic acid hydrogenation employs non-renewable and expensive N-dopants for the NDC synthesis, also most of them involve tedious and energy intensive synthesis.^{137–139} The detailed literature survey on the same is given in chapter 4.

- The objectives of this work were to synthesize ruthenium catalysts supported on nitrogen-containing carbon derived from chitosan using both the CCP method and the wet impregnation method with pre-synthesized N-doped carbon (NDC) from chitosan.
- Comparison of LA hydrogenation activity of Ru-CCP and Ru/NC catalysts with a non-nitrogen-containing Ru/C catalyst synthesized via wet impregnation.
- Additionally, this study aims to understand the role of nitrogen in tuning the catalytic properties of these materials and how different synthesis methods influence catalytic activity.

1.8. Reference

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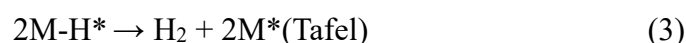
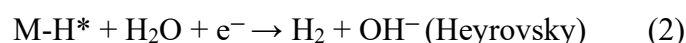
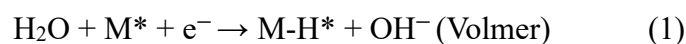
2. Tailoring ruthenium nanocatalyst via nitrogen doping for enhanced electrochemical HER in alkaline medium

2.1. Introduction

The rising energy demands, environmental pollution, and global warming caused by excess CO₂ emissions are major challenges that humankind faces in this era. The depletion of fossil fuels and their harmful environmental effects have created an urgent need for clean energy solutions. Renewable energy sources like solar and wind power can reduce reliance on fossil fuels, but their intermittent nature makes them unsuitable for consistent energy needs. One solution is to store this spasmodic energy during periods of excess in the form of chemical energy and reuse it when needed.^{1,2} Hydrogen stands out as a promising fuel alternative because of its carbon free emission, and it offers the highest energy density by weight among fuels.³ However, the lion share of the industrial hydrogen production involves the catalytic reforming of natural gas, where water and natural gas is converted into hydrogen and carbon dioxide.^{4,5} This process not only consumes fossil fuels and emits CO₂ but also produces hydrogen with low purity due to variable efficiency.⁵ A more sustainable method is to generate hydrogen through hydrogen evolution from water electrolysis, powered by electricity from renewable sources such as solar or wind energy.⁶

Water electrolysis involves two fundamental half reactions, Hydrogen evolution reaction (HER) occurring at the cathode and oxygen evolution reaction (OER) occurring at the anode of a water electrolyzer. However, water electrolysis is thermodynamically unfavorable, with a ΔG value of 237.2 kJ mol⁻¹ and a theoretical potential of 1.23 V.⁴ Hence in practice, it requires additional voltage to proceed, creating challenges for large-scale implementation of this promising technology. The use of appropriate and efficient catalysts can enhance the hydrogen production from water electrolysis by boosting the HER activity.^{7,8} Water electrolysis at room temperature can occur in both acidic and alkaline electrolytes, where platinum-based catalysts serve as the benchmark catalyst for HER.^{9,10} Even though numerous studies have focused on acid electrolyzers, the high cost of proton exchange membranes (PEM) and the slow kinetics of OER in acidic conditions limit their scalability. These challenges can be alleviated by using alkaline electrolyzers.¹¹⁻¹³ HER mechanism is typically discussed based on two key pathways (Volmer–Heyrovsky or Volmer–Tafel pathway) based on the three key steps involved (equation 1-3,

where M^* is the active site in the catalyst).⁸ The HER mechanism in alkaline medium involves a water dissociation step unlike in acid medium thus the energy barrier for water dissociation and the adsorption free energy of H in the catalyst surface plays a crucial role in deciding the activity.¹⁴



However, in alkaline conditions, platinum-based catalysts show significantly slower electron transfer kinetics for the HER, about two orders of magnitude lower than in acid electrolytes. Given this, along with the high cost and scarcity of platinum demands the research to find viable, cost effective and efficient electrocatalysts.^{15–18} Among the various electrocatalysts investigated Ru-based catalysts have gained attention recently because of their similar hydrogen bonding strength compared to Pt ($\sim 65 \text{ kcal mol}^{-1}$) and their efficient water dissociation ability in both alkaline and neutral electrolytes and they show comparable or better HER activity than Pt catalysts.^{18–20} Particularly, carbon-supported ruthenium catalysts have been opted due to their high electrical conductivity and large specific surface area, which facilitate electron transport.²¹ While using normal carbon as a support, it lacks the necessary functionality for a strong metal-support interaction. Consequently, metal particles aggregate, and cause a decline in the catalytic activity over time.²² Enhancing the metal-support interaction by engineering the carbon support for Ru-based catalysts can improve both their catalytic activity and stability in the HER.²³

Nitrogen doping is a prevalent technique for altering carbon supports.²⁴ Traditional methods for synthesizing N-doped carbon materials rely on non-renewable and costly nitrogen precursors, involving tedious synthesis procedures.^{24,25} Thus, achieving sustainable and cost-effective synthesis of N-doped carbon materials poses a challenge, necessitating the exploration of alternative solutions. The biopolymer chitosan can be used as a renewable N-precursor for the synthesis of N-containing carbon materials since it holds 7% nitrogen in its structure naturally.²⁶ The synthesis of ruthenium on nitrogen-doped carbon catalysts reported in literature required additional reagents, including nitrogen precursors and templates which are listed in Table 2.1.^{11,23,27–36} Even studies using chitin biomass used additional N-containing chemicals.^{37,38}

In this chapter, a straightforward synthetic procedure is described, involving the formation of a ruthenium–chitosan complex followed by a single-step pyrolysis process to synthesize Ru catalysts supported on N-containing carbon. Incorporating the metal before carbonization

ensures a more effective interaction between the metal and the amino and hydroxyl groups present in chitosan. This approach may also limit the growth of metal particles during pyrolysis. Unlike existing methods, this synthesis strategy does not require any additional nitrogen precursors or structure-directing templates. The electrochemical HER performance of the synthesized catalyst was evaluated in an alkaline medium, and the structure-activity correlation, along with the role of N-doping in enhancing catalytic activity, was studied.

Table 2.1. Literature reports on carbon supported Ru catalysts for electrochemical HER.

Catalyst	Precursor/Template	η_{10} (mV) ^a	Ref.
CNT/C/Ru	CNT ^b	38.3	27
Ru@GnP	Graphite + Dry ice ^c	22	28
Ru@C ₂ N	Hexaaminobenzene trihydrochloride + Hexaketocyclohexane	17	29
Ru/C ₃ N ₄ /C	Dicyandiamide	79 ^d	30
Ru/NC	Polyaniline	21	31
Ru-NC-T	Melamine formaldehyde + Te Nanowire template	12	11
RuNC	1,10-phenanthroline + SiO ₂ + Glucose	38	32
Ru _{1,n} -NC	Polypyrrole	14.8	33
Ru@NC/NG	Resorcinol + Formaldehyde + L-lysine	16	34
RuBCN	tris(2,20-bipyridine)Ru complex + closo-[B ₁₂ H ₁₂] ²⁻	20	23
Ru-NPs/OPC	ZIF-8 containing Ru(acac) ₃ + Polystyrene	22	35
Ru/BCN	Cucurbit [6]uril + closo-[B ₁₂ H ₁₂] ²⁻	33	36
Ru@CN	D-glucosamine hydrochloride + Melamine	32	37
Ru@NC	Chitin + Urea + NaOH	39	38

^aOverpotential at 10 mA cm⁻², ^bCarbon nanotubes synthesized by CVD method, ^cBall milled and reduced using NaBH₄, ^d0.1M KOH electrolyte.

2.2. Experimental section

2.2.1. Materials and Reagents

Low-molecular-weight chitosan (product code: 448869) was sourced from Sigma-Aldrich and microcrystalline cellulose was obtained from Maple India Bio Chem Lab. Ruthenium(III) nitrosyl nitrate solution (Ru(NO)(NO₃)₃, 1.5% w/v) was obtained from Alfa Aesar. Glacial acetic acid and 99% acetone were purchased from Loba Chemie. All solutions for this work were prepared with deionized water. All chemicals and reagents used were of analytical grade and were used without further purification.

2.2.2. Synthesis of Ruthenium-Chitosan complex pyrolyzed material (Ru-CCP)

For the synthesis of metal-chitosan complex a previously reported method was adopted with modifications.³⁹ Initially 1 g (6.2 mmol, based on monomer) chitosan was dissolved in 40 mL of acetic acid solution (1%, w/v) by stirring at room temperature for 12 hours. A transparent viscous solution of chitosan was obtained. To this solution, 5 mL (0.075 g of Ru, 0.74 mmol), 4.17 mL (0.063 g of Ru, 0.62 mmol), and 3.33 mL (0.05 g of Ru, 0.49 mmol) of 1.5 v/w % ruthenium(III) nitrosyl nitrate solution were added in order to achieve a final metal loading of 25% in all of the materials after the pyrolysis at 500, 600, and 700 °C, respectively. The required metal loading was calculated on the basis of the mass of carbon materials obtained from only chitosan during its pyrolysis at the mentioned temperatures. Acetic acid treated chitosan was stirred with the Ruthenium precursor solution for another 12 hours to form the Ruthenium–chitosan complex solution. This solution was then slowly poured into 150 mL of acetone to obtain the metal–chitosan complex hydrogel. This hydrogel was then filtered and washed three times with 10 mL of acetone. Subsequently, the filtered hydrogel was dried in a laboratory oven at 60 °C for 12 hours, followed by drying at 100 °C in a vacuum oven for 6 hours. The resulting dried hydrogels were referred to as the ruthenium–chitosan complex (Ru-CC). The Ru-CC was weighed and placed in a ceramic boat inside a quartz tube for pyrolysis in a tubular furnace. Pyrolysis was performed under a nitrogen atmosphere with a flow rate of 30 mLmin⁻¹ at 500, 600, and 700 °C for 2 hours, with a ramp rate of 10 °C min⁻¹ and the resulting material was named ruthenium–chitosan complex pyrolyzed material Ru-CCP-500, Ru-CCP-600, and Ru-CCP-700, respectively. The scheme for the synthesis of Ru-CCP materials is shown in Figure 2.1. The Ru-CCP catalysts were weighed, ground in a mortar and pestle, and used as such for experiments.

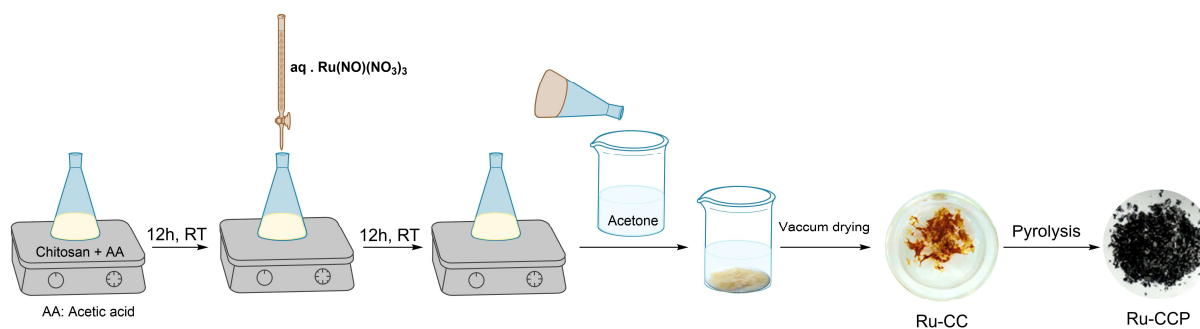


Figure 2.1. Scheme for the synthesis of Ru-CCP catalysts.

2.2.3. Synthesis of Ruthenium on cellulose derived carbon (Ru-CLC)

For the comparison of the effect of N-doping, a control sample was prepared based on cellulose derived carbon in a similar procedure as that of Ru-CCP catalyst. For the synthesis of Ru-CLC material, 1 g cellulose was treated with 1% (w/v) Acetic acid solution. To the obtained dispersion of cellulose 2.9 mL (0.043 g of Ru, 0.42 mmol) of ruthenium (III) nitrosyl nitrate solution (1.5 w/v %) was added to get a final metal loading of 25% and stirred for 12 h. The required metal loading is calculated based on the mass of carbon material obtained by the pyrolysis of cellulose at 500 °C. After removing the solvent using a rotary evaporator, the resulting solid was dried in a vacuum oven at 100 °C. The dried material was then pyrolyzed at 500 °C for 2 hours in a tubular furnace under a nitrogen atmosphere with a flow rate of 30 mLmin⁻¹ to obtain the Ru-CLC-500 material.

2.2.4. Characterization of catalysts

The bulk structure and phases purity of the catalysts were analyzed using X-ray diffraction (XRD) on a Desktop PXRD Miniflex 600 (Rigaku) diffractometer with Ni-filtered monochromatic Cu K α radiation of wavelength 1.5406 Å. The samples were scanned over a 2 θ range of 10 to 90° at a rate of 4°/min. Thermogravimetric analysis (TGA) was performed using an STD Q600 instrument at a heating rate of 10 °C/min under an oxygen atmosphere from 25 to 900 °C to determine metal loading on carbon. Elemental analysis for metals was conducted on a Spectro Arcos Germany FHS 12 instrument. Nitrogen adsorption isotherms and surface area measurements were carried out using a Quanta chrome BET surface area analyzer. Particle size, shape, lattice parameter analysis, elemental mapping, selected area diffraction (SAED), and high-resolution STEM images were obtained with a JEOL JEM-F200 (URP) transmission electron microscope operating at 200 kV. The electronic state of the elements in the catalyst were identified using XPS analysis on a Thermo K-alpha+ X-ray photoelectron spectrometer with an Al K α source. XPS data were processed with Casa XPS software, and binding energy corrections were made using the carbon 1s peak at 284.6 eV. Raman spectroscopy was performed to understand the bonding and crystallinity of the samples, using a Horiba LabRam HR800 spectrometer with a He–Ne laser (632.8 nm, 20 mW) in the range of 100 to 4000 cm⁻¹.

2.2.5. Experimental details for X-ray Absorption spectroscopy (XAS) studies

To determine chemical state and coordination environment of ruthenium in the catalysts, The Ru K-edge X-ray absorption spectra were recorded at the Scanning EXAFS Beamline (BL-09) of the INDUS-2 Synchrotron radiation source at the Raja Ramanna Centre for Advanced Technology (RRCAT) in Indore. The beamline was equipped with a Si (111) double crystal

monochromator for energy selection and meridional cylindrical mirror coated with Rh/Pt for collimation. Data were recorded when the synchrotron source's 2.5 GeV ring was operated at an injection current of 128 mA. XAS measurements were conducted at room temperature in transmission mode, with ion chambers filled with gases N₂, He, and Ar for the Ru foil and the samples. The X-ray absorption near edge spectra (XANES) and Extended X-ray absorption fine structure (EXAFS) measurements were done in the quick-XAS mode, allowing for continuous scanning over the energy or angle range instead of the conventional step-by-step scan. During data collection, the second crystal of the monochromator was 60% detuned to suppress higher harmonic components.⁴⁰ Energy calibration was performed using Ru metal foil at 22117 eV as a reference. Standard normalization and background subtraction procedures were executed using ATHENA software version 0.9.26 to obtain normalized XANES spectra.⁴¹ Fourier transforms (FT) of EXAFS oscillations were calculated to observe the $|\chi(R)|$ vs. R space spectra, with fitting performed using ARTEMIS software version 0.9.26, which employs FEFF6 and ATOMS⁴² programs to simulate theoretical scattering paths based on the crystallographic structure.

2.2.6. Electrochemical analysis

2.2.6.1. Evaluation of electrochemical HER activity

Electrochemical hydrogen evolution activity of the catalysts was monitored by BioLogic SP-300 potentiostat in 1 M KOH solution saturated with N₂ using a conventional three-electrode system with Hg/HgO as the reference electrode (RE) and graphite rod as the counter electrode (CE). The synthesized catalyst coated glassy carbon electrode was used as the working electrode (WE) with an active area of 0.196 cm². The three-electrode electrochemical system used is shown in Figure 2.2. The catalyst ink was prepared by ultrasonic assisted dispersion of 5 mg of the catalyst in 1 mL mixture of isopropyl alcohol (400 μ L), DI water (580 μ L), and Nafion (5 wt.%, 20 μ L). 10 μ L of catalyst ink was drop casted on the Rotating disk Electrode (RDE) and the electrode was dried at room temperature. 20wt% Pt/C ink was prepared in the same manner and was used as a standard sample to compare the HER activity. The data collection is carried out using EC Lab software. Cyclic voltammetry (CV) was conducted in a N₂-saturated 1 M KOH solution. 20 cycles of CV were carried out at 50 mV s⁻¹ at room temperature before performing linear sweep voltammetry (LSV) at a scan rate of 10 mVs⁻¹. The overpotential value was determined from the LSV plot, by applying iR correction value of 65%. 20 wt.% Pt/C commercial catalyst ink was coated on 0.196 cm² area with a loading of 0.01 mg and the LSV was measured under similar condition.

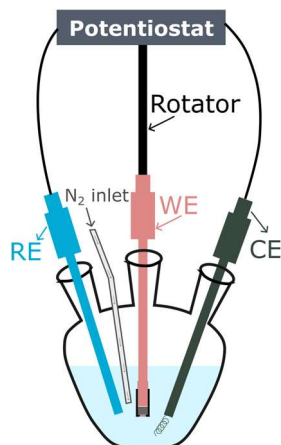


Figure 2.2. Illustration of three-electrode system used for electrochemical analysis.

2.2.6.2. Calibration of Hg/HgO electrode

The Hg/HgO electrode was calibrated using a three-electrode setup in a H₂-saturated 1 M KOH solution. A Platinum RDE served as the working electrode, Hg/HgO as the reference electrode, and a graphite rod as the counter electrode. The zero point on the Y-axis, where current flow was noted, was considered the thermodynamic potential for the hydrogen electrode reactions during LSV at a scan rate of 1.0 mV s⁻¹. The LSV calibration of the Hg/HgO reference electrode to the reversible hydrogen electrode (RHE) in 1 M KOH is shown in Figure 2.3, with the potential determined to be approximately 0.925 V. The potential was then referenced to RHE by adding 0.925 V as given in equation 4.

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.925 \text{ V} \quad (4)$$

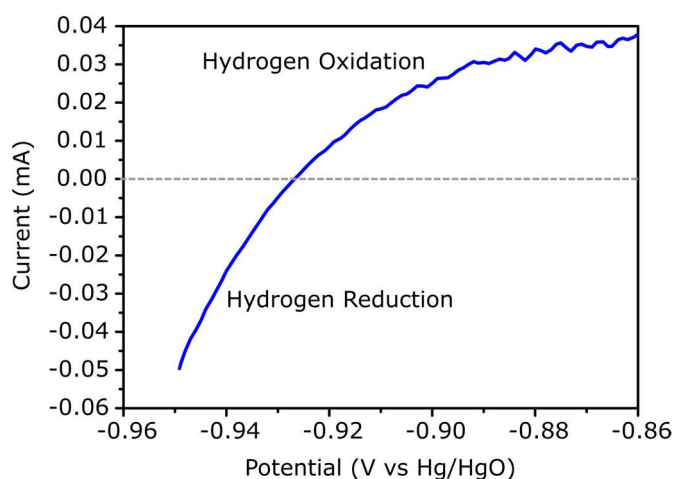


Figure 2.3. The LSV for Hg/HgO reference electrode calibration to RHE in 1 M KOH.

2.2.6.3. Determination of electrochemical active surface area (ECSA)

From the non-faradic region (0.065 V to 0.115 V vs. RHE) of CV performed at different scan rates, the peak current obtained at 0.09 V was plotted against the corresponding value of scan rate. The slope of the straight line obtained corresponds to the C_{dl} value. The ECSA can be calculated by dividing the C_{dl} value with specific capacitance (C_s).

2.3. Results and discussions

2.3.1. Catalyst synthesis and characterizations

The Ru-CCP materials were synthesized using chitosan-metal complexation followed by a single step pyrolysis method at different pyrolysis temperatures from 500 to 700 °C in order to study the effect of pyrolysis temperature on the formation of N-functionalities and its interaction with metal and subsequent change in the HER activity. The TGA analysis of chitosan in N_2 atmosphere shows the decomposition of the polymer at temperatures above 350°C (Figure 2.4). Hence the pyrolysis of chitosan was carried out at a minimum of 500 °C to ensure complete carbonization of the material.

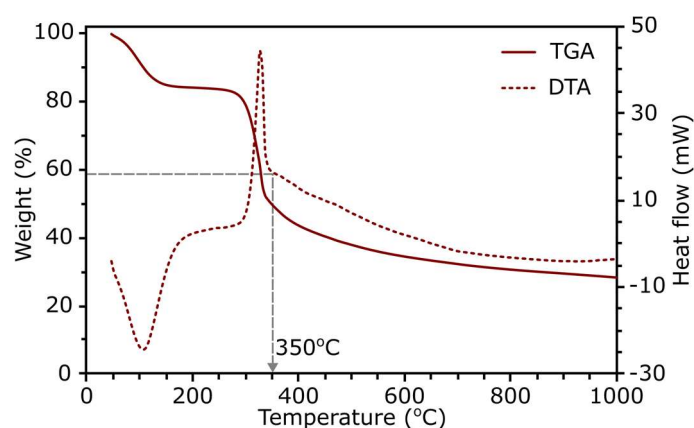


Figure 2.4. TGA of chitosan in N_2 atmosphere.

The nitrogen sorption isotherms of the Ru-CCP materials displayed type II adsorption isotherms, with the Ru-CCP-500 sample having the highest specific surface area of $888.6 \text{ m}^2\text{g}^{-1}$. As the pyrolysis temperature increased, the surface area of the Ru-CCP-600 and Ru-CCP-700 samples decreased to 626 and $436 \text{ m}^2\text{g}^{-1}$, respectively. The nitrogen adsorption isotherms and the measured surface area of the Ru-CCP materials by application of BET equation are given in Figure 2.5a & b, respectively. This trend in surface area results from two phenomena: initially, the carbonization of the hard Ru-CC material leads to a higher specific surface area at 500 °C, then as the pyrolysis temperature increases, the graphitization of the amorphous carbon structure causes a reduction in surface area.^{43,44}

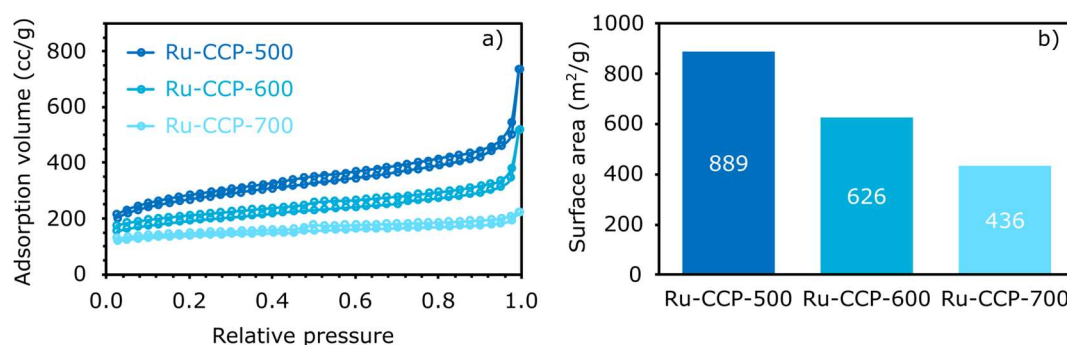


Figure 2.5. (a) N₂ adsorption isotherms of Ru-CCP catalysts, (b) The surface area of Ru-CCP catalysts.

The percentage of the ruthenium present in the catalysts was calculated from thermogravimetric analysis carried out in the presence of air. Due to the challenges associated with digesting Ru-containing materials^{45,46}, especially those with high metal loading, ICP-OES analysis was not conducted for these samples. For metal catalysts supported on carbon, carbon burn-off can be used to determine the overall metal content. The final percentage of weight obtained from TGA is considered to represent the weight of RuO₂. The percentage of ruthenium present in the catalysts were calculated using the formula as given below,

$$\text{wt. \% of Ru} = (\text{wt. \% from TGA}) \times \frac{\text{Atomic weight of Ru}}{\text{Molecular weight of RuO}_2}$$

The ruthenium loading was found to be 18.6, 23.6, 13.6 and 22.2 % for the Ru-CCP-500, Ru-CCP-600, Ru-CCP-700, and the control sample Ru-CLC-500, respectively. The TGA curves for the catalysts are shown in Figure 2.6.

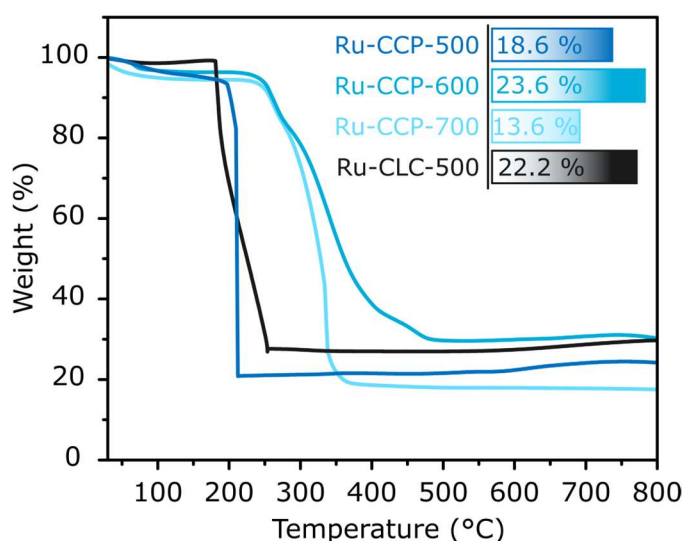


Figure 2.6. TGA curve for the Ru-CCP and Ru-CLC catalysts.

High-resolution transmission electron microscopy (HR-TEM) images of the catalysts and their particle size distribution profiles are shown in Figure 2.7(a-c). Ru-CCP-500 showed a fine size distribution of particles, with the majority of particles falling in the range of 1.5–2.75 nm size. With the increase in the pyrolysis temperature from 500 to 700 °C, the average size of the ruthenium particles increased slightly. However, these samples also exhibited a fine distribution of particles, where the majority belongs to the range of 1.7–3 nm for the Ru-CCP-600 sample and 1.9–3.6 nm for the Ru-CCP-700 sample. The interplanar spacing (d-spacing) of the particles was measured from the lattice fringes observed, where 0.2 nm corresponds to (101) and 0.16 nm corresponds to (102) planes of metallic ruthenium (Figure 2.7d) . Fast Fourier transform (FFT) analysis of the images further confirms the crystalline planes of the metallic ruthenium (shown as inset in Figure 2.7d). The STEM image and the elemental mapping of the elements Ru, C, and N are presented in Figure 2.7(e-h), and it shows even distribution throughout the material. Meanwhile the control sample Ru-CLC-500 exhibited severe particle clustering and a broad size distribution of particles. The HRTEM image and particle size distribution of Ru-CLC-500 is shown in Figure 2.8(a & b).

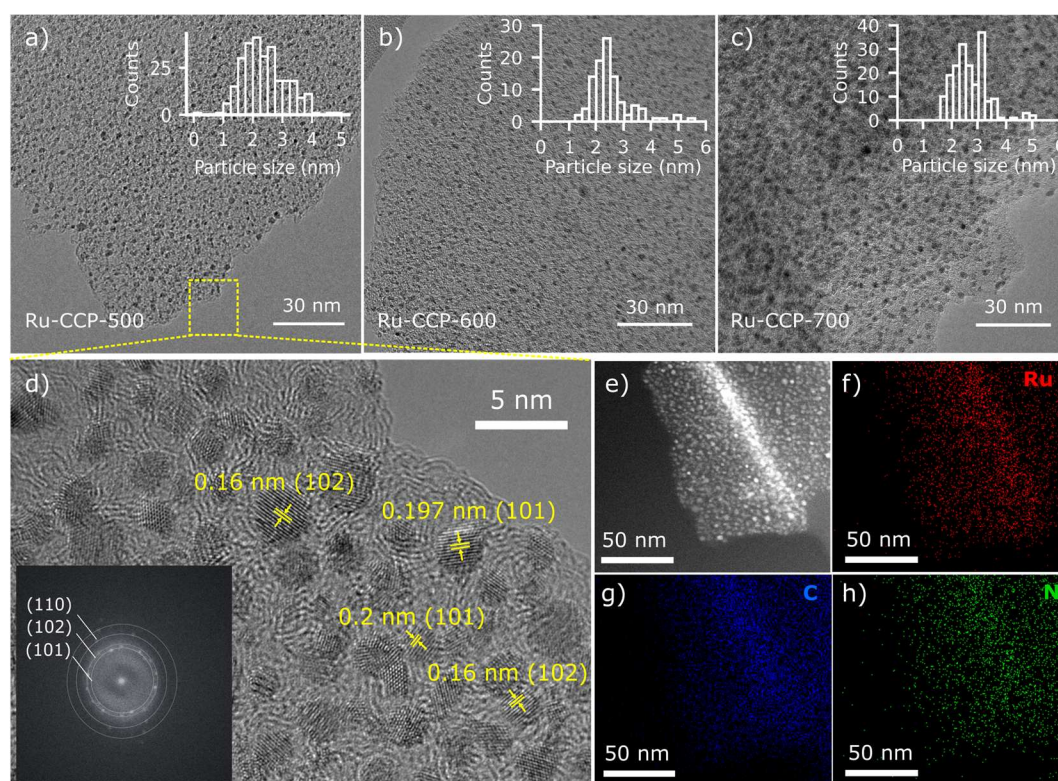


Figure 2.7. (a-c) HR-TEM images and particle size distribution of Ru-CCP-500, Ru-CCP-600, and Ru-CCP-700 catalysts, (d) HR-TEM image of Ru-CCP-500 showing lattice fringes and d-spacings and FFT of the image d is shown in inset, (e) STEM image of Ru-CCP-500 and (g-h) elemental mapping for Ru, C and N measured in the area of image e.

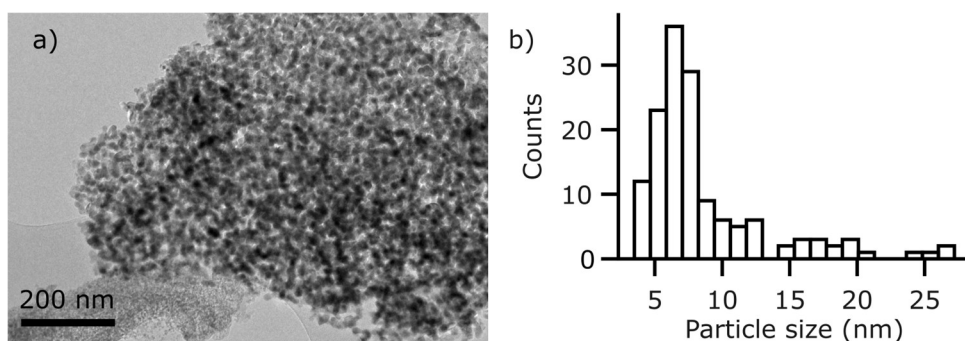


Figure 2.8. (a) HR-TEM image and (b) particle size distribution of Ru-CLC-500 sample.

The XRD patterns of the Ru-CCP materials are presented in Figure 2.9a. The XRD analysis reveals several sharp diffraction peaks that correspond well to metallic ruthenium with a hcp structure (JCPDS No: 00-006-0663). In addition to the Ru diffraction patterns, all materials exhibit a broad peak around $2\theta = 25^\circ$, which is attributed to the (002) facets of partially graphitized amorphous carbon.⁴⁷ Another broad diffraction peak at $2\theta = 44^\circ$ is observed, corresponding to the in-plane diffraction of the (101) facets of graphitic carbon, suggesting the formation of a layered graphitic phase within the carbon matrix.⁴⁸ The intensity of the graphitic carbon peak at $\sim 44^\circ$ increases with higher pyrolysis temperatures, indicating an increase in the graphitization of the carbon material. This trend is also observed in the XRD patterns of bare carbon materials obtained by pyrolyzing only chitosan at different temperatures (Figure 2.9b), referred to as CNC materials. No other phases, such as RuO_2 , were found in the XRD of CCP materials. Notably, the peaks for metallic Ru diffractions became more pronounced at higher annealing temperatures, indicating improved crystallinity of Ru in the material.

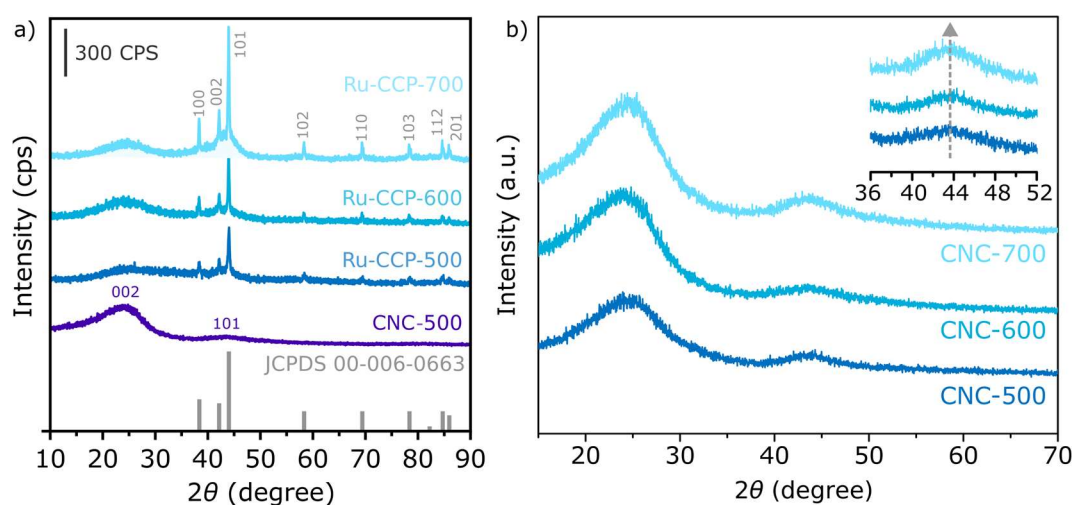


Figure 2.9. (a) XRD pattern of Ru-CCP materials and bare carbon CNC-500 and (b) XRD pattern of bare carbon (CNC) materials.

2.3.2. Electrochemical HER activity in alkaline medium

The electrochemical HER was monitored in N_2 saturated 1 M KOH electrolyte solution. Figure 2.10a represents the linear sweep voltammograms (LSVs) of Ru-CCP materials and Pt/C. Ru-CCP-500 catalyst exhibited higher current response compared to other catalysts as well as commercial Pt/C. The Current response for the catalysts follows the order: Ru-CCP-500 > Ru-CCP-600 > Pt/C (20 wt %) > Ru-CCP-700. The overpotential for HER for Ru-CCP-500 and Ru-CCP-600 were 46 mV and 78 mV, respectively, to achieve a current density of 25 mA cm^{-2} , compared to Pt/C which required 123 mV. On the other hand, Ru-CCP-700 showed a higher overpotential of 201 mV, and the metal-free carbon material CNC-500 displayed insignificant HER performance. The cellulose based control sample synthesized at 500°C (Ru-CLC-500) was also tested for the HER activity in similar conditions and the LSV for the same is given in Figure 2.10b. However, Ru-CLC-500 exhibited a poor HER performance compared to Ru-CCP-500 and Pt/C and displayed an overpotential of 349 mV to achieve a current density of 25 mA cm^{-2} . Overpotential at 25 mA cm^{-2} (η_{25}) for the materials is displayed in Figure 2.10c.

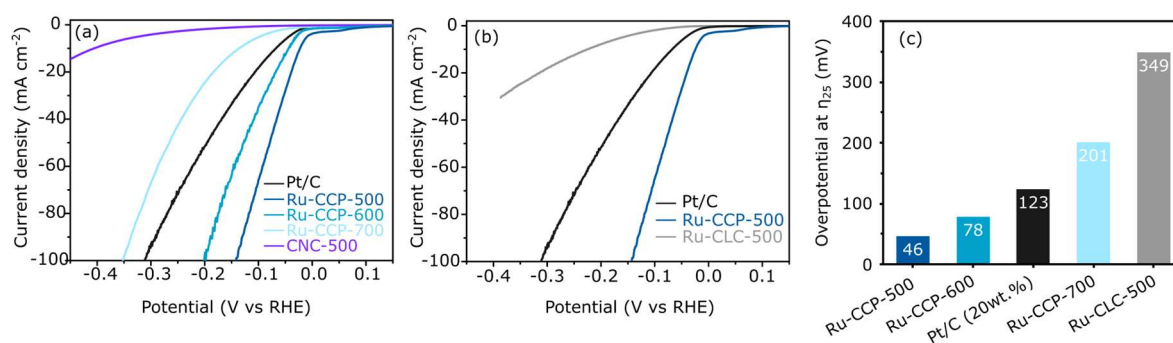


Figure 2.10. (a) LSV of Ru-CCP materials, Pt/C, and bare carbon samples, (b) LSV of Ru-CLC-500 in comparison with Ru-CCP-500 and Pt/C, (c) Overpotential at 25 mA cm^{-2} current density of the Ru-CCP catalysts and control samples.

Since the final ruthenium loading in the samples were different, for a fair comparison of the HER activity, the current density output was normalized with the ruthenium loadings calculated from the TGA. Figure 2.11a represents the LSV of catalysts where the potential vs RHE was plotted against the current density observed per mg of Ru. The HER activity of the samples followed a similar trend as discussed earlier. The overpotential corresponding to the normalized current density $1 \text{ A cm}^{-2}/\text{mg}_{\text{metal}}$ of the catalysts are presented in Figure 2.11b.

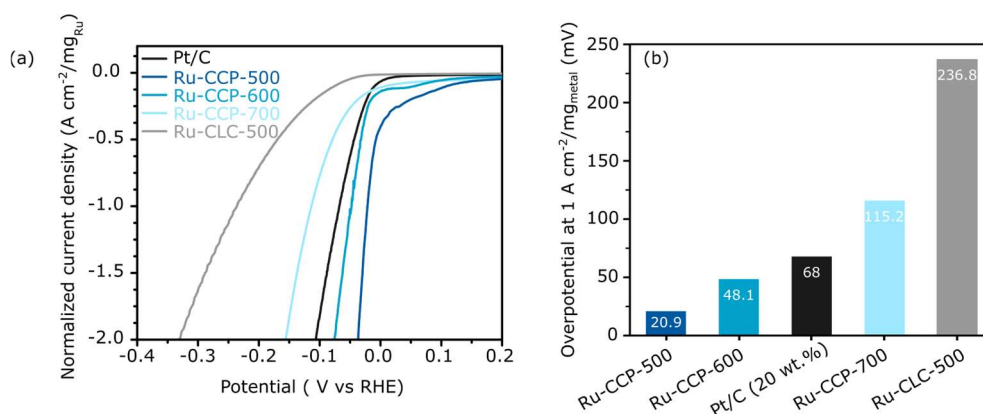


Figure 2.11. (a) LSV of the catalysts showing normalized current density with respect to metal loading, (b) overpotential of the samples to achieve current density of $1 \text{ A cm}^{-2}/\text{mg}_{\text{metal}}^{-1}$

2.3.3. Detailed electronic and structural characterization

The electrochemical analysis suggests that Ru-CCP-500 catalysts delivered high current output, and it outperformed the commercial Pt/C catalyst. Moreover, the results were even better and comparable to the reported Ru supported N-doped carbon catalysts in literature. For the detailed investigation of the higher activity of Ru-CCP-500 further characterization techniques were employed to understand its surface and bulk electronic structure. Using X-ray photoelectron spectroscopy (XPS), the chemical and electronic states of Ru and N in the samples were examined. Due to the overlap of Ru 3d with the C 1s region, Ru 3p was analyzed for Ru species. Figure 2.12 shows the XPS analysis of the Ru 3p region for all synthesized catalysts.

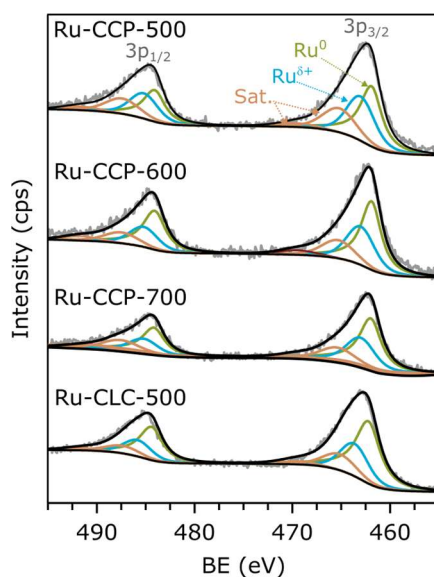


Figure 2.12. Deconvoluted Ru 3p XPS spectra of Ru-CCP catalysts and Ru-CLC-500.

Deconvolution of this region revealed two Ru species: Ru^0 with binding energies at 461.8 and 484.1 eV, and $\text{Ru}^{\delta+}$ at 462.9 and 485.2 eV.⁴⁹ As the pyrolysis temperature increased, the proportion of metallic ruthenium (Ru^0) increased relative to oxidized ruthenium ($\text{Ru}^{\delta+}$). The Ru 3p XPS spectra of Ru-CLC-500 displayed both metallic and oxidic Ru species and the intensity of Ru^0 was higher in this material compared to Ru-CCP catalysts. Also, Ru-CLC-500 exhibited a shift to higher binding energies by 0.3 eV, which means that Ru is present in higher oxidation state in the catalyst surface. Further characterizations were done to understand the same.

It is noteworthy that the XRD of the control sample Ru-CLC-500 revealed distinct peaks for both metallic ruthenium and RuO_2 phases (Figure 2.13a). Peaks at 28° , 35.2° , and 54.3° correspond to RuO_2 diffractions (JCPDS: 00–043–1027), while other peaks relate to metallic Ru and the carbon support. Compared to the Ru-CCP-500 material the diffractions were sharp and intense, which suggests that the Ru-CLC-500 sample has large sized particles and this observation corroborates well with the HR-TEM analysis. Interestingly, despite the absence of RuO_2 phases in the XRD of the Ru-CCP material, XPS indicated the presence of oxidized ruthenium species. This suggests that there may be small, oxidized ruthenium domains too tiny to be detected via XRD, possibly formed by the presence of nitrogen in the material. To confirm the nature of oxidized ruthenium in Ru-CCP and Ru-CLC-500, Raman spectroscopy was performed. The Raman spectra of the Ru-CCP samples are shown in Figure 2.13b, and a comparison of the Raman features of Ru-CCP-500, Ru-CLC-500, and RuO_2 is displayed in Figure 2.13c. All samples exhibited Raman shifts at 1353 and 1590 cm^{-1} , corresponding to the D-band and G-band, indicative of disordered carbon and crystalline graphitic structures, respectively.⁵⁰ Notably, Ru-CLC-500 showed two Raman bands at 512 cm^{-1} and 626 cm^{-1} , characteristic of the E_g and A_{1g} vibration modes of RuO_2 .^{51,52} These bands were absent in the Ru-CCP catalysts, suggesting that the oxidized ruthenium species in Ru-CCP materials do not correspond to RuO_2 structure.

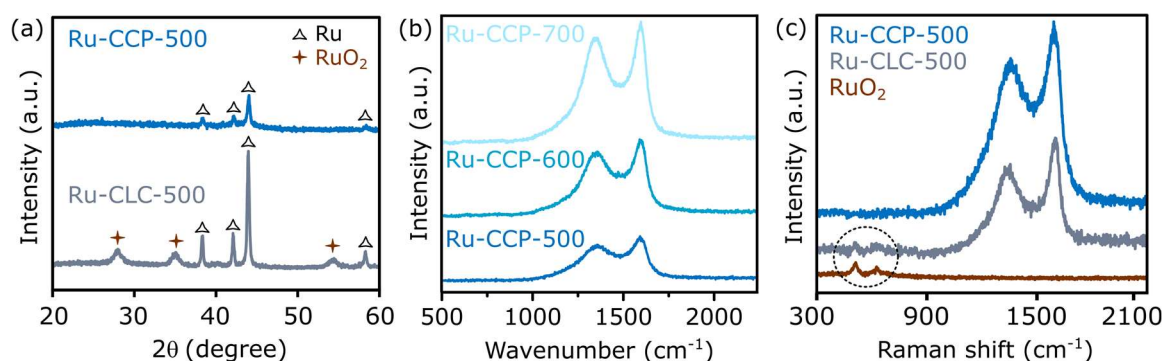


Figure 2.13. (a) XRD of Ru-CLC-500 in comparison with Ru-CCP-500, (b) Raman spectra of Ru-CCP-500 and Ru-CLC-500 along with RuO_2 , (c) Raman spectra of Ru-CCP catalysts.

From the wide scan of XPS the surface concentration of the elements was calculated, elemental surface concentrations are provided in Table 2.2, and the XPS survey spectra for Ru-CCP-500 is shown in Figure 2.14. Ru-CCP-500 had 3.3 % of surface N species and a decline in overall surface nitrogen species was observed with increasing pyrolysis temperature.

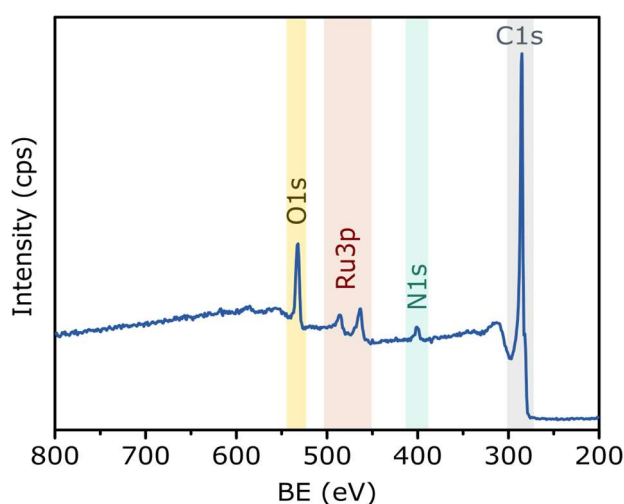


Figure 2.14. XPS survey scan of Ru-CCP-500

Table 2.2. Quantification the surface concentration of elements from XPS survey.

Sample	%C	%N	%Ru	%O
Ru-CCP-500	64.4	3.3	16.5	15.9
Ru-CCP-600	72.8	2.3	12.1	12.9
Ru-CCP-700	73	2	12	13
Ru-CLC-500	69.4	0	10.7	20

To investigate the nature of nitrogen species and their interaction with the metal, N1s XPS spectra were recorded. The deconvolution of the N1s XPS spectra for the bare carbon material CNC-500 revealed four N-species: pyridinic (Py-N) at 398.8 eV, pyrrolic (Pr-N) at 400.7 eV, graphitic (G-N) at 401.5 eV, and oxidized graphitic (O-N) at 402.8 eV. In the Ru-CCP-500 catalyst, a new peak appeared at 399.3 eV, indicating the presence of Ru–N species.⁵³ Additionally, a shift to lower binding energies was observed in Ru-CCP-500 compared to the bare N-doped carbon. The N1s XPS spectra of Ru-CCP-500 and CNC-500 is shown in Figure 2.15a. The N1s XPS spectra for all Ru-CCP catalysts are displayed in Figure 2.15b and the binding energies of the N-species in all the CNC and Ru-CCP materials are given in Table 2.3. In the Ru-CCP material reduction in pyridinic and pyrrolic nitrogen species was observed after the metal incorporation. This suggests that ruthenium in the Ru-CCP catalysts interacted with these nitrogen functionalities in the carbon support, transferring electron density from

ruthenium to nitrogen. This electron transfer causes a red shift in the nitrogen binding energies and results in positively charged ruthenium species and supporting the presence of oxidized ruthenium in the Ru-CCP catalyst despite the absence of RuO_2 .

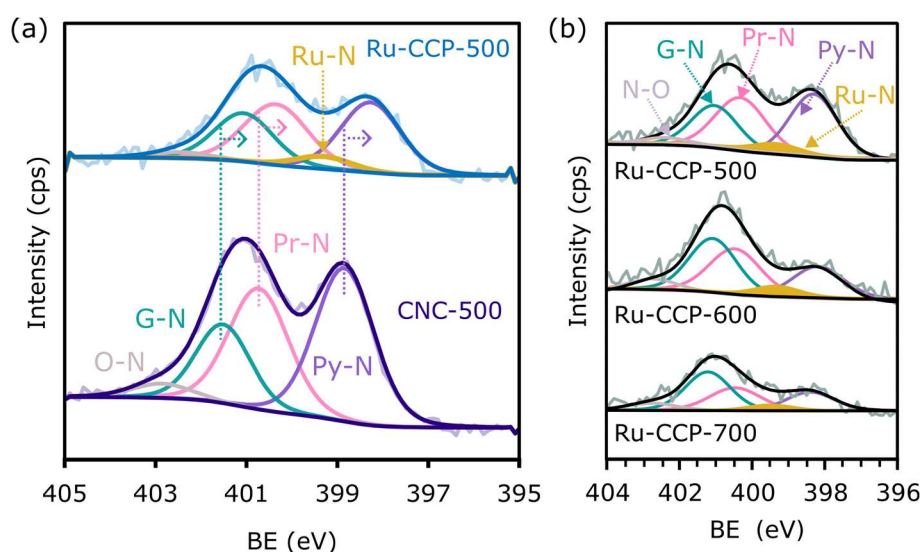


Figure 2.15. (a) Deconvoluted N 1s XPS scan of Ru-CCP-500 and CNC-500, (b) N1s XPS spectra of all Ru-CCP materials.

Table 2.3 binding energy of N-species in CNC and CCP materials

Catalysts	Binding energy of N-species (eV)				
	Py-N	Pr-N	Gr-N	O-N	Ru-N
CNC-500	398.84	400.73	401.47	402.85	
Ru-CCP-500	398.27	400.35	401.06	402.42	399.32
CNC-600	398.76	400.54	401.52	402.84	
Ru-CCP-600	398.20	400.50	401.11	402.76	399.33
CNC-700	398.70	400.36	401.50	402.84	
Ru-CCP-700	398.40	400.50	401.25	402.78	399.3

The quantification of nitrogen species in the CNC and CCP materials are represented in Figure 2.16a & b. Significant reductions in pyridinic (Py-N) and pyrrolic (Pr-N) nitrogen species was observed at higher annealing temperatures alongside a slight decrease in Ru-N species, which suggests that metal–nitrogen interactions are most pronounced at a pyrolysis temperature of 500 °C. The higher amounts of Py-N and Pr-N surface nitrogen species were present in Ru-CCP-500 compared to other samples, which imply increased interactions between ruthenium and these nitrogen species. Meanwhile, an increase in graphitic nitrogen (G-N) species is observed, reflecting enhanced graphitization of the carbon support at higher temperatures.

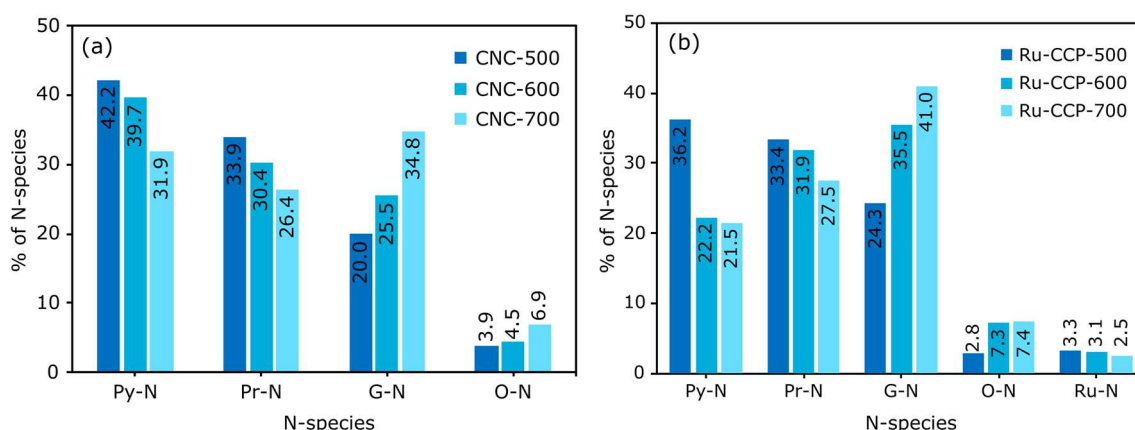


Figure 2.16. Quantification of the N-species in (a) CNC and (b) CCP materials

From the XPS analysis the ruthenium-nitrogen interaction was evident, another supporting evidence for the metal-nitrogen interaction was found in the line scan analysis of the Ru-CCP-500 sample using HAADF-STEM (high-angle annular dark-field scanning transmission electron microscopy) displayed in Figure 2.17a & b. The line scan intensity for nitrogen increased noticeably in tandem with the increase in the ruthenium scan intensity. This correlation is observed for both surface ruthenium and ruthenium particles embedded within the carbon layers of the material.

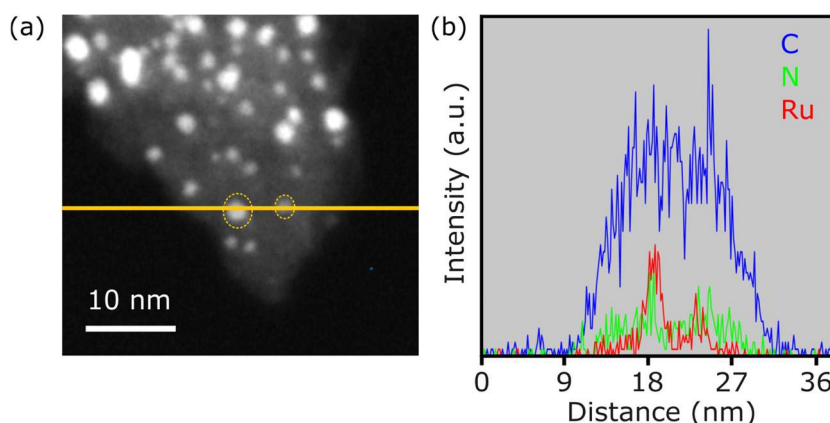


Figure 2.17. (a) HAADF-STEM image of Ru-CCP-500 and (b) the line scan analysis of elements Ru, N, and C (measured across the line marked in yellow colour)

To further investigate the bulk electronic structure of the catalysts and the nature and coordinating environment of ruthenium, X-ray absorption measurements were carried out at Ru K-edge using synchrotron radiation source for Ru-CCP materials and the control samples. Figure 2.18a shows the normalized X-ray absorption near-edge structure (XANES) for Ru-CCP-500, Ru-CLC-500, Ru-CC, and reference samples Ru foil and RuO₂. The absorption edge of Ru-CCP-500 lies between that of Ru foil and RuO₂, indicating an average positive valence

for Ru species in both Ru-CCP-500 and Ru-CLC-500.³³ Ru-CLC-500 has a slightly lower energy absorption edge, close to that of Ru-CCP-500, however, the near-edge region displayed a clear difference among both the samples. Ru-CLC-500 showed features resembling both Ru foil and RuO₂, with a stronger resemblance to metallic Ru. In contrast, near-edge of Ru-CCP-500 is closer to RuO₂ and the Ru-chitosan complex (Ru-CC), and it also displayed features of metallic Ru, but with lower absorbance than Ru-CLC-500. These findings indicate that both Ru⁰ and Ru^{δ+} species are present in the CCP and CLC catalysts and it corroborates well with the Ru 3p XPS data.

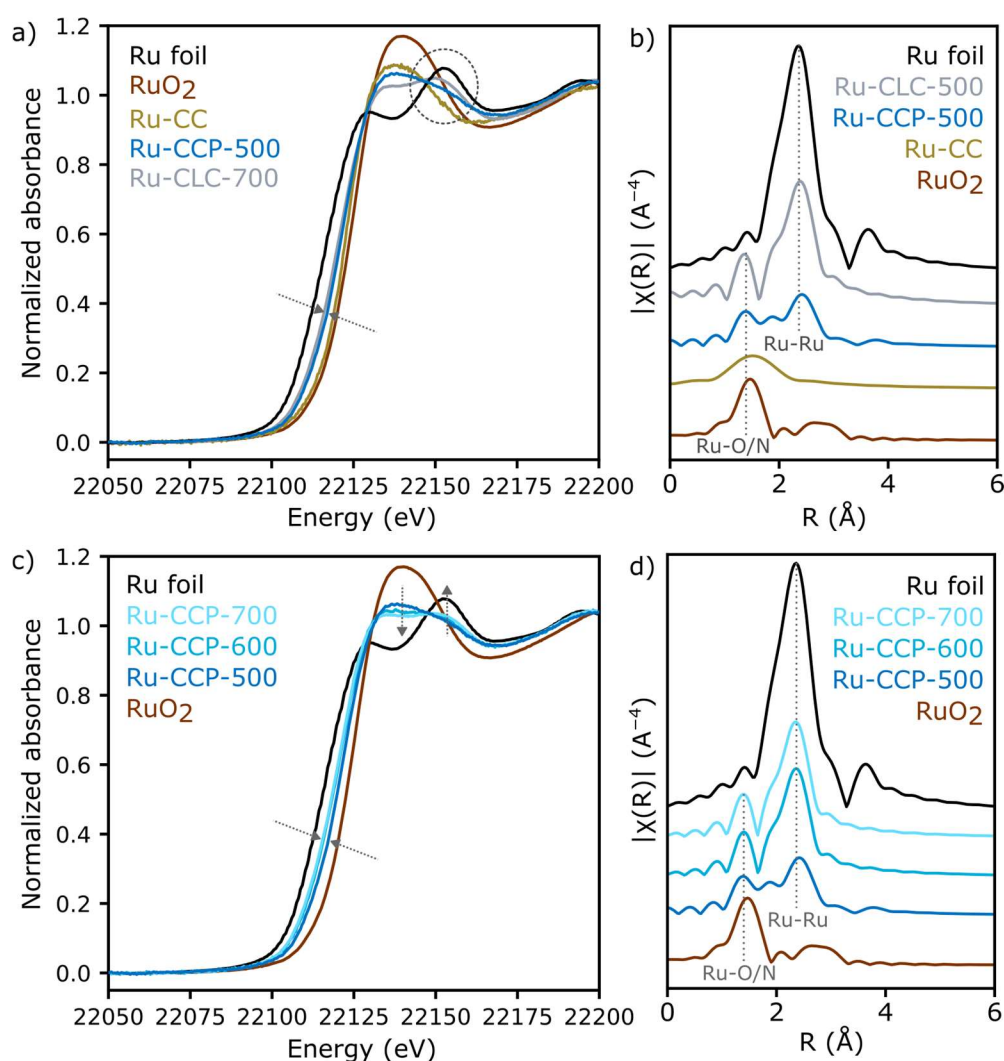


Figure 2.18. (a) Normalized absorbance in the XANES region of Ru K-edge (b) Fourier-transformed EXAFS of Ru K-edge for Ru-CCP-500 and control samples along with references. (c) Normalized absorbance in the XANES region and (d) Fourier-transformed EXAFS spectra for different Ru-CCP catalysts along with references.

Figure 2.18b shows the Fourier transform of the extended X-ray absorption fine structure (EXAFS) region of Ru-CCP-500 along with reference and control samples. In the Ru foil, the

Ru–Ru peak appears at 2.4 Å, while the RuO₂ sample shows a Ru–O peak at 1.5 Å. For the sample analysis, the prominent peaks were fitted using Ru–Ru paths for metallic ruthenium and Ru–O/N paths for Ru^{δ+} species. Ru-CLC-500 exhibits a prominent Ru–Ru peak at 2.4 Å, compared to Ru-CCP-500. The Ru–O peak was at 1.4 Å in Ru-CLC-500 whereas the Ru–N peak in Ru-CCP-500 was observed at 1.45 Å, suggesting the Ru–N coordination in the sample. Also, the Ru-CCP-500 showed a comparable intensity of both metallic Ru and oxidized ruthenium peaks. These observations line up with the Ru 3p XPS data. Furthermore, the Ru-CC sample features a unique peak at 1.6 Å with no Ru–Ru peak, indicating a different initial charge state for ruthenium in the ruthenium-chitosan complex before pyrolysis and suggests that Ru⁰ and Ru^{δ+} species were formed during pyrolysis. The EXAFS fitting parameters for the samples are given in Table 2.4 and the plots of EXAFS fitting results are given in Figure 2.19.

Table 2.4. EXAFS fitting parameters for all Ru-CCP catalysts, control samples and references.

Sample	Bond	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0 (eV)	<i>R</i> factor
Ru foil	Ru–Ru	12.0	2.67 ± 0.01	0.001 ± 0.0003	−4.13 ± 1.8	0.015
RuO ₂	Ru–O	6.0	1.91 ± 0.23	0.029 ± 0.041	−2.36 ± 5.14	0.019
Ru-CC	Ru–N	2.0	2.02 ± 0.03	0.017 ± 0.002	8.17 ± 3.09	0.018
Ru-CCP-500	Ru–Ru	2.6 ± 0.3	2.71 ± 0.02	0.007 ± 0.003	2.75 ± 1.76	0.018
	Ru–N	2.7 ± 0.5	1.98 ± 0.01			
Ru-CCP-600	Ru–Ru	5.7 ± 1.4	2.67 ± 0.01	0.004 ± 0.002	−6.11 ± 1.72	0.021
	Ru–N	2.3 ± 0.6	1.93 ± 0.01			
Ru-CCP-700	Ru–Ru	6.1 ± 1.2	2.66 ± 0.01	0.004 ± 0.001	−7.00 ± 1.37	0.016
	Ru–N	2.1 ± 0.5	1.93 ± 0.01			
Ru-CLC-500	Ru–Ru	6.8 ± 1.5	2.67 ± 0.01	0.003 ± 0.002	−4.31 ± 1.57	0.019
	Ru–O	2.7 ± 0.6	1.94 ± 0.01			

N: coordination numbers, *R*: bond distance, σ^2 : Debye–Waller factors, ΔE_0 : the inner potential correction, *R* factor: goodness of fit, S_0^2 was set to 1.

Despite Ru-CLC-500 and Ru-CCP-500 having similar Ru–O/N coordination numbers (2.71 and 2.67), their FT-EXAFS in R-space differ, suggesting different local environments for Ru^{δ+} species in Ru-CCP-500 compared to Ru-CLC-500 and RuO₂, hence confirming the Ru–N interaction in Ru-CCP-500 as observed seen from N 1s XPS. The Ru–Ru coordination number for Ru-CCP-500 is 2.6, and for Ru-CLC-500, it is 6.8, both significantly lower than Ru-foil (12).¹¹ This lowest coordination number for Ru–Ru in Ru-CCP-500 provides strong evidence for the formation of ultrasmall ruthenium nanoparticles, as seen in the HR-TEM images.

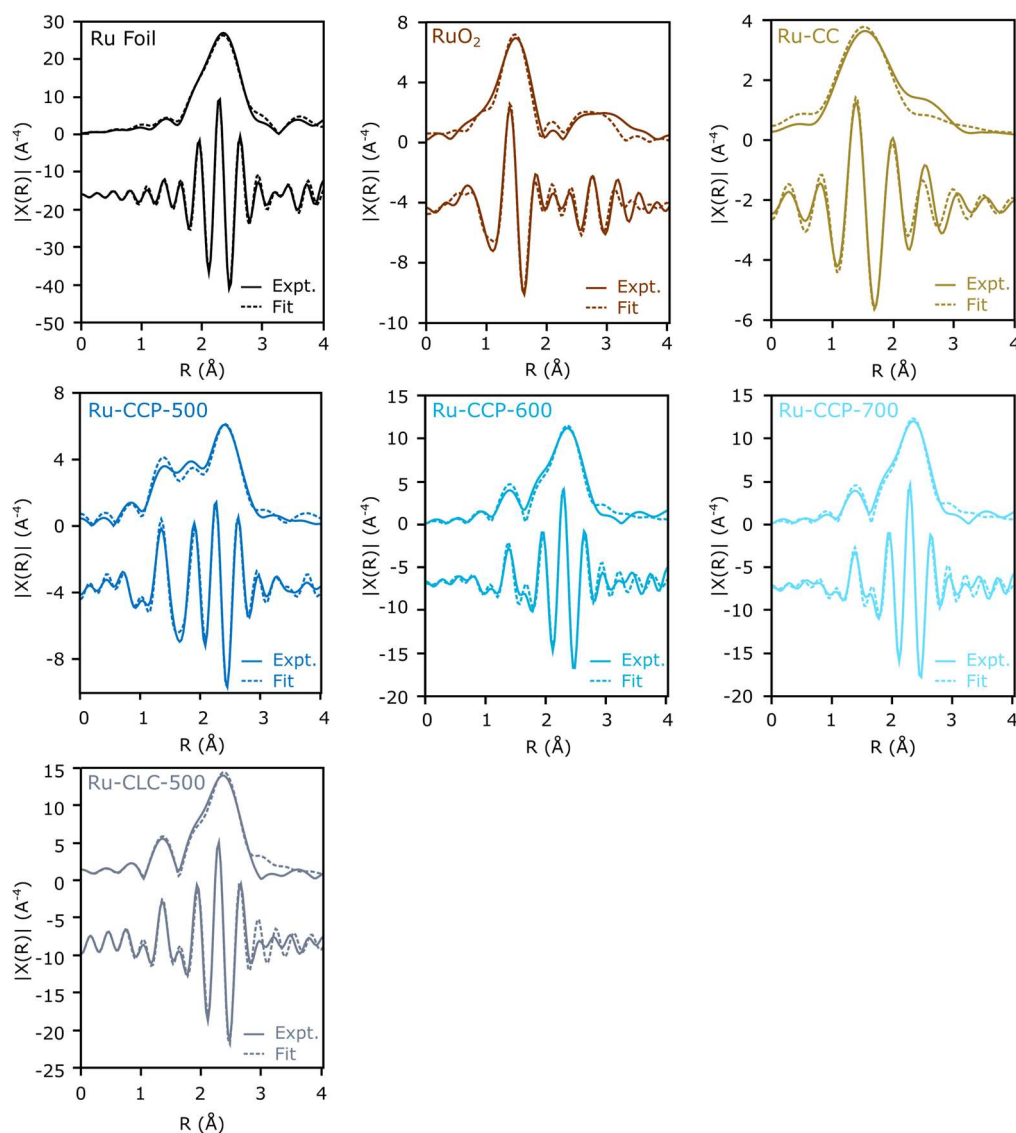


Figure 2.19. EXAFS fitting of the catalysts and references.

The XANES spectra of the Ru-CCP materials synthesized at different temperatures (500 to 700 °C), along with Ru foil and RuO₂, are shown in Figure 2.18c. It is noteworthy that the absorption edge shifted to lower energy levels as the pyrolysis temperature increased. All Ru-CCP materials exhibited both metallic and oxidic ruthenium near-edge features. Interestingly, as the pyrolysis temperature increased, the absorption intensity of the oxidic ruthenium near-edge decreased, while the intensity in the metallic ruthenium region increased. This trend suggests an increasing metallic character in the CCP catalysts with an increase in pyrolysis temperatures. The trend in the XANES data was supported by the Fourier-transformed EXAFS of these samples, which are presented in Figure 2.18d. As previously stated, the two main peaks in the Ru-CCP catalysts were fitted with Ru–Ru and Ru–O/N paths. The peak at 2.4 Å, indicative of metallic ruthenium, increased significantly with temperature. The peak at 1.4 Å, associated with Ru–N coordination, is distinct from RuO₂. Notably, the relative intensity of Ru⁰

species compared to $\text{Ru}^{\delta+}$ species increased at higher annealing temperatures, this trend also observed in Ru 3p XPS data. The Ru–Ru coordination number was 2.6 for Ru-CCP-500 and which increased to 5.7 and 6.1 for Ru-CCP-600 and Ru-CCP-700, respectively. This result suggested the growth of metallic ruthenium nanoparticles, at higher pyrolysis temperatures which was evident from both XRD and HR-TEM images. Additionally, the Ru–N coordination number decreases with higher pyrolysis temperatures, likely due to the reduction in nitrogen species.

2.3.4. Structure activity relationship and the role of nitrogen

Detailed structural and electronic characterizations reveal that nitrogen doping significantly impacts the catalytic activity for the HER. Figure 2.20a illustrates the correlation between HER activity, overall nitrogen content, and the percentage of Ru–N species in the catalysts, as calculated from N 1s XPS data. The Ru-CCP-500 sample, with the highest nitrogen content and a higher fraction of pyridinic and pyrrolic nitrogen, exhibited the lowest overpotential. HER activity progressively decreased in Ru-CCP-600 and Ru-CCP-700 samples as nitrogen content and surface nitrogen species decreased. Meanwhile, Ru-CLC-500, with a non-nitrogen-containing carbon support, demonstrated significantly higher overpotential and poorer HER activity.

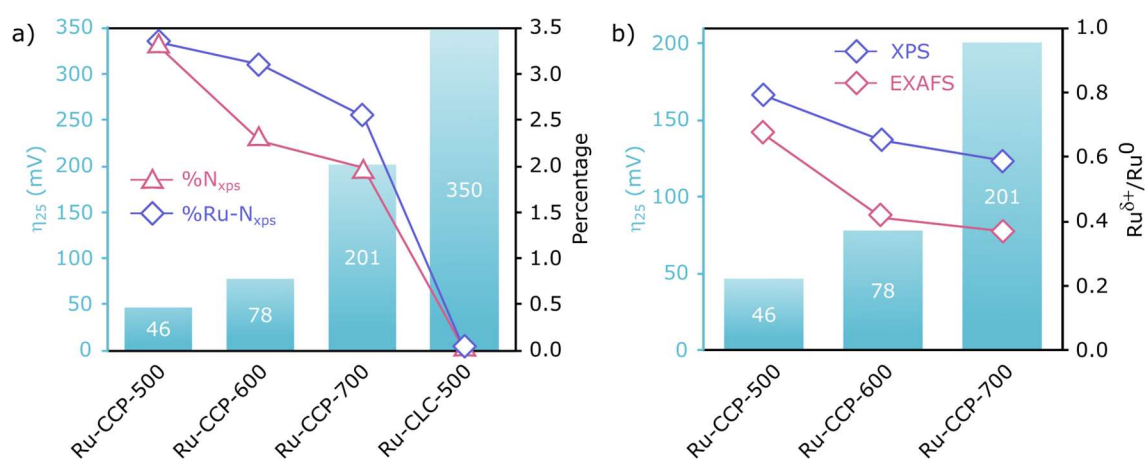


Figure 2.20. (a) HER activity trend in Ru-CCP and Ru-CLC catalysts based on overall N content and % Ru–N species from XPS and (b) Relationship between HER overpotential of Ru-CCP catalysts and $\text{Ru}^{\delta+}/\text{Ru}^0$ ratio found from XPS and EXAFS analysis.

HR-TEM analysis revealed that the formation of smaller ruthenium nanoparticles occurred only in the presence of nitrogen, while metal particles on non-nitrogen-containing cellulose-derived carbon appeared larger and in the absence of nitrogen, the formation of RuO_2 was observed from XRD in the Ru-CLC-500. However, having RuO_2 or metallic ruthenium species within

cellulose-derived carbon was insufficient for effective catalytic performance. Thus, the presence of nitrogen in the carbon support enhanced the electronic metal–support interaction in the Ru-CCP catalyst and significantly influenced the electrocatalytic activity. The metal–nitrogen interaction also explains the existence of oxidized ruthenium species in the catalyst and the presence of $\text{Ru}^{\delta+}$ species played a significant role in affecting the catalytic activity.

Figure 2.20b portrays the relationship between the overpotential and the ratio of $\text{Ru}^{\delta+}/\text{Ru}^0$. These values were deduced from the area of Ru^0 and $\text{Ru}^{\delta+}$ peaks in the Ru 3p XPS spectra and the intensity of the Ru^0 and $\text{Ru}^{\delta+}$ peaks from the EXAFS data. The $\text{Ru}^{\delta+}/\text{Ru}^0$ ratio decreased with increase in the pyrolysis temperature and consequently caused an increase in the overpotential. Hence, it is apparent that a certain proportion of oxidized and metallic ruthenium is necessary for attaining the desired HER activity. The Ru-CCP-500 material possessed a higher amount of the desired nitrogen species, facilitating enhanced interaction with the metal and which favored formation of a greater number of oxidized ruthenium species and exhibited higher activity toward the HER. Hence, the pyrolysis temperature of 500°C was optimum to form the ruthenium-containing nitrogen-doped carbon from the ruthenium–chitosan complex, with controlled graphitization and the most active metal centers for the HER activity.

2.3.5. Electrochemical HER kinetics and stability

To gain insight into the mechanistic aspects of HER reaction the Tafel slopes were calculated from the small polarization area of LSVs of the catalysts. For the Tafel slope calculation the current densities at specific potentials were calculated, and the linear portion was fitted to the Tafel equation; $\eta = b \log j + a$, where η represents overpotential, j denotes current density, and b represents the Tafel constant.⁵⁴ Tafel slopes obtained for Ru-CCP-500, Ru-CCP-600, Ru-CCP-700, and Pt/C (20 wt %) were 45, 47, 107, and 46 mV dec^{-1} , respectively (Figure 2.21a). The lowest Tafel slope was observed for Ru-CCP-500. However, Ru-CCP-600 and Pt/C also exhibited Tafel slopes in a similar range which suggests these samples follow similar HER kinetics. Based on literature and the obtained Tafel slope value ($\sim 40 \text{ mV dec}^{-1}$), the Ru-CCP-500 adheres to the Volmer–Heyrovsky mechanism for the HER, with Heyrovsky being the rate-determining step.^{13,55} From the electrochemical impedance spectroscopy (EIS) analysis the electrocatalytic charge transfer resistance between electrode/electrolyte interfaces was calculated. The charge transfer resistance (R_{CT}) values were calculated from the Nyquist plots shown in Figure 2.21b. The lowest R_{CT} value of 3.14 Ω was observed for Ru-CCP-500. Ru-CCP-600 and Pt/C showed the values 5.1 Ω and 6.19 Ω , respectively. The small R_{CT} values

indicated more active charge transfer kinetics for Ru-CCP-500 catalysts and the trend aligns well with the LSV performance.

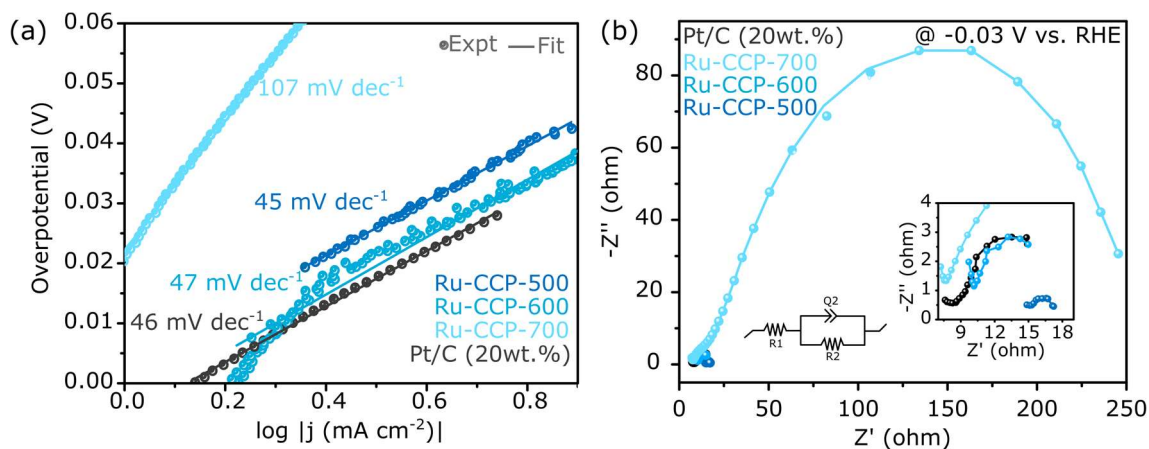


Figure 2.21. (a) Tafel plot showing the Tafel slope values for Ru-CCP catalysts and Pt/C and (b) Nyquist plots for Ru-CCP catalysts and Pt/C calculated from EIS, in 1 M KOH at -0.03 V vs RHE and inset shows the enlarged area in the range of 7 to 20 Ω .

The double-layer capacitance (C_{dl}) value for the samples were calculated from the CV run in the non-faradaic region at a potential range of 0.065 to 0.115 V vs RHE. The CV recorded at

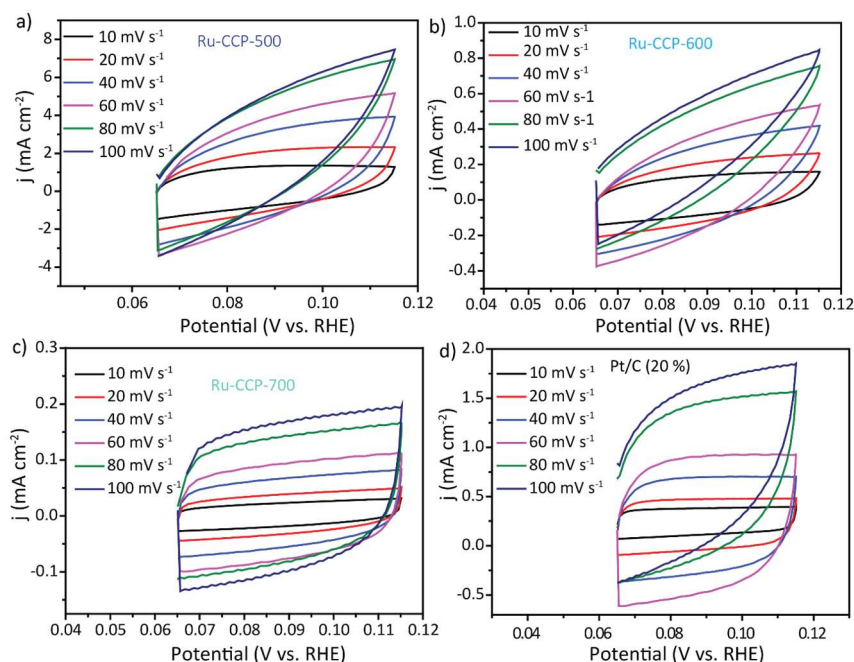


Figure 2.22. The cyclic voltammograms (CV) recorded for the catalysts in the non-faradaic region at different scan rates.

different scan rates in the N_2 saturated 1 M KOH for the Ru-CCP samples and Pt/C is shown in Figure 2.22. The slopes obtained from the scan rate vs current density plot were 53, 5, 2, and 15 mF cm^{-2} for Ru-CCP-500, Ru-CCP-600, Ru-CCP-700, and Pt/C respectively (Figure 2.23).

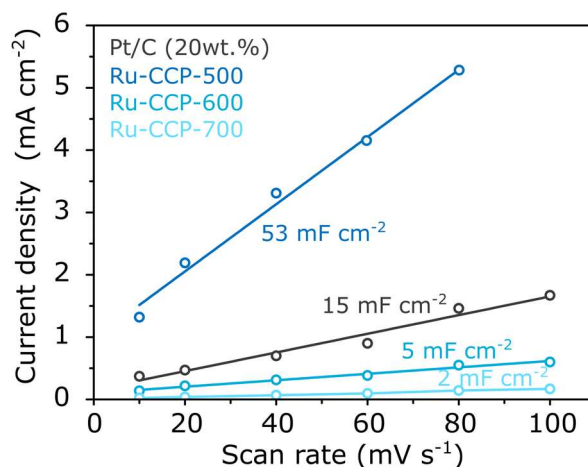


Figure 2.23. The plots for current density vs the scan rate in the non-faradaic region of the cyclic voltammograms of the catalysts.

The double layer capacitance (C_{dl}) was obtained from these values and the electrochemically active surface area (ECSA) of the samples were calculated by dividing the C_{dl} by the specific capacitance (C_s), which is assumed to be 0.040 mF cm^{-2} . The C_{dl} and ECSA values are presented in Table 2.5. Ru-CCP-500 exhibited higher ECSA compared to other catalysts and Pt/C and this confirmed the well exposed active sites on the conductive nitrogen-doped carbon support of the sample which accelerates the mass transfer in the HER kinetics.

Table 2.5. The C_{dl} values and ECSA calculated from the CV plot run in the non-faradic region at a potential range from 0.065 to 0.115 V vs. RHE.

Sample	C_{dl} (mF)	ECSA (cm ²)
Ru-CCP-500	10.38	295.5
Ru-CCP-600	0.98	24.5
Ru-CCP-700	0.40	10
Pt (20 wt%)/C	2.94	73.5

To evaluate the stability of the catalyst. LSV for Ru-CCP-500 in 1 M KOH was measured before and after 1000 cycles within a potential range of 0.005 to 0.05 V vs RHE. The HER polarization curve showed no notable change after 1000 cycles (Figure 2.24a). Additionally, the functional stability of Ru-CCP-500 was tested for 12 hours in 1 M KOH at -0.06 V vs RHE using chronoamperometry (electrode area of 1 cm^2). The results indicated consistent performance of

the catalyst with no current degradation (Figure 2.24b) and suggested a high structural integrity of the catalyst.

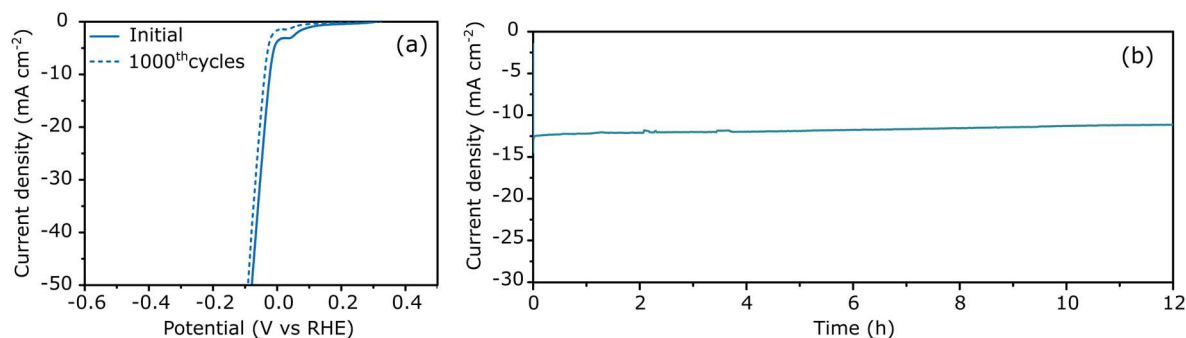


Figure 2.24 (a) LSV of Ru-CCP-500 measured within the potential window of -0.005 to 0.05 V vs RHE showing initial activity and after 1000 cycles and (b) Chronoamperometry analysis of Ru-CCP-500 in 1M KOH for 12 hours at a potential of -0.06 V vs. RHE.

2.3.6. Post HER characterization of the catalysts

Figure 2.25 shows the HR-TEM image of the Ru-CCP-500 catalyst after the stability test. The particle morphology remained intact, with only a minor increase in particle size and no significant agglomeration. This implies that the improved metal–support interaction due to nitrogen doping retained the properties and stability of the catalyst.

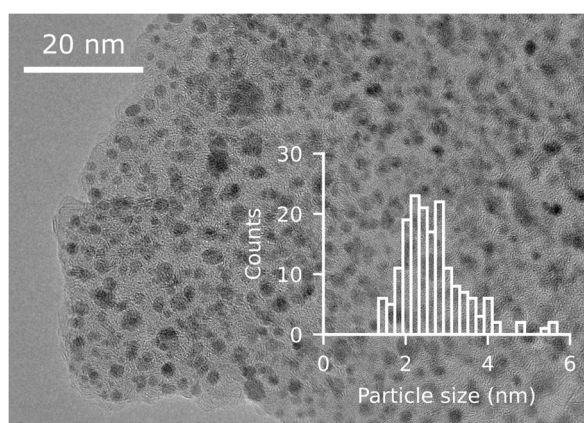


Figure 2.25. HR-TEM image and particle size distribution of Ru-CCP-500 catalyst after the stability test.

ICP-OES analysis of the electrolyte was conducted After the stability test, and it showed no ruthenium leaching. These results confirm that the Ru-CCP-500 catalyst is durable and consistently performs well under the test conditions. The Ru 3p and N1s XPS was recorded for the electrode with the spent Ru-CCP-500 catalyst after the stability test and they are presented in Figure 2.26a & b. The Ru 3p scan showed an overall decrease in intensity compared to the

fresh catalyst, due to the smaller amount of catalyst used to coat in the electrode. The Ru^0 peak intensity decreased significantly, while an increase in the $\text{Ru}^{\delta+}$ species was observed in the spent catalyst. It could be due to the conversion of Ru^0 species to $\text{Ru}^{\delta+}$ during the reaction. This is further supported by the N 1s XPS, which showed an increase in pyrrolic (Pr-N) and Ru-N species compared to the fresh catalyst, along with an overall decrease in other nitrogen species. This suggests that $\text{Ru}^{\delta+}$ species could be the active sites for the reaction and during the HER, More Pr-N functionalities have evolved which could interact with ruthenium, leading to the formation of more $\text{Ru}^{\delta+}$ species and contributing to the stable performance of the catalyst.

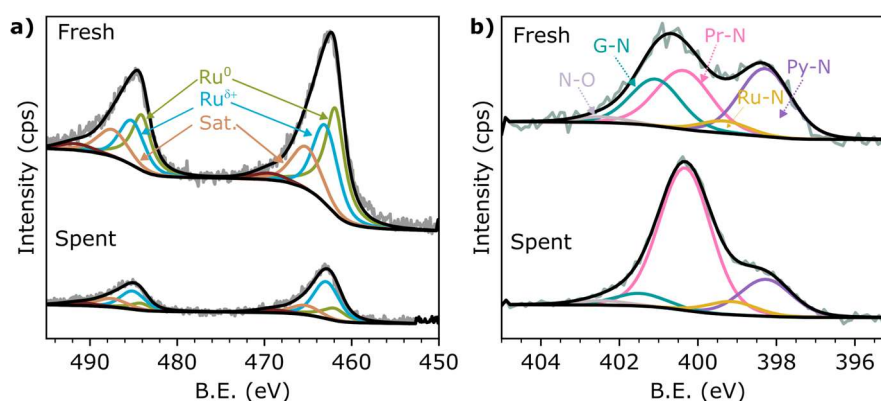


Figure 2.26. (a) deconvoluted Ru 3p and (b) deconvoluted N 1s XPS spectra of Ru-CCP-500 on the electrode after stability test.

2.4. Summary and Conclusion

A viable method for synthesizing N-containing carbon supported ruthenium catalyst was designed by complexing chitosan with ruthenium and performing a one-step pyrolysis process. Ru-CCP-500 demonstrated remarkable electrocatalytic activity for the HER, outperforming commercial Pt/C and other and other ruthenium-based catalysts on N-doped carbon support. This superior performance is attributed to its unique structural and electronic properties. Various characterizations revealed that the metal-nitrogen interaction in the material, which causes the formation of oxidized ruthenium species and the aid the formation of smaller and stable ruthenium nanoparticles within the carbon framework. The optimal synthesis temperature was identified as 500 °C with a fine balance of graphitization, desired nitrogen species and content to achieve the ideal proportion of oxidized and metallic ruthenium species. The tuning of electronic properties, metal and carbon support by improving the metal-support interaction was achieved by nitrogen doping. Ru-CCP materials present a sustainable alternative to platinum-based catalysts, addressing cost and scarcity concerns, and highlight the potential of chitin biomass derived materials for energy applications.

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3. Nitrogen containing carbon-supported Fe-Ni bimetallic catalyst for electrochemical OER and ORR

3.1. Introduction

In Chapter 2, we have identified that the M-CCP catalyst showed excellent electrochemical HER activities and the CCP synthesis method is a viable alternative for conventional N-doped carbon supported metal catalysts. Our next goal was to expand this method to bimetallic catalyst systems and investigate their electrochemical activity. In this work the catalyst design was intended to study fundamental oxygen electrochemical reactions; oxygen evolution (OER) and oxygen reduction (ORR). Understanding and optimizing these reactions are pivotal for improving the efficiency and performance of devices such as water electrolyzers, fuel cells, and metal air batteries (MAB). A schematic representation of water electrolyzer, metal air battery and fuel cell are shown in Figure 3.1.

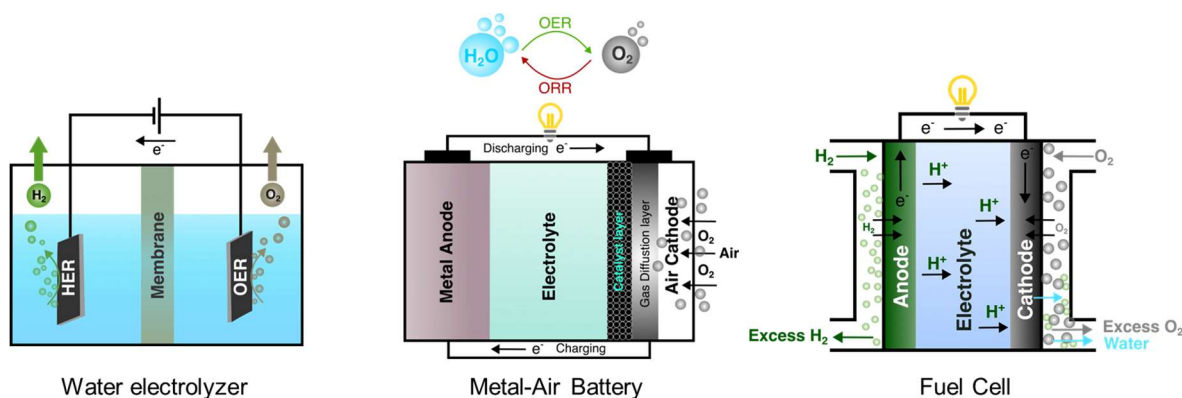
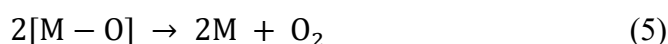
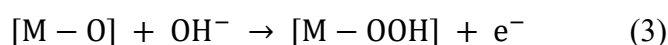
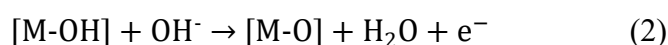
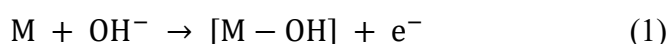


Figure 3.1. Schematic representation of water electrolyzer, metal air battery and fuel cell.

In electrochemical water splitting, the OER at the anode is coupled with the HER at the cathode to produce hydrogen and oxygen gases. Efficient OER catalysts are crucial for reducing the energy input required for water splitting, making hydrogen production more sustainable and which can be used as a clean fuel and energy carrier.¹ The ORR is a process where molecular oxygen is reduced to form water or hydroxide ions in an electrochemical cell. MABs, like zinc-air and lithium-air batteries, rely on the ORR during discharge and the OER during recharge.² The efficiency and reversibility of these reactions determine the energy density and cycle life

of the batteries. Metal-air batteries offer high energy density due to the use of oxygen from the air as a reactant, which is abundant and lightweight. Optimizing ORR and OER catalysts can further enhance their performance and make them more viable for applications such as electric vehicles and grid storage. In fuel cells, the ORR at the cathode combines electrons from the external circuit with oxygen and protons from the electrolyte to produce water.³

OER kinetically sluggish than is cathodic counterpart HER since it involves the formation O₂ double bond and a 4-electron pathway. Hence, the OER requires higher anodic potential. The OER reaction mechanism in alkaline medium is given in equations (1-5)⁴

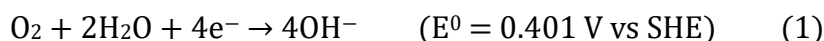


RuO₂ demonstrates exceptional activity in both acidic and alkaline environments. However, it shows instability at higher anodic potential, leading to the formation RuO₄ and its dissolution in the electrolyte.⁵⁻⁷ IrO₂ is another state-of-the-art catalyst used for OER electrodes which is comparatively stabler than RuO₂, However, it also experiences oxidation to IrO₃ under the reaction conditions.⁷⁻⁹ The widespread use of these catalysts is restricted by the high cost and limited availability of these precious metals.⁴

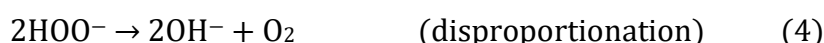
ORR is also kinetically sluggish since it involves the breaking of the strong double bond in oxygen. State-of-the-art catalysts for ORR in low-temperature fuel cells are Pt based catalysts, known for their high activity and efficiency.¹⁰ However, the scarcity and high cost of Pt have spurred research into reducing its usage and finding alternatives.^{11,12} The ORR is highly irreversible with multiple adsorption and desorption steps, making it crucial to minimize overpotential for high energy efficiency. The mechanism is complex due to intricate electron transfer and adsorption-desorption processes. Performing ORR in an alkaline medium is preferable as it reduces anion adsorption energies, enhances kinetics, and creates a less corrosive environment for the catalyst.¹³ The reaction can follow a direct four-electron pathway, converting oxygen directly to hydroxide ions, or a 2+2 indirect pathway, forming peroxide ions first followed by a 2-electron reduction to form hydroxide ion or disproportionation of the peroxide ion to form water and oxygen. The direct mechanism is preferred for fuel cells due to its efficiency and because peroxide in the indirect pathway can harm fuel cell components. The

two-electron mechanism leads to electrochemical peroxide synthesis. The reaction mechanism for ORR in alkaline medium is given in the equations (1-4).^{13,14}

Direct $4e^-$ pathway:



Indirect $2e^-$ pathway:



As mentioned previously the scarcity and stability issue of the state of art catalysts RuO_2 , IrO_2 for OER and Pt based catalysts for ORR has limited their use in scalable applications. Carbon based catalysts with different morphologies¹⁵ and non-noble metal-based systems^{16–18} have been emerged as a promising alternative as bifunctional OER-ORR catalysts. Among the various transition metal-based electrocatalysts, FeNi-based materials stand out for their excellent performance and low cost.^{16,19–21} Transition metal alloys, such as the FeNi bimetallic alloy, exhibit superior electrocatalytic properties due to their unique electronic and chemical characteristics. Notably, FeNi alloys are particularly promising because of their bifunctional activity for OER and ORR.^{19,22–25} However, multi-metallic alloys alone often encounter strong agglomeration, which hinder catalytic efficiency. Combining these metal alloys with a conductive carbon support, especially heteroatom-doped carbon, can enhance electron and mass transfer, disperse metallic species more effectively, and enhance chemical stability.^{26,27} Additionally, heteroatom doping boosts catalytic activities by introducing active configurations.^{12,15,23,26}

Nitrogen doped carbon supports have been proved to be efficient for FeNi based catalysts for OER and ORR. The formation of carbon core shell around FeNi catalysts was found to improve the corrosion and oxidation resistance of the alloy and improved the electrochemical stability of catalyst^{22,28,29}, The FeNi alloy supported on graphitic carbon layers to form the thin core shell around the alloy particles which can facilitate fast electron transfer from the core to the surface.^{21,25,30} The N- doping induces the formation of various functionalities among which, the graphitic and pyridinic nitrogen species found to improve the electric conductivity and surface wettability and diffusion-limited current density.^{25,31–33} Hence offer better electron charge transfer kinetics for both OER and ORR and reduce the over potential to a great extent. However, the FeNi catalysts supported on N-doped carbon materials mostly use non-renewable and

expensive N-precursors such as pyridine, aniline, NH_3 , ZIFs, PAN, Phthalocyanines, etc. and the synthetic procedures are often cumbersome. A compilation of the recent studies on N-doped carbon supported FeNi alloy catalysts and their OER over potential and ORR half wave potential are shown in Table 3.1.

Table 3.1. Literature reports for the recent studies on N-doped carbon supported FeNi alloy catalysts for electrochemical OER and ORR

Catalyst	Precursor/Template	OER η_{10} (mV) ^a	ORR $E_{1/2}$ (V) ^b	Ref.
FeNi/NC	Pluronic F127 + gC_3N_4	350	0.81	34
Fe-FeNi ₃ /NC	Pyridine (Plasma discharge)	360	0.79	35
FeNi@NCs	Guanine	379	0.84	36
FeNi @N-CNT/NCSs	gC_3N_4 + HCl + Aniline + $(\text{NH}_4)_2\text{S}_2\text{O}_8$	310	0.84	22
FeNi/N-CPCF	ZIF-8 + DMF + Polyacrylonitrile	385	0.86	37
FeNi@NC	ZIF-8 + Fe & Ni phthalocyanines	291	0.85	38
FeNi/PNG	FeNi-MOF-74+ PNG (laser irradiation)	353	-	29
P-FeNi/NC-900	FeNi-MOF + Polydopamine	390	0.85	33
FeNi-CNC-800	CTF ^c + NaCl	320	0.84	39
FeNi@NC	gC_3N_4 + Glucose	360	0.84	25
FeNi@C/NG	Dicyandiamide + Glucose	430	0.84	30
FeNi-NC	Peanut shell + KOH + Melamine	410	0.83	40
FeNiN@C/NC	Cellulose + melamine + NH_3	305	0.87	41
NC@NiFe	Chitosan + NaCl + Acetic acid + NH_3	339	-	42
FeNi ₃ @NC	Chitosan	277	0.86	43

^aOER over potential at 10 mA cm^{-2} , ^bORR half wave potential, ^cCovalent Triazine Framework.

Chitosan as a sustainable and cheap nitrogen containing carbon precursor with and without external N-dopant was used by couple of recent studies on FeNi catalyst system showing improved OER and ORR activity.^{42,43} In this work our aim was to synthesize FeNi bimetallic catalyst on nitrogen doped carbon via metal-chitosan complex pyrolysis method. The electrochemical OER and ORR activity of the synthesized catalyst was evaluated in alkaline medium, and the effect of nitrogen doping was studied by varying the pyrolysis temperature and the carbon support.

3.2. Experimental section

3.2.1. Materials and reagents

Low-molecular-weight chitosan (product code: 448869), Ruthenium (IV)oxide (RuO_2), Potassium hydroxide (KOH), and Isopropyl alcohol were bought from Sigma-Aldrich. Microcrystalline cellulose was obtained from Maple India Bio Chem Lab. Platinum on carbon (Pt/C, 20% w/w) was obtained from Alfa Aesar. Iron(III)nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Activated carbon (Pharma grade, product code: 0269000500), Glacial acetic acid 99% and Acetone were purchased from Loba Chemie. 5% Nafion aqueous solution was procured from Electrochem, Inc. All solutions for this work were prepared with deionized water. All chemicals and reagents used were of analytical grade and they were used as received.

3.2.2. Synthesis of FeNi-Chitosan complex pyrolyzed material (FeNi-CCP)

For the synthesis of metal-chitosan complex, with Fe and Ni, a previously reported method was adopted with certain modifications.⁴⁴ Initially 1g (6.2 mmol, based on monomer) chitosan was dissolved in 40 mL of acetic acid solution (1%, w/v) by stirring at room temperature for 12 hours. Transparent viscous solution of chitosan was obtained after this step, to this solution, a mixture 0.752 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.86 mmol of Fe) and 0.542 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.86 mmol of Ni) in 5 mL of distilled water was added dropwise. Then the solution was kept stirring for another 12 hours to form the FeNi–chitosan complex solution. This solution was then slowly poured into 150 mL of acetone to obtain the metal–chitosan complex hydrogel. This hydrogel was then filtered and washed three times with 10 mL of acetone. Subsequently, the filtered hydrogel was dried in a laboratory oven at 60 °C for 12 hours, followed by drying at 100 °C in a vacuum oven for 6 hours. The resulting dried hydrogels were referred to as the FeNi–chitosan complex (FeNi-CC). The FeNi-CC was weighed and placed in a ceramic boat inside a quartz tube for pyrolysis in a tubular furnace. Pyrolysis was performed under nitrogen atmosphere with a flow rate of 30 mL min⁻¹ at 700, 800, and 900 °C for 2 hours, with a ramp rate of 10 °C/min and the resulting material was named FeNi-chitosan complex pyrolyzed material FeNi-CCP-700, FeNi-CCP-800, and FeNi-CCP-900, respectively. The scheme for the synthesis of FeNi-CCP materials is shown in Figure 3.2. The FeNi-CCP catalysts were weighed, ground in a mortar and pestle, and used as such for experiments without any further treatments. To evaluate the activity of the FeNi bimetal system relative to its individual Fe and Ni components, we also synthesized catalysts containing only Fe (Fe-CCP-800) and only Ni (Ni-CCP-800) using the same procedure described above.

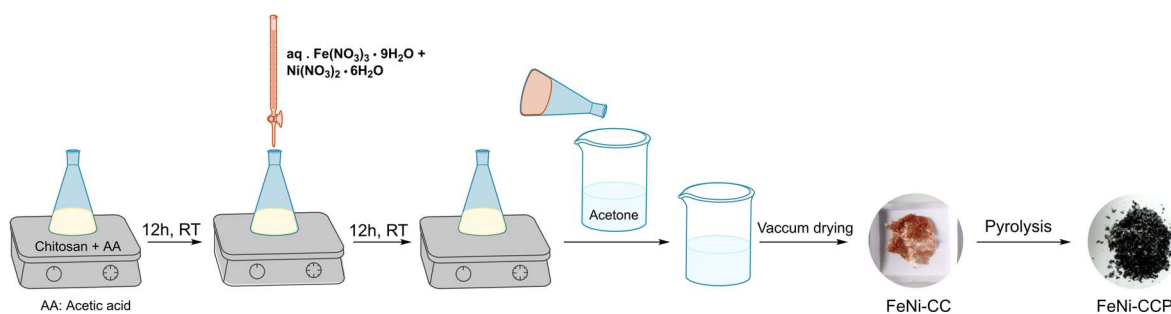


Figure 3.2. Scheme for the synthesis of bimetallic FeNi-CCP catalysts

3.2.3. Synthesis of FeNi bimetallic catalyst on cellulose derived carbon (FeNi-CLC)

For the comparison of the effect of N-doping, a control sample was prepared based on cellulose derived carbon in a similar procedure as that of FeNi-CCP catalyst. For the synthesis of FeNi-CLC material cellulose, 1g was treated with 1% (w/v) acetic acid solution. To the obtained dispersion of cellulose, 0.752 g of Fe(NO₃)₃·9H₂O (1.86 mmol of Fe) and 0.542 g of Ni(NO₃)₂·6H₂O (1.86 mmol of Ni) in 5 mL of distilled water was added dropwise followed by stirring at room temperature for 12 h. Then the solvent was removed using a rotary evaporator, the resulting solid was dried in a vacuum oven at 100 °C. The dried material was then pyrolyzed at 800 °C for 2 hours in a tubular furnace under a nitrogen atmosphere with a flow rate of 30 mL min⁻¹ to obtain the FeNi-CLC-800 material.

3.2.4. Synthesis of FeNi bimetallic catalyst on activated carbon (FeNi/C)

Another control sample was synthesized based on conventional impregnation method on activated carbon, To compare the effect of synthesis method as well as the influence of N-doping. Initially the activated carbon was vacuum dried at 150 °C for 6 hours to remove the adsorbed moisture. 1 g of activated carbon support was immersed in 10 mL of deionized water and kept stirring for 1 hour at room temperature (RT) to get a dispersion. To this 2.17 g of Fe(NO₃)₃·9H₂O (0.3 g of Fe) and 0.25 g of Ni(NO₃)₂·6H₂O (0.05g of Ni) in 5 mL of distilled water was added dropwise to obtain a final loading of 30 wt.% of Fe and 5 wt.% Ni on the carbon support. After the addition of metal precursor, the catalyst slurry was stirred for 12 hours at RT. After this step the water was evaporated using a rotary evaporator at 60 °C and 60 mbar. The powder obtained was then dried in a vacuum oven for 12 hours at 100 °C. The dried catalyst was pyrolyzed under flow of nitrogen (30 mL min⁻¹) in a furnace at 800 °C for 2 hours at a rate of 10 °C min⁻¹ to obtain FeNi/C catalyst.

3.2.5. Characterization of catalysts

The bulk structure and phases of the catalysts were analyzed using X-ray diffraction (XRD) on a Desktop PXRD Miniflex 600 (Rigaku) diffractometer with Ni-filtered monochromatic Cu K α radiation of wavelength 1.5406 Å. The samples were scanned over a 2 θ range of 10 to 80° at a rate of 4°min⁻¹. Nitrogen adsorption isotherms and surface area measurements were carried out using a Quanta chrome BET surface area analyzer. Particle size, shape, lattice parameter, elemental mapping, and high-resolution STEM images were obtained with a JEOL JEM-F200 (URP) transmission electron microscope operating at 200 kV. The electronic state of the elements in the catalyst were identified using XPS analysis on a Thermo K-alpha+ X-ray photoelectron spectrometer with an Al K α source. XPS data were processed with Casa XPS software, and binding energy correction was made using the carbon 1s peak at 284.6 eV. Elemental quantification of Fe and Ni was performed on Agilent 4200 MP-AES system (Microwave Plasma-Atomic Emission Spectroscopy). For the sample preparation, catalysts were microwave digested using concentrated HCl and HNO₃ mixture of ratio 1:6 (v/v).

3.2.6. Experimental details for X-ray Absorption spectroscopy (XAS) studies

To determine chemical state and coordination environment of iron and nickel in the catalysts, The K-edges of Fe (7112 eV) and Ni (8333 eV), X-ray absorption spectra were recorded at Scanning EXAFS Beamline (BL-09) of INDUS-2 Synchrotron Radiation Source, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore. The beamline was equipped with Si(111) based double crystal monochromator for energy selection and meridional cylindrical mirror (Rh/Pt coated) for collimation. The data was collected when the synchrotron source 2.5 GeV ring was operated at 100 mA injection current. XAS measurements were carried out at room temperature in transmission mode. An ion chamber was filled with N₂, He and Ar for Fe and Ni foil and for the samples. The XANES and EXAFS measurements were carried out in the quick-XAS mode which is a continuous scan over the energy or angle range, instead of a conventional step-by-step scan during acquisition of the XAS data. The second crystal of the monochromator was 60% detuned during the data collection to suppress the higher harmonic components. The energy calibration was performed using Fe and Ni metal foil as a reference. The standard normalization and background subtraction procedures were executed using the ATHENA software version 0.9.26 to obtain normalized XANES spectra.⁴⁵ Fourier transformed (FT) of EXAFS oscillations were calculated to observe the $|\chi(R)|$ vs R space spectra.

3.2.7. Electrochemical analysis

3.2.7.1. Catalyst ink preparation

The catalyst ink was prepared by mixing the synthesized catalyst (5 mg) in 1 mL of water-isopropyl alcohol (3:2) solution and 40 μL of 5% Nafion solution. This was further mixed by ultrasonication for about 1 hour. A 10 μL aliquot of the catalyst ink was coated over a glassy carbon electrode (Pine Research Instrument) of area 0.196 cm^2 and dried under an IR-lamp for 1 hour.

3.2.7.2. Evaluation electrochemical OER and ORR activity

The electrochemical performance was analyzed by linear sweep voltammetry (LSV) by utilizing a conventional three electrode system where, catalyst ink coated glassy carbon electrode was used as the working electrode, whereas a graphite rod and Hg/HgO were employed as the counter and reference electrodes, respectively. All the electrochemical analyses were done by using the Pine Research Instrument's rotating disk electrode (RDE) setup connected to a BioLogic SP300 potentiogalvanostat instrument. The linear sweep voltammograms (LSVs) corresponding to ORR were recorded in 0.1 M KOH at the voltage scan rate of 10 mV sec^{-1} under O_2 atmosphere while maintaining the working electrode rotation at 1600 RPM. The OER activity was evaluated in 1 M KOH at a voltage scan rate of 10 mV sec^{-1} under N_2 atmosphere at 1600 RPM. An IR correction of 65% was applied in both the analyses.

3.3. Results and discussion

3.3.1. Catalyst characterization

XRD of FeNi-CCP materials and control samples FeNi-CLC-800 and FeNi/C were performed to understand their bulk structure and phases. Figure 3.3a shows the XRD patterns of FeNi-CCP-800, FeNi-CLC-800, and FeNi/C. In all three catalysts, peaks at 43.7° , 50.9° , and 74.9° were observed, corresponding to the (111), (200), and (220) planes of the FeNi alloy, identified as Taenite syn form of FeNi alloy (PDF2: 00-047-1417). The FeNi alloy phase was the major phase present in all the catalysts. Additionally, the FeNi-CCP-800 catalyst also exhibited peaks corresponding to metallic Fe (44.7° , 65° ; PDF2: 00-006-0696) and the Fe_2O_3 oxide phase (30.1° , 35.4° , 57.1° , 62.6° ; PDF2: 00-04-0755). In contrast, the cellulose-derived catalyst FeNi-CLC-800 contained only FeNi alloy phases. The FeNi/C catalyst showed a higher fraction of the FeO phase (PDF2: 01-075-1550) alongside the FeNi alloy phase, and it also contained metallic Fe and Fe_2O_3 phases. With the increase in the pyrolysis temperature the FeNi-CCP catalysts

showed an increase in the FeNi alloy diffractions (Figure 3.3b). The intensity of metallic Fe and Fe₂O₃ peaks was diminished. This suggests that the crystallinity and phase purity of the FeNi alloy phase increases at higher pyrolysis temperature. Additionally, the alloy peaks shifted towards lower diffraction angles, suggesting lattice expansion of the FeNi alloy structure at higher annealing temperatures. No peaks corresponding to metallic Ni or NiO phases were observed from XRD.

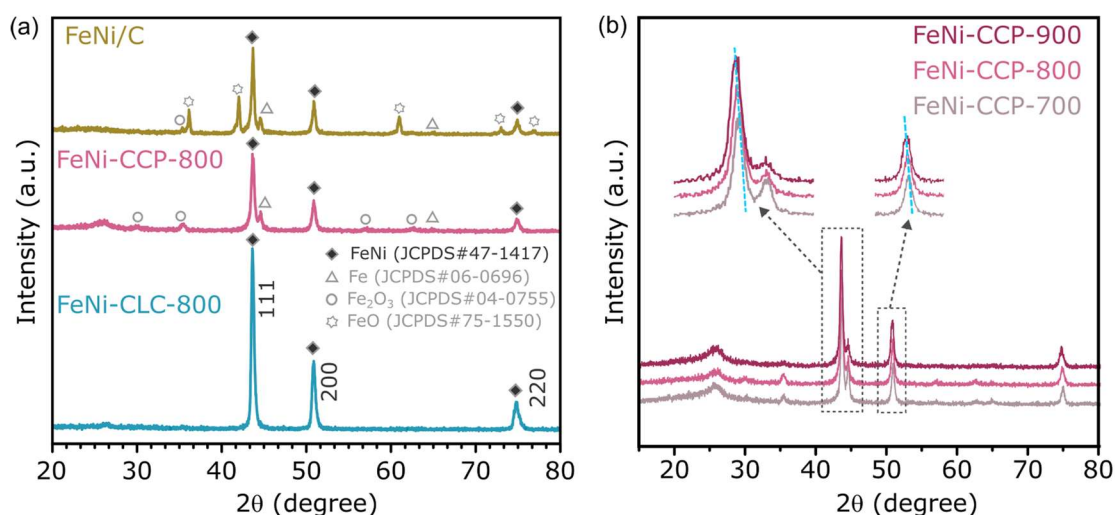


Figure 3.3. (a) XRD pattern of FeNi-CCP-800 and the control samples FeNi-CLC-800 and FeNi/C, (b) XRD pattern of FeNi-CCP catalysts synthesized at different pyrolysis temperatures 700, 800, and 900 °C

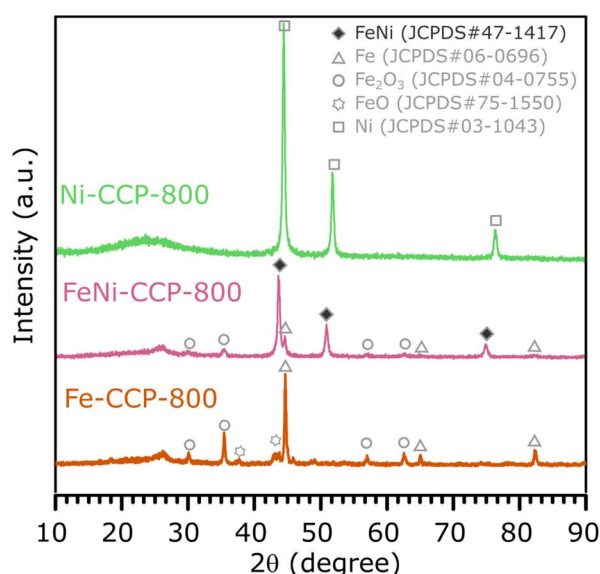


Figure 3.4. XRD pattern for the monometallic Fe-CCP-800 and Ni-CCP-800 catalysts in comparison with FeNi-CCP-800

The XRD pattern for the monometallic Fe-CCP-800 and Ni-CCP-800 catalysts are shown in Figure 3.4. The only Fe containing CCP catalysts showed mix of phases including metallic Fe, Fe_2O_3 , and FeO with higher intensity for metallic Fe. Whereas The only Ni containing CCP catalysts did not show any oxidized phase of Ni and only metallic Ni phase was present in the catalyst.

The particle size distribution of the FeNi-CCP catalysts was determined using high-resolution transmission electron microscopy (HR-TEM) images. Figure 3.5 presents the HR-TEM images and particle size distribution of the FeNi-CCP catalysts. All the catalysts showed the particle present in the carbon layers and some particles were found to be surrounding the carbon shell. The FeNi-CCP-700 catalyst exhibited an average particle size of 34.5 nm with a broad size distribution. In contrast, FeNi-CCP-800 and FeNi-CCP-900 showed smaller average particle sizes of 22.1 nm and 20.5 nm, respectively.

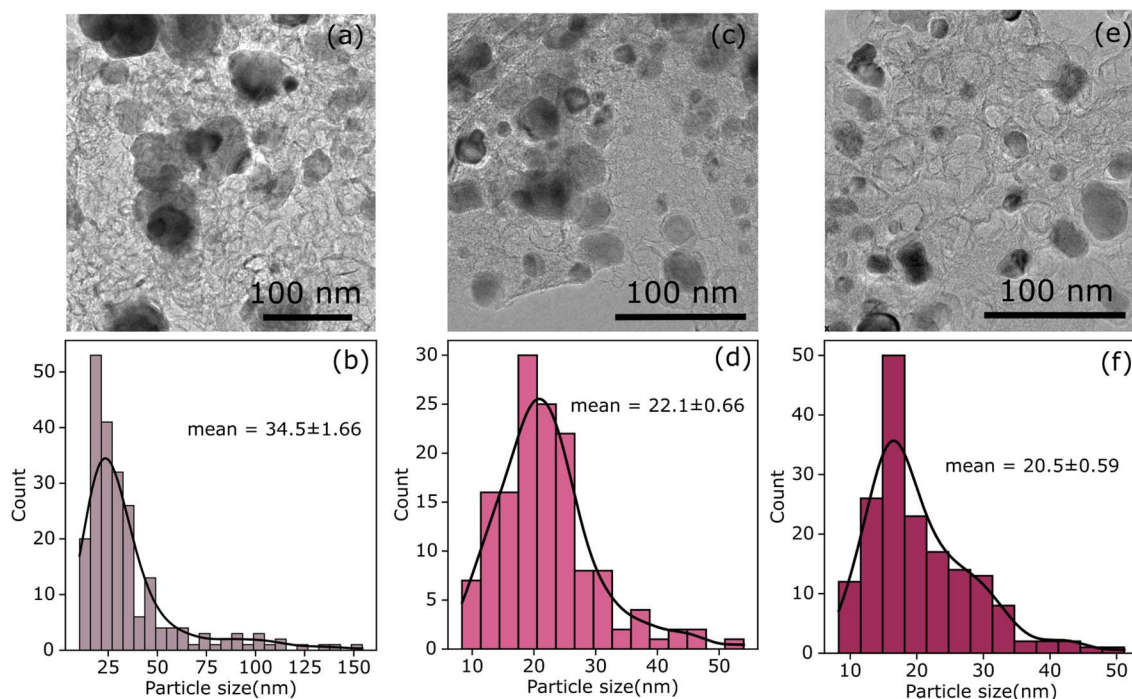


Figure 3.5. HR-TEM image and particle size distribution of (a-b) FeNi-CCP-700, (c-d) FeNi-CCP-800, and (e-f) FeNi-CCP-900 catalysts.

Figure 3.6a shows the lattice fringes observed in FeNi-CCP-800, with 0.34 nm corresponding to the graphitic carbon layers present in the catalyst, 0.2 nm to the (110) metallic Fe lattice spacing, and 0.208 nm and 0.18 nm to the interplanar spacings of the (111) and (200) planes of the FeNi alloy phase, respectively. Figure 3.6b and c display the STEM image of FeNi-CCP-800 and the corresponding line analysis of the elements. Figure 3.6d shows the STEM image, while Figure 3.6(e-k) presents the elemental mapping of Fe, Ni, the FeNi overlay, C, N, O, and

the overlay of all elements. The elemental mapping indicates that Fe and Ni alloy formation occurs in the catalyst, but the lower intensity of the Ni signal suggests a lower amount of Ni compared to Fe in the alloy composition.

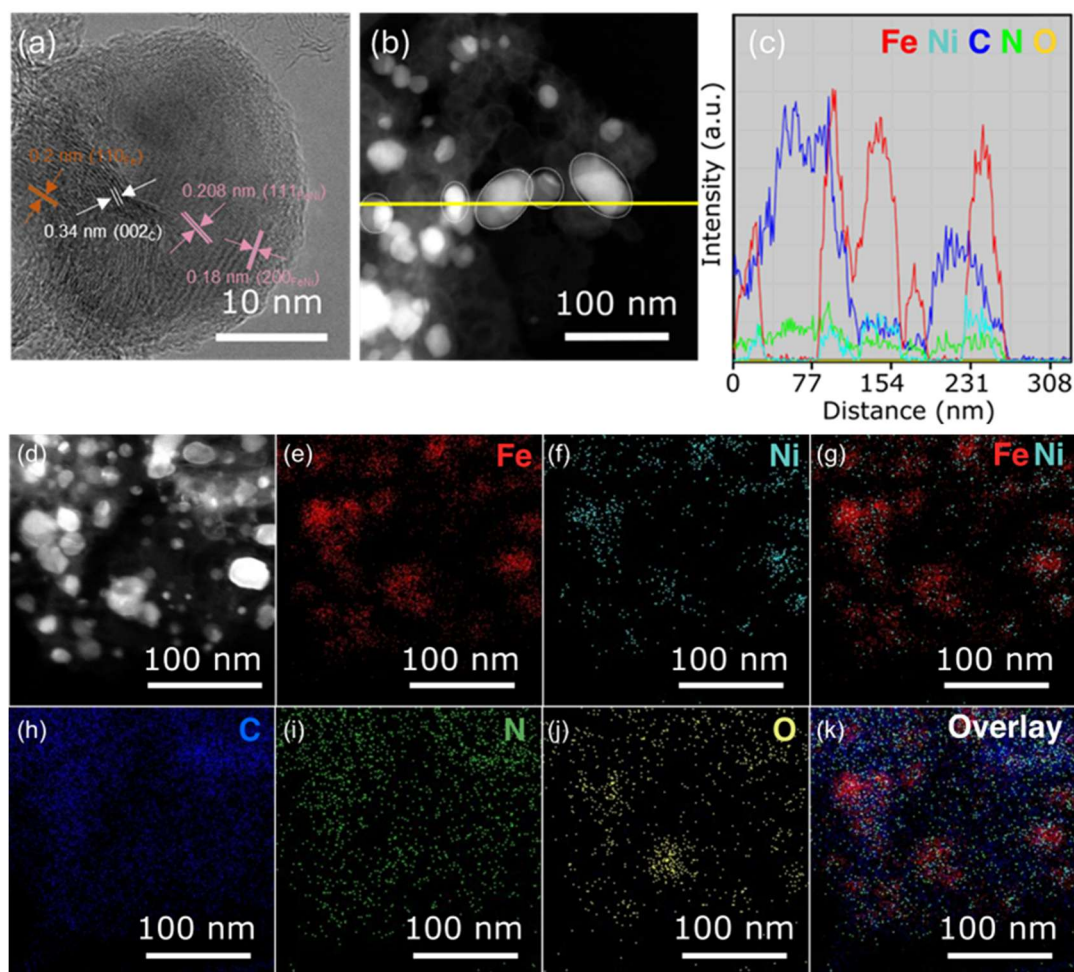


Figure 3.6. (a) HRTEM image of FeNi-CCP-800 showing the lattice fringes, (b) STEM image of FeNi-CCP-800 (yellow line denotes the region of line analysis), (c) line analysis of FeNi-CCP-800, (d-k) STEM images of FeNi-CCP-800 and elemental mapping in the corresponding area for Fe, Ni, FeNi overlay, C, N, O and overlay of all elements.

The control samples FeNi-CLC-800 and FeNi/C displayed particles of large size and particle aggregation were very pronounced in the materials. Figure 3.7a & h represents the HR-TEM images of the catalysts. Figure 3.7(b-g) depicts the STEM image and elemental mapping for C, Fe, Ni, O and overlay corresponding to the STEM image for FeNi-CLC- 800. Figure 3.7(i-n) displays the same for FeNi/C catalyst. TEM data suggests that the FeNi catalyst on chitosan derived, N-containing carbon formed comparatively small particles compared to the normal carbon supported catalyst.

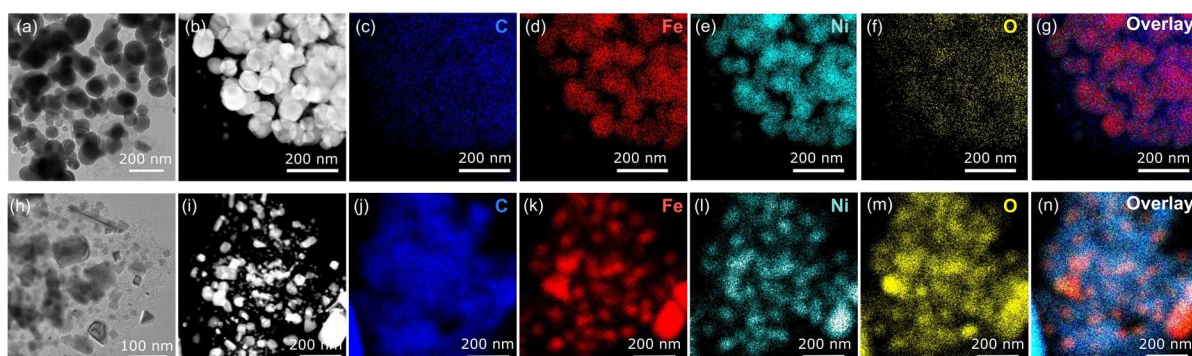


Figure 3.7. HR-TEM image, STEM image and elemental mapping (a-g) for FeNi-CLC-800 and (h-n) FeNi/C.

The nitrogen adsorption of the FeNi-CCP catalysts and the control samples show type II adsorption isotherm with a hysteresis (Figure 3.8a-b). Among the FeNi-CCP catalysts FeNi-CCP-800 showed the highest specific surface area of $303 \text{ m}^2 \text{ g}^{-1}$. Whereas the catalysts annealed at 700 and 900 °C, shows a less surface area of 183, $174 \text{ m}^2 \text{ g}^{-1}$ respectively (Figure 3.8c). The control samples FeNi-CLC-800 and FeNi/C showed surface area of 161 and $694 \text{ m}^2 \text{ g}^{-1}$ respectively.

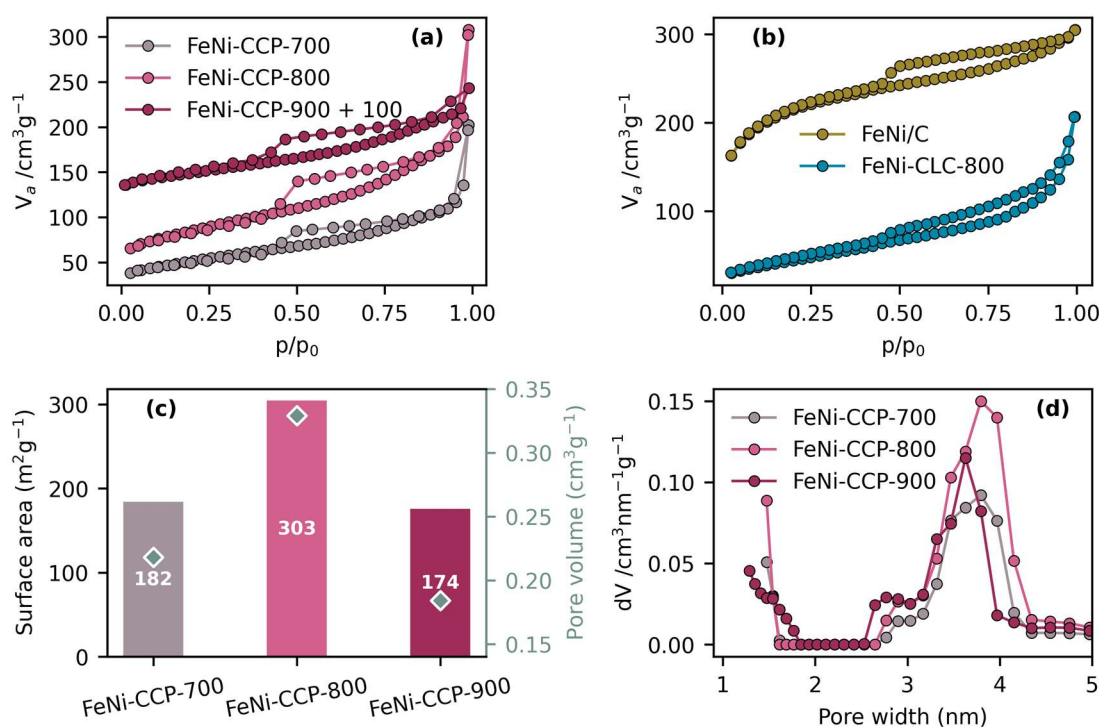


Figure 3.8. (a) N_2 sorption isotherm of FeNi-CCP catalysts (100 unit in the y axis is added in the isotherm for FeNi-CCP-900 catalyst), (b) N_2 sorption isotherm of the control samples FeNi-CLC-800 and FeNi/C, (c) surface area and pore volume of FeNi-CCP catalysts, and (d) pore size distribution of FeNi-CCP catalysts.

It was found from the pore size distribution and the pore volume data that; at lower pyrolysis temperature the material has a smaller number of meso and micropores and with increase in the temperature to 800 °C the pore volume and surface area increases because of the increase in number of pores. Further higher temperature pyrolysis resulted in decrease of the surface area and pore volume, this could be probably due to the higher graphitization leading to the collapse of the smaller pores.^{46,47} The correlation with surface area and pore volume in the FeNi-CCP catalysts are depicted in Figure 3.8c and the pore size distribution data are shown in Figure 3.8d.

3.3.2. Electrochemical OER activity in alkaline medium

The OER performances of FeNi-CCP catalysts and other control samples were measured by a three-electrode system in 1 M KOH electrolyte using Hg/HgO as the reference and graphite rod as the counter electrode. The LSV polarization curve of the catalysts are obtained at a scan rate of 10 mV s⁻¹, all the potential values presented in this work are iR-corrected and data are represented with reference to the RHE. The polarization curves are represented in Figure 3.9a. The FeNi-CCP-800 catalyst shows the lowest potential of 310 mV at 10 mA cm⁻² current density (η_{10}), even better than the commercial RuO₂ (η_{10} = 340 mV). The other CCP catalysts, FeNi-CCP-900 and FeNi-CCP-700, displayed higher overpotentials of 330 and 360 respectively. The η_{10} values for all the catalysts are represented in Figure 3.9b. The OER data illustrates that the FeNi-CCP-800 shows enhanced catalytic properties feasible for OER compared to the other catalysts.

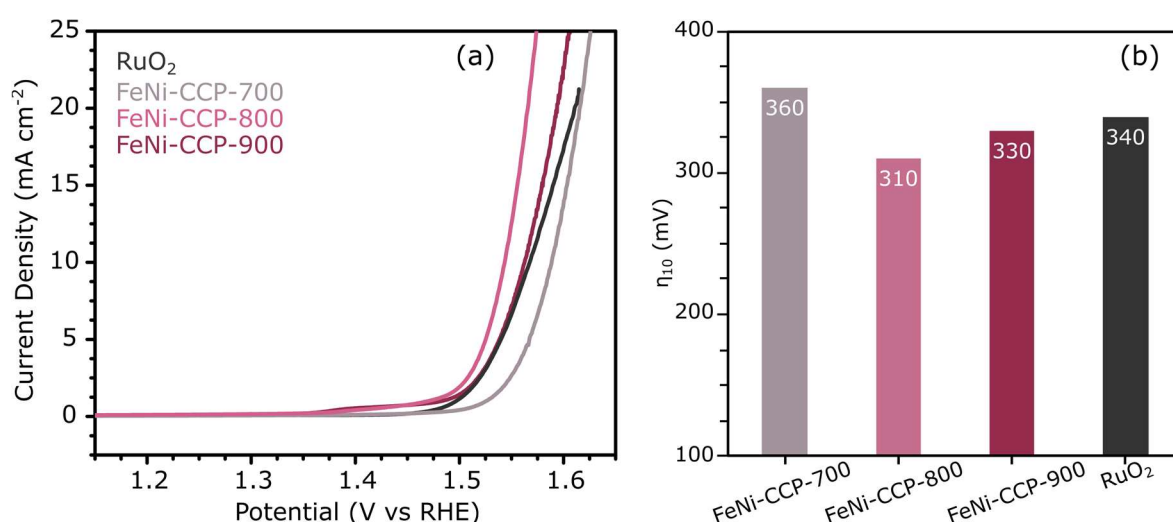


Figure 3.9 (a) OER polarization curves for FeNi-CCP catalysts in comparison to RuO₂, and (b) overpotential at 10 mA cm⁻² for the catalysts.

The OER activity of FeNi-CCP-800 was compared to monometallic Fe-CCP-800 and Ni-CCP-800, as well as to control samples derived from non-nitrogen-containing carbon, FeNi-CLC-

800, and FeNi/C. The LSV for OER activity of the catalysts are given in Figure 3.10a, and the calculated overpotential values are depicted in Figure 3.10b. FeNi-CCP-800 catalysts demonstrated superior activity compared to the control samples. The monometallic CCP catalysts exhibited very poor OER activity, indicating that the FeNi bimetallic combination is essential for catalytic activity. Additionally, the poor performance of FeNi-CLC-800 and FeNi/C suggests that the presence of nitrogen and the synthesis method play a crucial role in enhancing OER performance.

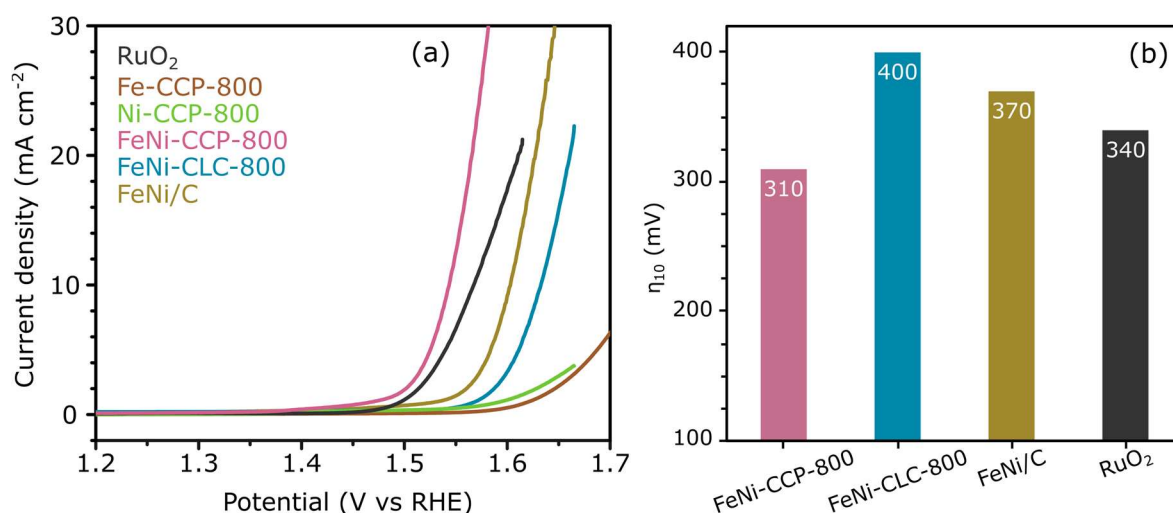


Figure 3.10. (a) OER polarization curves for FeNi-CCP-800 catalyst in comparison to Control samples and RuO₂, and (b) overpotential at 10 mA cm⁻² for the catalysts.

3.3.3. Electrochemical ORR activity in alkaline medium

The electrochemical ORR activity of the catalysts was measured in 0.1M KOH solution using three electrode system using Hg/HgO as the reference and graphite rod as the counter electrode. The ORR activity of the FeNi-CCP catalysts were compared with the commercial 20 wt.% Pt/C catalyst as well as the control samples. It was seen that FeNi-CCP-800 catalyst exhibited better ORR activity in terms of the onset potential, limiting current density (J_L) and half wave potential ($E_{1/2}$), however all the catalytic activity was not comparable to the Pt/C. The ORR performance LSVs are shown in Figure 3.11(a-b) and the ORR activity parameters of the catalysts are tabulated in Table 3.2.

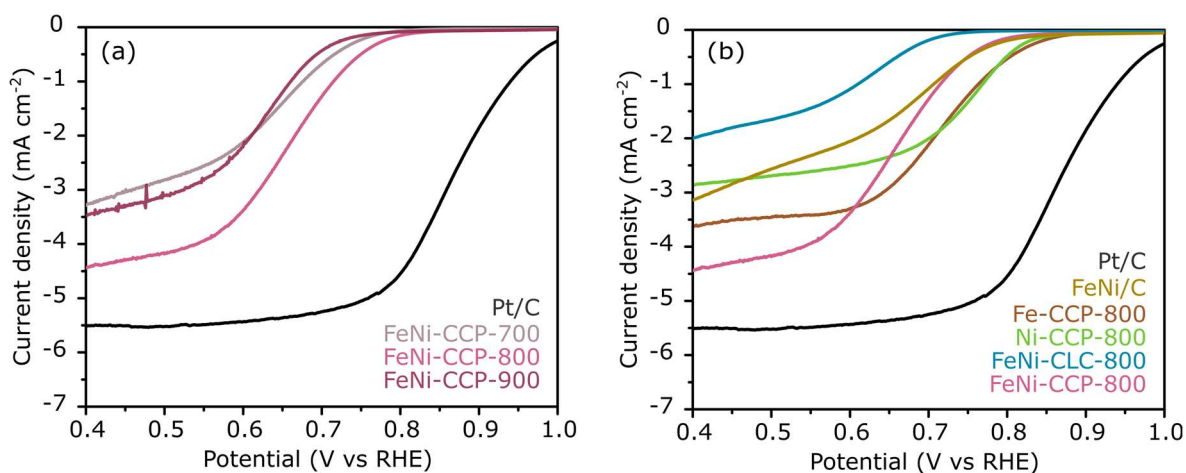


Figure 3.11. (a) ORR LSVs of FeNi-CCP catalysts and Pt/C and (b) ORR LSVs of FeNi-CCP-800 and control samples in comparison to Pt/C.

Table 3.2. ORR performance parameters of FeNi-CCP catalysts and control samples.

Catalyst	Onset potential (V)	E _{1/2} (V)	J _L (mA cm ⁻²)
Pt/C	1.0	0.86	5.5
FeNi-CCP-700	0.83	0.64	3.1
FeNi-CCP-800	0.84	0.67	4.4
FeNi-CCP-900	0.80	0.62	3.4
Fe-CCP-800	0.90	0.72	3.6
Ni-CCP-800	0.87	0.75	2.8
FeNi-CLC-800	0.78	0.61	1.9
FeNi/C	0.86	0.65	3.5

3.3.4. Detailed electronic and structural characterization

The electrochemical analysis revealed that FeNi-CCP-800 exhibits superior OER activity compared to RuO₂; however, its ORR activity was not as significant as expected for FeNi bimetallic systems. To understand the correlation between structure and activity, we conducted a detailed study of the bulk and surface electronic properties of the catalysts. Using XPS, we examined the chemical and electronic states of Fe, Ni, N, and O in the catalysts. The deconvoluted Fe 2p XPS spectra of FeNi-CCP-800 and Fe-CCP-800 catalysts are shown in Figure 3.12a. The Fe-CCP-800 catalyst, which contains only Fe, showed completely oxidized Fe species on the surface, with no Fe⁰ present. In contrast, the FeNi-CCP catalyst exhibited a significant increase in Fe⁰ species (706.7 eV). The intensity of Fe⁰ species increased with higher pyrolysis temperatures, correlating directly with the XRD patterns of the samples (Figure 3.12b). The comparison of Fe 2p XPS spectra with control samples is shown in Figure 3.12c.

The FeNi-CLC-800 control sample also displayed both Fe^0 and Fe^{3+} species. However, the intensity ratio of Fe^0 to Fe^{3+} species was higher in the CLC sample compared to the CCP catalyst, suggesting that surface Fe^0 species were more prevalent in the FeNi-CCP-800 catalyst. No peak shift was observed in the FeNi-CCP samples; however, the control sample, FeNi-CLC-800, showed a shift towards higher binding energy by 0.2 eV. This suggests that the Fe species on the alloy surface in FeNi-CLC-800 are oxidized, even though no bulk iron oxides were detected in the XRD analysis. The FeNi/C sample showed completely oxidized Fe surface species. Fe is typically considered more reactive and more reducible than Ni, Since Fe ($E_0 = -0.44\text{eV}$) has a more negative reduction potential than Ni ($E_0 = -0.25\text{ eV}$), it means Fe^{2+} ions are less stable than Ni^{2+} and will be reduced more readily. Hence, the Fe 2p XPS analysis indicates that the addition of Ni to the Fe-CCP system promotes the formation of metallic Fe surface species in the catalyst. Furthermore, the in-situ synthesis method, rather than conventional impregnation, is crucial for forming these metallic Fe species.

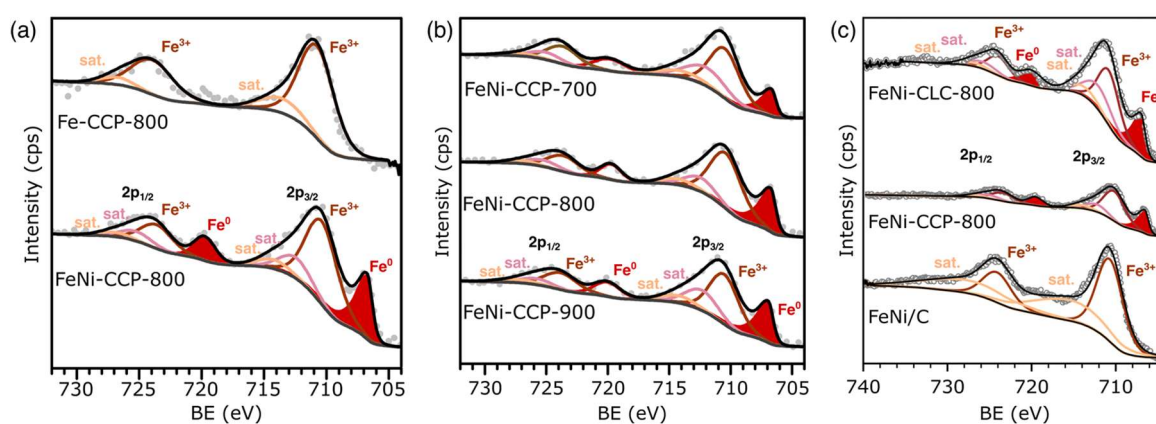


Figure 3.12. Deconvoluted Fe 2p XPS spectra of (a) Fe-CCP-800 and FeNi-CCP-800, (b) all FeNi-CCP catalysts and (c) FeNi-CCP-800 and the control samples FeNi-CLC-800 and FeNi/C.

The Ni 2p XPS spectra of the Ni-CCP-800 and FeNi-CCP-800 shows both Ni^0 as well as Ni^{2+} oxidation states. However, the intensity of Ni^0 species was more in the monometallic CCP catalyst. There was no considerable difference between the CCP catalysts synthesized at different pyrolysis temperatures. The deconvoluted Ni 2p XPS spectra of the Ni-CCP-800 and FeNi-CCP catalysts are represented in Figure 3.13(a-b). FeNi-CLC-800 control sample showed a higher fraction of Ni^0 species compared to FeNi-CCP-800 and FeNi/C. This could be probably due to the higher concentration of Ni in this sample. FeNi/C species showed a much lower intensity of Ni^0 . The Ni 2p XPS spectra of the control samples and FeNi-CCP-800 is shown in Figure 3.13c.

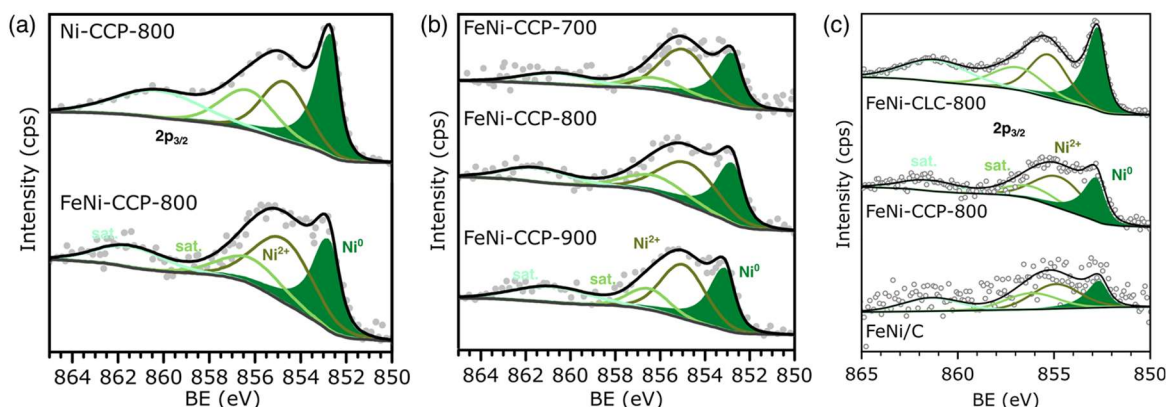


Figure 3.13. Deconvoluted Ni 2p XPS spectra of (a) Ni-CCP-800 and FeNi-CCP-800, (b) all FeNi-CCP catalysts and (c) FeNi-CCP-800 and the control samples FeNi-CLC-800 and FeNi/C.

To investigate the nature of nitrogen species and their interaction with metal the N1s XPS spectra of the samples were recorded. The deconvolution of N1s XPS spectra of the bare carbon material synthesized from chitosan at 800 °C (denoted as NC-800) showed four different species of nitrogen namely Pyridinic (Py-N), Pyrrolic (Pr-N), Graphitic (G-N) and oxidized graphitic nitrogen (O-N) nitrogen functionalities at binding energies 398.16, 400.03, 400.83, and 402.79 eV respectively. Meanwhile in the FeNi-CCP-800 catalyst, along with these N-species, an additional binding energy of 399.14 eV appeared, which can be attributed to the presence of metal nitrogen (denoted as M-N) interaction in the catalyst.^{48,49} Additionally, the binding energy shift to higher energy was observed in the FeNi-CCP catalyst compared to the NC-800 (Figure 3.14a).

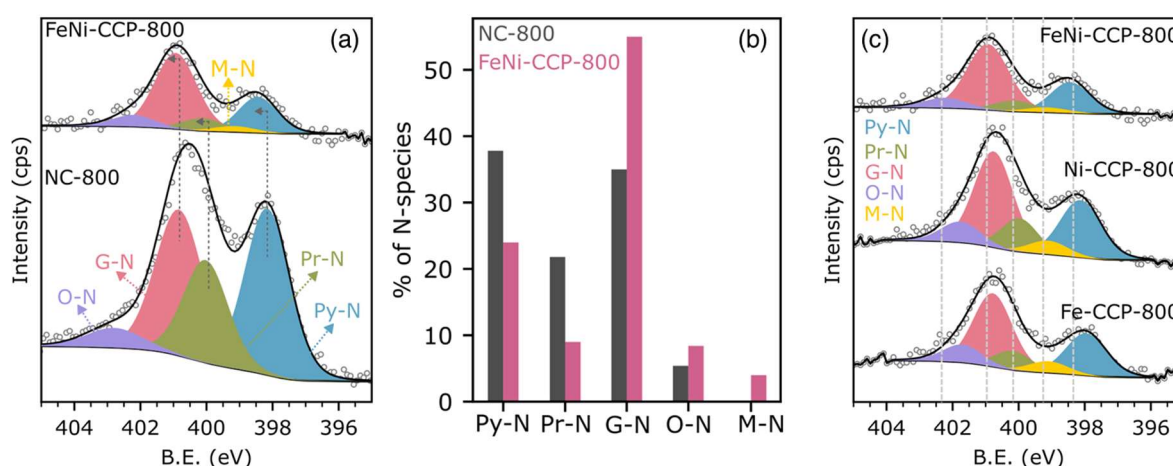


Figure 3.14. (a) N1s XPS spectra of FeNi-CCP-800 and NC-800, (b) quantification of N-species in NC-800 and FeNi-CCP-800, and (c) N1s XPS spectra of mono metallic Ni-CCP-800, Fe-CCP-800 in comparison with FeNi-CCP-800 catalyst.

This indicates that there could be a probable electron transfer from the N-species to the metal in the catalyst and existence of metal-nitrogen interaction. It was interesting to note that the pyridinic and pyrrolic functionalities reduced significantly in the FeNi-CCP-800 catalyst compared to NC-800, at the same time considerable increase in the graphitic nitrogen species was observed in the catalyst, this could be due to the enhanced graphitization of the carbon support in presence of metal.^{12,46} The quantification of the N-species is represented graphically in Figure 3.14b. The comparison of N1s XPS spectra of FeNi-CCP-800 with monometallic catalysts Fe-CCP-800 and Ni-CCP-800 also showed a binding energy shift to the higher energy region, suggesting enhanced electron transfer from the N- species in the carbon support to the metal in the FeNi-CCP-800 catalyst.

The variation in the surface N-species were understood from the N1s XPS spectra of the FeNi-CCP catalysts synthesized at different pyrolysis temperatures (Figure 3.15a). With the increase in the pyrolysis temperature increase in the G-N species were observed and simultaneously the other N-functionalities showed a decrease. A graphical representation of the quantification of the nitrogen species is displayed in Figure 3.15b. From the wide scan of the XPS the surface elemental concentration of nitrogen was calculated. The percentage of nitrogen were 2.2, 1.8, and 1.6% for the samples FeNi-CCP-700, FeNi-CCP-800 and FeNi-CCP-900 respectively.

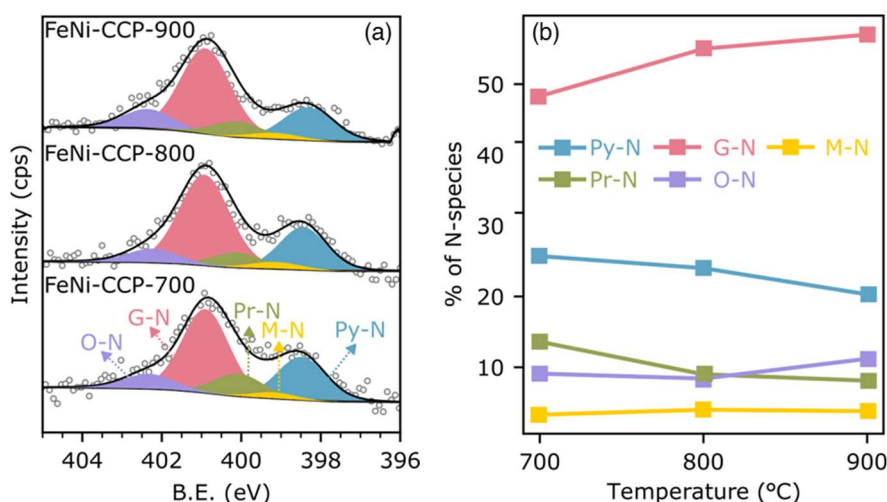


Figure 3.15. (a) Deconvoluted N 1s XPS of FeNi-CCP catalysts pyrolyzed at different temperatures, (b) quantification of surface nitrogen species in FeNi-CCP catalysts with respect to the pyrolysis temperature.

The overall observations from XPS analysis suggested that the FeNi alloy formation moreover the existence of surface Fe^0 and Ni^0 species happened effectively in the CCP and CLC catalysts due to the pyrolysis process of polysaccharides chitosan and cellulose, where the in situ

reduction is highly favorable compared to normal activated carbon support. However, the CLC catalyst showed more oxidized Fe and Ni surface species whereas in the CCP catalyst the surface oxidation was comparatively low. The presence of surface nitrogen induced electron transfer to the metals and aided the surface Fe and Ni to be in reduced state, which could be one probable reason for the higher activity of the FeNi-CCP-800 catalyst.

The bulk electronic and chemical state of the catalysts were probed by X-ray absorption spectroscopy (XAS) of the Fe and Ni K-edge using synchrotron radiation source. The normalized absorbance in the XANES region for the Fe K-edge of the catalysts and reference samples are shown in Figure 3.16a and b. The absorption edge of the FeNi-CCP catalysts lies near to the Fe foil implies that Fe was in the zero oxidation state in all the FeNi-CCP catalysts. However, the near edge and post edge absorbance features were different from both Fe foil and Fe_2O_3 suggesting possibility of different local environment. The monometallic Fe-CCP-800 catalyst showed an absorption edge situated between Fe foil and Fe_2O_3 , indicating average positive valence for the Fe species. The near edge was close to Fe foil and exhibited different post edge features. This could be due to the existence of oxide phases of Fe with metallic Fe in the bulk.

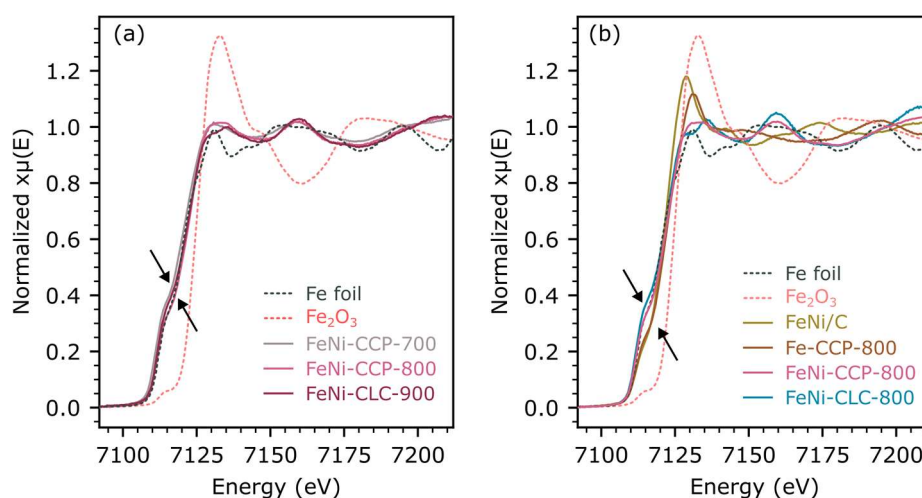


Figure 3.16. (a) Normalized absorbance in the XANES region for Fe K-edge for different FeNi-CCP catalysts and the reference samples Fe foil and Fe_2O_3 . (b) Normalized absorbance for Fe K-edge in the XANES region of FeNi-CCP-800 in comparison with Fe-CCP-800, FeNi-CLC-800, FeNi/C, and reference samples.

This observation matches with XRD analysis of Fe-CCP-800 as well as the XPS. FeNi-CLC-800 control sample showed similar features to that of FeNi-CCP-800 suggesting that the FeNi alloy formation in both catalysts, however near edge feature was slightly different and the post edge features were almost similar. FeNi/C catalyst also exhibited an absorption energy in

between Fe foil and oxide suggesting the existence of average positive valence of Fe. This ample also showed very distinct near and post edge features suggesting that the Fe existed in different forms in the catalyst, which was also evident from the XRD analysis.

Fourier transformation of the EXAFS region was performed to see the local environment in the materials. Figure 3.17a and b show the FT-EXAFS of the Fe K-edge for the FeNi-CCP-800 catalyst and control samples along with reference Fe foil and Fe_2O_3 . The main peak for Fe in the first coordination sphere appeared at 2.17 Å. The FeNi-CCP-800 sample, and other control samples also displayed a peak at a similar position suggesting the presence of metallic Fe in the samples. Neither FeNi-CCP-800 nor the control samples FeNi-CLC-800 and FeNi/C displayed any features similar to Fe_2O_3 . A clear distinction in the scattering was observed in the secondary coordination sphere between Fe foil and the FeNi catalysts, all the three systems displayed similar secondary scattering features (3-5 Å region, marked with dotted rectangle), suggesting the formation of FeNi alloy phase. The secondary features of Fe-CCP-800 were similar to Fe foil and Fe_2O_3 , which confirmed the secondary features in FeNi catalysts are due to the presence of Ni.

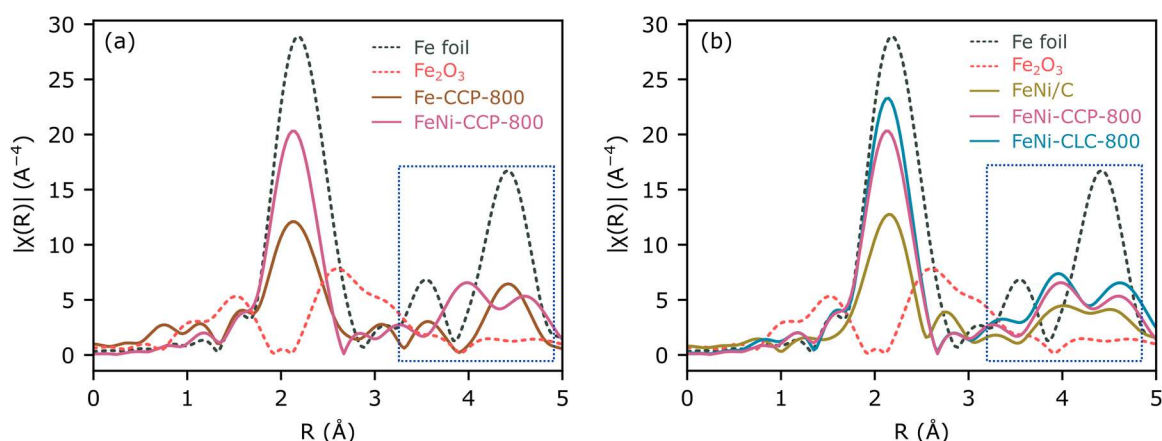


Figure 3.17. (a) FT-EXAFS of Fe K-edge for FeNi-CCP-800 and Fe-CCP-800 along with references, (b) FT-EXAFS of Fe K-edge for FeNi-CCP-800 and the control samples FeNi-CLC-800 and FeNi/C along with references.

The normalized absorbance in the XANES region of the Ni K-edge for the FeNi-CCP catalysts are shown in Figure 3.18a. All the CCP catalysts show absorption edge near to metallic Ni and the near and post edge features were also like the Ni foil. All the control samples also showed features like Ni foil. These observations suggest that Ni was present in the metallic form in the materials and no features of NiO were observed, which was in line with the XRD data.

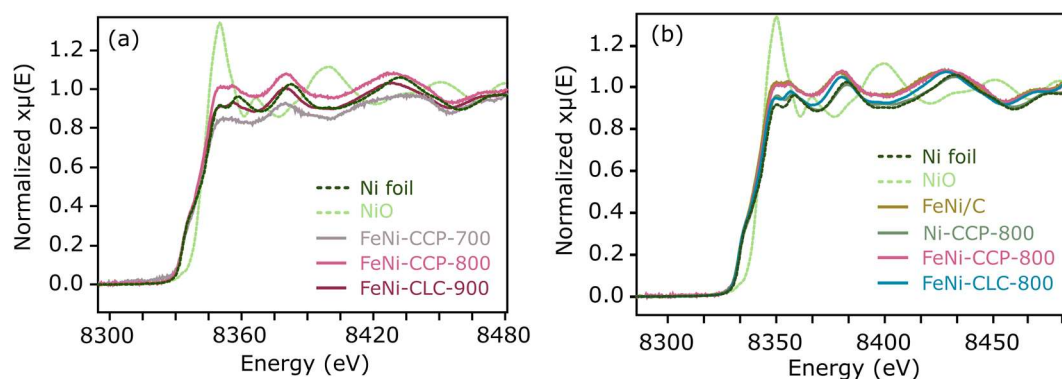


Figure 3.18. (a) Normalized absorbance in the Ni K-edge XANES region for different FeNi-CCP catalysts and the reference samples Fe foil and Fe_2O_3 . (b) Normalized absorbance for Ni K-edge in the XANES region of FeNi-CCP-800 along with Ni-CCP-800, FeNi-CLC-800, FeNi/C, and reference samples.

The FT-EXAFS of the Ni K-edge in the R-space for the FeNi-CCP-800 and the monometallic Ni-CCP-800 catalyst is shown in Figure 3.19a. The spectra of both the samples showed similar features as Ni foil and were different from NiO, which again confirmed the existence of Ni in the metallic form as seen from XANES and suggesting that in the FeNi-CCP catalyst Ni must be alloyed with Fe, since no separate phase of Ni was observed from XRD.

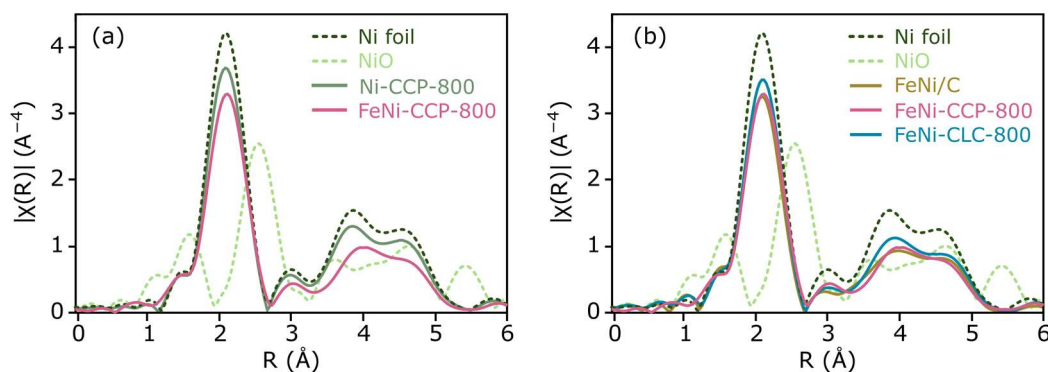


Figure 3.19. (a) FT-EXAFS of Ni K-edge for FeNi-CCP-800 and Ni-CCP-800 along with references, (b) FT-EXAFS of Fe K-edge for FeNi-CCP-800 and the control samples FeNi-CLC-800 and FeNi/C along with references.

The FT-EXAFS for control samples and FeNi-CCP-800 are given in Figure 3.19b. All the control samples and FeNi-CCP-800 showed similar features as that of Ni-foil and no match was seen with the NiO standard. Hence it is clear that in all the CCP catalysts and the control sample Ni existed in metallic state. Overall, the XAS data confirms that in the bulk of FeNi-CCP catalyst Fe and Ni exist in the metallic state and the major phase present is the FeNi alloy.

The nominal Fe and Ni loadings in CCP catalysts and control samples, quantified using MP-AES, are shown in Table 3.3. In the FeNi-CCP catalyst, the Ni loading was found to be six times lower than Fe, despite planning for equal amounts of both metals. This discrepancy is likely due to competitive adsorption during chitosan-metal complexation, with non-interacting metal ions being lost to the acetone bath during precipitation. Lower Ni content was also evident from TEM elemental and line profile analysis. The cellulose-derived FeNi-CLC material, which avoids the precipitation step, maintained the Fe and Ni ratio in the final catalyst. The FeNi/C catalyst was synthesized based on the observed Fe and Ni loading for the FeNi-CCP-800 catalyst, yielding values close to theoretical loading. For a fair comparison of the activities, the cellulose-derived FeNi-CLC-800 material was synthesized again using the Fe and Ni loading values same as that of FeNi-CCP-800, and this sample, labeled FeNi-CLC-800R, showed comparable metal loading to the FeNi-CCP-800 catalyst.

Table 3.3. Quantification of Fe and Ni loading from MP-AES analysis.

Catalyst	Fe (wt%)	Ni (wt%)
FeNi-CCP-700	28.4	5
FeNi-CCP-800	32.9	6.9
FeNi-CCP-900	24.6	8.4
FeNi/C	27	4.4
FeNi-CLC-800	39.7	42.5
FeNi-CLC-800R	28.9	4.3

The OER and ORR activity of the FeNi-CLC-800R catalyst was evaluated and compared with the FeNi-CCP-800 catalyst. A considerable increase in the activity of the sample was observed for the OER ($\eta_{10} = 344$ mV) from the FeNi-CLC-800 ($\eta_{10} = 400$ mV) material, however the activity was less than that of the best performing FeNi-CCP-800 catalyst ($\eta_{10} = 310$ mV). There was no considerable change in the ORR activity of the material. The OER and ORR LSV of the FeNi-CLC-800R are shown in Figure 3.20a and b along with FeNi-CCP-800 and FeNi-CLC-800. The XRD of the FeNi-CLC-800R was carried out to identify the Fe and Ni phases present. The diffraction patterns observed correspond to the FeNi alloy phase as seen for the FeNi-CLC-800. The XRD pattern for the same is shown in Figure 3.21. The HR-TEM images of the catalyst showed change in morphology compared to the FeNi-CLC-800 sample and the average particle size obtained was 56 nm, and the particles exhibited a broad size distribution (Figure 3.21b). shows the HRTEM image and size distribution of the particle in FeNi-CLC-800R control sample. The surface area calculated for the catalyst was $204 \text{ m}^2 \text{ g}^{-1}$, which was higher than the

FeNi-CLC-800. These changes in the catalyst properties could be a probable reason for activity enhancement observed for FeNi-CLC-800R sample.

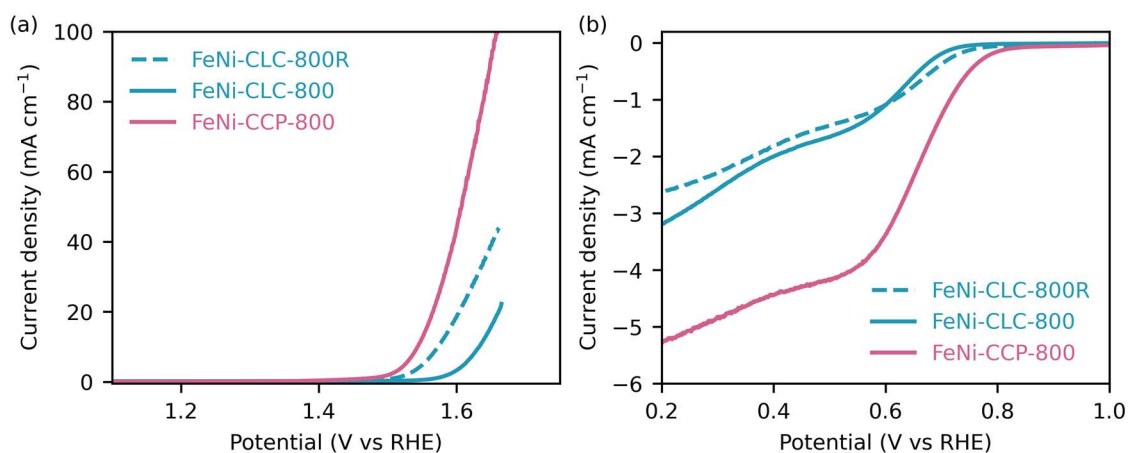


Figure 3.20. (a) LSVs of FeNi-CLC-800R, FeNi-CLC-800 and FeNi-CCP-800 for (a) OER and (b) ORR activity.

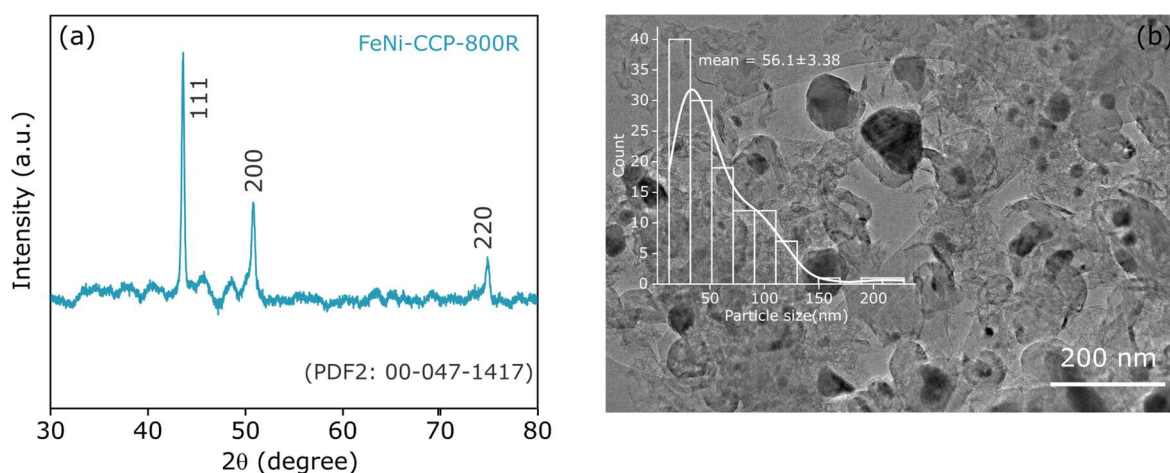


Figure 3.21. (a) The XRD pattern and (b) HR-TEM image with particle size distribution of the FeNi-CLC-800R catalyst.

3.3.5. Electrochemical OER kinetics and stability of the catalyst

The details of the kinetics and mechanistic aspects of the OER, Tafel slopes were also obtained from the small polarization area in the LSV. For the Tafel slope calculation the current densities at specific potentials were calculated, and the linear portion was fitted to the Tafel equation; $\eta = b \log j + a$, where η represents overpotential, j denotes current density, and b represents the Tafel constant. The Tafel slope of FeNi-CCP-800 was about 73 mV dec⁻¹, much smaller than that of RuO₂ catalyst (130 mV dec⁻¹). The Tafel slope obtained for the other catalysts FeNi-CCP-900, FeNi-CCP-700, FeNi-CLC-800, FeNi/C, Fe-CCP-800, and Ni-CCP-800 were 80, 75,

77, 86, 108, and 120 mV dec^{-1} , respectively. The Tafel plots for the catalysts are shown in Figure 3.22a and b. The Tafel slopes obtained for the catalysts (130 to 73 mV dec^{-1}) typically indicates that the rate-determining step involves the transfer of one electron, during the initial step of OER where OH^- ion is adsorbed onto the catalyst surface and loses an electron to form the OH^* intermediate.^{50,51} The lowest Tafel slope of FeNi-CCP-800 implies active electron transfer kinetics compared to other catalysts.

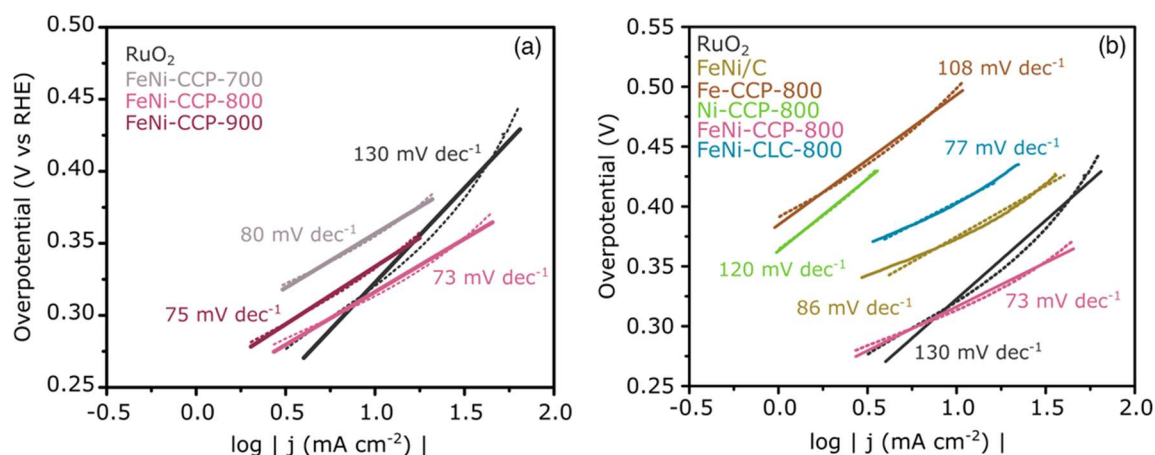


Figure 3.22. Tafel plots showing the Tafel slope values for (a) FeNi-CCP catalysts and RuO_2 and (b) FeNi-CCP-800 catalyst and control samples Fe-CCP-800, Ni-CCP-800, FeNi-CLC-800, and FeNi/C.

The electrochemically active surface area (ECSA) values were also examined to find out the accessible active site density of the various catalysts. For platinum-free systems, double-layer capacitance (C_{dl}) in the non-faradaic region is a reasonable parameter to measure the ECSA. The plots for current density vs the scan rate in the non-faradaic region of the cyclic voltammograms of the catalysts are displayed in Figure 3.23a and b. The obtained results showed the higher C_{dl} values for FeNi-CCP-800 as compared to the of the control samples FeNi-CLC-800 and other FeNi-CCP catalysts. The calculated C_{dl} values and ECSA are listed in Table 3.4.

Table 3.4. List of C_{dl} and ECSA values calculated from the cyclic voltammetry of the FeNi-CCP catalysts and control samples.

Catalyst	C_{dl} (mF)	ECSA (cm^2)
FeNi-CCP-700	3.1	0.08
FeNi-CCP-800	3.5	0.09
FeNi-CCP-900	3.0	0.07
FeNi-CLC-800	0.7	0.02

FeNi/C	8.1	0.20
Ni-CCP-800	1.1	0.03
Fe-CCP-800	6.4	0.16

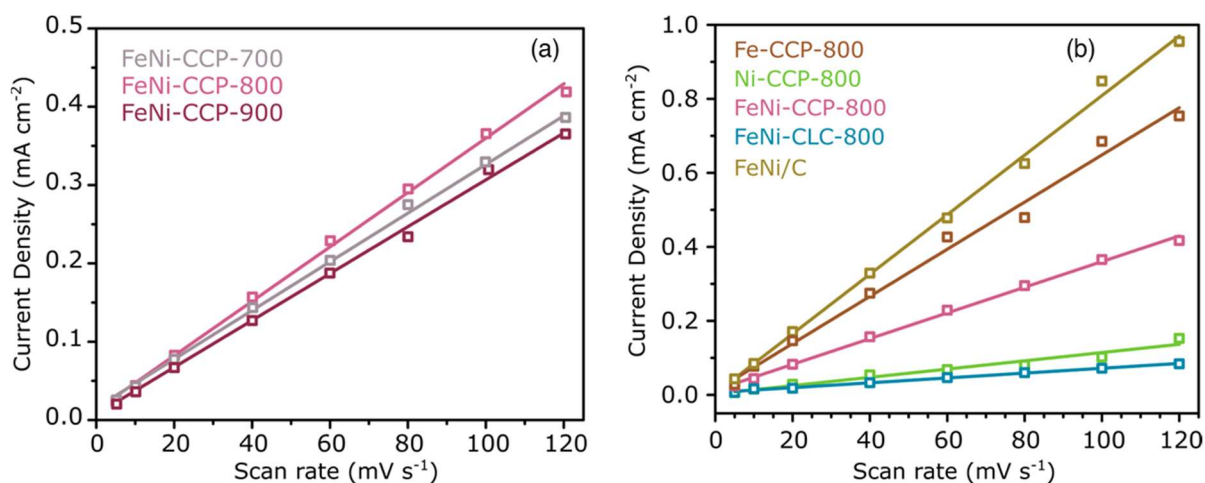


Figure 3.23. The plots for current density vs the scan rate in the non-faradaic region of the cyclic voltammograms of (a) FeNi-CCP catalysts and (b) FeNi-CCP-800 and the control samples Fe-CCP-800, Ni-CCP-800, FeNi-CLC-800, and FeNi/C.

The accelerated durability test (ADT) for the catalyst FeNi-CCP-800 towards OER was conducted to evaluate the surface structure stability. The potential at 10 mA cm^{-2} showed a difference of only 0.036 V after 5000 cycles, which indicated that the structural integrity of the catalyst is maintained during the OER under alkaline condition. LSV of the catalyst FeNi-CCP-800 before and after 5000 cycles during the ADT is given in Figure 3.24.

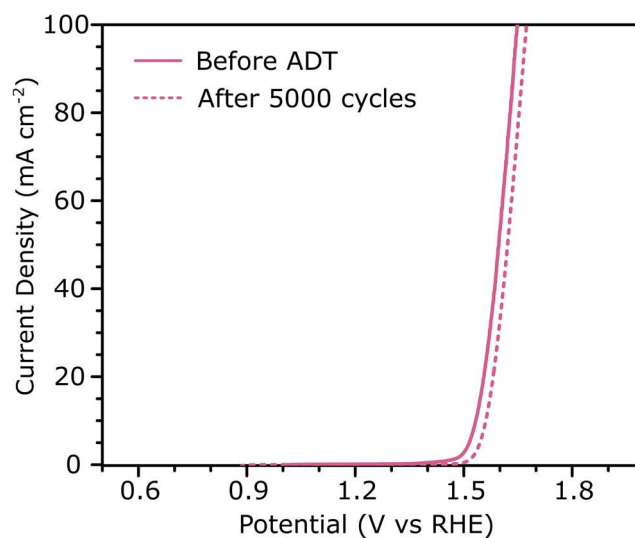


Figure 3.24. LSV of the catalyst FeNi-CCP-800 before and after 5000 cycles during the ADT.

3.3.6. Post OER characterization of the catalyst

The HR-TEM images of the spent catalysts and the elemental mapping are displayed in Figure 3.25(a-d). The images show similar morphology for both fresh and spent catalysts, only a slight increase in the particle size was observed for the spent catalyst (average particle size 23.9 ± 0.62 nm). The elemental mapping also showed similar distribution of elements in the spent catalyst. These observations suggest that the catalyst retains structural integrity during the OER.

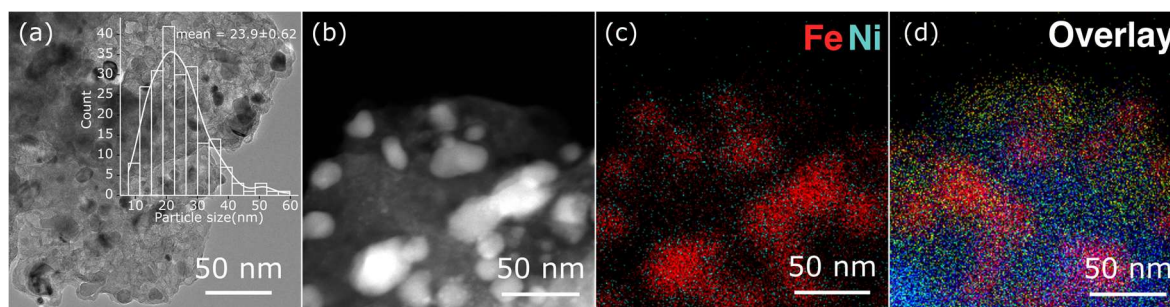


Figure 3.25. (a) HR-TEM image and particle size distribution, (b) STEM image, (c) elemental mapping for Fe and Ni in the corresponding area, and (d) overlay of elements of the FeNi-CCP-800 catalyst after the ADT for OER.

AES analysis of the electrolyte solution after the stability test showed no presence of Fe or Ni, which implied that there is no leaching of the metal during the reaction. The fresh and spent electrode after ADT was followed by XPS to identify the changes in the surface chemical structure of the catalyst. The Ni 2p and Fe 2p XPS spectra of the samples are shown in Figure 3.26. The spectra looked similar, and no significant change was seen. These results confirm that the FeNi-CCP-800 catalyst is durable and consistently performs well under the reaction conditions.

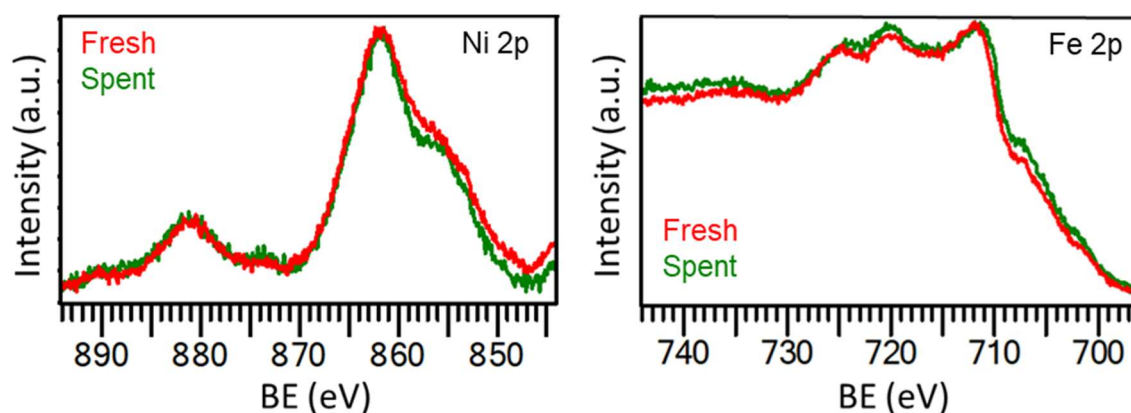


Figure 3.26. Ni 2p and Fe 2p XPS spectra of the fresh and spent electrodes after the ADT.

The deconvoluted N 1s XPS spectra of the fresh and spent electrodes are shown in Figure 3.27. After the reaction, the graphitic and pyridinic N species decreased and with a significant increase in the pyrrolic N species. These results indicate that surface N-species underwent modification during the reaction and the pyrrolic nitrogen species could be the desirable form of nitrogen to enhance the OER reaction and to stabilize the metal species or intermediates formed on the surface of the catalyst.

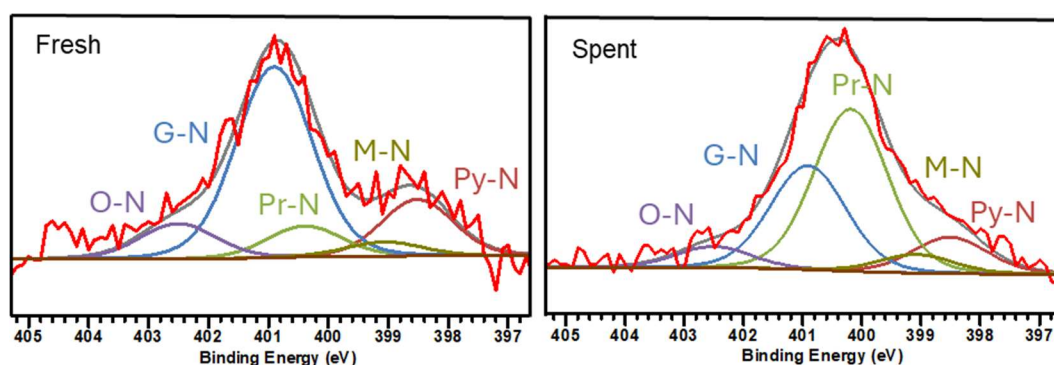


Figure 3.27. N1s XPS spectra of the fresh and spent electrodes after the stability test.

3.4. Conclusion

In this work, bimetallic FeNi-CCP catalyst was synthesized by the pyrolysis of FeNi-chitosan complex at temperature of 800°C. The FeNi-CCP-800 catalyst showed remarkable lower over potential compared to the control samples as well as commercial RuO₂ towards OER in alkaline medium. The effect of nitrogen doping is studied by varying the pyrolysis temperature and by comparing the activity with non-nitrogen containing carbon catalysts. However, the catalyst did not show comparable performance to that of Pt/C in ORR. The XRD and XAS analysis of the catalyst showed the formation of FeNi alloy as the major phase in the catalyst. The presence of N aided the formation of smaller particles in the CCP catalyst compared to the control samples. The XPS analysis revealed that in the absence of N-doping the surface of the alloy species shows more oxidized species of Fe and in the presence of N and Ni the Fe species become electronically rich and aid the formation of stable surface alloy species. We anticipate that the surface stabilization of FeNi alloy by nitrogen species caused the enhanced OER activity of the catalyst. The future prospects of this work could focus on improving the ORR activity of the catalyst and making the catalysts bifunctional for both OER and ORR and to be used in applications such as metal air batteries.

3.5. References

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4. The effect of nitrogen doping in ruthenium supported carbon catalyst and its activity towards Levulinic acid hydrogenation

4.1. Introduction

Fossil fuels have long been the major source for both fuel and chemical synthesis, powering industries and transportation worldwide. However, the rapid depletion of these non-renewable reserves poses significant challenges. The extensive use of fossil fuels contributes heavily to global warming due to the emission of greenhouse gases, particularly CO₂, which traps heat in the atmosphere and leads to climate change and environmental pollution. The global CO₂ emission has reached its highest in April 2024 to the value of 426.57 ppm, which has contributed almost 1.6°C rise in the temperature.¹ This alarming scenario underscores the need for clean and renewable alternatives for fossil fuel. The present scientific research indicates that transitioning from conventional fuels to electricity can significantly reduce emissions.^{2,3} However, despite progress in the energy sector, chemical processes are still essential to meet material demands. In this scenario, biomass stands out as a carbon neutral, sustainable, cheap and renewable alternative.⁴ Biomass-derived chemicals and fuels can replace those traditionally sourced from fossil fuels, helping to mitigate environmental impacts and create a more resilient and eco-friendly energy system. The thermo catalytic conversion of plant derived lignocellulosic biomass to value added chemicals has been a major area of scientific research for the last two decades.⁵⁻⁷ Through catalytic processes, biomass is usually converted into intermediates known as platform compounds, which are then used for the downstream synthesis of energy fuels and fine chemicals.⁸⁻¹²

Levulinic acid (LA) or 4-oxopentanoic acid is one such top platform chemical that can be obtained from lignocellulosic biomass. LA can be further converted to various useful chemicals and biofuels.¹³⁻¹⁵ The catalytic hydrogenation of LA produces gamma valerolactone (GVL) which is considered as a potential precursor for various fine chemicals and fuels. GVL is utilized as a green solvent in reactions due to its high boiling point, stability in air and water, and low flammability risk.¹⁶ It has also been successfully used as a fuel additive in gasoline and diesel.¹⁷⁻²⁰ Hydrogenation products of GVL, such as 2-methyltetrahydrofuran, can blend with gasoline at concentrations up to 70%.²¹ Additionally, GVL can be converted into valeric acid or its esters,

serving as potential fuel precursors.²² Methylpentenoate and GVL esters are promising intermediates for polymer synthesis.^{23,24} The potential transformation of GVL to fuels and chemicals is shown in Figure 4.1.

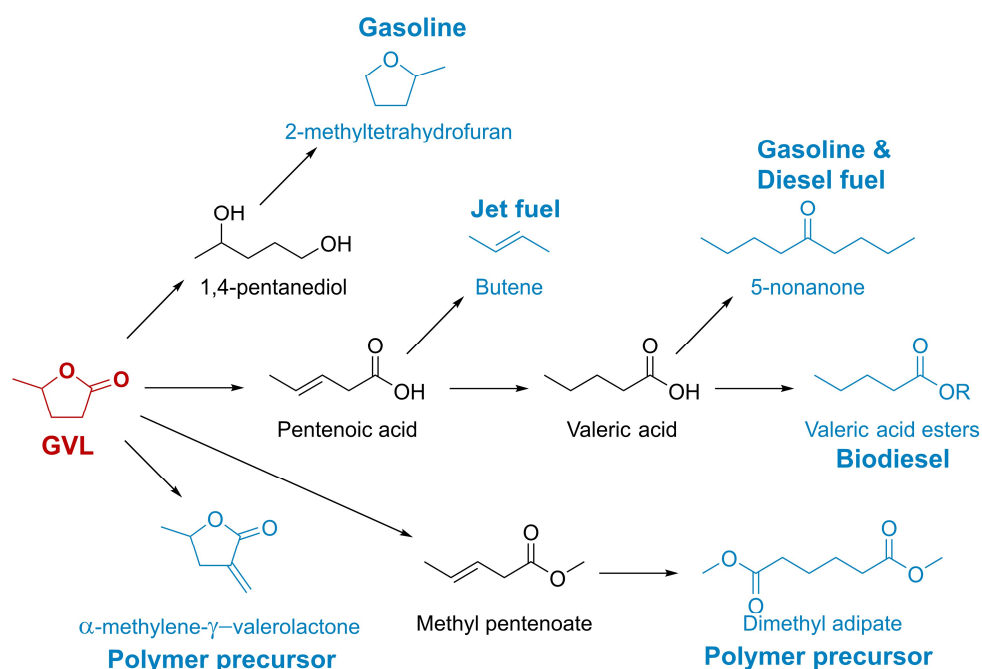


Figure 4.1. Transformation of GVL to fuels and chemicals

The extensive applications of GVL have led to studies focused on its production from biomass-derived LA. LA is obtained by dehydrating C6-sugars, which are produced through the hydrolysis of cellulose. Additionally, LA can be derived from furfural and furfuryl alcohol, which come from xylose produced through the hydrolysis of hemicellulose.²⁵ The possibility of production of LA from both cellulose and hemicellulose enhances the economic viability of GVL production. Typically, LA is hydrogenated using either heterogeneous^{25–27} or homogeneous²⁸ catalysts to produce GVL. This process uses molecular hydrogen or other hydrogen-donor molecules²⁹ such as formic acid or isopropanol as the hydrogen source. Due to the advantages in product separation and catalyst recyclability, heterogeneous catalysts, particularly supported metal catalysts, are preferred over homogeneous catalysts. Various supported metal catalysts, including both noble and non-noble metals such as Pt, Pd, Rh, Re, Ru, Ni, Co, Cu, Fe, and Zr, and their combinations, have been utilized. These metals are supported on materials like carbon, SiO₂, TiO₂, Al₂O₃, ZrO₂, and zeolites. Among these, Ru-based catalysts, especially those on carbon supports, demonstrate efficient and selective hydrogenation of the carbonyl group in LA to form GVL.^{25,30,31} Comparative studies of activated carbon-supported noble metal catalysts for LA hydrogenation revealed that the 5% Ru/C catalyst achieves higher LA conversion and GVL selectivity.^{32–34} These reactions were

tested in various solvents in which 1,4-dioxane showed highest selectivity for GVL.³⁴ However, reaction in water medium is preferred because of the environmental concerns. Ru catalysts on different supports (TiO_2 , SiO_2 , and Al_2O_3) were also evaluated, and carbon-supported Ru again outperformed others.³⁵ The higher activity of Ru/C was attributed to the high dispersion of ruthenium particles on the high surface area carbon support. However, the Ru/C catalyst exhibited a significant drop in the activity during recycling, even in the second catalytic run.^{32,35} It was found that catalyst deactivation can be caused by ruthenium leaching, particle aggregation at higher temperatures, or the adsorption or deposition of products and byproducts on the catalyst surface.^{36,37} A primary reason for leaching or particle aggregation is the inert nature and hydrophobic surface properties of the carbon support, which result in a weak metal-support interaction in the supported metal catalyst.

To enhance metal-support interaction and increase the stability of carbon-supported catalysts, various strategies have been employed. One common approach is surface functionalization or heteroatom doping to modify the surface and electronic properties of carbon materials. Several studies have shown that modified carbon-supported ruthenium catalysts significantly improve stability and enable reactions under milder conditions compared to commercial Ru/C catalyst. The details of some important studies on ruthenium-based carbon supported catalysts are given in Table 4.1. The use of cocatalysts, such as acid resins, allows reactions with Ru/C catalysts to occur under milder conditions and with a lower substrate-to-metal molar ratio.³⁵ Choline chloride has proven effective as a promoter by preventing carbonyl group adsorption and enhancing acyl group adsorption on the catalyst surface.³⁸ The acid functionalization of ordered mesoporous carbon material with H_3PO_4 was showing improved conversion of LA under mild reaction conditions compared to the untreated carbon. However, the GVL selectivity was decreased due to the formation of 2-methyl furan and pentanoic acid.³⁹ Carbon materials based on graphene and graphene oxide have shown effectiveness in converting LA at low temperatures, although higher H_2 pressure is required.^{40,41} Zirconia-supported ruthenium catalyst embedded in a carbon matrix remains stable under highly acidic conditions.⁴²

Catalyst systems based on N-doped carbon supports have demonstrated superior activity, enabling reactions at ambient temperatures and reduced hydrogen pressures with low ruthenium loading.^{43–46} The presence of specific nitrogen (notably pyridinic and graphitic) functionalities on the carbon support was found to be enhancing the electron enrichment of ruthenium and thereby boosting the catalyst's hydrogenation ability. To improve the metal support interaction

Table 4.1. Various ruthenium-based carbon catalysts reported in literature for Levulinic acid hydrogenation.

Catalyst	Support/ Precursor/ Template	Reaction condition	Solvent	S/M ^a	X _{LA} ^b (%)	S _{GV} ^c (%)	Ref.
5Ru/C	Activated carbon	130 °C, 2.6 h, 12 bar H ₂	Water	359	99.5	86.6	34
			Methanol		99	85.3	
			1,4-Dioxane		98.8	97.7	
5Ru/C + A70 ^d	Activated carbon	70 °C, 3 h, 5 bar H ₂	Water	1	98	99.9	35
5Ru/C + ChCl ^e	Activated carbon	150 °C, 2.5 h, 50 bar H ₂	Neat	348	100	100	38
1Ru/OMC 1Ru/OMC-P ^f	Resorcinol + Formaldehyde + Pluronic F127	70 °C, 9 h, 7 bar H ₂	Water	1000	65 99	98 93	39
2Ru/RGO ^g	Graphene oxide (Hummer's method)	40 °C, 2 h, 40 bar H ₂	Water	1450	100	99.9	40
2Ru/FLG ^h	Thermal exfoliation of graphite oxide	20 °C, 12 h, 40 bar H ₂	Water	4400	99	100	41
0.85Ru/ZrO ₂ @C	ZrCl ₄ + Terephthalic acid + Acetic acid	140 °C, 2 h, 10 bar H ₂	Water	1000	97	96	42
3Ru/HPNC ^j	Dopamine + 1,3,5-trimethylbenzene + NH ₃ + Pluronic F127	100 °C, 2.5 h, 25 bar H ₂	Water	1654	99	99	43
3Ru/NHPC ^k	Cellulose + (NH ₄) ₂ C ₂ O ₄ + NaHCO ₃	50 °C, 3 h, 10 bar H ₂	Water	337	99	99	44
1.6Ru/PNC-I ^l	Azobis(isobutyronitrile) + Acrylonitrile	30 °C, 3.5 h, 10 bar H ₂	Water	310	97.8	99	45
1Ru/N-CS ^m	3-aminophenol + Formaldehyde + NH ₃	70 °C, 1 h, 40 bar H ₂	Water	2500	99	99	46
3Ru/TiO ₂ @CN	NH ₂ MIL 125 (MOF)	30 °C, 13 h, 60 bar H ₂	Water	3610	100	100	47
5Ru-NOMC ⁿ	SBA-15 + Glucosamine hydrochloride	120 °C, 4 h, 13 bar H ₂	Methanol	34.8	100	100	48
8.3Ru@CN	Tannic acid + gC ₃ N ₄ + Tris ^o + Dopamine	100 °C, 1.5 h, 20 bar H ₂	Water	524	100	99.5	49

^aS/M: mole ratio of LA to Ru, ^bX_{LA}: LA conversion, ^cS_{GV}: GVL selectivity, ^dA70: Amberlist 70, ^eChCl: Choline chloride, ^fOMC-P: Ordered mesoporous carbon functionalized with phosphoric acid, ^gRGO: Reduced graphene oxide, ^hFLG: Few layered graphene, ⁱOMC: Ordered mesoporous carbon, ^jHPNC: Hierarchical porous N-doped carbon, ^kNHPC: N-doped hierarchically porous carbon, ^lPNC: Pyridinic-N-doped carbon, ^mN-CS: nitrogen-doped nanoporous carbon spheres, ⁿNOMC: N-doped ordered mesoporous carbon, ^oTris: Tris(hydroxymethyl)aminomethane.

and to prevent the leaching and sintering of ruthenium from the catalyst, embedding strategies were adopted along with N-doping.^{48,49} For instance, ruthenium nanoparticle embedded on ordered mesoporous carbon was synthesized by Wei et. al., where they annealed the SBA-15 impregnated with Ru precursor followed by N-precursor, Glucosamine hydrochloride.⁴⁸ This embedding strategy was effective compared to conventional impregnation method due to higher stability of ruthenium nanoparticles. Recently Guan et al., have adopted a similar strategy, where the synthesized Ru-embedded N-doped carbon nanosheets, which were found to be highly stable and showed an increased activity during the recycle studies.⁴⁹

While N-doped carbon support catalysts offer excellent performance and recyclability, their synthesis often relies on non-renewable and expensive nitrogen-containing chemicals and involves tedious, multi-step processes. Likewise, the carbon support obtained from biomass materials also require additional N-containing reagents and templates to incorporate nitrogen and to tune the pore size respectively.^{44,48} Building on this literature background, the objectives of this work were established to synthesize nitrogen-containing carbon supports from biomass-derived chitosan without using any additional reagents or templates, through pyrolysis. The ruthenium-supported catalyst was synthesized using a wet impregnation strategy on the N-containing carbon materials synthesized at various pyrolysis temperatures. Additionally, inspired by literature on Ru-embedding strategies, Ru catalysts were prepared by pyrolyzing a Ru-chitosan complex to compare their LA hydrogenation activity. For comparison, a ruthenium catalyst supported on activated carbon was also prepared. The overall aim of this work is to study how nitrogen doping, and various synthesis methods impact the performance of carbon-supported ruthenium catalysts for LA hydrogenation to GVL.

4.2. Experimental section

4.2.1. Materials and reagents

Low-molecular-weight chitosan (product code: 448869) and Levulinic acid (98%) were obtained from Sigma-Aldrich. Activated charcoal (pharma grade, product code: 0269000500) and glacial acetic acid and 99% acetone were purchased from Loba Chemie. Ruthenium(III) nitrosyl nitrate solution ($\text{Ru}(\text{NO})(\text{NO}_3)_3$, 1.5% w/v) and γ -valerolactone (98%) were obtained from Alfa Aesar. All solutions for this work were prepared with deionized water. All chemicals and reagents were used as received.

4.2.2. Synthesis of Ru(1)/C catalyst

For the synthesis of 1 wt.% Ru on activated carbon support (Ru(1)/C), wetness impregnation

method was used. Initially the activated carbon was vacuum dried at 150 °C for 6 hours to remove the adsorbed moisture. 1 g of activated carbon support was immersed in 10 mL of deionized water and kept stirring for 1 hour at room temperature (RT). To this 0.667 mL (0.01 g of Ru) of 1.5% (w/v) $\text{Ru(NO)(NO}_3)_3$ solution was added dropwise to obtain a final loading of 1 wt.% on the carbon support. After the addition of metal precursor, the catalyst slurry was stirred for 16 hours at RT. After this step the water was evaporated using a rotary evaporator at 60 °C and 60 mbar. The powder obtained was then dried in a vacuum oven for 12 hours at 150 °C. The dried catalyst was reduced under flow of hydrogen (16 mL min^{-1}) in a furnace at 400 °C for 2 hours. The temperature was increased at a rate of $2.2 \text{ }^\circ\text{C min}^{-1}$. A schematic representation of the catalyst synthesis process is presented in Figure 4.2.

4.2.3. Synthesis of Ru(1)/NC catalyst

For the synthesis of 1 wt. % Ru on nitrogen doped carbon (Ru(1)/NC) the carbon support used was obtained from pyrolysis of chitosan. For the synthesis of nitrogen containing carbon (NC), chitosan was pyrolyzed at temperatures of 500, 600 and 700 °C in a tubular furnace fitted with a quartz tube under the flow of nitrogen (30 mL min^{-1}). The temperature was increased at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ and held for 2 hours. The N-containing carbon material obtained after the pyrolysis of chitosan at 500, 600 and 700 °C was termed NC500, NC600, and NC700 respectively. For the impregnation of 1 wt.% ruthenium the wetness impregnation method was used as described earlier and same reduction procedure was performed to obtain the final catalyst.

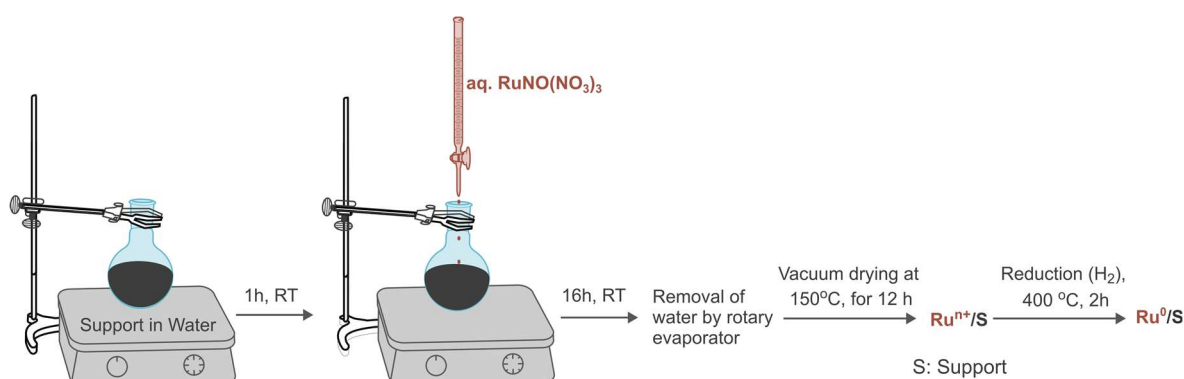


Figure 4.2. Schematic representation for the synthesis of Ru(1)/C and Ru(1)/NC catalyst.

4.2.4. Synthesis of Ru(1)-CCP catalyst

Ru-CCP catalyst was prepared by following the ruthenium chitosan complex pyrolysis process mentioned in chapter 2 (section 2.2.2). To obtain the final ruthenium loading of 1 wt. %, 0.2 mL (0.003 g of Ru) 0.167 mL (0.0025 g of Ru) , and 0.133 mL (0.002 g of Ru) of 1.5 % (w/v)

$\text{Ru}(\text{NO})(\text{NO}_3)_3$ solution was used in synthesizing chitosan-metal complex pyrolyzed at 500, 600 and 700 °C respectively. The required metal amount was estimated on the basis of the mass of carbon materials obtained from chitosan during its pyrolysis at the mentioned temperatures. After the synthesis of Ru-CCP materials, they were subjected to a reduction treatment at 400 °C under hydrogen flow as mentioned earlier in the case of Ru/C and Ru/NC catalysts.

4.2.5. Catalyst characterisation

The electronic state of the elements in the catalyst were identified using XPS analysis on a Thermo K-alpha+ X-ray photoelectron spectrometer with an Aluminum $\text{K}\alpha$ source. XPS data were processed with Casa XPS software, and binding energy corrections were made using the carbon 1s peak at 284.6 eV. Nitrogen adsorption isotherms were recorded using a Quantachrome Quadrasorb *SI* instrument and surface area was determined BET equation. Particle size, shape, lattice parameter analysis, elemental mapping, and high-resolution STEM images were obtained with a JEOL JEM-F200 (URP) transmission electron microscope operating at 200 kV. Bulk structural information of the catalysts was analyzed using X-ray diffraction (XRD) on a desktop PXRD Miniflex 600 (Rigaku) diffractometer with Ni-filtered monochromatic Cu $\text{K}\alpha$ radiation of wavelength 1.5406 Å. The samples were scanned over a 2θ range of 10 to 90° at a rate of 4°/min. NH_3 and CO_2 temperature programmed desorption (TPD) experiments were conducted to gain insight into the acidic and basic sites in the catalysts using Microtrac BELCAT II instrument. For the NH_3 -TPD analysis, initially, catalyst was activated at 250 °C for 1 hour at a heating rate of 5 °C min^{-1} in helium flow of 30 mL min^{-1} . Then the temperature was decreased to 100 °C and the samples were exposed to 10% NH_3 (flow rate 50 mL min^{-1}) in He for 30 minutes and followed by He flush for another for 15 minutes at 100 °C to remove all the physisorbed NH_3 . The desorption of chemisorbed NH_3 was done in helium flow by increasing the temperature from 100 to 700 °C at the rate of 10 °C min^{-1} . The desorbed species at different temperatures were detected by the TCD. For the CO_2 TPD experiments the activation of the catalyst was done at 250 °C for 1 hour then the temperature was reduced to 50 °C. Catalyst was exposed to 20% CO_2 in He for 30 minutes and then flushed with He (50 mL min^{-1}) for another 15 minutes to remove the physisorbed CO_2 . The desorption of chemisorbed CO_2 was carried out in helium flow by increasing the temperature from 100 to 700 °C at the rate of 10 °C min^{-1} . The desorbed species at different temperatures were detected by the TCD. Elemental analysis for ruthenium was performed on Agilent 4200 MP-AES system (Microwave Plasma-Atomic Emission Spectroscopy). For the sample preparation, catalysts were microwave digested using concentrated HCl and HNO_3 mixture of ratio 1:6.

4.2.6. Levulinic acid hydrogenation reaction

4.2.6.1. Catalytic runs

The hydrogenation reaction of Levulinic acid (LA) was carried out in a 50 mL Amar equipment high pressure autoclave reactor. In a typical reaction, the reactor was charged with 5 mmol (0.5805 g) of LA, 0.05 g of catalyst ($\frac{n_{LA}}{n_{Ru}} = 1000$) in 30 mL of water. The reactor was purged with N₂ gas 3-4 times to remove the air. After the nitrogen purge, the reactor was heated under slow stirring of 180 rpm until it reached the desired reaction temperature. After attaining the reaction temperature, the reactor was pressurized with 10 bars of hydrogen and the stirring was increased to 900 rpm and this time was counted as the starting time of the reaction. After the reaction was completed at desired time, the reactor was cooled down to room temperature and the pressure was released.

4.2.6.2. Analysis of the reaction mixture

The reaction mixture was centrifuged to separate the catalyst and liquid. The liquid was then filtered using a 0.22 µm PTFE syringe filter and it was analyzed using High Performance Liquid Chromatography (HPLC). An Agilent 1260 infinity HPLC system was equipped with a Rezex ROA-organic acid H⁺ column (length: 300 mm, Inner diameter: 7.8 mm, particle size: 8µm) and refractive index detector (RID). 0.005 M H₂SO₄ was used as the mobile phase with a flow rate of 0.6 mL min⁻¹. The column temperature was maintained at 30 °C and RID cell temperature was kept at 35 °C.

4.2.6.3. Calculations

Known concentration of LA and GVL standards were prepared and injected in HPLC, and a calibration curve was obtained from the plot of, the area under the peak vs concentration for both LA and GVL. The concentration and the number of moles of LA and GVL in the reaction mixture was calculated from the calibration curve. The conversion of LA (X_{LA}), yield of GVL (Y_{GVL}), selectivity of GVL (S_{GVL}) and turn over frequency (TOF) were calculated using the following formulas.

$$X_{LA} = \left(100 - \frac{n_{LA_{remaining}}}{n_{LA_{taken}}}\right) \times 100\%$$

$$Y_{GVL} = \frac{n_{GVL_{formed}}}{n_{LA_{taken}}} \times 100 \%$$

$$S_{\text{GVL}} = \frac{Y_{\text{GVL}}}{X_{\text{LA}}} \times 100 \%$$

$$\text{TOF} = \frac{n_{\text{GVL}_{\text{formed}}}}{n_{\text{Ru}} \times \text{reaction time}}$$

4.3. Results and discussions

4.3.1. LA hydrogenation using Ru(1)/C and reaction optimization

Initially the Ru(1)/C was tested for LA hydrogenation using 10 bar molecular hydrogen in water medium. The reaction temperature and time were optimized using the same catalyst. At 100 °C the selectivity of GVL obtained was the highest (92.9%) with a conversion of 54.1 % of LA. By increasing the temperature, the GVL selectivity, and the reaction mass balance (MB) decreased, hence 100 °C was chosen as the optimized temperature to do further reactions. The results of temperature optimization are shown in Figure 4.3. At 100 °C temperature the reaction time course was studied, in 3 hours 97.6 % of LA conversion was observed with 89% of GVL yield. The time course of the reaction is displayed in Figure 4.4. Further the substrate concentration was varied by keeping the catalyst amount same at the optimized temperature and time (Figure 4.5). A decrease in the conversion and yield was observed when 10 mmol of LA was used and thus, LA amount of 5mmol was used to study further reactions. At the optimized reaction condition of 100 °C, 3 hours with S/M ratio of 1000, the Ru (1)/C catalyst showed 97.6 % of LA conversion and 89.1 % of GVL yield with a selectivity of 91.3 %.

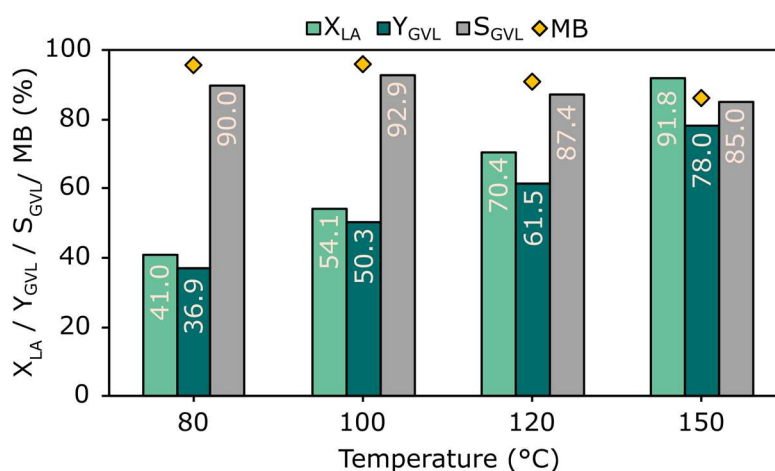


Figure 4.3. LA hydrogenation at different temperatures (Reaction conditions: LA (5 mmol), Ru(1)/C (0.05 g), Water (30 mL), 0.5 h, 10 bar H₂).

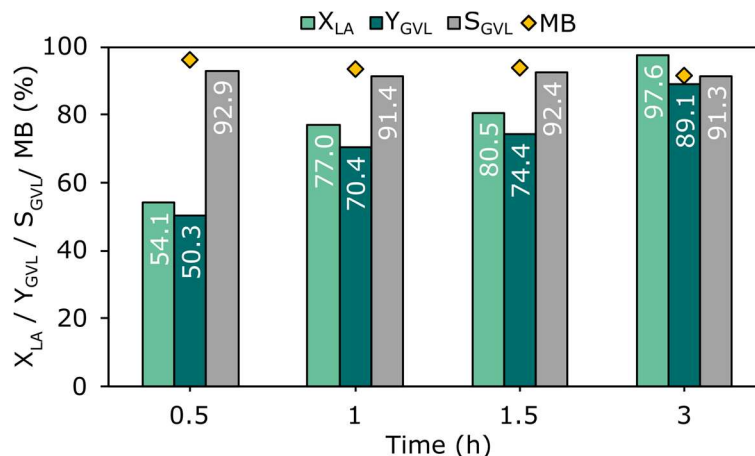


Figure 4.4. Optimization of reaction time (Reaction conditions: LA (5 mmol), Ru(1)/C (0.05 g), Water (30 mL), 100 °C, 10 bar H₂).

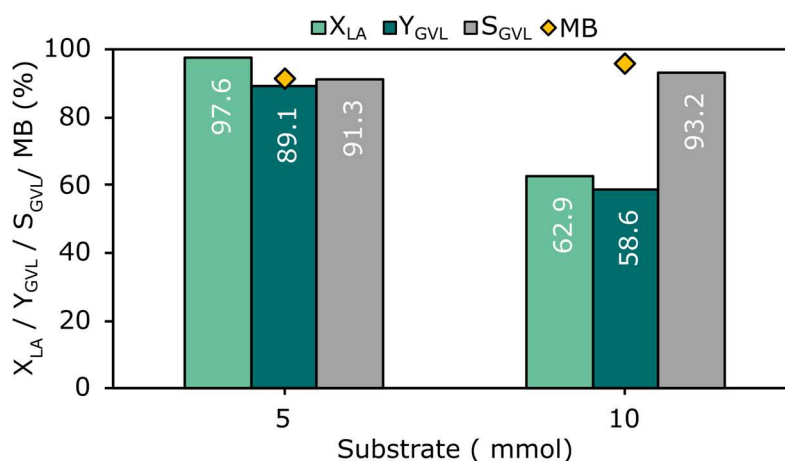


Figure 4.5. Effect of substrate concentration (Reaction conditions: Ru(1)/C (0.05 g), Water (30 mL), 100 °C, 3 h, 10 bar H₂).

4.3.2. Chitosan derived N-containing carbon supported Ru catalysts for LA hydrogenation

4.3.2.1. LA hydrogenation using Ru(1)/NC catalyst

Nitrogen containing carbon (NC) synthesized by the pyrolysis of chitosan at different temperatures were used as support to make Ru(1)/NC catalysts. These catalysts were then used for the hydrogenation of LA. The Ru(1)/NC catalysts synthesized from NC material at different pyrolysis temperatures were screened at reaction conditions of 100 °C, 10 bar H₂, using 5 mmol of LA and 0.05 g of catalyst in 30 mL water. The result of catalyst screening is shown in Figure 4.6.

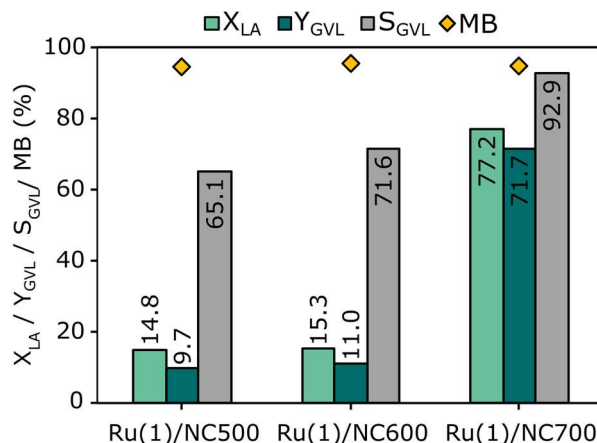


Figure 4.6. LA hydrogenation activity of Ru(1)/NC catalyst on NC support synthesized at different pyrolysis temperature (Reaction conditions: LA (5 mmol), catalyst (0.05 g), Water (30 mL), 100 °C, 1 h, 10 bar H₂).

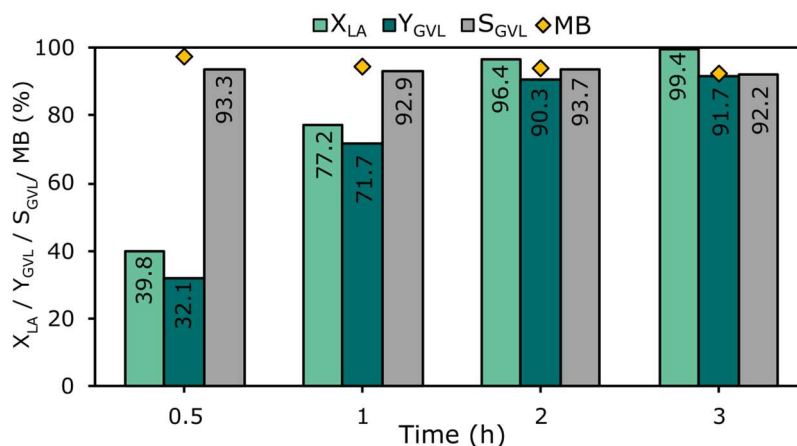


Figure 4.7. Reaction time course using Ru(1)/NC700 catalyst (Reaction conditions: LA (5 mmol), catalyst (0.05 g), Water (30 mL), 100 °C, 10 bar H₂).

The reaction was carried out for 1 hour and it was observed that the Ru(1)/NC700 catalyst showed the highest activity among the NC support catalysts. Further with the Ru(1)/NC700 catalyst the reaction time course was studied (Figure 4.7). The LA conversion and GVL yield displayed an exponential increase with respect to the reaction time and after 3 hour reaction, 99.4 % LA conversion was observed with 91.7% yield of GVL.

4.3.2.2. LA hydrogenation using Ru(1)-CCP catalyst

Ru(1)-CCP catalysts synthesized at different pyrolysis temperatures were also screened for LA hydrogenation at 100 °C using 2 mmol LA, 0.05 g catalyst, 30 mL water and 10 bar H₂ for 3 hours. It was found that Ru(1)-CCP catalysts were not showing a significant activity compared to Ru(1)/C and Ru(1)/NC catalysts. Also, a similar trend in the activity with respect to pyrolysis

temperature was found as in the case of Ru/NC catalyst, where the Ru(1)-CCP-700 exhibited a comparatively higher conversion of LA and GVL yield and selectivity. The reaction data for Ru(1)-CCP catalysts are shown in Figure 4.8.

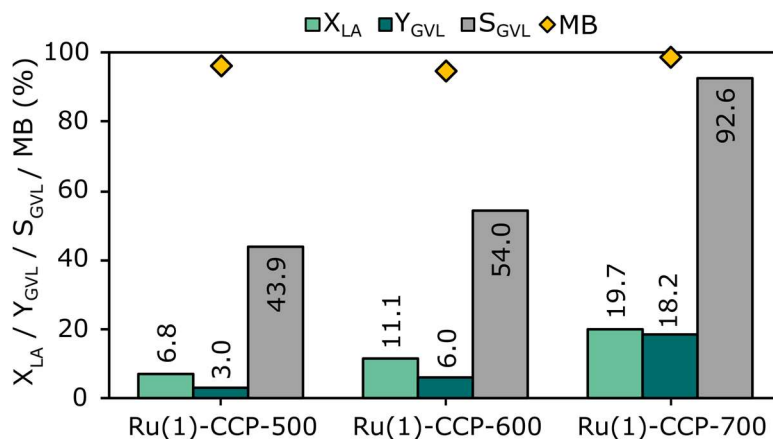


Figure 4.8. LA hydrogenation activity of Ru(1)-CCP catalysts (Reaction conditions: LA (5 mmol), catalyst (0.05 g), Water (30 mL), 100 °C, 3 h, 10 bar H₂).

4.3.3. Characterizations of Ru(1)/C, Ru(1)/NC and Ru(1)-CCP catalysts

The surface area of the carbon supports, and Ru impregnated carbon catalysts were calculated by application of BET equation in relative pressure range 0.05 to 0.35 of N₂ adsorption isotherms and pore volume were calculated using NLDFT method, which are listed in Table 4.2.

Table 4.2. Surface area and pore volume of the supports and catalysts.

Catalyst	Surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)
Activated carbon (C)	1144.5	0.587
Ru(1)/C	1101	0.527
NC500	21.4	0.023
NC600	351	0.151
NC700	558.3	0.234
Ru(1)/NC700	530.4	0.216
Ru(1)-CCP-700	86.9	0.072

It was seen that the commercial activated carbon has a higher surface area compared to the NC support made from chitosan. Upon the metal impregnation both Ru(1)/C as well as Ru(1)/NC700 showed a decrease in the surface area. This could be caused by the occupancy of the pores and surface by metal, and which is again confirmed by the reduction in the pore volume of the metal impregnated catalyst compared to the support. The adsorption isotherms

activated carbon and Ru(1)/C, NC-700, and Ru(1)/NC-700, and Ru(1)-CCP-700 are displayed in Figure 4.9 a, b and c respectively. It was also observed that in the NC catalysts the surface area was very low for NC500, and it increases with temperature of pyrolysis. Hence, it can be inferred that the surface area of the support is a vital parameter in determining the activity.

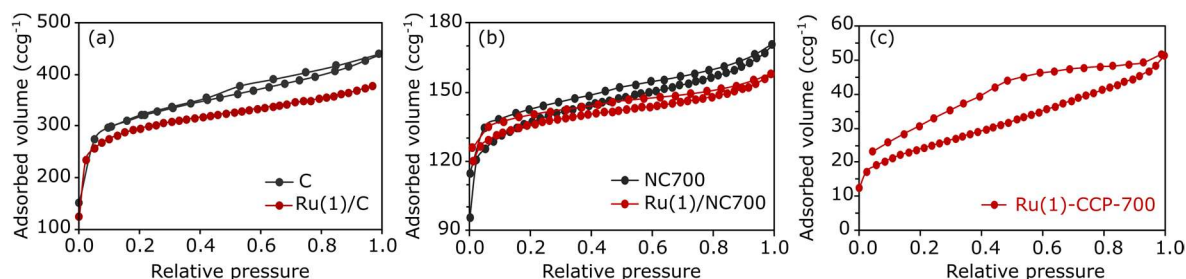


Figure 4.9. N₂ sorption isotherms for (a) C and Ru(1)/C, (b) NC700 and Ru(1)/NC700 and, (c) Ru(1)-CCP-700.

HRTEM images of the Ru(1)/C catalyst displayed finely distributed ruthenium particles of average size 1.95 nm (Figure 4.10a). The STEM image elemental mapping of Ru and C is shown in Figure 4.10(b-e), which also confirms the presence of uniformly distributed ruthenium particles on carbon support.

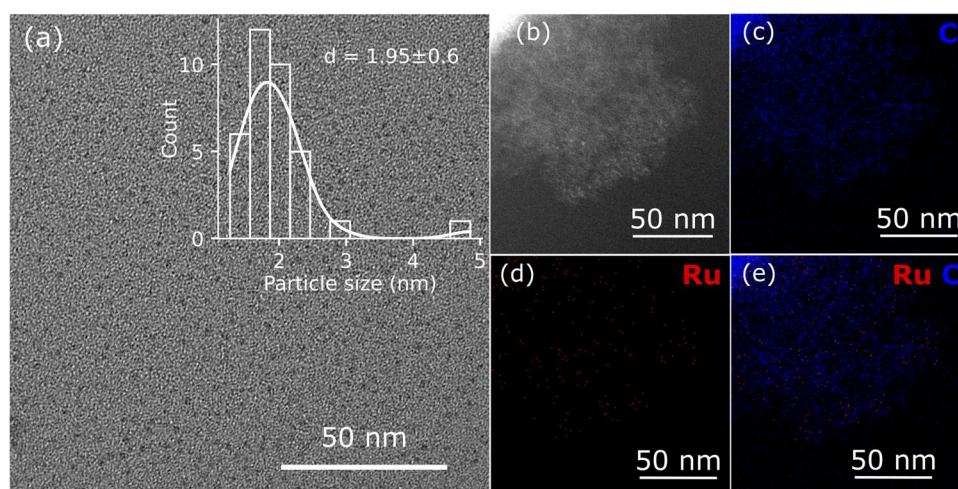


Figure 4.10. (a) HRTEM image and particle size distribution of Ru(1)/C, (b) HAADF-STEM image and, (c-e) elemental mapping of C, Ru, and their overlay, respectively.

Meanwhile the Ru(1)/NC700 exhibited slightly big particles of average size 2.66 nm which is presented in Figure 4.11a. The elemental mapping confirms the presence of nitrogen in the catalyst along with Ru and C. Figure 4.11 (b-g) represents the HAADF-STEM image and elemental mapping of C, Ru, N, and overlay of elements respectively. Elemental mapping suggests that Ru and N are uniformly distributed throughout the carbon matrix.

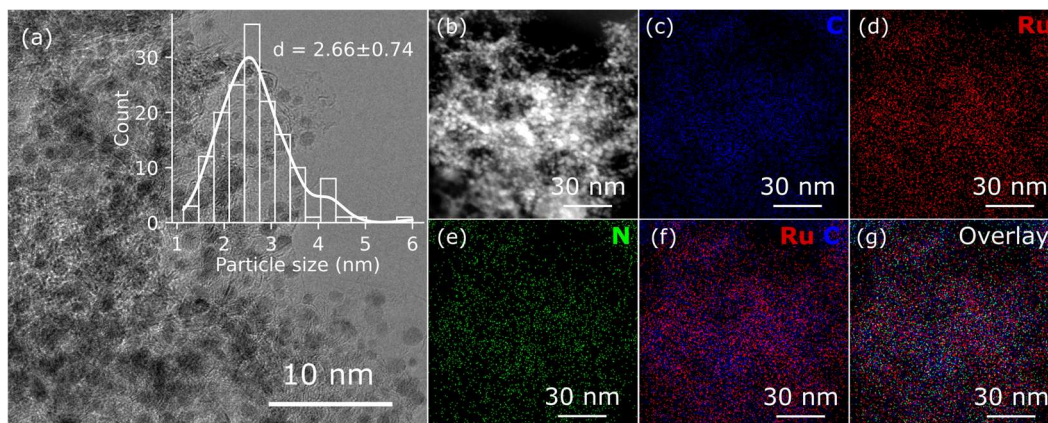


Figure 4.11. (a) HRTEM image and particle size distribution of Ru(1)/NC700, (b) HAADF-STEM image and, (c-g) elemental mapping of C, Ru, N, and the overlay of elements.

It was interesting to observe that Ru(1)-CCP-700 displayed relatively bigger particles (average size 6.26 nm) compared to Ru(1)/C and Ru(1)/NC700. This could be one of the probable reasons for poor LA hydrogenation performance of Ru(1)-CCP catalyst. The HRTEM image and the particle size distribution of Ru(1)-CCP-700 is shown in Figure 4.12a and the elemental mapping for C, Ru, N and their overlay is shown in Figure 4.12 (b-e).

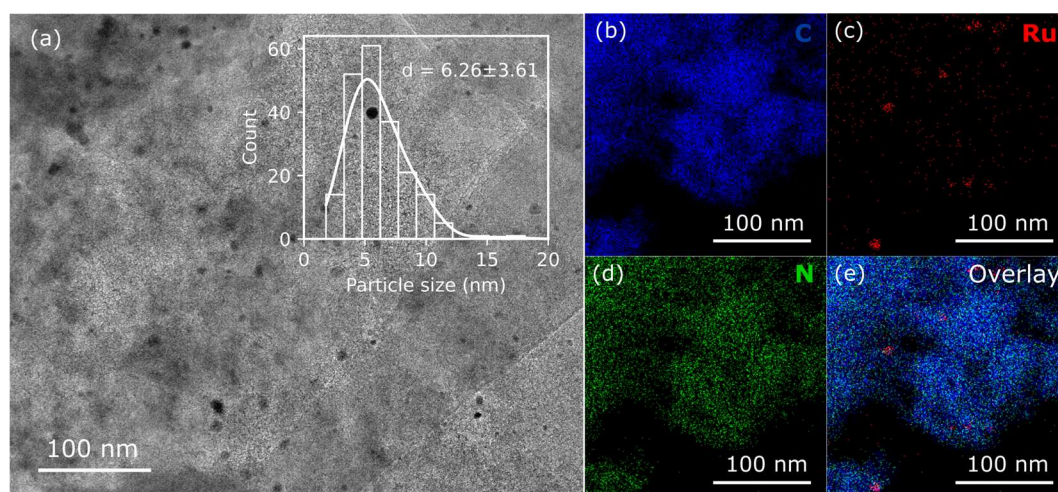


Figure 4.12. (a) HRTEM image and particle size distribution of Ru(1)-CCP-700 catalyst and (b-e) elemental mapping for C, Ru, N, and their overlay.

The XRD patterns of the catalysts Ru(1)/C, Ru(1)/NC700 and Ru(1)-CCP-700 are shown in Figure 4.13. All the three samples exhibited similar diffractions at $2\theta \sim 25^\circ$ and $2\theta \sim 44^\circ$ which corresponds to the 200 and 101 diffractions characteristic of amorphous carbon support. No visible peaks corresponding to ruthenium were observed in the diffraction patterns, likely due to the low concentration of the metal and the small size of the ruthenium particles within the carbon support, as confirmed by TEM images.

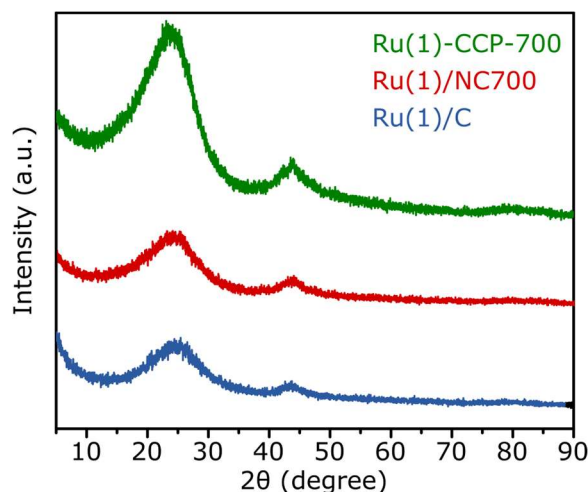


Figure 4.13. XRD patterns of the catalysts

From the XPS analysis of Ru 3p region of the catalysts the electronic state of ruthenium was identified. Ru 3d was not chosen for the analysis since this region overlaps with the C 1s region. As shown in the deconvoluted Ru 3p region, all the three catalysts exhibited both Ru^0 and $\text{Ru}^{\delta+}$ oxidation states (Figure 4.14a). However, the amount of these species was different in all the three samples. Ru/C had 23.4% of Ru^0 while the same in Ru/NC and Ru-CCP had 16.7% and 9.3% respectively. This suggests that in nitrogen doped carbon support ruthenium existed in oxidized state majorly. The details of Ru 3p binding energies and the relative fraction of Ru^0 and $\text{Ru}^{\delta+}$ species calculated from the area ratio the Ru^0 and $\text{Ru}^{\delta+}$ peaks are given in the Table 4.3.

Table 4.3. List of binding energies of Ru^0 and $\text{Ru}^{\delta+}$ species and the ratio $\text{Ru}^{\delta+}/\text{Ru}^0$ in the Ru(1)/C, Ru(1)/NC700 and Ru(1)-CCP-700 catalysts.

Catalysts	Ru^0 (BE in eV)	$\text{Ru}^{\delta+}$ (BE in eV)	$\text{Ru}^{\delta+}/\text{Ru}^0$
Ru(1)/C	461.13	462.74	3.3
Ru(1)/NC700	461.2	462.71	5
Ru(1)-CCP-700	461.1	463.16	9.8

The N1s XPS spectra of the Ru(1)/NC700 sample is shown in Figure 4.14b. It was observed that in the NC700 support exhibited peaks corresponding to pyridinic (Py-N), pyrrolic (Pr-N), graphitic (G-N), and oxidized (O-N) nitrogen species at binding energies 398.92, 400.65, 401.71 and 402.95 eV respectively. Among these nitrogen species G-N was the highest (50.1%), Py-N, Pr-N and O-N were 19.9, 14.1 and 15.9% respectively. After the impregnation of Ru and reduction treatment a considerable change in these functionalities was observed. The surface concentration of Py-N and Pr-N has increased to 20.3 and 23.9% respectively.

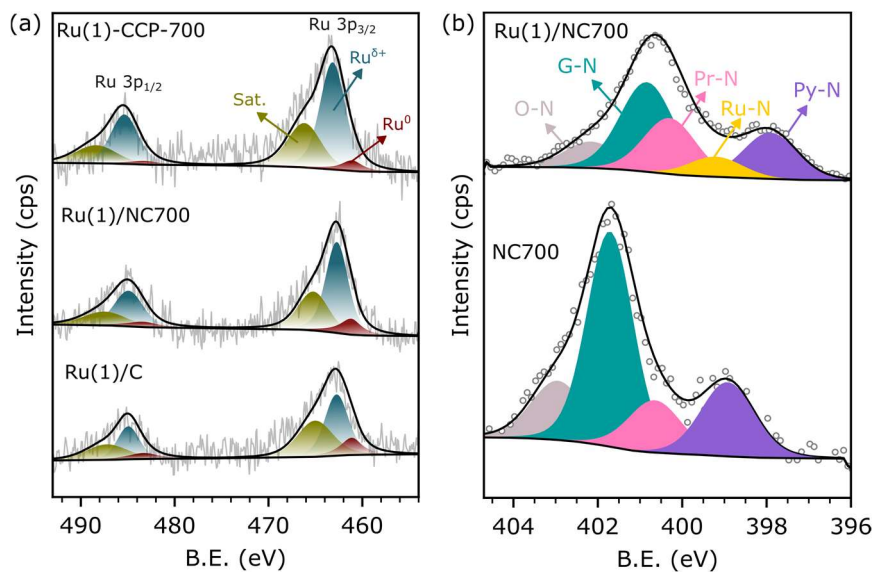


Figure 4.14. (a) Ru 3p XPS spectra of the catalysts Ru(1)/C, Ru(1)/NC700, and Ru(1)-CCP-700, and (b) N1s XPS spectra of NC700 support and Ru(1)/NC700.

Interestingly, the G-N species decreased significantly to 39.3%, along with a reduction in oxidized nitrogen species. Additionally, a metal-nitrogen binding energy peak at 399.2 eV was observed, indicating an interaction between Ru and N. A shift towards lower binding energy was noted for all the N species in the Ru catalyst. These observations suggest that in the Ru/NC catalyst, there is likely a charge transfer from the ruthenium species to the nitrogen species in the support.⁵⁰ This results in the N-containing carbon support becoming electron-rich, which could enhance the metal-support interaction in the catalyst. The details of deconvoluted binding energy and the quantification of surface nitrogen functionalities are given in Table 4.4.

Table 4.4. Binding energy position and quantification of surface nitrogen species in NC-700 and Ru(1)/NC700

N-species	NC700		Ru(1)/NC700	
	B.E (eV)	Quantification (%)	B.E (eV)	Quantification (%)
Py-N	398.92	19.9	397.91	20.3
Pr-N	400.65	14.1	400.30	23.9
Gr-N	401.71	51.1	400.83	39.3
O-N	402.95	15.9	402.16	11.6
Ru-N	-	-	399.26	4.7

The NH₃ and CO₂-TPD profiles and the quantification of acid and basic sites are displayed in Figure 4.15 a, b and c. The acid and basic site concentration was lowest in the activated carbon and after the metal impregnation an increase in the total number of acid and basic sites was

observed, suggesting that the incorporation of metal and the reduction treatment alters the surface acidity as well as the basicity of the carbon support.

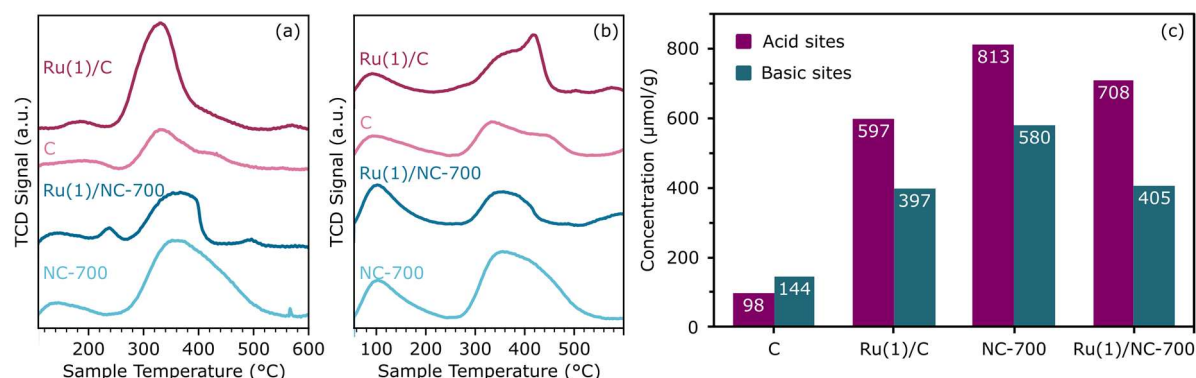


Figure 4.15. (a) NH₃ TPD profile, (b) CO₂ TPD profile and, (c) the acid base site concentration measured from TPD experiments.

The number of acidic and basic sites in NC700 was higher compared to activated carbon, likely due to the N and O functionalities present on the carbon surface. In the Ru(1)/NC700 sample, the number of acidic and basic sites decreased. This reduction could be attributed to the interaction of the metal with the N and O functionalities present in the carbon, which evolved from the pyrolysis of chitosan. This finding aligns with the N1s XPS data, showing a higher number of G-N and O-N species in NC700, which decreased upon metal incorporation.

The nominal loading of the catalysts, quantified using MP-AES, is listed in Table 4.5. Due to inherent acid resistance of metallic ruthenium, acid digestion methods are not entirely effective in solubilizing the metal, resulting in comparatively lower measured values for ruthenium loading.^{51,52} Consequently, a theoretical metal loading of 1% was used for the calculation of TOF in this work.

Table 4.5. Quantification of ruthenium loading using MP-AES

Catalyst	Ru loading (%)
Ru(1)/C	0.76
Ru(1)/NC700	0.72
Ru(1)-CCP-700	0.56

4.3.4. Comparison of activity of Ru(1)/C and Ru(1)/NC700

At the optimized time and temperature conditions using Ru(1)/C catalyst, the LA hydrogenation activity of Ru on nitrogen containing carbon catalysts were evaluated. It was seen that Ru(1)/C

and Ru(1)/NC700 exhibit comparable performance. Figure 4.16a represents the comparison of activity of these catalysts.

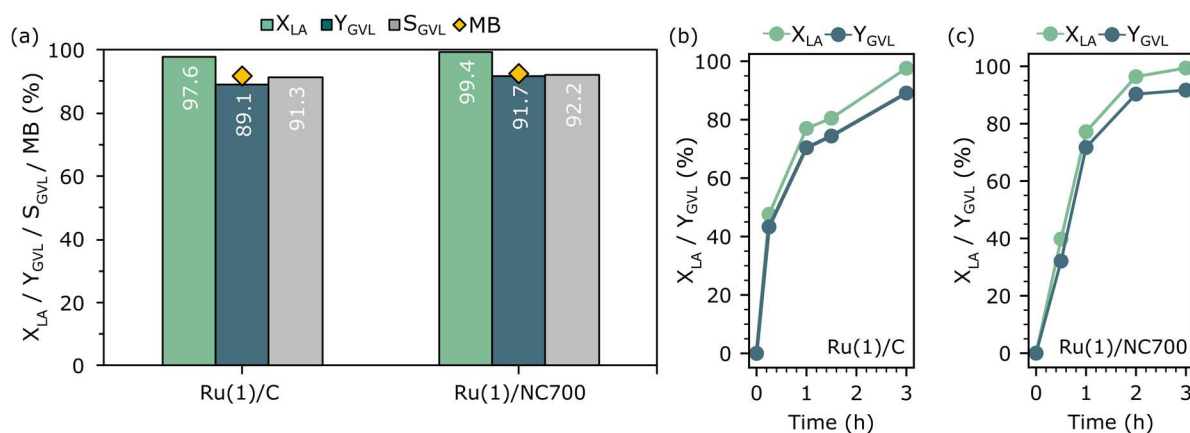


Figure 4.16. (a) Comparison of the LA hydrogenation activity of Ru(1)/C, Ru(1)/NC700 and Ru(1)-CCP-700 at the reaction conditions; LA (5 mmol), catalyst (0.05 g), Water (30 mL), 100 °C, 3 h, 10 bar H_2 . (b-c) Time course of the LA hydrogenation reaction using Ru(1)/C and Ru(1)/NC700 at the same reaction conditions.

The reaction time course of both Ru/c and Ru/NC catalysts are shown in Figure 4.16 (b-c). In the first glance the results for Ru(1)/C and Ru(1)/NC700 catalysts looks similar. However, to understand the intrinsic activity of these catalysts we have done the TOF calculation at conversions in the range of 40-55%. TOF was calculated as the number of moles of GVL formed per ruthenium (mols) per hour. Ru(1)/C showed a TOF of 1011 h^{-1} and Ru(1)/NC700 had a TOF value of 749 h^{-1} . Given that the surface area of the catalyst plays a crucial role in gearing the catalytic activity, The TOF values were normalized with surface area. It was seen that Ru(1)/NC700 showed 1.41times better activity than Ru(1)/C catalyst. The TOF and Surface area normalized TOF (SNTOF) values for the catalysts are shown in Table 4.6.

Table 4.6. TOF and SNTOF values for the catalysts Ru(1)/C and Ru(1)/NC700

Catalyst	Surface area (m^2/g)	TOF ($mol_{GVL}mol_{Ru}^{-1}h^{-1}$)	SNTOF ($mol_{GVL}mol_{Ru}^{-1}h^{-1}m^{-2}$)
Ru(1)/C	1101	1011	0.92
Ru(1)/NC700	530	749	1.41

4.3.5. TOF comparison with NDC supported Ru catalysts in literature

The TOF value of the Ru(1)/NC700 was also compared to the TOF of the nitrogen doped carbon supported ruthenium catalysts reported for Levulinic acid hydrogenation in the literature, also a comparison of the C and N precursors or reagents used for the catalyst synthesis is compared.

These details are enlisted in Table 4.7. The number of moles of ruthenium was calculated in all the cases with respect to the nominal loading of ruthenium in the catalysts. TOF frequency was calculated at less than 50% conversion. We can see that the previously reported systems have utilized expensive nitrogen containing reagents for the synthesis of catalysts. Also, the TOF values are less compared to Ru(1)/NC700 catalyst except in one case. It is important to note that the synthesized NC catalyst was derived from only chitosan without using any additional reagents and only 1% ruthenium loading was used in the catalyst. Hence the Ru/NC catalyst shows better performance and holds great potential in terms of its benign synthesis method.

Table 4.7. The Comparison of C,N precursor used for the synthesis of the N-doped carbon supported Ru catalysts in literature and their TOF with Ru(1)/NC700.

Catalyst	C,N precursor/ template	TOF (h ⁻¹)	Ref.
3Ru/HPNC	Dopamine + NH ₃ + TMB + Pluronic F127	776	43
3Ru/NHPC	Cellulose + (NH ₄) ₂ C ₂ O ₄ + NaHCO ₃	338	44
1.6Ru/PNC-I	Azobis(isobutyronitrile) + Acrylonitrile	168	45
1Ru/N-CS	3-aminophenol + Formaldehyde + NH ₃	5100	46
0.14Ru/TiO ₂ @NC	NH ₂ MIL 125 (MOF)	279	47
5Ru-NOMC	SBA-15 + Glucosamine hydrochloride	14.3	48
8.3Ru@CN	Tannic acid + gC ₃ N ₄ + Tris + Dopamine	304	49
Ru(1)/NC700	Chitosan	749	This work

4.3.6. Catalyst recyclability

For Ru(1)/NC700 catalyst recycling, the reaction was conducted for 15 minutes to maintain conversion rates within the kinetic region. After the first cycle, the reaction mixture and reactor washings were carefully collected and centrifuged to isolate the catalyst from the liquid. The catalyst was washed with distilled water and centrifuged again to remove any adsorbed reactant or product. This procedure was repeated four times. The catalyst was not dried and was used as is for the next cycle. The spent wet catalyst in known quantity of water was added to the reactor with the substrate and the remaining solvent required for the next reaction cycle. This process was repeated for four consecutive cycles. It was observed that the conversion of Levulinic acid remained same for the first three cycles (18.6-18.8%) and it dropped after the 4th cycles to 15.3%. The selectivity of GVL decreased from 93% in the first cycle to 86% after the 4th cycle. This suggests that the catalyst is stable, and only slight deactivation is happening during the recycling. The reaction results of catalyst recycle experiments are presented in Figure 4.17. The MP-AES analysis of the reaction mixture shows no leaching of ruthenium. Also, we have

carried out a reaction using the reaction mixture after the first cycle without the using the catalyst and the no LA conversion observed in the same.

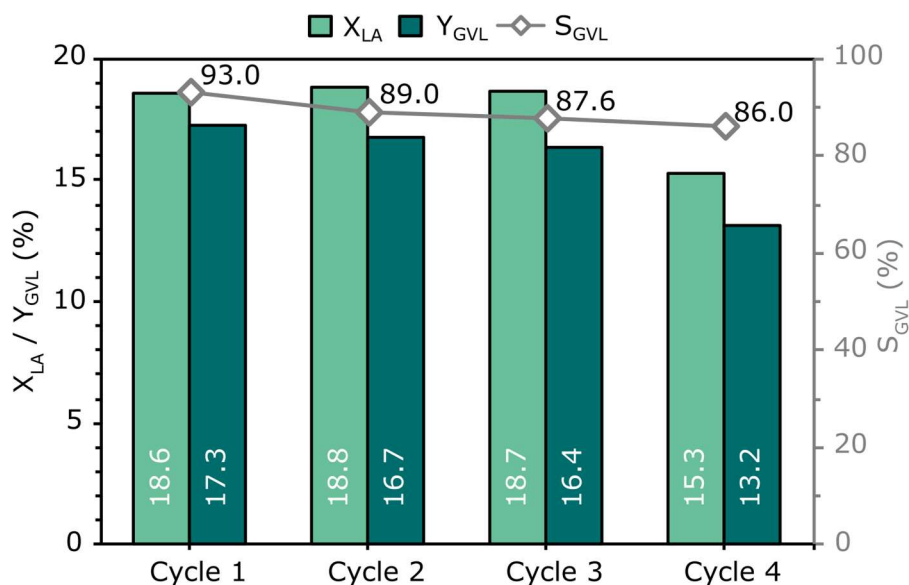


Figure 4.17. Recycle study of Ru(1)/NC700 (Reaction conditions: LA (5 mmol), catalyst (0.05 g, cycle1), Water (30 mL), 100 °C, 15 min, 10 bar H₂).

4.3.7. Characterization of spent catalysts

The spent Ru(1)/NC700 catalyst was characterized using HRTEM and XPS analysis to understand if any structural and electronic change has occurred during the catalyst recycle process. The HRTEM images of the spent catalyst and the particle size distribution are shown in Figure 4.18. The average particle size was 2.68 nm which was almost similar to the fresh catalyst and no severe aggregation was seen in the spent catalyst.

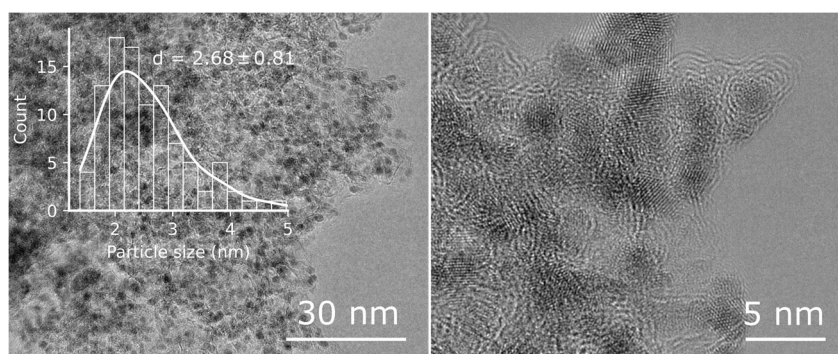


Figure 4.18. HRTEM images and particle size distribution of Ru(1)/NC700.

The Ru 3p and N1s XPS spectra of the spent catalyst are displayed in Figure 4.19. Ru 3p XPS analysis revealed a slight increase in the amount of oxidized ruthenium species compared to the fresh catalyst. N1s XPS showed a further decrease in G-N species, accompanied by an increase

in Pr-N and Ru-N species. These findings suggested that oxidized ruthenium species formed under reaction conditions and that N-species are effectively interacting with the metal.

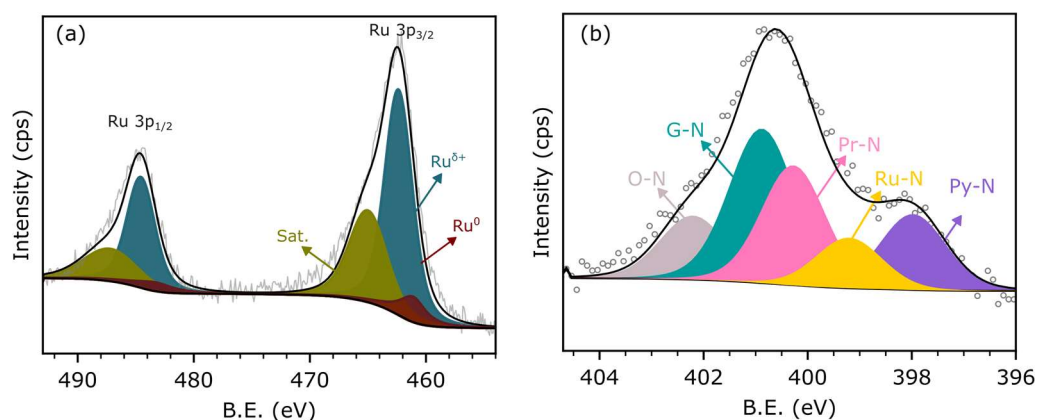


Figure 4.19. (a) Deconvoluted Ru 3p XPS and (b) Deconvoluted N1s XPS of spent Ru(1)/NC700 catalyst

4.3.8. Probable mechanism of LA hydrogenation

Insights from XPS revealed that in the Ru/NC catalyst, the majority of ruthenium existed in an oxidized state. The nitrogen functionalities in the catalyst influenced the electronic structure of the metal, resulting in charge transfer from the metal, evidenced by the Ru-N binding energy and the binding energy shift of nitrogen moieties. These Ru-N centers likely serve as active sites for the reaction. Based on this, we propose the following mechanism for LA hydrogenation using the Ru/NC catalyst, which is illustrated in the Figure 4.20. Hydrogen may undergo heterolytic cleavage at the Ru-N sites. The Ru^{δ+} species effectively polarizes the carbonyl group of adsorbed LA, facilitating the hydrogenation step to form 4-hydroxypentanoic acid (HPA). HPA is a short-lived intermediate that quickly undergoes intramolecular cyclization to form a cyclic diol in the reaction conditions. This diol then undergoes dehydration to form GVL. The dehydration step is facilitated by the N-basic sites in the catalyst, which abstract the diol proton. The abstracted proton combines with the hydroxyl ion to form water, freeing the catalytic site for the next reaction.

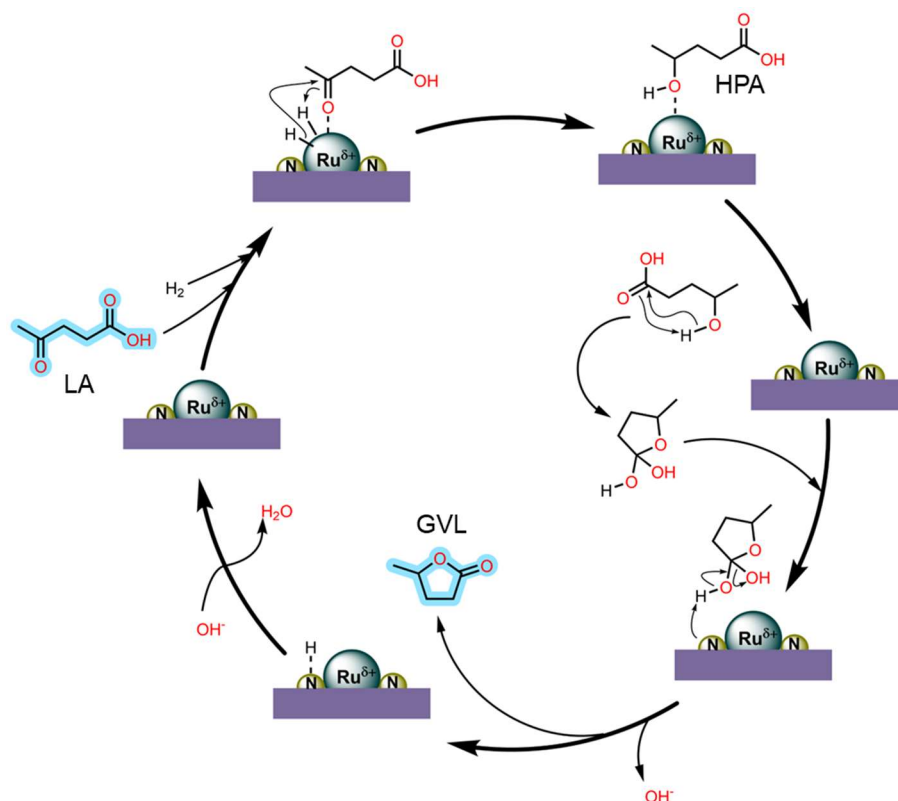


Figure 4.20. The proposed mechanism of LA hydrogenation to GVL over Ru(1)/NC700.

4.4. Conclusion

Among the synthesized N-containing carbon supported ruthenium catalyst, Ru(1)/NC700 showed comparable performance to Ru/C catalyst. The intrinsic activity of the Ru/NC catalyst was determined by the TOF and surface area normalized TOF, proved the superior activity of the catalyst compared to Ru/C. The Ru-CCP catalyst showed suboptimal performance, likely due to the formation of larger particles of Ru on the surface and the embedding of ruthenium sites during pyrolysis, which could mask most of the active sites. XPS data suggest the interaction of Ru and N species and shows the existence of higher fraction of oxidized ruthenium species. Based on these data, the probable mechanism is proposed, where the $\text{Ru}^{\delta+}$ enhances the carbonyl group activation during the hydrogenation step and the N-basic sites in the carbon support can aid the dehydration step to GVL, thereby increasing the overall rate of the reaction. The recycle experiment and post recycle characterization suggest that the catalyst is recyclable and stable and validate the improved metal-support interaction in the catalyst. The NC support synthesis based on chitosan is green and sustainable compared to previously studied N-doped carbon-based catalysts. Additionally, the NC catalyst exhibited better TOF values compared to many reported catalysts in the literature.

4.5. References

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5. Summary and Conclusions

In chapter 1 of the thesis a general introduction to carbon materials and biomass derived carbon materials as catalysts and catalyst support was discussed in detail. Carbon materials, due to their unique properties, serve as efficient catalysts and supports in thermo- and electrocatalytic reactions. Their diverse forms, including graphite, graphene, activated carbon, and carbon nanotubes, enable a wide range of applications. Synthesizing these materials from renewable biomass is crucial for sustainability, offering a low-cost, carbon-neutral alternative to conventional methods. Biomass-derived carbon materials often exhibit superior performance in catalysis and energy storage. This approach leverages the natural presence of heteroatoms in biomass, enhancing the efficiency of carbon-based materials. Nitrogen-doped carbon (NDC) materials are crucial in catalysis due to their nitrogen species-induced structural defects, which enhance catalytic activity by supporting stable metal nanoparticles and single atoms. This leads to strong metal-support interactions and favorable electronic states. However, the NDC materials have been typically synthesized from No-containing molecular precursors which are non-renewable and expensive. Chitin, the second most abundant biopolymer, is an ideal precursor for NDC synthesis due to its high nitrogen content and availability from crustacean shells. Chitin is deacetylated to chitosan, which is more soluble and suitable for NDC production, making it a sustainable resource for advanced catalytic materials. NDC from chitin biomass can be synthesized through various methods such as chemical vapor deposition, hydrothermal/solvothermal treatment, and pyrolysis. Each method adjusts the nitrogen content and structural properties of the NDC for specific applications. Pyrolysis strategy is promising in terms of producing direct synthesis of carbon materials with high degree of graphitization and porosity. Incorporation of metals into NDC can be achieved by post-synthesis impregnation or in situ formation from metal-chitosan composites by utilizing chitosan's chelation properties. In this thesis, we have synthesized metal@NDC catalyst using only chitosan as C and N source and have explored the role of N-incorporation in tuning the catalytic properties of the synthesized catalyst towards electrochemical HER, OER, ORR and Thermo catalytic biomass derived LA hydrogenation.

Chapter 2 presents a sustainable approach for synthesizing Ru on Nitrogen doped carbon catalyst, Ru-CCP via chitosan complexation with ruthenium, followed by a one-step pyrolysis process. The electrochemical HER activity of the Ru-CCP materials were evaluated and the

role of N-doping in tuning the catalytic activity was studied using advanced characterization tools. The overall conclusions from this study are,

- Synthesized a ruthenium catalyst on nitrogen-doped carbon without using toxic or non-renewable chemicals or templates.
- Studied the effect of nitrogen doping by varying the pyrolysis temperature of the catalysts.
- The Ru-CCP-500 catalyst outperformed commercial Pt/C, demonstrating remarkable performance and stability in HER compared to Ru catalysts on conventionally synthesized NDC.
- Enhanced performance is attributed to the unique structural and electronic properties of Ru-CCP catalysts, as revealed by HR-TEM, XPS, and XAS studies.
- Nitrogen doping stabilized and formed small nanoparticles within the carbon framework, as indicated by XPS and XAS analyses.
- The relative fraction of $\text{Ru}^{\delta+}$ compared to Ru^0 is crucial in controlling electrocatalytic activity.
- Optimal synthesis temperature was identified as 500°C, balancing graphitization and nitrogen content to achieve the desired ratio of charged and reduced ruthenium species.
- This study highlights a sustainable approach for synthesizing Ru@NDC catalyst, utilizing strong metal-support interactions facilitated by nitrogen doping.

Chapter 3 explores the synthesis of a bimetallic FeNi catalyst via chitosan metal complex pyrolysis and its activity towards electrochemical OER and ORR. The effect of N-doping in modulating the catalytic properties was studied using various characterization tools. The conclusion from this chapter is,

- The FeNi-CCP-800 catalyst demonstrated significantly lower overpotential for OER in alkaline medium compared to control samples and commercial RuO_2 . However, the catalyst underperformed compared to Pt/C in ORR.
- Nitrogen doping effects were studied by varying pyrolysis temperatures and comparing the activity with non-nitrogen carbon-based catalysts.
- XRD and XAS analyses confirmed FeNi alloy as the major phase in the catalyst.

- XPS analysis showed that, in the absence of N-doping, the alloy surface had more oxidized Fe species, while the presence of nitrogen and nickel facilitate the formation of stable surface FeNi alloy species.
- Nitrogen doping resulted in smaller particle formation in the CCP catalyst and likely enhanced OER activity by stabilizing FeNi alloy species.

In Chapter 4, The effect of nitrogen doping in ruthenium supported carbon catalyst and its activity towards biomass derived Levulinic acid hydrogenation was studied. Ruthenium catalysts were synthesized by wet-impregnation on chitosan derived carbon and Ru-Chitosan complex pyrolysis and their LA hydrogenation activity was compared with Ru/C catalyst.

- Among the synthesized nitrogen containing carbon supported ruthenium catalysts, Ru(1)/NC700 showed comparable performance to Ru/C.
- The intrinsic activity of the Ru/NC catalyst, determined by TOF and surface area normalized TOF, proved higher than that of Ru/C
- The TOF of the Ru(1)/NC700 was higher and comparable to the Ru catalysts based on conventional NDC support.
- The Ru-CCP catalyst performed sub optimally due to larger ruthenium particles and the embedding of ruthenium sites during pyrolysis, which masked most active sites.
- XPS data indicated Ru-N interaction and a higher fraction of oxidized ruthenium species.
- A proposed mechanism suggests that $\text{Ru}^{\delta+}$ enhances carbonyl group activation during hydrogenation, while N-basic sites in the carbon support aid dehydration to GVL, increasing the overall reaction rate.
- Recycle experiments and post-recycle characterization demonstrated the catalyst's recyclability and stability, confirming improved metal-support interaction.
- The NC support synthesis from chitosan is green and sustainable compared to previously studied N-doped carbon-based catalysts.

Overall, This thesis explores the synthesis and application of biomass-derived, nitrogen-doped carbon materials as efficient catalysts and catalyst supports. By leveraging chitosan from chitin, sustainable and high-performance mono metallic Ru and Bimetallic FeNi catalysts were developed. These catalysts demonstrated superior activity in electrochemical HER and OER respectively. Ru impregnated on NC material derived from chitosan pyrolysis showed better performance for LA hydrogenation compared to the reported NDC supported catalysts. These

studies emphasize the importance of nitrogen doping in enhancing catalytic properties and achieving strong metal-support interactions. N- incorporation induced the formation of stable and smaller nanoparticles in all the catalysts. In the case of Ru catalysts, metal to nitrogen electron transfer and in FeNi system nitrogen to metal electron transfer interactions were observed. These metal-N interactions influence the catalytic properties of the material. This work highlights a green approach to catalyst synthesis, offering environmentally friendly alternatives to conventional methods of nitrogen doped carbon catalysts. A graphical summary of the thesis working chapters is given in Figure 5.1.

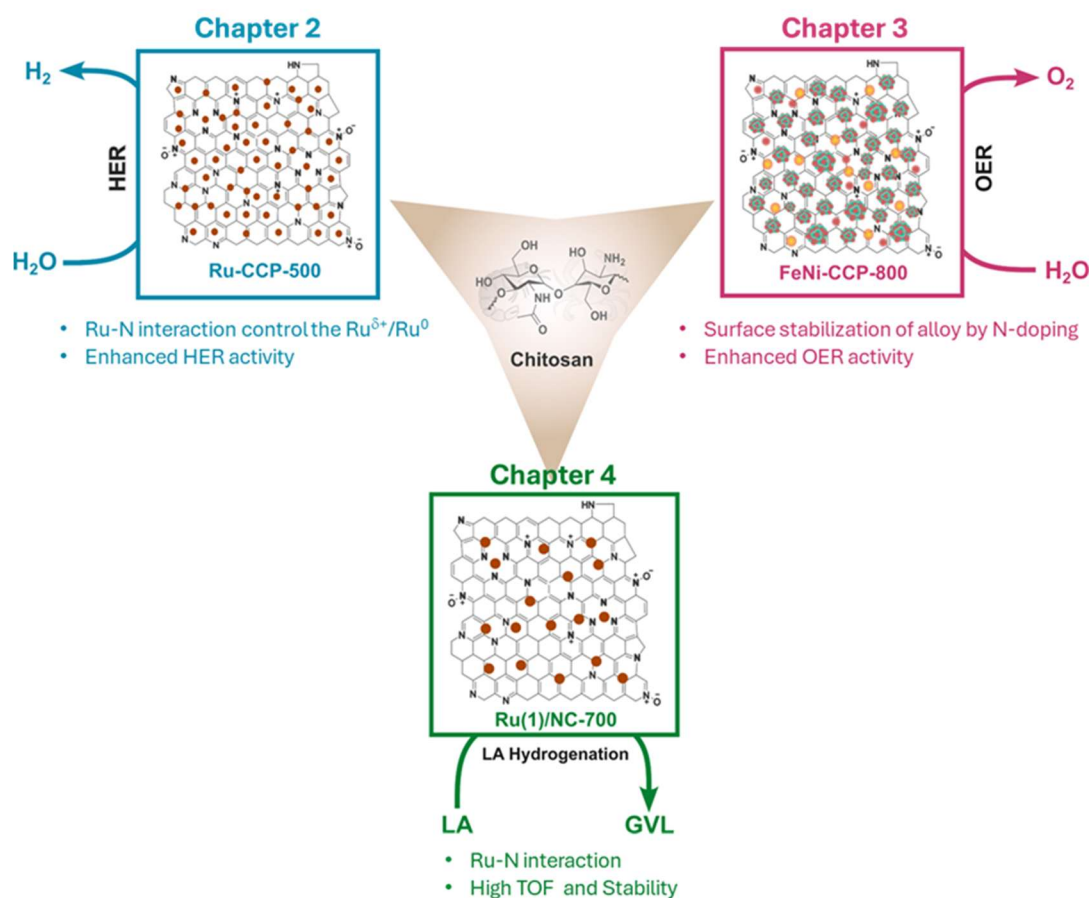


Figure 5.1. A graphical summary of the thesis working chapters.

The future perspective on this work includes the expansion of the CCP method of synthesis of M-CCP catalysts to various monometallic and multi metallic systems and explore the catalytic activity of those materials, the design optimization of the M-CCP catalysts for bifunctional activity for HER and OER, OER and ORR, and other thermo catalytic reactions and fine tuning the M/NC catalysts for various thermo catalytic reactions and detailed study of the structure activity correlation.

ABSTRACT

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Year of Submission: 2024

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Name of the Supervisor(s): Dr. Paresh L. Dhepe

Title of the thesis: Exploring the effect of nitrogen incorporation in modulating the catalytic properties of chitosan derived carbon supported metal catalysts for electrochemical HER, OER, ORR and biomass hydrogenation

Carbon materials are extensively used in catalysis due to their unique and tunable properties. Among various carbon materials, activated carbon is preferred for its high surface area, porosity, availability, and low cost. Traditionally synthesized from non-renewable resources, the focus is now on renewable biomass sources for carbon material synthesis. Biomass-derived carbon materials are utilized in numerous applications, with hetero-atom doping, particularly nitrogen doping, enhancing their properties. Current methods for nitrogen doping involve non-renewable and toxic chemicals. Chitosan, derived from chitin, offers a sustainable alternative, containing ~7% biologically fixed nitrogen. This study explores chitosan-derived nitrogen-containing carbon materials for catalytic applications and studies the effect of nitrogen incorporation in tuning catalytic properties.

The thesis comprises three main studies on the catalytic application of nitrogen-containing carbon-supported metal catalysts. The first work (chapter 2) details the synthesis of a nitrogen-containing carbon-supported ruthenium catalyst (Ru-CCP-500) via chitosan complexation and pyrolysis. This catalyst demonstrated remarkable HER performance, surpassing commercial Pt/C and other ruthenium-based catalysts due to its unique structural and electronic properties. Characterizations revealed that the metal-nitrogen interaction facilitated the formation of oxidized ruthenium species and stable, small ruthenium nanoparticles. The optimal synthesis temperature was identified as 500°C, balancing graphitization and nitrogen content to achieve the desired proportion of oxidized and metallic ruthenium species.

Chapter 3 describes the synthesis of a bimetallic FeNi-CCP catalyst by pyrolyzing FeNi-chitosan complex at 800°C. This catalyst exhibited significantly lower overpotential for OER in alkaline media compared to control samples and commercial RuO₂. XRD and XAS analyses confirmed the formation of FeNi alloy as the major phase, while XPS analysis showed that nitrogen doping made the Fe species electronically rich, aiding the formation of stable surface alloy species. Future work aims to improve the catalyst's ORR activity and develop bifunctional catalysts for applications like metal-air batteries.

Chapter 4 investigates the biomass derived Levulinic acid hydrogenation activity of three carbon-supported Ru catalysts with 1 wt.% metal loading: Ru/C and Ru/NC (prepared via wetness impregnation) and Ru-CCP (via Ru-chitosan complex pyrolysis). Ru(1)/NC700 exhibited higher intrinsic activity than Ru/C, as determined by TOF. Ru-CCP's poor performance was due to larger ruthenium particles and masked active sites. XPS data revealed Ru-N interactions and more oxidized ruthenium species. The catalysts were recyclable and stable, with chitosan-based NC support offering a sustainable alternative. Ru/NC also showed superior TOF values compared to many reported catalysts.

In all three works the chitosan-based carbon offers a viable and sustainable way of synthesizing the catalysts. The role of nitrogen doping was understood by the analysis of catalysts via various characterization methods. The Electronic structure modulation of the Ru catalysts was found to be caused by the Ru-N electron transfer interaction, meanwhile the in the FeNi catalysts the N-metal electron transfer was seen. Also, the presence of nitrogen in the catalyst aids the formation of small and stable metal particles and caused the overall enhancement of the catalytic performance in the studied reactions.

List of publication(s) in SCI Journal(s) (published & accepted) emanating from the thesis work

1. **Lavanya Korampattu**, Sidharth Barik, Ajmal Pandikassala, Rajashri R. Urkude, Sreekumar Kurungot*, Paresh L. Dhepe*, '*The Role of Nitrogen Doping in Modulating Ruthenium Nanocatalysts for Enhanced Electrochemical Hydrogen Evolution Reaction in Alkaline Medium*' Chemistry of Materials, **2024**, 36 (9), 4262–4274.
2. **Lavanya Korampattu**, Neha Ghosh, Paresh L. Dhepe*, '*Shell Waste Valorization to Chemicals: Methods and Progress*'. Green Chemistry, **2024**, 26 (10), 5601–5634.

List of papers with abstract presented (oral/poster) at national/international conferences/seminars

1. 3- Minute Thesis presentation at **NCL-RF 5th Annual Students' Conference**, CSIR-NCL, Pune | 30th November – 1st December 2023, received Best 3-MT presentation runner-up award.
2. Oral presentation at 'International Conference on Sustainable Chemistry & Engineering' (**SusChemE 2.0**), ICT, Mumbai | 14th -16th September 2023, received best paper award in oral presentation.
3. Poster presentation on **National Science Day**, CSIR-NCL, Pune | 23rd February 2023
4. Poster presentation at **NCL-RF 4th Annual Students' Conference**, CSIR-NCL, Pune | 29th - 30th November 2022
5. Poster presentation on 'International Conference of H₂ and CO₂' (**ICH₂CO₂'22**) (Virtual) by S & T Digital | 17th -19th November 2022
6. Poster presentation on 'Conference on Advances in Catalysis for Energy and Environment (**CACEE -2022**) & CO₂ India Network 1st Annual Meet', TIFR, Mumbai | 31st October – 4th November 2022
7. Poster presentation on **National Science Day**, CSIR-NCL, Pune | 26th - 28th February 2020
8. Poster presentation on Symposium on 'Catalysis & Multiphase Reactor Engineering' (**CATMUR**) held at CSIR-NCL, Pune | 23rd December 2019
9. Poster presentation on 'The 8th Asia Pacific Congress on Catalysis' (**APCAT-8**), Bangkok, Thailand | 4th - 7th August 2019

The Role of Nitrogen Doping in Modulating Ruthenium Nanocatalysts for Enhanced Electrochemical Hydrogen Evolution Reaction in Alkaline Medium

Lavanya Korampattu, Sidharth Barik, Ajmal Pandikassala, Rajashri R. Urkude, Sreekumar Kurungot,* and Paresh L. Dhepe*



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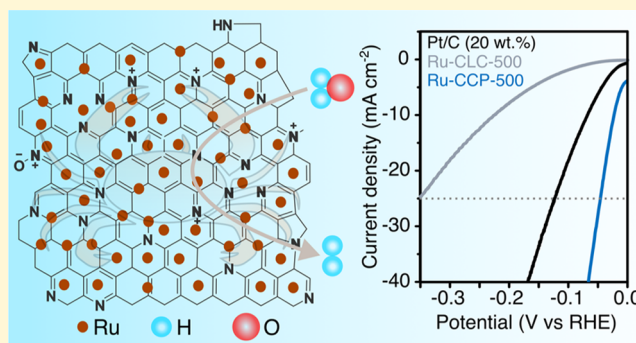
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ABSTRACT: Nitrogen doping has become a fundamental approach to enhance the catalytic performance of carbon materials across various applications. The introduction of nitrogen creates defects and active sites, promoting the formation of small metal particles and strengthening the metal–support interaction within carbon materials. However, the challenge lies in developing sustainable and cost-effective methods for synthesizing nitrogen-doped carbon materials. In this study, we present a sustainable approach for the synthesis of ruthenium on nitrogen-doped carbon catalysts (Ru-CCP) using chitosan as a nitrogen and carbon source. Unlike traditional methods, our process avoids the use of additional nitrogen precursors and templates, streamlining the synthesis while using a renewable resource. The synthesized material exhibits an exceptional performance in the electrochemical hydrogen evolution reaction (HER) in alkaline conditions by achieving a current density of 25 mA cm⁻² at an impressively low overpotential of 46 mV, outperforming Pt/C under similar conditions. The detailed studies on structural and electronic properties of the materials using X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and transmission electron microscopy (TEM) revealed that the remarkable catalytic activity is upheld by the unique interplay between Ru^{δ+} and surface nitrogen moieties, notably pyridinic and pyrrolic nitrogen. Here, we demonstrate the control of particle size and electronic environment around the metal atom via the interaction of nitrogen and unravel the role of nitrogen doping in tuning the catalytic performance. In addition, this work offers insights into efficient HER catalyst design and emphasizes the potential of biomass-derived materials like chitosan in advancing clean hydrogen production for renewable energy applications.



INTRODUCTION

The growing energy crisis, coupled with the urgent threat of global warming, emphasizes the critical need for renewable energy sources and sustainable methods to produce chemicals and fuels. Among the renewable energy sources, hydrogen energy is considered clean and efficient because of its carbon-free emission and its high energy density.¹ One of the promising approaches for obtaining renewable hydrogen is the hydrogen evolution from water electrolysis.² Pt-containing catalysts have generally demonstrated the best performance for the hydrogen evolution reaction (HER) due to their efficient reaction kinetics. However, the increased cost and scarcity of Pt limit its practical use on an industrial scale, necessitating research into cost-effective catalysts.^{3,4} Recently, Ru-based catalysts have emerged as a promising low-cost alternative to Pt. Ru has a similar hydrogen bond strength (~65 kcal mol⁻¹) as Pt and a superior water dissociation ability, particularly in neutral or alkaline electrolytes, contributing to its comparable or even better HER performance than that of Pt and other

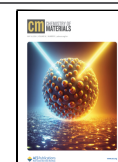
metals.^{5–8} Specifically, carbon-supported ruthenium catalysts have been used for the purpose because of their increased electrical conductivity and large specific surface area that can aid in electron transport.⁹ However, when carbon is used as a support, it lacks the necessary functionality to have a strong metal–support interaction. Consequently, the metal particles tend to aggregate, leading to a loss of catalytic activity over time.¹⁰ Hence, engineering the carbon support for Ru-supported catalysts by improving the metal–support interaction can enhance their catalytic activity and stability toward the HER.

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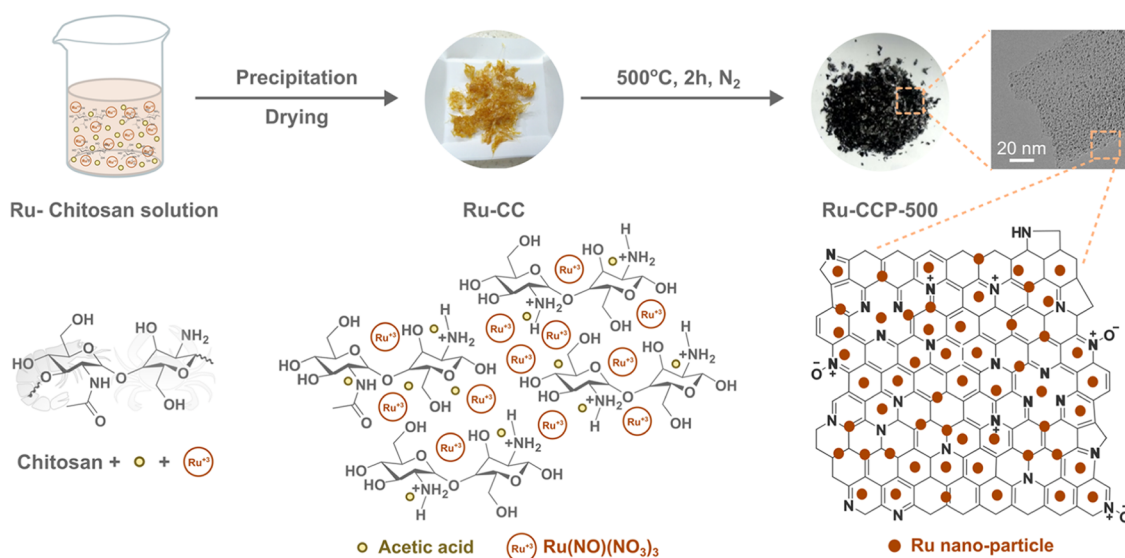
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Scheme 1. Synthesis of the Ru-CCP Material via Metal–Chitosan Complexation Followed by the Pyrolysis Method



Surface functionalization and heteroatom doping are used as key strategies to improve the metal–support interaction to enhance the catalyst stability of metal-supported carbon catalysts.^{11,12} Nitrogen is an ideal dopant for carbon materials; being a neighboring element to carbon, it allows precise control in altering the number of electrons when substituted. Also, its similar atomic size to carbon prevents lattice mismatches. The electron surge due to nitrogen doping alters the electrical conductivity, surface basicity, and hydrophobicity of carbon materials by introducing defects and various nitrogen moieties, creating catalytically active sites within the carbon framework.^{13,14} Also, the increase in the electronegativity due to nitrogen doping facilitates a strong metal–support interaction, which helps in the stabilization of small metal particles. This consequently boosts the catalytic activity and overall stability of metal catalysts supported on nitrogen-doped carbon in heterogeneous catalytic reactions.^{15–17}

Traditionally, N-doped carbon is synthesized either by heat treatment of undoped porous carbon materials in the presence of N-containing precursors or via direct synthesis using N-containing precursors, either independently or in combination with carbon-containing precursors, and the metal nanoparticles are introduced either during the synthesis or via postsynthetic impregnation.^{18–20} Commonly, N-containing chemicals such as ammonia, urea, melamine, acetonitrile, cyanamide, dicyandiamide, and ionic liquids or N-containing polymers such as polypyrrole, polyaniline, and metal–organic frameworks (MOFs) were being used for the synthesis.^{21–25} However, the above-mentioned chemicals are rather toxic and expensive and are nonrenewable. Hence the sustainable production of nitrogen-doped carbon materials poses a persistent challenge and demands devising cost-effective and sustainable methods for fabrication of these materials.

Chitin is a naturally occurring nitrogen-containing polysaccharide found in the shell waste of crustaceans and it is recognized as the second-largest abundant biopolymer on earth.²⁶ Chitin is a polymer of N-acetyl-D-glucosamine (NAG), a sugar structurally similar to glucose. Unlike glucose, NAG has an acetamido group in place of the $-\text{OH}$ group at the C2 position. Chitin undergoes deacetylation to form chitosan, wherein the removal of the acetyl group from NAG units

results in the formation of D-glucosamine (GA). Depending on the degree of deacetylation, chitosan can exhibit a variable number of monomer units of GA and NAG. The natural occurrence of nitrogen in chitin coupled with its abundance renders it as an economical and sustainable feedstock for the synthesis of various chemicals²⁷ and materials.²⁸ Chitin or chitosan can be carbonized to synthesize nitrogen-doped carbon materials, which have been employed as catalysts and catalyst supports in various organic transformations^{29–32} and electrochemical applications.^{33–36} The amino groups, along with the hydroxyl groups in chitosan, serve as excellent chelating ligands capable of coordinating with transition metal ions.^{37,38} Consequently, they are utilized in various applications, including the adsorption of heavy metal atoms^{37,39} and the synthesis of metal-containing catalysts for chemical conversions.^{31,40} Additionally, the biological properties of metal–chitosan complexes, such as antibacterial activity, were studied.⁴¹ Despite chitin or chitosan inherently containing 7% biologically fixed nitrogen in their structure, many studies, particularly in electrochemical applications, employ additional nitrogen-containing chemicals to enhance the support's conductivity and catalytic activity.^{42–44} In order to tune the porosity of the carbon material, templates are often utilized during synthesis.^{45–48} The use of additional reagents and templates in catalyst synthesis can make the process expensive and tedious. Furthermore, postsynthesis incorporation of the metal often necessitates oxidation or reduction treatments. Hence, it is highly desirable to design sustainable catalyst materials that eliminate the need for extra reagents and chemicals, avoiding multiple steps and streamlining the synthesis process.

Herein we report the synthesis of Ru nanoparticles supported on N-self-doped carbon from chitosan, as an efficient catalyst for the electrochemical HER, by a simple synthetic procedure that involves the formation of a ruthenium–chitosan complex followed by a single-step pyrolysis process. Chitosan was chosen over chitin because of its higher abundance of amino groups, which are effective ligands compared to acetamido groups present in chitin.⁴⁰ Additionally, incorporating the metal before carbonization ensures a more effective interaction between the metal and

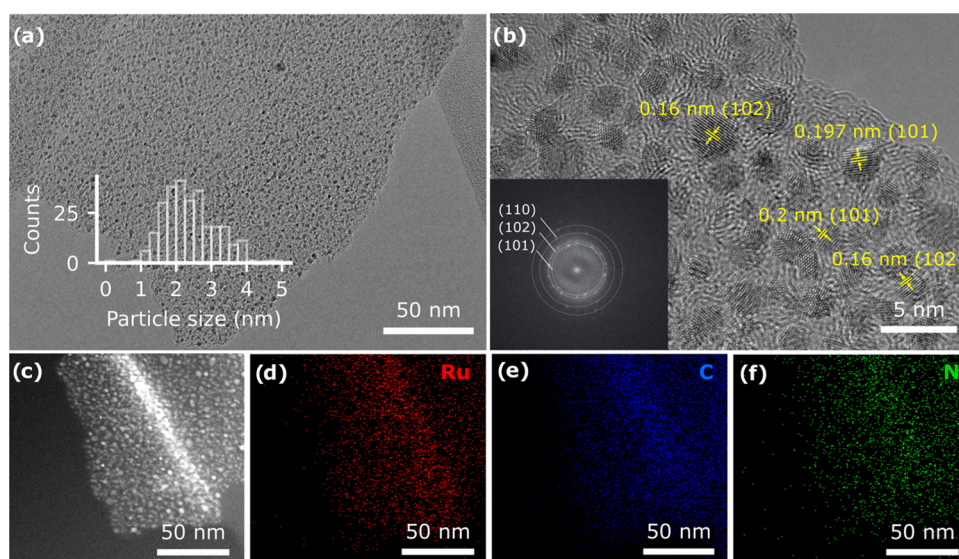


Figure 1. (a) HR-TEM image and particle size distribution histogram of Ru-CCP-500, (b) HR-TEM image of Ru-CCP-500 at a 5 nm scale with lattice fringes and the corresponding FFT image in the inset, (c) STEM image area of the Ru-CCP-500 material chosen for elemental mapping, and (d–f) elemental mapping images of Ru, C, and N in Ru-CCP-500.

chitosan. This process may also limit the growth of metal particles during pyrolysis. Unlike the existing reports on Ru-based carbon catalysts, our synthesis strategy does not involve the use of any additional N precursors or structure-directing templates. The synthesized Ru-CCP catalyst demonstrated a remarkable performance in the electrochemical HER in alkaline medium compared with the state-of-the-art Pt/C catalyst. Also, the catalyst exhibited a lower overpotential compared to similar ruthenium-containing carbon catalysts derived from chitin and D-glucosamine. Furthermore, the synthesis of previously reported catalysts involved the use of additional reagents. In the case of the chitin-derived material, urea and NaOH were used along with chitin, and freeze-drying was additionally employed during synthesis.⁴² For the D-glucosamine-derived material, melamine was used additionally, and a two-step pyrolysis process was involved.⁴³ The detailed structural and electronic characterization of the synthesized catalysts revealed the enhanced electronic metal–support interaction and the formation of ultrasmall ruthenium nanoparticles in the material induced by the metal–nitrogen bonding. Through detailed catalyst characterization, we also revealed how nitrogen plays a crucial role in modulating the electronic structure of ruthenium nanoparticles. The electronic structure modulation through nitrogen doping ensures a precise balance between positively charged and reduced ruthenium species, thereby being the key factor responsible for the enhanced activity.

RESULTS AND DISCUSSION

Catalyst Synthesis and Characterizations. Chitosan was used as both the source of nitrogen and carbon for the materials synthesized in this work. The synthesis of the Ru-CCP material is illustrated in Scheme 1 and the detailed procedure for the material synthesis is given in the Experimental Section. Initially, chitosan was dissolved in acetic acid. It protonates the amino groups present in chitosan, weakens the hydrogen bonding in the rigid polymer network of chitosan, and forms a viscous solution of it. The metal precursor used for ruthenium was ruthenium(III) nitrosyl

nitrate. The choice of the nitrate precursor was intended to ensure that the anion group was removed completely during pyrolysis. The ruthenium precursor solution was added to dissolved chitosan in acetic acid. Further the formed metal–chitosan solution was precipitated as a spongy hydrogel in an excess of acetone. This ruthenium–chitosan hydrogel was then dried to remove the trapped solvent and water, and the obtained material is termed as the ruthenium–chitosan complex (Ru-CC). The Ru-CC material is then pyrolyzed under an inert (N_2) atmosphere in a single step at 500, 600, and 700 °C to obtain the ruthenium–chitosan complex pyrolyzed (Ru-CCP) materials Ru-CCP-500, Ru-CCP-600, and Ru-CCP-700, respectively. The composition of the metal and chitosan used, along with the anticipated ruthenium loading in each material, is presented in Table S1. The Ru-CCP materials were used for the experiments as synthesized without any post-treatments.

The nitrogen sorption isotherms of the Ru-CCP materials are given in Figure S1a. All of the materials exhibited a type II adsorption isotherm, and the Ru-CCP-500 sample showed the highest specific surface area ($888.6 \text{ m}^2 \text{ g}^{-1}$). With a further increase in the pyrolysis temperature, the surface area of the samples Ru-CCP-600 and Ru-CCP-700 decreased to 626 and $436 \text{ m}^2 \text{ g}^{-1}$, respectively (Figure S1b). This trend in the surface area is due to the interplay of two phenomena. Initially, the carbonization of the hard Ru-CC material results in a higher specific surface area at 500 °C. Later, the graphitization of the amorphous carbon structure causes the decrease in the surface area at higher annealing temperatures.^{47,49} The percentage of the ruthenium loading was calculated from thermogravimetric analysis of the materials in the presence of air. The metal loading was found to be 18.6, 23.6, and 13.6% for the Ru-CCP-500, Ru-CCP-600, and Ru-CCP-700 samples, respectively. The thermogravimetric analysis (TGA) curve for Ru-CCP-500 is given in Figure S2 and the % metal content of the materials is listed in Table S2.

High-resolution transmission electron microscopy (HR-TEM) analysis was carried out to realize the catalyst morphology and the size distribution of the metal nano-

particles in the synthesized catalysts. Among the synthesized materials, Ru-CCP-500 showed a very fine size distribution of particles, where the majority of particles fall in the range of 1.5–2.75 nm size (as depicted in Figure 1a,b). The interplanar spacing of the particles was observed; 0.2 and 0.16 nm correspond to (101) and (102) planes of metallic hcp ruthenium (Figure 1b). Fast Fourier transform (FFT) analysis of the images further confirms the crystalline planes of the Ru metal (Figure 1b, inset). The STEM image and the elemental mapping of Ru, C, and N (Figure 1c–f) show the even distribution of the elements throughout the material. The HR-TEM images of Ru-CCP-600 and Ru-CCP-700 and their particle size distributions are shown in Figure S3(a–b). With the increase in the pyrolysis temperature from 500 to 700 °C, the average size of the ruthenium particles increased slightly. However, these samples also exhibited a fine distribution of particles, with the majority falling within the range of 1.7–3 nm for the Ru-CCP-600 sample and 1.9–3.6 nm for the Ru-CCP-700 sample. While the majority of nanoparticles in all of the Ru-CCP catalysts are under 3 nm in size, the TEM images also revealed the presence of a small population of larger particles. Additional TEM images of the Ru-CCP catalysts showing the presence of larger particles are displayed in Figure S4.

X-ray diffraction patterns of the Ru-CCP material have a number of sharp diffraction peaks that can be well indexed to metallic ruthenium in a hexagonal close packed (hcp) structure (JCPDS No: 00–006–0663). No other phases of Ru or RuO₂ were observed from X-ray diffraction (XRD). The XRD pattern of the Ru-CCP materials are shown in Figure 2. Sharp

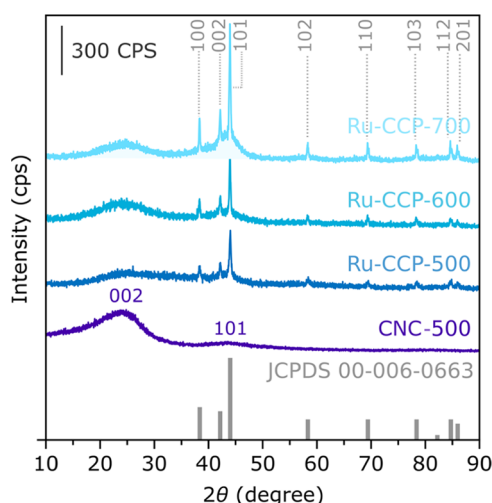


Figure 2. XRD of Ru-CCP materials pyrolyzed at different temperatures, the bare carbon material CNC-500, and the reference XRD pattern for metallic ruthenium (JCPDS: 00–006–0663).

and significant peaks for metallic Ru were observed at higher annealing temperatures, which suggests the improved crystallinity of Ru in the material. Even though the majority of the particles, as observed from the TEM images, were smaller (<3 nm), the XRD peaks observed were significantly sharper. The crystallite size calculated using the Scherrer equation for the catalysts Ru-CCP-500, Ru-CCP-600, and Ru-CCP-700 were 27.6, 32.5, and 36.5 nm, respectively. The presence of the sharp peaks could be attributed to the minor population of the larger particles within the catalyst.⁵⁰ The detail of the crystallite

size calculation is given in the Supporting Information, and its comparison with the particle size calculated from TEM is shown in Table S3. Apart from the diffraction patterns for Ru, all of the materials showed a broad peak in the region of 2θ –25° and can be assigned to (002) facets of partly graphitized amorphous carbon.⁵¹ A second broad diffraction at 2θ –44° can be attributed to the in-plane diffraction of (101) facets of graphitic carbon, which indicates the formation of a layered graphitic phase in the carbon matrix.⁵¹ The graphitic carbon peak at ~44° also shows an increase in the intensity with the increase in the pyrolysis temperature, which suggests the increase in graphitization of the carbon material, and this can be seen from the XRD pattern of the bare carbon materials termed as CNC materials. The XRD patterns of the other bare carbon materials synthesized at different temperatures are given in Figure S5.

Electrochemical HER Performance. The electrochemical analysis of all of the synthesized catalysts was conducted in a 1 M KOH electrolyte solution using a three-electrode system, where Hg/HgO was used as the reference electrode. The detailed procedure for the electrochemical analysis is given in the Experimental Section, and the linear sweep voltammogram (LSV) for Hg/HgO electrode calibration is given in Figure S6. Figure 3a represents the linear sweep voltammograms (LSVs) for Ru-CCP materials along with commercial Pt/C (20 wt %). The HER activity trend was observed in the following order: Ru-CCP-500 > Ru-CCP-600 > Pt/C (20 wt %) > Ru-CCP-700. Among the synthesized catalysts, Ru-CCP-500 exhibited a remarkably lower overpotential compared to the commercial Pt/C catalyst. The overpotential for the Ru-CCP materials to achieve a current density of 25 mA cm^{−2} is depicted in Figure 3b. Ru-CCP-500 and Ru-CCP-600 exhibited low overpotentials of 46 and 78 mV, respectively, to reach the current density of 25 mA cm^{−2}, while Pt/C required 123 mV. In contrast, Ru-CCP-700 displayed a higher overpotential of 201 mV, and the metal-free carbon material CNC-500 exhibited a poor HER performance. Furthermore, the HER activity of Ru-CCP-500 stands remarkable and makes it competitive with or even superior to many catalysts reported in previous studies.^{42,43,52–58} A comparison of the HER overpotential in the alkaline medium for both previously reported catalysts and this study is provided in Table S4.

Structural and Electronic Characterizations. In order to investigate the underlying factors contributing to the improved electrochemical performance of Ru-CCP-500 in the HER, we conducted thorough investigations of its structural and electronic properties. Using X-ray photoelectron spectroscopy (XPS), the chemical and electronic states of the constituent elements of the samples were studied. Due to the overlap of C 1s and Ru 3d regions, Ru 3p was chosen for the analysis of Ru species. XPS analysis of the Ru 3p region of Ru-CCP-500 is given in Figure 4a and the Ru 3p XPS spectra of all of the Ru-CCP materials are shown in Figure S7. Upon deconvolution of the Ru 3p region, two different species of Ru can be found. The binding energies of 461.8 and 484.1 eV correspond to Ru⁰ and 462.9 and 485.2 eV correspond to Ru^{δ+} species.⁵⁹ With the increase in the pyrolysis temperature, the metallic ruthenium (Ru⁰) fraction showed an increase relative to oxidized ruthenium (Ru^{δ+}). We were particularly intrigued by the presence of oxidized ruthenium species in the XPS of the Ru-CCP material, as we observed no evidence of RuO₂ phases in XRD. Hence, we assumed that there might be a possibility that there are small ruthenium oxide domains in the

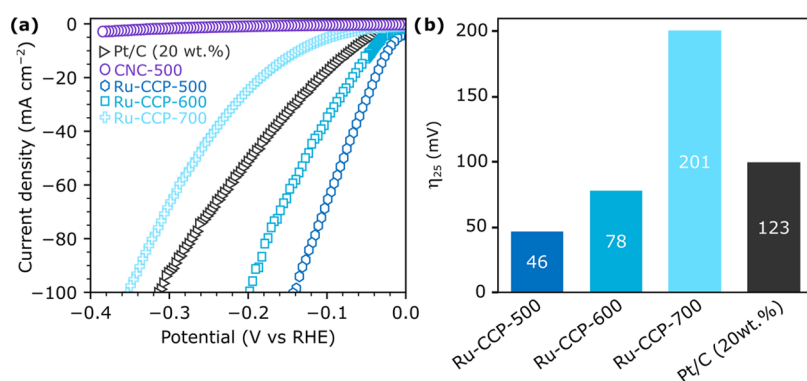


Figure 3. (a) Comparative HER polarization curves of the CCP catalysts recorded at a scan rate of 10 mV s⁻¹ in the N₂-saturated 1 M KOH solution and (b) overpotential of Ru-CCP catalysts and the commercial Pt/C catalyst observed at the current density of 25 mA cm⁻².

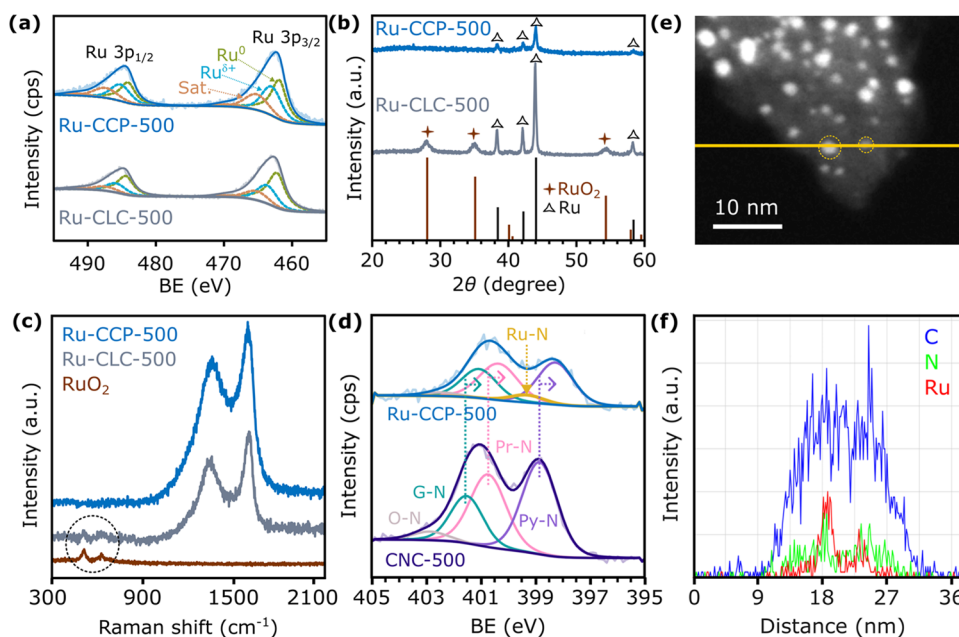


Figure 4. (a) Deconvoluted Ru 3p XPS spectra of Ru-CCP-500 and Ru-CLC-500, (b) XRD of Ru-CLC-500 in comparison with Ru-CCP-500 along with the reference XRD patterns of metallic Ru (JCPDS: 00-006-0663) and RuO₂ (JCPDS: 00-043-1027), (c) Raman spectra of Ru-CCP-500, Ru-CLC-500, and RuO₂ (Raman bands for RuO₂ are marked in the dotted circle), (d) N 1s XPS spectra of Ru-CCP-500 and CNC-500, and (e, f) HAADF-STEM image of Ru-CCP-500 and the corresponding line scan analysis of elements Ru, N, and C across the line (marked with yellow color).

material, but they are too small to be visible in XRD or else the presence of nitrogen in the material may be influencing the electronic state of ruthenium.

To understand the reason for the existence of multiple oxidation states of ruthenium in the catalyst, we synthesized a control sample and examined its structural and electronic properties alongside Ru-CCP-500. For a fair comparison of nitrogen doping effects, we synthesized a nitrogen-free counterpart, Ru-CLC-500, using cellulose as the carbon source through the same synthetic procedure followed for Ru-CCP-500 (see the Experimental Section for the details). The Ru 3p XPS spectra of Ru-CLC-500 also showed both metallic and oxidic Ru species (Figure 4a); however, the relative fraction of Ru⁰ to Ru^{δ+} species was the highest in Ru-CLC-500 compared to all the Ru-CCP materials. It was interesting to note that the XRD of Ru-CLC-500 exhibited visible features corresponding to both metallic ruthenium and RuO₂ phases (Figure 4b). The peaks at 28, 35.2, and 54.3° correspond to the RuO₂ diffractions (JCPDS: 00-043-1027) and the other diffractions

correspond to metallic Ru and the carbon support. To further confirm the nature of oxidized ruthenium in both Ru-CCP-500 and Ru-CLC-500, we conducted Raman spectroscopy on both samples. Ru-CLC-500 exhibited two Raman bands at 512 and 626 cm⁻¹, which are characteristic of the E_g and A_{1g} vibration modes for RuO₂, as predicted by group theory.^{60,61} However, in the case of Ru-CCP-500, these Raman features were not present (Figure 4c), suggesting that the oxidized ruthenium species in Ru-CCP-500 do not conform to the RuO₂ structure. In both the samples, we observed Raman shifts at 1353 and 1590 cm⁻¹, corresponding to the D-band and G-band, respectively, which are indicative of the disordered carbon structure and the crystalline graphitic structure within the carbon materials, respectively.⁶² The Raman spectra for other Ru-CCP catalysts are shown in Figure S8 in the Supporting Information.

With the exclusion of the presence of RuO₂ species in the Ru-CCP materials, our focus was narrowed down to one remaining avenue for confirming the identity of ruthenium

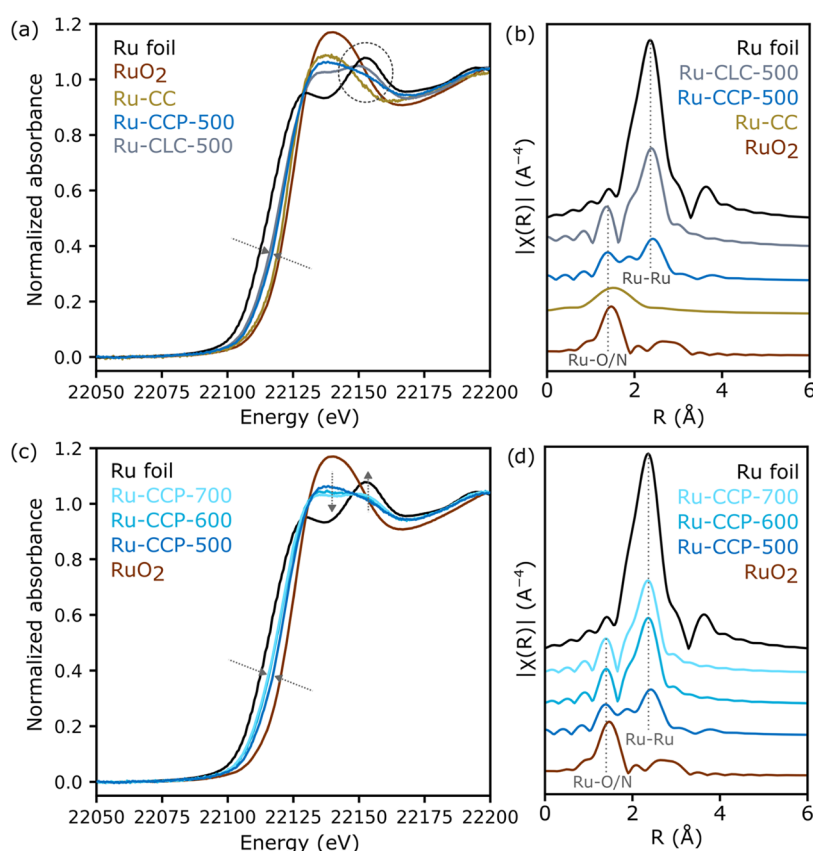


Figure 5. (a) Normalized XANES spectra and (b) Fourier-transformed EXAFS of Ru K-edge for Ru-CCP-500 and control samples along with references (Ru foil and RuO₂). (c) Normalized XANES and (d) Fourier-transformed EXAFS spectra for Ru-CCP catalysts along with references.

species: investigating the nature of the nitrogen species and how they interact with ruthenium in the material. The N 1s XPS of the bare carbon materials (CNC) can be deconvoluted into four different species of nitrogen, viz, pyridinic (Py-N), pyrrolic (Pr-N), graphitic (G-N), and oxidized graphitic (O-N). Figure 4d shows the N 1s core level spectra of the bare carbon material CNC-500 and Ru-CCP-500. The peaks at binding energies 398.8, 400.7, 401.5, and 402.8 eV correspond to Py-N, Pr-N, G-N, and O-N, respectively, for CNC-500. Meanwhile, for Ru-CCP materials, a new peak emerged at a binding energy (BE) of 399.3 eV, which can be attributed to the presence of Ru-N species.⁶³ Furthermore, it was notable that the Py-N, Pr-N, G-N, and O-N species in Ru-CCP-500 exhibited a lower binding energy compared to that in CNC-500. In Ru-CCP-500, a substantial reduction in the intensity of Py-N and Pr-N was observed. These observations imply that a fraction of ruthenium in the catalyst is involved in interactions with the nitrogen species in the carbon support, particularly with Py-N and Pr-N. The metal–nitrogen interaction could lead to the dissipation of the electron density from the metal to the nitrogen species, causing the red shift in their BE and consequently making the ruthenium species positively charged. This phenomenon could plausibly account for the presence of oxidized ruthenium species in the Ru-CCP materials despite the absence of any RuO₂. The XPS analysis also reveals a clear trend of a decline in the overall surface nitrogen species with an increase in the pyrolysis temperature. The quantification of the surface concentration of the elements calculated from the XPS survey is given in Table S5 and the XPS survey spectra for Ru-CCP-500 is given as an example in Figure S9. From the N 1s XPS spectra, a significant reduction in the pyridinic (Py-N)

and pyrrolic (Pr-N) nitrogen species is evident. This suggests a higher likelihood of the interaction between the ruthenium nanoparticles and these nitrogen species in the Ru-CCP-500 sample compared with the other samples. On the other hand, the increase in graphitic nitrogen (G-N) species is apparent, as the higher pyrolysis temperatures facilitate graphitization of the carbon support. A slight decrease in the Ru–N species is also found, which suggests that the metal–nitrogen interaction is more at a pyrolysis temperature of 500 °C. The N 1s XPS spectra of all of the Ru-CCP catalysts and the quantification of the different surface nitrogen species are given in Figure S10a,b, respectively.

The decline in the proportion of Ru^{δ+} species can be directly correlated to the reduction in the nitrogen content as the pyrolysis temperature increases. The sharpening of hcp ruthenium peaks in XRD indicates the formation of more metallic ruthenium at higher pyrolysis temperatures. Conversely, the absence of nitrogen in the Ru-CLC-500 sample promotes the formation of a greater proportion of metallic ruthenium along with the ruthenium oxide phase. Consequently, HR-TEM images of the Ru-CLC-500 sample reveal a pronounced particle clustering (Figure S11a,b) and a broad distribution of particle sizes ranging from 3 to 30 nm, with the majority falling within the 5–8 nm size range. This observation further underscores the role of nitrogen doping in enhancing the metal–support interaction in the catalyst, which, in turn, restricts the growth of the metal particles. The more direct evidence for the metal–nitrogen interaction can be seen from the line scan analysis of the Ru-CCP-500 sample carried out in HAADF-STEM (high-angle annular dark-field scanning transmission electron microscopy) mode (Figure 4e). As depicted

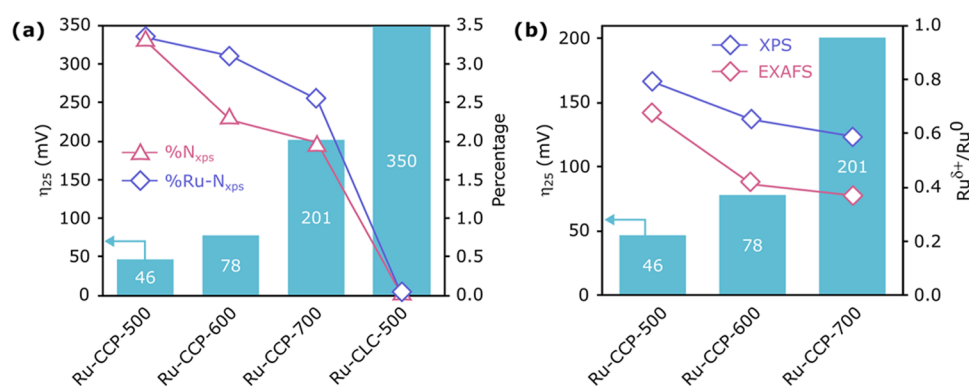


Figure 6. (a) Trend in the HER activity of Ru-CCP and Ru-CLC catalysts with respect to the overall N content and % Ru–N species calculated from XPS and (b) relationship between the HER overpotential of different Ru-CCP catalysts vs the ratio of Ru^{δ+}/Ru⁰ calculated from XPS and EXFAS analysis.

in Figure 4f, there is a noticeable increase in the line scan intensity for N that coincides with an increase in the Ru scan intensity. This observation holds true for both surface ruthenium and the ruthenium particles embedded within the carbon layers of the material. Therefore, the presence of specific nitrogen species and its interaction with the metal play a pivotal role in determining the material's activity in the HER. Ru-CCP-500, which exhibits the highest concentration of pyridinic and pyrrolic nitrogen species, likely fosters an increased interaction with the ruthenium nanoparticles, thus resulting in its better performance toward the HER.

To further explore the bulk electronic structure of the catalysts, Ru K-edge X-ray absorption spectroscopy (XAS) experiments were carried out for Ru-CCP materials and the control samples. The experimental details for the XAS analysis are given in the Supporting Information. Figure 5a shows the normalized X-ray absorption near-edge structure (XANES) of Ru-CCP-500 and the control samples Ru-CLC-500 and Ru-CC along with references. The absorption edge of Ru-CCP-500 lies in between the absorption edge of the Ru foil and RuO₂, which suggests that the Ru species in Ru-CCP-500 shows an average positive valence.⁶⁴ Ru-CLC-500 has a slightly low energy absorption edge lying near Ru-CCP-500. However, a clear difference among these samples were displayed by the near-edge region. The near-edge region of Ru-CLC-500 displays characteristics that resemble both the Ru foil and RuO₂, with a stronger resemblance to metallic Ru. In contrast, Ru-CCP-500's near-edge is positioned closer to RuO₂ and the Ru–chitosan complex (Ru-CC), and it also exhibits near-edge features corresponding to metallic Ru, albeit with a lower absorbance compared to Ru-CLC-500. These observations suggest the coexistence of both Ru⁰ and Ru^{δ+} species in both the CCP and CLC catalysts. These data are further supported by the Fourier transform of the extended X-ray absorption fine structure (EXAFS) region of these samples (Figure 5b). In the Ru foil, the prominent Ru–Ru peak is observed at 2.4 Å, and the Ru–O peak in RuO₂ is observed at 1.5 Å. The two main peaks in the samples were fitted with a Ru–Ru path for metallic ruthenium and Ru–O/N paths for Ru^{δ+} species. Ru-CLC-500 shows a prominent Ru–Ru peak compared to the Ru–O/N peak at 1.4 Å, whereas the Ru-CCP-500 sample shows a relatively small peak for Ru–Ru compared to Ru-CLC-500. The relative intensity of the Ru–Ru peak was higher compared to the Ru–O/N peak in Ru-CLC-500, while Ru-CCP-500 showed a comparable intensity of these peaks. These observations align with the Ru 3p XPS data. The Ru–O/N

peak is observed at 1.45 Å and can be assigned to Ru–N coordination in the Ru-CCP-500 material, and it is clearly distinct from the Ru–O peak position of RuO₂ and Ru-CLC-500. Moreover, Ru-CC has an entirely different peak at 1.6 Å with no Ru–Ru peak, which clarifies that the ruthenium species in Ru-CC carry a different charge initially, and during the pyrolysis process, Ru⁰ and Ru^{δ+} species have formed. Even though the Ru-CLC-500 sample shows the same coordination number (2.7) as that of Ru-CCP-500 for the Ru–O/N bond, their FT-EXAFS in the R-space clearly shows a difference. The EXAFS fitting for all of the samples is shown in Figure S12. This again suggests that the local environment of Ru^{δ+} species in Ru-CCP-500 is different from RuO₂ and Ru-CLC-500, hence confirming the existence of the Ru–N interaction as observed from N 1s XPS. The EXAFS fitting parameters of the catalysts and references are given in Table S6. The Ru–Ru coordination number for Ru-CCP-500 is 2.6 and that for Ru-CLC-500 is 6.8 and these numbers are significantly lesser than that (12) of bulk Ru.⁶⁵ The markedly low coordination number for Ru–Ru in the Ru-CCP-500 sample provides compelling evidence for the formation of ultrasmall ruthenium nanoparticles, which is clearly seen from the HR-TEM images of the catalyst.

Figure 5c shows the XANES spectra of all of the Ru-CCP materials synthesized at different temperatures from 500 to 700 °C along with the Ru foil and RuO₂. Notably, this edge shifts to lower energy levels as the pyrolysis temperature increases. Across all of these materials, both metallic and oxidic ruthenium near-edge features are observed. It is intriguing to observe a particular trend where an increase in the pyrolysis temperature corresponds to a decrease in the absorption intensity of the oxidic ruthenium near-edge, accompanied by a simultaneous increase in the intensity of the near-edge in the metallic ruthenium region. This trend implies a growing metallic character in the CCP catalysts as the pyrolysis temperature is raised. Figure 5d shows the Fourier-transformed EXAFS data for different Ru-CCP catalysts along with the references. As mentioned previously, the two main peaks in the Ru-CCP catalysts can be fitted with the Ru–Ru and Ru–O/N paths. The peak at 2.4 Å is indicative of metallic ruthenium, and its intensity significantly improves with increasing temperature. Meanwhile, the peak at 1.4 Å can be associated with Ru–N coordination, given its distinct position in comparison to RuO₂. Another significant observation was that the relative intensity of the Ru⁰ species compared to Ru^{δ+} species exhibits a notable increase at higher annealing

temperatures; this trend was consistent with the observations from the Ru 3p XPS data. The coordination number for the Ru–Ru bond was found to be 2.6 for Ru-CCP-500 and this number increases to 5.7 and 6.1 for Ru-CCP-600 and Ru-CCP-700, respectively. The increase in the coordination number is directly associated with the higher pyrolysis temperature and the concurrent reduction in nitrogen moieties. This phenomenon promotes the growth of metallic ruthenium nanoparticles, a transformation that is clearly evident in the HR-TEM images of the materials. Additionally, the Ru–N coordination number shows a decrease with the increase in pyrolysis temperatures due to the decrease in the amount of nitrogen species.

Structure Activity Relationship. The surface and bulk structural and electronic characterizations of the materials reveal that the nitrogen doping strongly influences the catalytic activity toward the HER. Figure 6a represents the trend in the HER activity with respect to the overall nitrogen content and the percentage of Ru–N species in the catalysts as calculated from N 1s XPS. The Ru-CCP-500 sample with the highest N content and a higher fraction of pyridinic and pyrrolic nitrogen shows the lowest overpotential. The HER activity successively decreases in Ru-CCP-600 and Ru-CCP-700 samples, as the N content and required surface nitrogen species reduce. At the same time, Ru-CLC-500 with the non-nitrogen-containing carbon support shows a far higher overpotential of 349 mV at the current density of 25 mA cm^{-2} . The comparative LSVs for Ru-CLC-500 and Ru-CCP-500 are given in Figure S13. These data prove that the mere presence of RuO_2 or metallic ruthenium species within cellulose-derived carbon is inadequate in achieving an effective catalytic performance and nitrogen doping strongly influences the electrocatalytic activity. As seen from HR-TEM, the formation of smaller ruthenium nanoparticles is favored only in the presence of nitrogen, while the metal particles on non-nitrogen-containing cellulose-derived carbon appear to be larger. Therefore, the presence of nitrogen enhanced the electronic metal–support interaction in the catalyst. Consequently, this interaction is the reason for the existence of charged ruthenium species in the catalyst. It is noteworthy that the presence of $\text{Ru}^{\delta+}$ species plays a vital role in the activity of different catalysts. Figure 6b depicts the trend in the overpotential at 25 mA cm^{-2} versus the ratio of $\text{Ru}^{\delta+}/\text{Ru}^0$. This ratio is calculated using the area of Ru^0 and $\text{Ru}^{\delta+}$ peaks in the Ru 3p XPS spectra and the intensity of the Ru^0 and $\text{Ru}^{\delta+}$ peaks from the EXAFS. The $\text{Ru}^{\delta+}/\text{Ru}^0$ ratio decreases with an increase in the pyrolysis temperature and consequently causes an increase in the overpotential. Hence, it is apparent that a certain proportion of oxidized and metallic ruthenium is necessary for attaining the desired overpotential. At lower pyrolysis temperatures, the material possesses a maximum amount of the desired nitrogen species, facilitating an enhanced interaction with the metal. This strong metal–support interaction favors a higher activity toward the HER. Hence, the pyrolysis temperature of 500°C was optimum to form the ruthenium-containing nitrogen-doped carbon from the ruthenium–chitosan complex, with controlled graphitization and the most active metal centers for the HER activity.

Electrochemical Activity and Stability. To explore the reason behind the better HER performance of Ru-CCP-500 than Pt/C (20 wt %), the HER reaction kinetics of all of the samples were analyzed by comparing the Tafel slopes calculated from the small polarization area of LSVs and are shown in Figure 7a. The current densities at certain potentials

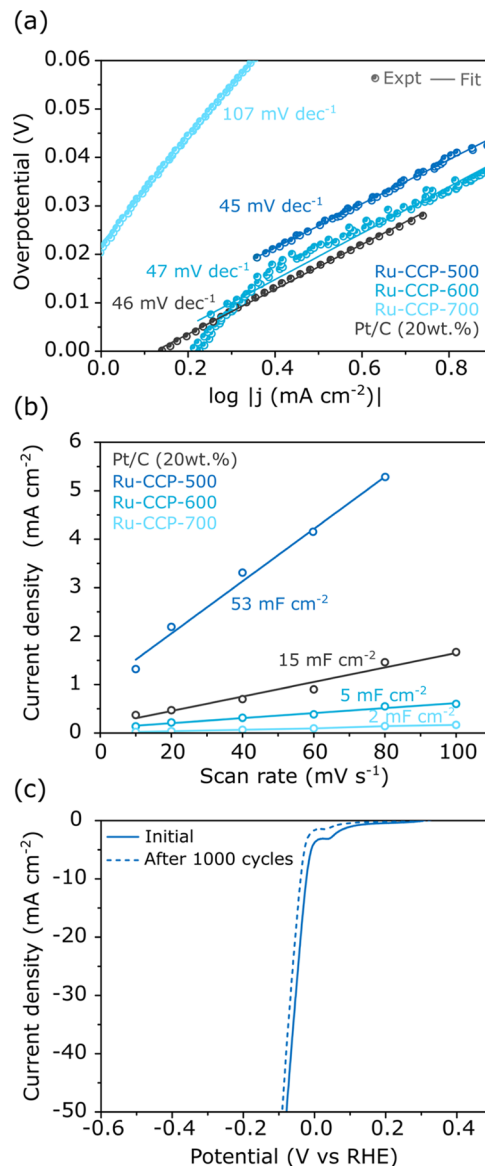


Figure 7. (a) Tafel slopes for Ru-CCP-500, 600, and 700 along with Pt/C, (b) plots of the current density vs the scan rate in the nonfaradaic region of the CVs, and (c) stability test of Ru-CCP-500 in 1 M KOH before and after 1000 cycles within the potential window of -0.005 to 0.05 V vs RHE .

were calculated and the linear part is fitted in the Tafel equation ($\eta = b \log j + a$; η : overpotential, j : current density, b : Tafel constant). The corresponding Tafel slopes of Ru-CCP-500, Ru-CCP-600, Ru-CCP-700, and Pt/C (20 wt %) are 45, 47, 107, and 46 mV dec^{-1} , respectively. The lowest Tafel slope was observed in the case of Ru-CCP-500. Ru-CCP-600 and Pt/C were also found to have a Tafel slope of a similar range ($\sim 40 \text{ mV dec}^{-1}$). This indicates that Ru-CCP-500, Ru-CCP-600, and Pt/C follow similar HER kinetics. According to the literature and the Tafel slope obtained, they follow the Volmer–Heyrovsky mechanism for the HER and Heyrovsky as the rate-determining step.^{66,67} The electrocatalytic charge transfer resistance between electrode/electrolyte interfaces was calculated from the electrochemical impedance spectroscopy (EIS) analysis in the 1 M KOH electrolyte solution in the same three-electrode setup. Figure S14 displays Nyquist plots of Ru-CCP-700, Ru-CCP-600, Ru-CCP-500, and Pt/C (20%)

in 1 M KOH at -0.03 V vs RHE. The lowest R_{CT} value of $3.14\ \Omega$ for Ru-CCP-500 and $5.1\ \Omega$ for Ru-CCP-600 compared to Pt/C ($6.19\ \Omega$) shows the active charge transfer kinetics of Ru-CCP-500 and Ru-CCP-600, which is in good agreement with the trend of the performed LSVs. Further, the double-layer capacitance (C_{dl}) value for the Ru-CCP samples and Pt/C was calculated from the CV plot run in the nonfaradic region at a potential range from 0.065 to 0.115 V vs RHE, as shown in Figure S15. The slope values obtained for Ru-CCP-500, Ru-CCP-600, Ru-CCP-700, and Pt/C (20 wt %) were 53 , 5 , 2 , and $15\ \text{mF cm}^{-2}$, respectively (Figure 7b). Accordingly, the C_{dl} values obtained for Ru-CCP-500, Ru-CCP-600, Ru-CCP-700, and Pt/C (20 wt %) were 10.38 , 0.98 , 0.40 , and $2.94\ \text{mF}$, respectively. As the C_{dl} is directly proportional to the electrochemical active surface area (ECSA), the calculated C_{dl} values of the catalysts give insight into the active sites. The ECSA was calculated by dividing the C_{dl} by the specific capacitance (C_s), which is assumed to be $0.040\ \text{mF cm}^{-2}$. The ECSA values obtained for Ru-CCP-500, Ru-CCP-600, Ru-CCP-700, and Pt/C (20 wt %) were 259.5 , 24.5 , 10 , and $73.5\ \text{cm}^2$, respectively. The C_{dl} and ECSA values calculated for the samples are listed in Table S7 in the Supporting Information. The ECSA was also determined using the Cu underpotential deposition method (Cu_{UPD}) for the best-performing Ru-CCP-500 catalyst and Pt/C. The experimental detail for the same is described in the Supporting Information. Figure S16a,b shows the background and the Cu_{UPD} stripping peak in the voltammograms of Pt/C and Ru-CCP-500 catalysts, respectively. The ECSA values obtained for the studied catalysts were $1214.2\ \text{cm}^2 \text{mg}_{Ru}^{-1}$ for Ru-CCP-500 and $380.95\ \text{cm}^2 \text{mg}_{Pt}^{-1}$, for commercial Pt/C (20 wt %). The higher ECSA of Ru-CCP-500 compared to Pt/C describes that the material has well-exposed active sites on the conductive nitrogen-doped carbon support and facilitates better mass transfer in the HER kinetics.

For the stability test, the LSV for Ru-CCP-500 in 1 M KOH was conducted before and after 1000 cycles within a potential window of 0.005 to 0.05 V vs RHE (Figure 7c). There was no significant change in the HER polarization curve after 1000 cycles. Along with this, the operational stability of the catalyst was evaluated by chronoamperometry analysis in 1 M KOH at a potential of -0.06 V vs RHE for 12 h. The results are shown in Figure S17, and it is evident from the data that the catalyst performs consistently without degradation in the current output, hence referring to the higher structural integrity of the catalyst. The HR-TEM image of the spent catalyst from the electrode is shown in Figure S18. The particle morphology observed was intact as the fresh catalyst. Though a slight increase in the particle size has been observed, the spent material does not show any severe agglomeration, which suggests that the enhanced metal–support interaction helps in retaining the structure and stability of the catalyst. After the stability test, inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the electrolyte solution was carried out, and no ruthenium leaching was found in the electrolyte. These results suggest that the Ru-CCP-500 catalyst is durable and delivers a stable performance under the experimental conditions. Post the stability test, the electrode with the spent Ru-CCP-500 catalyst was subjected to Ru 3p and N 1s XPS. Ru 3p XPS shows (Figure S19a) an overall decrease in the intensity compared to the fresh catalyst, which is due to the smaller quantity of the catalyst used to coat on the electrode. The Ru^0 peak shows a considerable decrease in the

intensity, while the $\text{Ru}^{\delta+}$ peak shows an increase in the intensity compared to the fresh catalyst. This suggests that $\text{Ru}^{\delta+}$ is the active species in the catalyst. During alkaline electrolysis, some of the Ru^0 species have transformed to $\text{Ru}^{\delta+}$ species. This observation is supported by the N 1s XPS (Figure S19b) of the spent catalyst, where we can see a significant increase in the pyrrolic (Pr–N) nitrogen species and Ru–N species compared with the fresh Ru-CCP-500 catalyst. An overall decrease in the other nitrogen species was also observed in the same. During the HER, the interaction of this Pr–N species with ruthenium might have happened and hence more $\text{Ru}^{\delta+}$ species formed in the catalyst, which eventually contributed to the stable performance of the catalyst.

CONCLUSIONS

In conclusion, this study presents a sustainable approach for synthesizing Ru/N-codoped carbon catalysts (Ru-CCP) through chitosan complexation with ruthenium, followed by a one-step pyrolysis process. Ru-CCP-500 exhibited an outstanding electrocatalytic activity for the HER, surpassing the commercial Pt/C catalyst and the other ruthenium-based catalysts. The exceptional performance of Ru-CCP-500 can be attributed to its unique structural and electronic properties. Characterization of Ru-CCP materials revealed the presence of ultrasmall ruthenium nanoparticles with a significant proportion of Ru–N coordination, as evidenced by XPS and XAS studies. The nitrogen doping not only stabilized the ruthenium nanoparticles but also created active sites within the carbon framework, contributing to the enhanced HER activity. The synthesis temperature of $500\ ^\circ\text{C}$ was identified as optimal, striking a balance between graphitization and N content in the catalyst to achieve the desired ratio of charged and reduced ruthenium species. This study also demonstrates the modulation of electronic properties of the carbon support via the strong metal–support interaction aided by nitrogen doping. Ru-CCP materials offer a viable alternative to platinum-based catalysts, addressing cost and scarcity issues. Also, it highlights the potential of biomass-derived materials like chitosan as a valuable resource for sustainable energy applications.

EXPERIMENTAL SECTION

Materials. All of the chemicals and reagents used were of analytical grade, and they were used as received. Low-molecular-weight chitosan (product code: 448869) was procured from Sigma-Aldrich. Ruthenium(III) nitrosyl nitrate solution ($\text{N}_4\text{O}_{10}\text{Ru}$, Ru-1.5% w/v) was obtained from Alfa Aesar. Glacial acetic acid and acetone (99%) were purchased from Loba Chemie. Microcrystalline cellulose was procured from the Maple India Bio Chem Lab. All of the solutions required for this work were prepared using deionized water.

Synthesis of Chitosan-Derived Nitrogen-Doped Carbon (CNC). The chitosan-derived nitrogen-doped carbon (CNC) material was prepared by a one-step pyrolysis method in a tubular furnace under a nitrogen atmosphere. One gram of chitosan was added to $40\ \text{mL}$ of 1% (w/v) acetic acid solution and stirred at room temperature for 12 h to get a transparent viscous solution. This solution was then poured slowly into $150\ \text{mL}$ of acetone to precipitate out the chitosan hydrogel. The hydrogel was then filtered and washed 3 times with $10\ \text{mL}$ of acetone. The filtered hydrogel was then dried in a laboratory oven at $60\ ^\circ\text{C}$ for 12 h and then dried at $100\ ^\circ\text{C}$ in a vacuum oven for 6 h. The dried chitosan hydrogel material was taken in a ceramic boat and kept in a quartz tube for pyrolysis. The nitrogen flow was adjusted to $30\ \text{mL/min}$, and a $10\ ^\circ\text{C/min}$ ramp rate was given to attain the set temperature. It was pyrolyzed at three different temperatures, viz, 500 , 600 , and $700\ ^\circ\text{C}$ for a period of 2 h to obtain nitrogen-doped carbon

CNC-500, CNC-600, and CNC-700, respectively. After the pyrolysis, the obtained carbon material was weighed and ground well using a mortar and pestle and used as such for the experiments. The percentage weight of CNC materials obtained at different pyrolysis temperatures was calculated with respect to the initial chitosan weight. The weight percentage of carbon materials CNC-500, CNC-600, and CNC-700 obtained was 30, 25, and 20%, respectively. These values were considered for the calculation of the desired metal loading for the synthesis of M-CCP materials at different pyrolysis temperatures.

Synthesis of the Metal–Chitosan Complex (M-CC). The metal–chitosan complex was synthesized by following a previously reported procedure, with certain modifications.⁴¹ One gram of chitosan (6.2 mmol, monomer basis) was added to 40 mL of 1% (w/v) acetic acid solution and stirred at room temperature for 12 h to get a transparent viscous solution of chitosan. To this solution, 5 mL (0.075 g of Ru, 0.74 mmol), 4.17 mL (0.063 g of Ru, 0.62 mmol), and 3.33 mL (0.05 g of Ru, 0.49 mmol) of 1.5 v/w % ruthenium(III) nitrosyl nitrate solution were added in order to achieve a final metal loading of 25% in all of the materials after the pyrolysis at 500, 600, and 700 °C, respectively. The chitosan and metal amounts used for the synthesis of M-CCP catalysts are shown in Table S1. Acid-treated chitosan was allowed to stir with the metal salt solution for another 12 h to get the metal–chitosan complex solution. The metal–chitosan solution was then poured slowly into 150 mL of acetone to form the metal–chitosan complex hydrogel. The hydrogel was filtered and washed 3 times with 10 mL of acetone. The filtered hydrogel was then dried in a laboratory oven at 60 °C for 12 h and then dried at 100 °C in a vacuum oven for 6 h. The dried hydrogels were named the metal–chitosan complex (M-CC).

Synthesis of the Metal–Chitosan Complex Pyrolyzed (M-CCP) Material. The metal–chitosan complex (M-CC) was weighed and transferred to a ceramic boat and placed in a quartz tube fitted in a tubular furnace. The pyrolysis was done at a nitrogen atmosphere with a flow of 30 mL/min at 500, 600, and 700 °C for 2 h, and a temperature ramp rate of 10 °C/min was given to attain the pyrolysis temperature. The material obtained after pyrolysis was named as the metal–chitosan complex pyrolyzed material (M-CCP-T, where M & T stand for the metal and the temperature of pyrolysis, respectively). The material was weighed and ground well in a mortar and pestle and used as such for the experiments.

Synthesis of the Metal-Doped Cellulose-Derived Carbon (M-CLC) Material. For the synthesis of M-CLC materials, cellulose was used instead of chitosan as the biomass carbon source for the catalyst synthesis. Initially, 1 g of cellulose was pyrolyzed at 500 °C for 2 h under a nitrogen atmosphere (a 30 mL min^{−1} flow) and the final weight of the carbon material obtained was calculated with respect to the initial cellulose weight. This weight was considered as the weight of the support for the calculation of the metal loading at 500 °C (Table S1). One gram (6.2 mmol, monomer basis) of cellulose was taken in 40 mL of 1% (w/v) acetic acid and stirred at room temperature to get a dispersion of cellulose. 2.9 mL of 1.5 v/w % ruthenium(III) nitrosyl nitrate solution (0.043 g of Ru, 0.42 mmol) was added into the cellulose dispersion and stirred for 12 h. The solvent was removed by rotary evaporation, and the solid was dried in a vacuum oven at 150 °C. The dried material was pyrolyzed at 500 °C for 2 h under a nitrogen atmosphere (a 30 mL min^{−1} flow) in a tubular furnace to obtain the Ru-CLC-500 material.

Material Characterization. The synthesized materials were characterized using various characterization techniques, such as XRD, XPS, XAS, HR-TEM, TGA, ICP-OES, Raman, and N₂ adsorption. The X-ray diffraction measurements were performed on a Desktop PXRD Miniflex 600 (Rigaku) diffractometer using Ni-filtered monochromatic Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The samples were scanned between a 2θ range of 10 and 90° at a scan rate of 4°/min. The catalyst morphology, analysis of the lattice parameter, elemental mapping, selected area diffraction (SAED), and high-resolution STEM images were obtained using a JEOL JEM-F200 (URP) transmission electron microscope working at an accelerating voltage of 200 kV. The chemical state of elements in the catalyst was identified by XPS analysis using a Thermo K-alpha+ X-ray

photoelectron spectrometer using an Al K α source. XPS data were fitted using Casa XPS software and the binding energy correction was done using carbon 1s energy (284.6 eV). Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C/min under an oxygen atmosphere from 25 to 900 °C to determine the metal loading over carbon using an STD Q600 thermogravimetric instrument. Elemental analysis for metals was performed on a Spectro Arcos Germany FHS 12 instrument. Raman analysis was performed on a Horiba LabRam HR800 Raman spectrometer using a He–Ne laser (632.8 nm, 20 mW) in the range of 100–4000 cm^{−1}. The nitrogen adsorption isotherms and surface area analysis were carried out on a Quantachrome BET surface area analyzer. Experimental details for the X-ray absorption spectroscopy (XAS) studies are given separately in the Supporting Information.

Electrochemical Analysis. A potentiostat (Bio-Logic-SP-300) was used for the electrochemical analysis of the synthesized materials in 1 M KOH solution using a three-electrode setup. Hg/HgO was used as the reference electrode, a graphite rod was used as the counter electrode, and an as-prepared catalyst-coated glassy carbon electrode was used as the working electrode with an active area of 0.196 cm². The Hg/HgO electrode was calibrated in a H₂-saturated 1 M KOH solution. The potential was referenced with respect to RHE by adding 0.925 V. The experimental details for the Hg/HgO electrode calibration, CV and Cu_{UPD} measurements are given in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c03169>.

Experimental details of additional electrochemical analysis; experimental details of XAS analysis; additional HRTEM images; TGA curve; XRD; Raman spectra; XPS; EXFAS fitting; EXAFS fitting parameters; literature comparison of Ru based HER catalysts; additional electrochemical analysis data (PDF)

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Author Contributions

L.K. designed and directed the research and was involved in the synthesis of materials, data analysis, data curation, writing of the original manuscript, and the revision of the manuscript. S.B. and A.P. conducted the electrochemical analysis and was involved in the revision of the manuscript. R.R.U. did the EXAFS data fitting and analysis. P.L.D. and S.K. gave critical insights into the work and reviewed the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Shell waste valorization to chemicals: methods and progress

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In light of growing energy and resource demands, the conversion of biomass materials into diverse chemicals and fuels holds significant importance. This process enables the utilization of biomass as a valuable and renewable resource to meet these escalating needs. The current biomass valorization processes are largely based on plant-derived lignocellulosic biomass materials. Studying new genres of biomass materials and their value addition is highly desirable, and they would complement and expand the existing biorefinery system. Crustacean shell waste represents a highly potential bioresource that is composed of a set of useful chemicals, among which chitin, the amino polysaccharide, has come to the fore as a promising material for a plethora of applications. In terms of the abundance of biopolymers on Earth, cellulose is the most prevalent biopolymer, and chitin ranks as the second. The presence of biologically fixed nitrogen in the structure of chitin opens up new possibilities for making useful chemicals, notably nitrogen-containing chemicals, which are otherwise impossible to produce directly from lignocellulosic biomass. In the last two decades, several attempts have been made by researchers in this area to convert chitin and its derivatives into valuable chemicals. This review comprehensively summarizes the transformation of the chitin fraction from shell waste to various chemicals through different thermo-catalytic processes and appraises the advancements in this area. The effect of various catalytic systems on chitin biomass valorization processes and the challenges and opportunities allied to this are discussed.

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1 Introduction

The excessive release of carbon dioxide (CO₂) has emerged as a significant cause for concern due to its contribution to the



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global warming phenomenon. The primary culprits behind this surge in CO₂ emissions are human activities involved in processing fossil fuel feedstocks to fulfil energy and material demands. Over the past two decades, this has prompted a notable shift in scientific focus towards exploring alternative energy sources and feedstocks. As per current scientific understanding, transitioning from conventional fuels to electricity can substantially mitigate emissions. However, despite progress in the energy sector, there is still a reliance on chemical processes to meet material needs. A potential solution lies in adopting renewable feedstocks, such as waste biomass. This approach not only aids in reducing our carbon footprint but also aligns with the imperative of fulfilling chemical requirements more sustainably.^{1,2}

While plant-based biomass is primarily composed of carbon, hydrogen, and oxygen, animal biomass waste, such as shell waste, additionally contains nitrogen in the structure as a result of biological nitrogen fixation. This makes shell waste an appealing alternative feedstock to traditional nitrogen-containing chemicals, which rely heavily on the energy-intensive Haber process for ammonia synthesis. The current biomass utilization is largely focused on lignocellulosic biomass.^{3–5} In contrast, much less attention is given to the valorization of animal-derived biomass. In this context the horizon of exploring new types of biomass resource will benefit the expanding horizon of biobased products and complement the current lignocellulose-based biorefinery system.

The FAO's 2022 report states that the annual production of crustaceans, including both aquaculture and capture fisheries, reached 17.2 million tons in 2020.⁶ Most of it comprises crabs, shrimps, lobsters, and prawns. With the increase in the overall production of crustaceans, the shell waste management facilities also have to be improved. The disposal of the waste produced after shellfish processing represents a practical chal-

lenge, as in developing and poor countries, often the shellfish waste is discarded back into the ocean, dumped in landfill sites, burned, or left out to spoil, whereas in developed countries like the UK, the disposal cost for landfill sites is about £80.⁷ Unregulated disposal can be a nuisance and polluting if not controlled. Shell waste contains several useful chemicals, such as chitin (an amino polysaccharide), protein, minerals like calcium carbonate, and pigments (the detailed composition is discussed in the next section). Hence, the valorization of shell waste by separating its components into different fractions, up-grading of each fraction, and converting them into useful chemicals can be a strategy for the management of shell waste.

The chitin fraction derived from shell waste constitutes a potent biopolymer, ranking as the second most abundant biopolymer in nature, following cellulose. Given its origin, chitin is both inexpensive and abundant, deriving from biomass, rendering it carbon-neutral and aligning well with the principles of the circular economy. Its natural nitrogen content further enhances its appeal as a feedstock. Considering the structural homology between chitin and cellulose, researchers have contemplated a parallel synthetic pathway for the production of value-added chemicals and platform compounds, particularly those featuring nitrogen moieties. Notably, several thermo-catalytic methodologies have been developed for the transformation of chitin biomass. These encompass the depolymerization, hydrolysis, hydrogenation, and oxidation of chitin and chito-oligosaccharides, yielding various nitrogen-containing and non-nitrogen-containing sugars, heterocyclic compounds, polyols, and acids *etc.* These methods serve the purpose of enhancing the value and utility of chitin-derived chemicals through systematic upgradation processes.

Chitin valorization to chemicals was in its budding stage in the initial years of the last decade. In recent times, there has been a discernible surge in interest surrounding the conversion of chitin, resulting in a substantial body of research and publications on the subject. Fig. 1 illustrates the increasing number of publications related to the thermo-catalytic trans-



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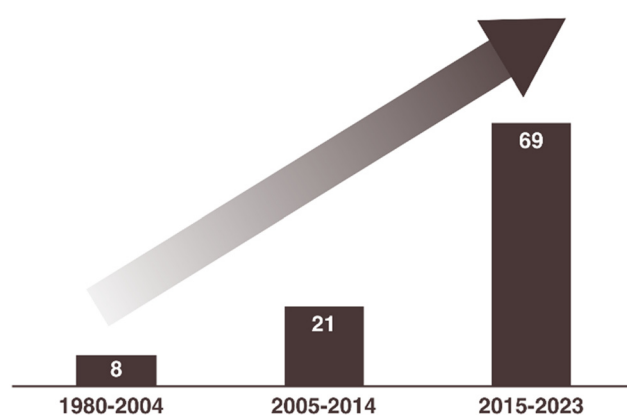


Fig. 1 Number of publications on the transformation of chitin and chitin-derived chemicals.

formation of chitin biomass into various chemicals. This data compilation is derived from the literature results obtained through searches using specific keywords and their combinations, such as 'valorization of chitin and chitosan', 'depolymerization of chitin and chitosan', 'catalytic conversion of chitin biomass', 'value-added chemicals from chitin', 'transformation of chitin', and 'nitrogen compounds from chitin' in the SciFinder database.

The transformation of chitin into various chemicals and the aspects of shell biorefinery have been previously addressed in a limited number of earlier reviews and perspectives.^{8–19} While a few reviews have provided detailed descriptions of various aspects of shell waste valorization and offered insights into the potential of chitin valorization, the majority of other reviews have focused on specific areas, such as the synthesis of one particular category of chemicals. Notably, a comprehensive compilation and discussion on recent advancements in catalytic transformations of chitin biomass is conspicuously absent in the existing literature. This gap in knowledge has motivated our exploration into the intricacies of the valorization of chitin from shell waste. The primary objective of this review is to scrutinize the diverse transformations of chitin leading to the production of valuable chemicals. Through an extensive examination of relevant literature, we present a categorization of chitin valorization methods based on the various products synthesized from chitin biomass. The review also delves into the discussion of the different catalytic systems employed and the distinct types of reaction process utilized in the conversion of chitin. In this review, our major focus is on the value addition of only the chitin fraction from shell waste. Given the abundance of detailed reviews on shell waste components¹⁰ and fractionation methods,²⁰ we have included only a general and short description of other shell waste components and methods of shell waste fractionation for them in this review.

2 Shell waste components and uses

The exoskeleton of crustaceans such as crabs, shrimps, lobsters, krill, and prawns consist of mainly four components: the amino polysaccharide chitin (15–40%), protein (20–40%), minerals like calcium carbonate (20–50%), and lipids and pigments like astaxanthin (0–14%).^{21–23} This composition is different and can vary from species to species, depending on the habitat, geographical area, and season as well. An illustration of shell waste composition and the area of application of each component is presented in Fig. 2.

Calcium carbonate is the major component of shell waste. It is also commonly found in rocks, shells of snails and mollusks, and eggs. It has three polymorphic forms in nature. The β , λ and μ -CaCO₃ forms are named calcite, aragonite, and vaterite, respectively.²⁴ CaCO₃ has a wide range of applications in industry. It is mainly used as a construction material in the building industry, and as an extender in the paint industry. Recent reports have highlighted the importance of shell waste-

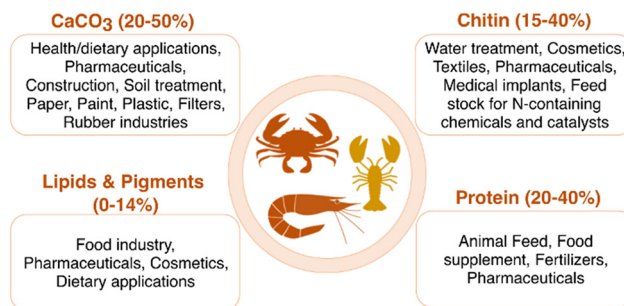


Fig. 2 Shell waste components and their applications.

derived CaCO₃ as a green additive to commercial cement.^{25,26} In medicine, CaCO₃ is used for health and dietary applications such as gastric antacids, phosphate binders, *etc.* It also plays a vital role in soil treatment in the agricultural industry.²⁴ About 20–50% of shell waste is composed of CaCO₃. This biological occurrence makes shell waste-derived calcium carbonate a reliable component in food and medicinal applications. The extraction of CaCO₃ to usable forms is discussed in some of the previous reports.^{27–29} Briefly, shell waste undergoes washing with water to remove dirt, salt and remaining flesh, drying and calcination at 500 °C to 1000 °C to produce the CaCO₃ as the final powder.

Chitin is a nitrogen-containing polysaccharide that is the second major component of the shell waste of crabs, shrimp, prawns *etc.* It also occurs in the exoskeletons of arthropods and in certain fungal species. The annual global production of chitin exceeds 100 billion tons.³⁰ The principal source of chitin is shellfish waste, which constitutes about 15–40% of the shell waste. Shrimp-processing wastes contain around 14–27% chitin in terms of their dry weight, while crab-processing wastes contain approximately 13–15% chitin. Chitin acts as a protective component in the cell wall, where the chitin filaments are integrated into a mixture of calcium carbonate, phosphate, and protein, forming a matrix. This protein-based matrix undergoes a hardening process known as tanning.³¹ Chemically, chitin is defined as a linear homopolymer of *N*-acetyl-D-glucosamine (NAG), or 2-(acetyl-amino)-2-deoxy-D-glucose linked *via* β -(1 → 4) glycosidic bonds. The structure of chitin is very comparable to that of cellulose, where the hydroxyl groups at the C-2 position of the glucose units are replaced by an acetamido group. There are three different polymorphic forms of chitin, namely α , β , and γ -chitin; they vary in the packing and polarities of adjacent chains in successive layers.³² The stacking configuration of different polymorphs of chitin is shown in Fig. 3a.

Thermodynamically, α -chitin is the most stable form of chitin, with an antiparallel arrangement of polymeric chains with alternating sense. The parallel arrangement of chains with the same sense makes the β -chitin whereas γ -chitin has a both antiparallel and parallel stacking of chains, which was also considered as a variant of the α -chitin family by recent studies. The conversion of β -chitin to α -chitin is possible while

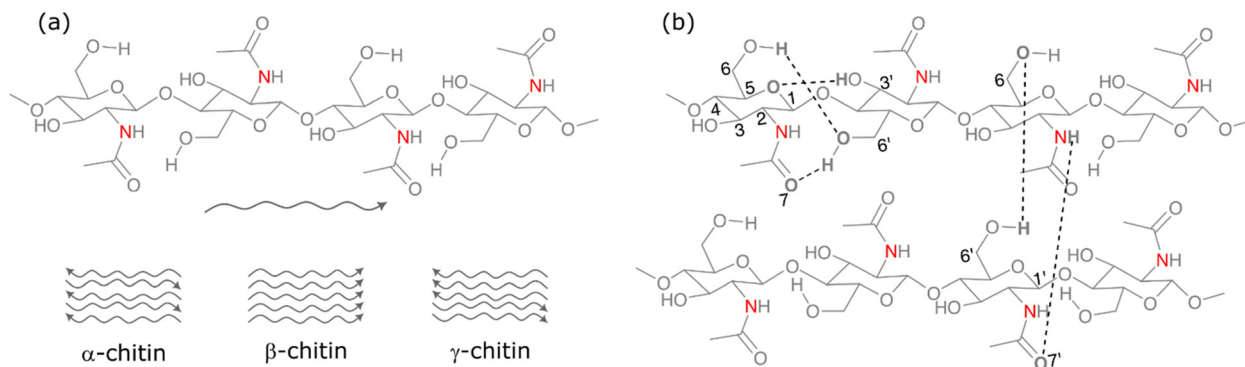


Fig. 3 (a) Stacking of polymer chains in different polymorphs of chitin and (b) intra- and inter-chain hydrogen bonding in chitin.

the reverse cannot be done. The crystallinity of α -chitin is due to the presence of intra-chain (C3'-OH to O5, C6'-OH to acetamido carbonyl O7 and C6'-OH to O6') and interchain (between NH and the acetamido carbonyl O7' and C6'-OH to O6) hydrogen bonding between the polymeric chains of the chitin.³³ The intra- and inter-chain hydrogen bonding in chitin is shown in Fig. 3b.

α -Chitin is the most abundant among all of the chitin polymorphs, due to its thermodynamic stability, which makes it insoluble in most of the common solvents, consequently making it difficult to break into monomers and other chemicals. Chitin can undergo deacetylation of the acetamido group when treated with a base at elevated temperature to form chitosan, where an amino group is present instead of an acetamido group. The monomer unit of chitosan is D-glucosamine (GA) or 2-(amino)-2-deoxy-D-glucose. Chitosan can have a varying degree of deacetylation (DD) according to the deacetylation conditions. Chitin with more than 50% of DD is considered to be chitosan. The transformation of chitosan is easier since it is less crystalline and has reduced rigidity compared with chitin.³⁴ Chitin and chitosan contain nitrogen along with carbon, hydrogen, and oxygen in their structure which makes them an excellent resource to produce various valuable chemicals. The attractive aspect of chitin valorization lies in its ability to produce nitrogen-containing chemicals, which are particularly valuable compared with those derived from its cellulose counterparts. Moreover, the production of N-containing chemicals requires ammonia or ammonia derivatives, and it is typically a laborious and energy intensive process. The Haber-Bosch process for ammonia synthesis requires high temperature and high pressure, and the hydrogen supply for the process is mainly from the reforming of fossil fuel. Hence, chitin can be a potential resource which is inexpensive and sustainable to produce nitrogen-containing chemicals. Section 4 provides a detailed discussion on the application of chitin as a feedstock and its valorization process.

Apart from the fact that chitin is a sustainable feedstock material, in its native form chitin has got so many interesting properties. The biological properties of both chitin and chito-

san such as antibacterial, antioxidative, biocompatibility, biodegradability, *etc.* have made both chitin and chitosan versatile materials for a variety of applications in the biomedical,³⁵ pharmaceutical,³⁶ and food processing³⁷ fields *etc.* The advantageous feature of chitin's structure lies in its ease of transformation into diverse physical forms, including fibers, membranes, films, spheres, beads, mats, disks, and more. This inherent flexibility facilitates the creation of chitin-based materials for applications such as wastewater treatment³⁸ and innovative biomedical solutions like tissue engineering, drug delivery, and the fabrication of medical implants with notable effectiveness.³⁹⁻⁴² Chitin is thermally and chemically stable and it has an abundance of hydroxyl, primary amino, and acet-ylamino functional groups that can bind to a diverse range of metal ions. Notably, the occurrence of the amino group is uncommon in polysaccharides, and that makes the tuning and functionalization of chitin a feasible process. The chemically modified chitin in the form of various organo-catalysts and metal incorporated catalysts is explored and utilized in many reactions.^{13,43-46}

In addition to fine chemicals, chitin is also used as a feedstock for biobased nitrogen-doped carbon.⁴⁷ This is a greener alternative to conventional nitrogen-doped carbon, as it reduces the use of expensive and toxic nitrogen sources like NH_3 , amines such as urea, melamine, dicyanodiamine, DMF, ethylenediamine, N_2H_4 , aniline,⁴⁸⁻⁵² or nitrogen-containing polymers, ionic liquids, and metal-organic frameworks (MOFs).⁵³⁻⁵⁵ The synthesis procedure and utilization of these nitrogen-doped carbons as catalysts,⁵⁶⁻⁵⁸ catalyst supports,⁵⁹⁻⁶¹ adsorbents^{61,62} *etc.* are discussed in several earlier literature works. The majority of them are being utilized for electrochemical applications⁶³⁻⁶⁸ and various organic transformations.^{58,59,69,70} Readers are redirected to the references for further reading.

Minor fractions of proteins and lipids are also found in the shell waste. The protein hydrolyzate which is found in some shrimp shells can be used in applications such as animal feed, pharmaceuticals, human nutrition, and cosmetics.⁷¹ The essential amino acid percentage in protein hydrolyzate determines the food protein nutritional value. Several species of

shrimp shells found to have proteins constituting amino acids glutamic acid, lysine, histidine, and valine which represent shell waste can be used as a nutritious protein source as animal feed and a food supplement.⁷² Lipids are biomolecules which contain hydrocarbons and are vital building blocks for the structure and functioning of cells. Examples of lipids are fats, waxes, oils, hormones, certain vitamins, and cell membrane *etc.* The lipids in shrimp shells comprise fatty acids as the majority. These fatty acids are composed of 30–50% saturated and 50–70% unsaturated fats. Eicosanoic acid is the prevalent saturated fatty acid found in the shells of shrimps. Additionally, fatty acids such as docosahexaenoic acid and eicosapentaenoic acid are polyunsaturated, and can also be found in crustacean shells.⁹ These lipids are used in cosmetics, food, and pharmaceutical applications.

Pigments like astaxanthin, astathin, lutein, canthaxanthin and β -carotene *etc.* are found in crustacean shells.⁷³ When the crustaceans are alive, they appear in different colors or even as transparent, as the pigments in their shells are bound to the protein. However, upon denaturation when the protein unfolds, the pigment is released. This is the reason for the transformation of seafood to a reddish hue when cooked. Astaxanthin has remarkable antioxidant activity, 10-fold higher than carotenoids and 500 times more advanced than vitamin E; hence, it is used as a dietary compound.⁷⁴ Since astaxanthin shows antioxidant, anti-immunomodulating, and anti-inflammatory effects it is widely used as a coloring agent in pharmaceuticals, food, and the cosmetics industry. The separation of lipids, proteins and pigments is mainly biochemical using enzymes and microorganisms and is briefly discussed in section 3.

3 Shell waste fractionation methods for the extraction of chitin

Fractionation protocols for shell waste have been developed primarily to extract chitin from discarded shells. Several methods exist for extracting chitin from shell waste (as shown in Fig. 4), in which the chemical extraction method is commonly employed industrially (Industrial method), whereas there are biological extraction procedures based on enzymes and microorganisms (Biological methods). Additionally, ionic liquid and deep eutectic solvent-based solvent extraction procedures have emerged recently (Solvent extraction methods).

3.1 Industrial method

Industrially, chitin extraction from shell waste follows a well-established chemical method starting from demineralization followed by deproteinization, and decolouration steps.⁷⁵ The demineralization step is conducted after the drying and powdering of waste shells. Mineral acids like hydrochloric acid (HCl), sulphuric acid (H₂SO₄), nitric acid (HNO₃) and even acetic acid or formic acid are used for demineralization. However, commonly, HCl is used for the treatment, in a concentration ranging from 0.2 to 2 N.³⁰ The time and tempera-

ture conditions for extracting chitin from shell waste can vary depending on the type of shells and the desired quality of the chitin. It usually takes a few hours to a couple of days, and the temperature can range from room temperature to around 100 °C. During the acid treatment, the calcium carbonate and other minerals are removed: $(\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2\uparrow)$.

Deproteinization is typically performed by alkaline treatment using 0.1 to 2 M concentration of NaOH at temperatures of 50 to 100 °C.⁷⁶ Proteins and lipids are hydrolysed and removed from the shell waste in this step. The process of base treatment not only removes proteins but also causes the chitin to undergo hydrolysis, resulting in a decrease in its molecular weight and partial deacetylation. After the deproteinization process, residual NaOH is removed by repeated washing with water and oven dried to obtain the chitin. Sometimes, to remove the pigments and to get colorless chitin for commercial applications oxidative bleaching is carried out using H₂O₂ or NaOCl. The depigmentation step can be carried out before the demineralization to extract valuable pigments like astaxanthin. Even though this method is widely used for commercial processes, the procedure is costly, destructive, and not environmentally friendly. Since it involves corrosive mineral acids and bases it requires corrosion-resistant equipment, and a huge amount of wastewater is generated from the neutralization process which causes extra treatment expenses. These factors account for the high price of chitin in the market. The need for a green and cost-effective method for shell fractionation resulted in many novel strategies, namely, solvent-extraction methods and bioprocessing methods.

3.2 Biological method

Biological extraction of chitin involves the use of enzymes and microorganisms for the isolation of chitin. Biological methods for extracting chitin typically involve two processes: deproteinization using enzymes and microorganism-mediated fermentation. Proteolytic enzymes like proteases, which are found in plants, microbes, and animals, are used for deproteinization of shell waste.³⁰ These protease enzymes (*e.g.* pepsin, papain, trypsin, devolvase *etc.*) can remove proteins from shells with minimal depolymerization and deacetylation during the extraction of chitin.⁷⁷ Enzymatic deproteinization of shrimp shells after demineralization has yielded chitin and protein hydrolysate.⁷⁶ Deproteinization can be conducted later or before the demineralization using crude enzymes as well as pure enzymes. Crude proteases can be obtained from bacteria and fish viscera. Even though enzymatic methods offer high-quality products and remain an eco-friendly process, they are costly, and the overall efficiency is lower than that of chemical processes.⁷⁸ Around 5 to 10% of residual proteins are found associated with isolated chitin. Additional alkali treatment can carry out the purity enhancement of the isolated chitin fraction.

The fermentation method can be utilized effectively by introducing specific microbial strains and endogenous microbes for deproteinization instead of using high-cost

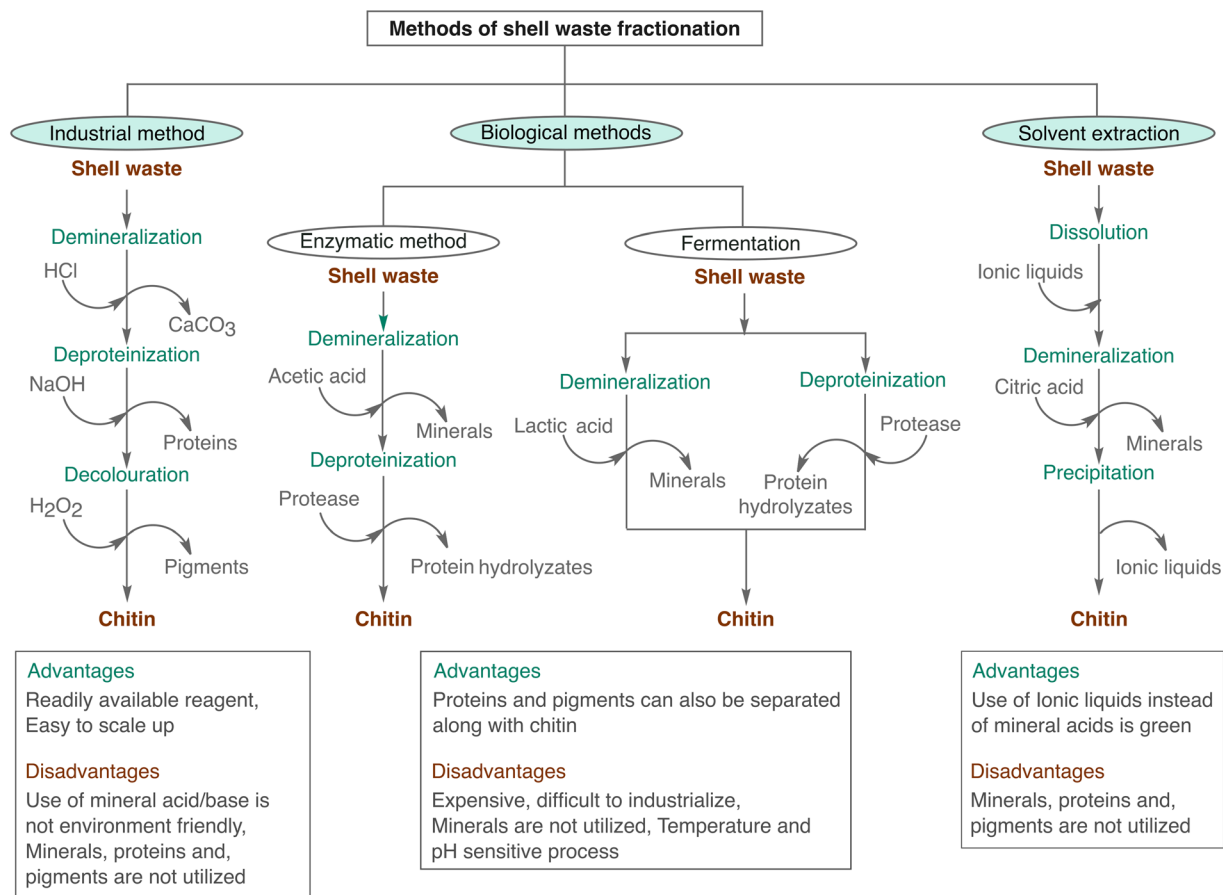


Fig. 4 Methods of shell waste fractionation.

enzymes.⁷⁵ The fermentation process combines the processes of deproteinization and demineralization into a single step. As a result of fermentation, a water-soluble liquor enriched with Ca²⁺ and protein hydrolysates is produced, which can be utilized as a supplement in animal feed. It should be noted that the efficiency of deproteinization and demineralization of shrimp shells can vary substantially based on the specific types of microorganism employed and the conditions of fermentation.⁹

There are two types of fermentation process, lactic acid-mediated fermentation and non-lactic acid-mediated fermentation. Lactic acid fermentation of shell waste uses *Lactobacillus* sp. bacterial strains which are capable of producing proteases and lactic acid during the fermentation process.⁷⁹ Glucose is converted to lactic acid, which causes a lowering of the overall pH of the feed. This acidic environment helps to inhibit the development of harmful microorganisms. Several factors affect the efficiency of the lactic acid fermentation process. These include the amount and composition of the microbial inoculum, initial pH, change in pH throughout fermentation, concentration and source of carbon, duration, and temperature of fermentation.⁸⁰ In non-lactic acid-based fermentation processes, various fungi and bacterial species such as *Bacillus*, *Pseudomonas*, and *Aspergillus* etc. have been

employed. Among these, the protease-producing bacteria *Pseudomonas aeruginosa* demonstrated the highest deproteinization efficiency (74.8%) and demineralization efficiency (78.5%).⁸¹

3.3 Solvent extraction methods

Even though chitin cannot be solubilized in normal solvents, ionic liquids (ILs)⁸² in the category of alkyl imidazolium halides or acetates or its acid functionalized derivatives and deep eutectic solvents (DES) (e.g., choline chloride-urea (CCU), choline chloride-thiourea and betaine hydrochloride-urea etc.) can dissolve chitin.⁸³ The literature extensively describes the dissolution of various biopolymers, such as cellulose, lignin, keratin, and others, in several ionic liquids. These studies provide detailed information on the capability of ionic liquids to effectively dissolve these biopolymers.⁸⁴ The strong interaction of anions in the ionic liquids with the hydroxyl group of the chitin helps to reduce the extent of hydrogen bonding in the structure and aids the dissolution of chitin. This dissolution ability of ILs has been utilized for the extraction of chitin in shell waste. The use of 1-ethyl-3-methylimidazolium acetate ([Emim]OAc) was reported for chitin extraction from shrimp shells. For 0.4 g shell waste with 10 g IL, loading under microwave heating for 2 minutes extracted chitin with high

purity and molecular weight.⁸⁵ Along with chitin, the dissolution of minerals and other components in the shell waste was also observed. Introducing a further step of demineralization by employing citric acid was found to be effective in reducing the mineral contamination in chitin extraction by ILs.⁸⁶ Recently *in situ* extraction of chitin was reported using 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim]HSO₄) acidic ionic liquid. This [Bmim]HSO₄ acidic ionic liquid facilitates the extraction of chitin and effectively separates it from the protein–mineral matrix simultaneously. This innovative approach offers a more streamlined and efficient method for chitin extraction.⁸⁷ Acidic and natural DES systems have been found to be effective in the dissolution and extraction of superior quality chitin from raw shell waste effectively.^{88,89} Extraction methods based on mechanochemistry where the solid-state milling of shell waste with solid acids is followed by aging are emerging as novel and sustainable methods nowadays.⁹⁰

As we discussed earlier, the methods intended to extract chitin from shell waste involve demineralization using acids, in which minerals are often decomposed to carbon dioxide and metal oxide or metal hydroxides, which means that they cannot be used as is. Similarly, base-aided deproteinization causes the denaturation of proteins and they cannot be isolated successfully. Hence, the traditional chemical methods of shell waste fraction can recover only a single component of it. However, the simultaneous extraction of protein, chitin, minerals, and pigments is highly desirable.

Biological extraction methods using protease enzymes have been successful in recovering the protein part in the form of protein hydrolyzate along with the recovery of chitin, astaxanthin and minerals.^{91,92} *Recombinant aspartic proteases P6281* (protease A) and *saccharopepsin* (protease B) showed high rates of deproteinization and could yield 40–71% of protein portions with an EAA (essential amino acid) content of 45–49%.⁹¹ The extraction of minerals, particularly CaCO₃, is highly desirable as they can serve as a reliable component in food and pharmaceutical applications because of their biological origin. The extraction of minerals from crustacean shell waste is not as popular as the mineral extraction from eggshells or the shells of mollusks. However similar methods can be adopted for mineral recovery from crustacean shell wastes. A typical method involves acid digestion of the shell waste followed by Na₂CO₃ treatment to precipitate out the CaCO₃.⁹³

4 Conversion of chitin biomass to chemicals

Chitin, being the bearer of naturally occurring nitrogen in its structure along with carbon, hydrogen, and oxygen, holds the potential for the production of biobased chemicals. Chitosan, the deacetylated chitin derivative, is more suitable for chemical transformation since it has enhanced solubility and less crystallinity than chitin. Hence, both chitin and chitosan are considered as substrates for chemical transformations. There

are different classes of chemicals derived from the valorization of chitin and its derivatives. Examples of chitin biomass-derived chemicals explored so far are given in Fig. 5. As the monomers of chitin and chitosan are the amino-sugars, *viz.*, *N*-acetyl-D-glucosamine (NAG) and D-glucosamine (GA), they are the first set of products that can be made from chitin or chitosan. In further cascade reactions, they can be converted to different chemicals. For example, the hydrogenation of amino sugars leads to the formation of amino or amide polyols, and dehydration reactions lead to various nitrogen heterocycles and nitrogen-containing furan derivatives or even furan derivatives without nitrogen. Oxidation leads to the formation of amino acids as well as acids without nitrogen. The following sections provide a comprehensive discussion on each of these transformations.

4.1 Conversion of chitin to nitrogen-containing chemicals

4.1.1 Conversion of chitin biomass to chito-oligomers and monomers. The first step in the chemical conversion of chitin and chitosan is their depolymerization or hydrolysis into chito-oligomers or monomeric amino sugars (Scheme 1). Chito-oligomers and amino sugars, GA and NAG, are used in the biomedical,⁹⁴ pharmaceutical and food industries for various applications.⁹⁵ The depolymerization methods can be chemical, physical, enzymatic and combinations of any of these methods as well. Chemical methods include hydrolysis in the presence of acids and bases,⁹⁶ oxidative degradation using hydrogen peroxide^{97,98} and ozone treatment⁹⁹ at elevated temperatures. Specific enzymes *viz.* chitinase, chitosanase and lysozyme and some non-specific enzymes like cellulose, protease, lipase, and pepsin are effective for enzymatic hydrolysis.¹⁰⁰ Physical methods like microwave,¹⁰¹ ultrasound^{102,103} and mechanical milling¹⁰⁴ techniques were also found to be useful along with chemical and enzymatic methods which can reduce the reaction time and increase the solubility of chitin by reducing its recalcitrant nature.

The acid-catalyzed hydrolysis of chitin and chitosan mostly involves the use of homogeneous acid catalysts like mineral acids in either water or ionic liquid media. The hydrolysis process for both chitin and chitosan comprises two important steps: the breakdown of the glycosidic bonds that link the NAG units and the deacetylation of the acetamido group within the NAG units. The rate of acid-catalyzed hydrolysis of the glycosidic linkage in chitin has been observed to be 2–3 times faster than that in chitosan.^{105,106} The probable reason is that the acetamido group at C2 helps in stabilizing the oxo carbonium ion transition state and accelerates the cleavage of the glycosidic bond. Meanwhile the protonated amino group in the C2 position of the GA unit hinders the proton attack on the glycosidic oxygen atom. The use of HCl (6.0 wt%) promoted the hydrolysis of chitosan in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) ionic liquid media resulting in a mixture of total reducing sugars (TRS) with a total yield of 60% within 7 hours at 100 °C.¹⁰⁷ The H₂SO₄-catalysed liquefaction of chitin in ethylene glycol (EG) medium has been reported by the same group; at 165 °C within 90 minutes, 75%

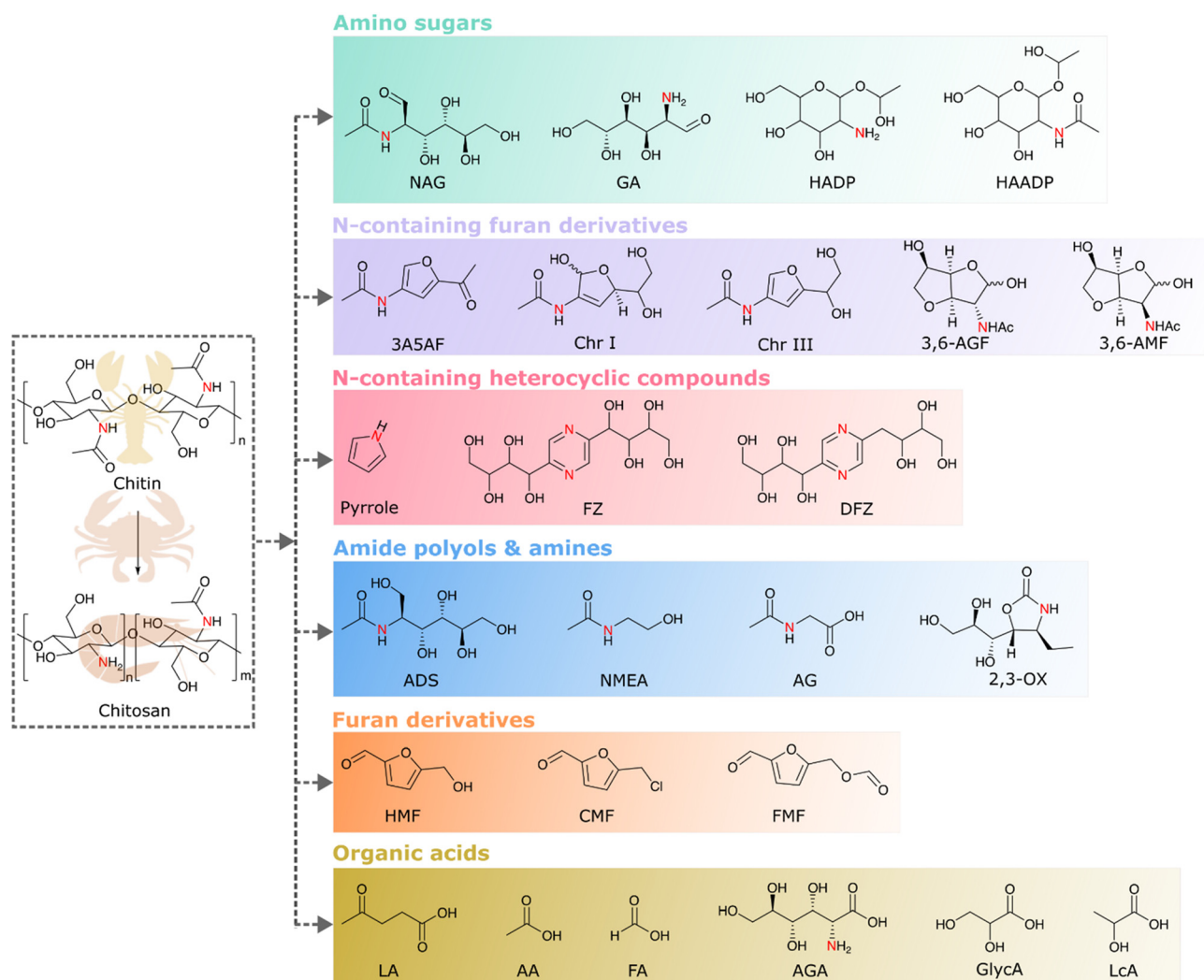
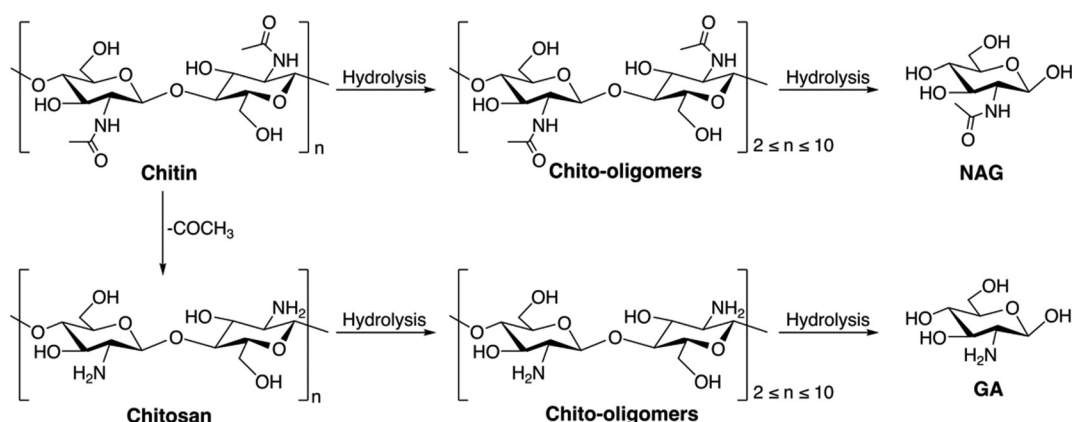


Fig. 5 Different classes of chemicals derived from chitin biomass valorization.



Scheme 1 Reaction pathway for chitin biomass hydrolysis to chito-oligomers and amino sugars.

of chitin was liquefied by using 8 wt% of acid. Hydroxyethyl-2-amino-2-deoxyhexopyranoside (HADP) and hydroxyethyl-2-acetamido-2-deoxyhexopyranoside (HAADP) were obtained as the major products in approximate yields of 30%.¹⁰⁸ In an attempt

to avoid the use of corrosive mineral acids, sulfonic acid functionalized imidazolium ILs have been used for the microwave-assisted hydrolysis of chitosan¹⁰⁹ where the IL 1-(3-sulfonic acid) propylpyridinium hydrogen sulfate ($[\text{C}_3\text{SO}_3\text{Py}]\text{HSO}_4$)

showed the best activity in DMSO because of its higher Brønsted acidity. The highest yield of 90% of TRS was obtained within 2 minutes at 640 W microwave power. Although these processes allow direct hydrolysis of chitin under mild reaction conditions, the use of strong mineral acids or other homogeneous alternatives is not desirable as they are corrosive and require a high post-processing cost.

In this context, the ball milling process has been successfully used to reduce the use of large amounts of mineral acids and ionic liquids, as mechanochemical forces can aid the hydrolysis process. Chitin depolymerization using a catalytic amount of H_2SO_4 was reported by Kobayashi *et al.* Ball milling of acid-impregnated chitin under solvent-free conditions yielded soluble short-chain oligomers, and further hydrolysis and methanolysis of the ball-milled (BM) sample at 170 °C for 1 hour gave 53% of NAG and 1–70% of *O*-methyl-*N*-acetylglucosamine (MeNAG) yield.¹¹⁰ Ning Yan *et al.* employed a similar strategy for the hydrolysis of chitin, where instead of a water medium, co-solvent systems were used. Various polar aprotic solvents were screened in which with a 4 : 1 diethylene glycol diethyl ether (DGDE)/water co-solvent system along with sulfuric acid, an 80% yield of glucosamine was achieved at 175 °C in 1 h from ball-milled chitin.¹¹¹ The depolymerization and functionalization of ball-milled chitin and chitin from shrimp shells were achieved during formic acid-mediated chitin liquefaction. The total yield of monomeric products obtained was 60% at 100 °C in 12 h.¹¹² Upon longer reaction times, the monomeric products underwent dehydration, resulting in the formation of 5-(formyloxymethyl)furfural (FMF) as the final product.

Another way to reduce the use of mineral acids was using lithium halide molten salt hydrate (MSH) systems due to their greater ability to disrupt the hydrogen bonding network of chitin.¹¹³ The use of only 40 mM HCl along with 60 wt% LiBr AMSH resulted in the formation of 71.5% NAG at 120 °C in 30 min. The higher acidity of the catalyst, the higher nucleophilicity of Br^- anions and the interaction of Li^+ cations with acetamide oxygen helps in breaking the glycosidic bonds without losing the acetamido groups and in turn increases the swelling and dissolution of the chitin. Other successful MSH systems constitute the use of 50% CaCl_2 along with 1a 0% ZnBr_2 mixture which resulted in a 67% yield of NAG at 120 °C in a 1 h reaction time. However, the chitin was aged in H_2SO_4 in this case.¹¹⁴

In an attempt to completely get rid of mineral acids, the same group studied use of zeolites in the lithium halide salt hydrate-mediated hydrolysis of chitin.¹¹⁵ Among various zeolites used, both commercial and synthesized SAPO-34 (CHA-type zeolite system) zeolite was found to be a suitable catalyst and gave an NAG yield up to 60%. The authors proposed that the Li^+ ions exchange with H^+ ions during the reaction and hence the hydrolysis reaction does not happen inside the pores of the catalyst and the released proton hydrolyzed the chitin dissolved in the LiBr molten salt hydrolysate. While the catalytic activity was not related to the zeolite morphology, the higher Brønsted acidity of the SAPO-34 had the key role to

play. Meanwhile, the low concentration of Lewis acid sites avoided the formation of undesirable side products.

Carbon-based solid catalysts possess higher stability compared with zeolite catalysts. A glucose-based carbon solid acid catalyst (GCSA) was employed for the hydrolysis of chitosan successfully, with a 98.1% yield of GA at 110 °C in 6 h. The presence of the amino groups in chitosan possesses challenges for solid acid catalysts as they can poison the acid sites. The authors overcame the problem by acidification of the chitosan amino group prior to the reaction. Along with higher activity the catalyst was found to be stable up to 6 catalytic cycles.¹¹⁶ Recently Kobayashi *et al.* overcame the use of any mineral acids and solvents by employing the mechanochemical hydrolysis of chitin using air-oxidized carbon as a catalyst (AC-Air).¹¹⁷ The weak acid sites induced by air oxidation of carbon in the form of carboxylic acid and hydroxyl groups were found to be responsible for the selective formation (94%) of chito-oligosaccharides. The solid carbon catalyst was able to hydrolyze chitin in a non-aqueous state and when compared with mineral acids and other solid acid catalysts, the selectivity of oligomers was higher in case of carbon catalyst.

Even though acid-catalyzed depolymerization is most favorable for chitin, the base-catalyzed depolymerization of chitin and chitosan has also been explored. Chebotok and co-workers studied the effects of bases on the depolymerization of chitin and chitosan.¹¹⁸ The hydrolysis was performed in various conditions such as in solutions of NaOH, KOH, NaCl, NaI, and KI, and also in air, under O_2 , and under N_2 . It was observed that the changes in molecular weight of chitin during its hydrolysis were essentially similar. It was found that neither hydroxide ions nor oxygen initiates the cleavage of the glycosidic bonds, but the excess water present in the system is playing this role. The H^+ ions formed by the dissociation of water (even trace amounts) caused the formation of carbenium ions which act as electrophiles in the reaction. Yan *et al.* studied the base-catalyzed mechano-chemical conversion of chitin and raw shrimp shell waste into low molecular weight chitosan.¹¹⁹ Chitin was ball milled along with different bases such as NaOH, KOH, LiOH, $\text{Ba}(\text{OH})_2$, and $\text{Ca}(\text{OH})_2$. It was observed that both NaOH and LiOH are effective in depolymerization as since Li^+ and Na^+ are small, they can easily coordinate to the C1 and C4 oxygens. However, NaOH is more effective in doing both deacetylation and depolymerization. A certain base concentration is necessary, but higher amounts of base cause the absorption of water which hinders the mechanical process. The amount of base used does not significantly affect the conversion of chitin, but notable improvements in conversion have been observed by optimizing ball milling parameters such as the number of balls, mill-cycles, *etc.* Chitosan obtained from raw shell waste had more than 90% purity and this process enabled a degree of deacetylation and a molecular weight in the range of 40–83% and 1–13 kDa, respectively.

The overall analysis of the conversion of chitin/chitosan to monomeric products shows that conventional acid and base systems are not very selective in forming the monomers, and

Table 1 Oligomers and amino sugar monomers from chitin biomass

Substrate	Catalyst	Reaction conditions			Product (% yield)	Ref.
		Solvent	Temperature (°C)	Time (h)		
Chitosan	HCl	[Bmim]Cl	100	7	TRS (60)	107
Chitin	H ₂ SO ₄	EG	165	1.5	HADP + HAADP (30)	108
Chitosan	[C ₃ SO ₃ Py]HSO ₄	DMSO	640 W (MW ^a)	0.03	TRS (90)	109
Ball milled chitin	H ₂ SO ₄	Water	170	1	NAG (53)	110
		Methanol	190	1	MeNAG (70)	
		DGDE/water (4 : 1 v/v)	175	1	GA (80)	
Ball milled chitin	Formic acid	Formic acid	100	12	Monomeric products (60)	112
Chitin	LiBr + HCl	Water	120	0.5	NAG (71.5)	113
Acid aged chitin	CaCl ₂	Water	120	1	NAG (51)	114
	CaCl ₂ + ZnBr ₂	—	—	—	NAG (66.8)	
Chitin	LiBr + SAPO-34	Water	130	2	NAG (61)	115
Chitosan	GCSA	HCl	110	6	GA (98.1)	116
Ball milled chitin	AC-Air	—	—	48	Oligomers (66) NAG (8.3)	117
Chitin	NaOH (50%)	Water	150	0.25	Chitosan (DD, 65%)	118
Ball milled chitin	NaOH	—	—	3	Chitosan (DD, 83%)	119

^a MW: microwave heating.

moreover they often require extreme reaction conditions. At the same time the incorporation of ball milling or aging techniques was found to be very effective along with acid–base catalysts. The use of carbon-based catalysts results in an improved yield and selectivity for monomeric products. The combination of MSH and acid catalyst systems gives better yields of products. Further improvements in the process can be expected when heterogeneous catalyst systems are explored. The literature reports on the conversion of chitin biomass to chito-oligomers and amino sugars are tabulated in Table 1.

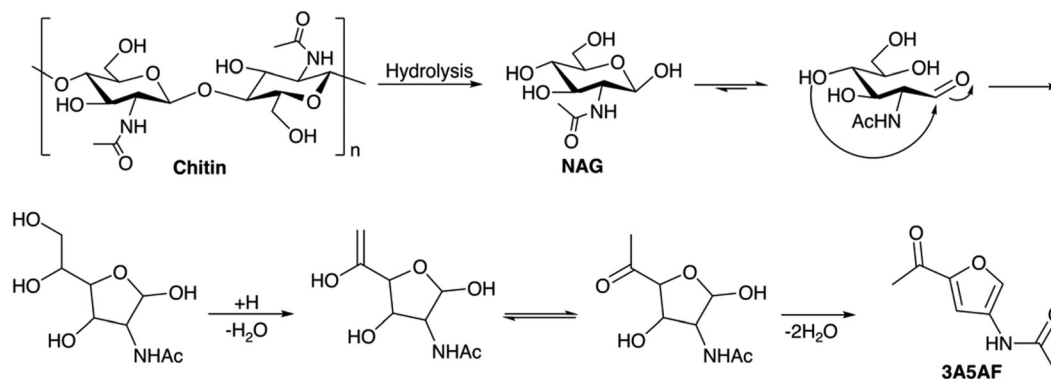
4.1.2 Synthesis of N-containing furan derivatives

4.1.2.1 Synthesis of 3-acetamido-5-acetylfuran (3A5AF). The utilization of cellulosic biomass for producing furan derivatives such as HMF and furfural has been extensively researched. Similarly, researchers have investigated the chemical conversion of chitin and chitin-derived compounds like GA and NAG to obtain nitrogen-containing furan derivatives, which are more valuable substitutes compared with those derived from cellulose valorization. 3-Acetamido-5-acetylfuran (3A5AF) is the first reported N-containing furan compound from animal biomass sources. It was first obtained as a pyrolysis product of NAG with a yield of 2% along with 3-acetamidofuran (5%) and acetamidoacetaldehyde (3%).¹²⁰ Later in the thermal degradation of NAG at 200 °C various degradation products were obtained and 3A5AF was identified as the major compound, along with 2-acetylfuran, 3-acetamidofuran, pyrazine, pyridine, ethylpyrazine, methylpyrazine, 2-ethyl-6-methylpyrazine, 2,3-dimethylpyrazine, and acetamide.¹²¹

The use of imidazolium ILs for the conversion of glucose and fructose to HMF is known. Drover *et al.* were pioneers in reporting the chemical conversion of NAG to 3A5AF using ILs. The inherent acidity of imidazolium ionic liquids and the effect of chloride counter-anions aid the dehydration process. They achieved a 25.5% yield of 3A5AF by subjecting NAG to microwave heating at 180 °C for 3 minutes in the presence of [Bmim]Cl.¹²² The freely bound chloride ions had a positive

effect on the reaction and the addition of NaCl could make only a 38.3% yield of 3A5AF. Meanwhile, the use of boric acid (H₃BO₃) as an additive at 180 °C increased the yield up to 60% during a 1 hour reaction. The Lewis acidity of the H₃BO₃ along with the formation of a borate–hexose complex accelerated the dehydration process; however due to the presence of the *N*-acetyl group in NAG, higher amounts of the additive were required.¹²² Furthermore, they tried the combination of NaCl and boric acid in a ratio 2 : 1 in the presence of dimethylacetamide (DMA) as the solvent under microwave heating at 220 °C for 15 minutes. The yield of 3A5AF could be maximized to 62% by using of 4 equivalents of NaCl.¹²³ The formation of 3A5AF directly from chitin was reported by Yan *et al.*, where they screened 6 organic solvents and 27 additives, including organic/inorganic acids, metal chlorides, bases, and heteropolyacids for the reaction. At 215 °C for 1 h, a 7.5% yield of 3A5AF was obtained with 50% chitin conversion by using *N*-methyl-2-pyrrolidone (NMP) as the solvent and H₃BO₃, LiCl and HCl as additives.¹²⁴ In addition to 3A5AF, several other products, including levoglucosenone, acetic acid, 4-(acetylamino)-1,3-benzenediol, and humins, were also identified in the reaction mixture, which offers insights into the reaction network. A mechanistic exploration through NMR studies highlights the formation of a boron complex intermediate, explaining boric acid's role. Kinetic analysis underscores the importance of disrupting hydrogen bonding in the chitin crystalline region for improved yields. A probable mechanism for the formation of 3A5AF from chitin is depicted in Scheme 2.

Subsequently, their research extended to the conversion of chitin and NAG to 3A5AF, involving the testing of 10 different ionic liquids (ILs) and 25 various additives. Replacing NMP with IL resulted in improved yields while lowering the required reaction temperature. In the presence of [Bmim]Cl, along with H₃BO₃ and HCl as additives, they achieved a 6.2% product yield at 180 °C in just 1 hour.¹²⁵ This work emphasized the importance of using additives and mineral acids in combi-



Scheme 2 Plausible pathway for the formation of 3A5AF from chitin.

nation with ILs to enhance chitin conversion. The crystalline nature of chitin posed a challenge in its conversion, prompting the exploration of different pre-treatment methods, including ball milling, steam explosion, alkaline treatment, phosphoric acid treatment, and dissolution/precipitation using ionic liquids.¹²⁶ Ball milling in dry conditions was found to be effective in reducing the crystallinity and H-bonding in chitin; ball-milled chitin yielded 28% 3A5AF, when boric acid and HCl were used as additives and [Bmim]Cl as the solvent at 180 °C and 1 h reaction time.¹²⁶

While ILs proved to be efficient in this transformation, their higher cost is a notable concern. Therefore, several efforts have been made to render them more cost-effective and tailored to specific tasks. Wang *et al.* studied the amino acid ionic liquid (AIL) catalyzed conversion of NAG to 3A5AF. Among them, glycine chloride ionic liquid, without any additive, yielded 43.2% 3A5AF in just 10 minutes at 200 °C. When CaCl₂ was introduced as an additive, the yield of 3A5AF increased to 52.6%, with improved conversion.¹²⁷ The AIL proved to be reusable, maintaining yields ranging from 43.22% to 36.59% over eight cycles. Zang *et al.* utilized pyridinium-based ionic liquids to produce 3A5AF from NAG. They achieved a 37.5% yield of 3A5AF with the 1-carboxymethyl pyridinium chloride ([CMPy]Cl) ionic liquid catalyst. This yield was further enhanced to 67.37% at 180 °C in 20 minutes by incorporating B₂O₃ and CaCl₂ as additives. However, this system was applicable to chitin monomer only. Additionally, ethanolamine ionic liquids were employed for NAG conversion, resulting in a 62% yield using triethanolamine hydrochloride (TEA-HCl) at 170 °C within 20 minutes.¹²⁸ This catalyst proved to be recyclable for five reaction runs. In another study Zang and co-workers tried a series of quaternary ammonium ionic liquids for the conversion of NAG to 3A5AF. Using pyrazine hydrochloride ([Pyz]Cl) in combination with boric acid and CaCl₂ as additives in DMA at 190 °C for 60 minutes, they achieved a remarkable (69.5%) yield of 3A5AF.¹²⁹ The catalyst, [Pyz]Cl, exhibits strong acidity, and when heated, it ionizes to release protons, facilitating the hydrolysis of NAG. This aligns with the known impact of ionic liquid acidity on NAG degradation. The acidic nature of [Pyz]Cl

allows H⁺ and Cl⁻ ions to disrupt the original intramolecular hydrogen bonds in NAG, enhancing the degradation process. In contrast, substituted pyrazinyl ionic liquids show weaker degradation effects, with methyl-substituted ionic liquids exhibiting limited catalytic efficiency due to steric hindrance and hindered interaction with NAG. However, the catalytic activity of [Pyz]Cl was poor for the chitin degradation.

Deep eutectic solvents (DESs), similar to ionic liquids, have gained prominence for their eco-friendly nature. They are formed by mixing hydrogen-bond donors and acceptors, resulting in solutions with lower melting points than their components. DESs offer advantages like easy preparation, low toxicity, and cost-effectiveness. They prove to be effective as catalysts and solvents in biorefining processes for biomass and its derivatives.^{130,131} Zhang and his team introduced an innovative method for converting NAG and chitin into 3A5AF using a DES based on choline chloride and citric acid (CCCA).¹³² They explored a range of biobased DESs, incorporating choline chloride and various acids like citric, succinic, malonic, malic, and lactic acids, along with urea and glycerol. By introducing CaCl₂·2H₂O as an additive along with CCCA, they achieved a 47 mol% yield of 3A5AF from NAG at 210 °C in 20 minutes, with a 1:2 NAG to CCCA ratio. The addition of H₃BO₃ also improved yields when used as a catalyst. The catalyst proved to be reusable for at least 5 cycles, maintaining a 30 mol% yield in the fifth cycle. Notably, the study also accomplished the direct conversion of chitin to 3A5AF using the same system, achieving a maximum yield of 5 mol% with chitin concentrations of 1 wt% at 210 °C in 120 minutes. Furthermore, they successfully isolated 99% pure 3A5AF from the crude product using a simple extraction followed by concentration, decolorization, crystallization, and drying processes.

Previously mentioned methods have commonly required high temperatures exceeding 180 °C, N-containing aprotic solvents, and chloride additives. However, Padovan *et al.* recently introduced an alternative approach involving the dehydration of NAG using AlCl₃·6H₂O and *N,N*-dimethylformamide (DMF) solvent at a notably lower temperature of 120 °C. This marks a significant reduction in the required temperature for NAG conversion *via* conventional heating.¹³³ They could achieve a 30%

yield of 3A5AF within 30 minutes and also presented a straightforward procedure for obtaining high-purity (98%) 3A5AF through column chromatography with an isolated yield of 18%. Zhang and Chen explored NH_4Cl as an economical catalyst for converting NAG to 3A5AF. In the presence of LiCl and DMF, they achieved a 43% product yield at 160 °C in 5 minutes.¹³⁴ NH_4Cl outperformed other chloride compounds tested as a catalyst. Notably, it surpassed a recent study using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The catalyst maintained 94% residual activity through five reaction runs. Scaling up the reaction to 200 mL demonstrated consistent results, and a purification protocol similar to that of Padovan *et al.* enabled the isolation of 99% pure 3A5AF with an isolated yield of 30%. Another study using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ achieved a 41.6% yield of 3A5AF from NAG, at 180 °C in 1 hour with B_2O_3 as an additive. They evaluated various N-containing polar aprotic solvents, with NMP demonstrating superior performance. Interestingly, under lower temperatures (120 °C), MoCl_5 outperformed $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.¹³⁵

The analysis of the literature highlights the effectiveness of ionic liquids and Lewis acid catalysts in the formation of 3A5AF from NAG. However, these methods typically require higher temperatures and N-containing aprotic solvents. The use of chloride salts and boric acid as additives plays a pivotal role in the reaction. Direct conversion of chitin to 3A5AF remains challenging due to chitin's structural rigidity. Pretreatment methods like ball-milling have proved effective but necessitate the use of mineral acids. Addressing the commercial feasibility issue with expensive ILs, the utilization of bio-based ILs, deep eutectic solvents (DES), and cost-effective Lewis acids shows potential. However, N-containing solvents are often unavoidable. Hence, these studies underscore the need for a heterogeneous catalytic system together with suitable pretreatment methods for chitin conversion. It is significant to tune the catalyst's acidic properties to accommodate chitin's recalcitrant nature and preserve the amino groups

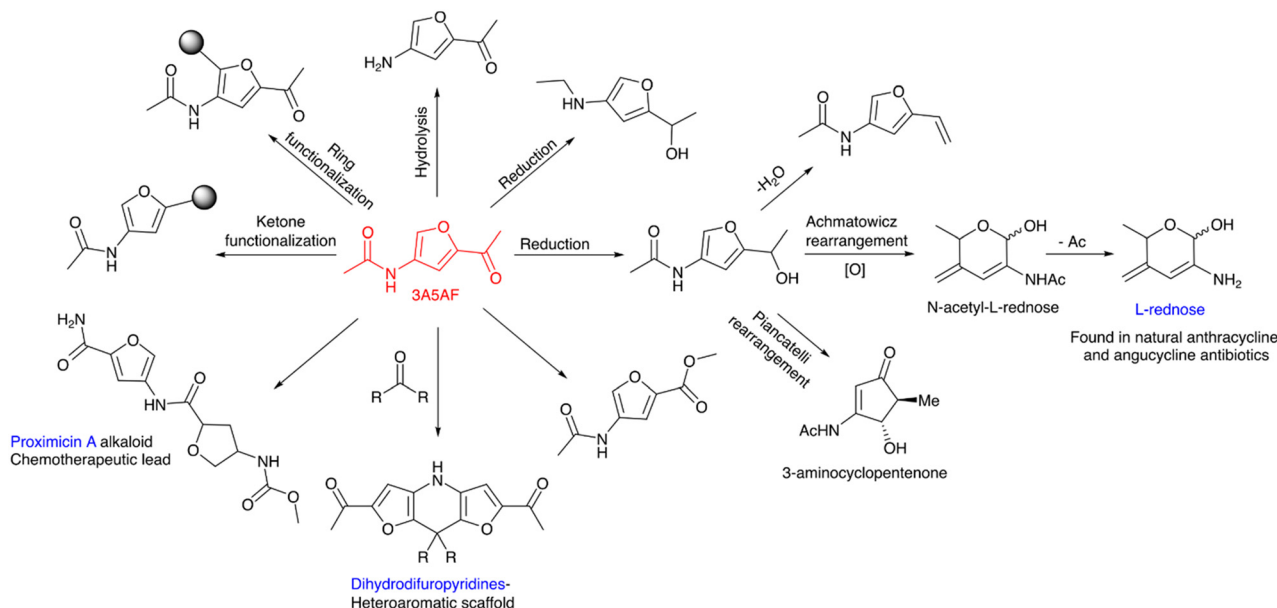
during conversion. The successful isolation and purification of 3A5AF on a lab scale holds promise for further valuable transformations into N-containing chemicals. Table 2 provides an overview of literature reports on the conversion of chitin and NAG to 3A5AF.

The potential of 3A5AF as an important organic compound and building block for the synthesis of other valuable chemicals has been explored by several groups. 3-Aminofuran is a molecule with unique substitution and its chemical transformations provide synthetic scope for novel heterocycles. Moreover, this is the only way of sustainably producing N-heterocycles. The hydrolysis of amido groups and reduction of acetyl groups in 3A5AF have resulted in 2-acetyl-4 aminofuran and 3-acetamido-5-(1-hydroxyethyl)furan.¹³⁷ Sperry *et al.* have studied the synthesis scopes for 3-amidofuran from 3A5AF by various ring and keto group functionalizations of 3A5AF.¹³⁸ Proximicins are excellent chemotherapeutic drug leads. Sperry and co-workers have attempted the synthesis of proximicin A, from chitin-derived 3A5AF. The synthetic steps were found to be greener and more sustainable than the conventional route.¹³⁹ The oxidative ring expansion of 3A5AF to 2-amino sugars like *N*-acetyl-L-rednose (RedNac) was reported with good yield and enantiopurity.¹⁴⁰ Deacetylation of RedNac gives L-rednose. Natural antibiotics such as anthracycline and angucyline contain L-rednose. The compound 3A5AF undergoes Pincatelli rearrangement, resulting in the formation of a 3-aminocyclopentenone. This 3-aminocyclopentenone can be easily transformed into diverse 4-aminocyclopentanones and 4-aminocyclopentene-1,3-diones. These compounds have significant utility in the synthesis of various nitrogen-containing heterocycles.¹⁴¹ The reaction between 3A5AF and aliphatic ketones resulted in the formation of a dihydrodifurapyridine and it is an important heteroaromatic scaffold.¹⁴² The chemical transformations of 3A5AF are schematically presented in Scheme 3.

Table 2 Conversion of chitin and NAG to 3A5AF

Substrate	Catalyst	Reaction conditions			3A5AF (% yield)	Ref.
		Solvent	Temperature (°C)	Time (min)		
NAG	[Bmim]Cl	Water	180 (MW ^a)	3	25.5	122
NAG	$\text{H}_3\text{BO}_3 + \text{NaCl}$	DMA	220 (MW)	15	58	123
Chitin	$\text{H}_3\text{BO}_3 + \text{LiCl} + \text{HCl}$	NMP	215	60	7.5	124
Chitin (8 wt%)	[Bmim]Cl + $\text{H}_3\text{BO}_3 + \text{HCl}$	[Bmim]Cl	180	60	6.2	125
NAG	[Bmim]Cl + H_3BO_3	EtOAc	180 (MW ^a)	3	32	
NAG	[Bmim]HSO ₄ + NaCl				19.7	
Ball milled chitin	$\text{H}_3\text{BO}_3 + \text{HCl}$	[Bmim]Cl	180	60	28	126
NAG	[Gly]Cl + CaCl_2	DMAc	200	10	52.6	127
NAG	TEA·HCl		170	20	62	128
NAG	[Pyz]Cl + $\text{B}_2\text{O}_3 + \text{CaCl}_2$	DMAc	190	60	69.5	129
NAG	CCCA + $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	DMAc	210	20	47	132
Chitin (1 wt%)				120	5	
NAG	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	DMF	120	30	30	133
NAG	$\text{NH}_4\text{Cl} + \text{LiCl}$	DMF	160	5	43	134
NAG	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{B}_2\text{O}_3$	NMP	180	60	41.6	135
NAG	[CMPy]Cl + $\text{B}_2\text{O}_3 + \text{CaCl}_2$	NMP	180	20	67.4	136

^a MW: microwave heating.



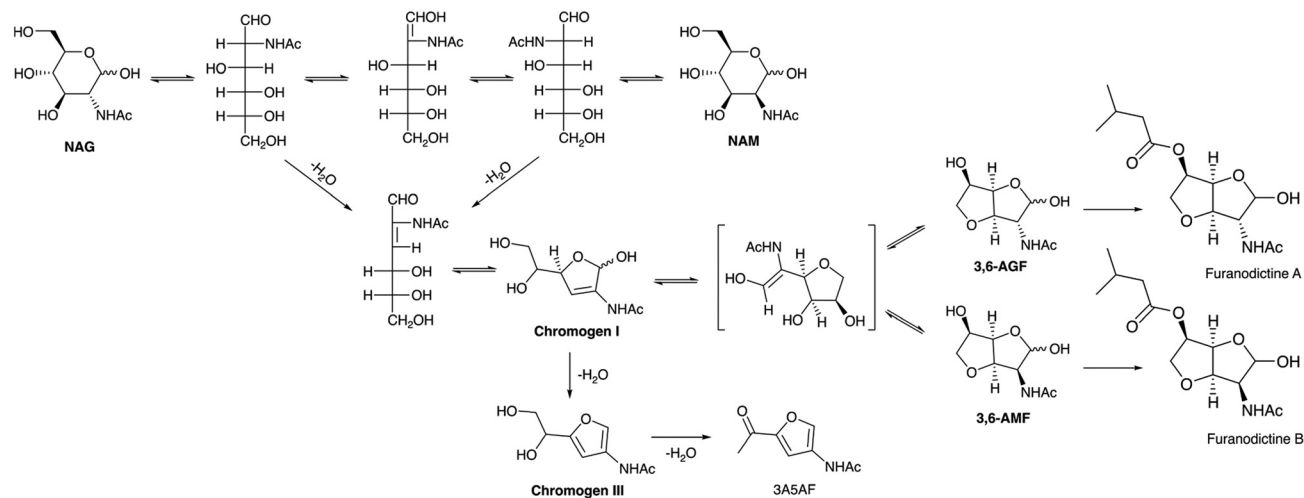
Scheme 3 Potential chemical transformation of 3A5AF.

4.1.2.2 Synthesis of chromogens and bicyclic 3,6-anhydro sugars. Derivatives of NAG such as Chromogen I (2-acetamido-2,3-dideoxy-D-erythro-hex-2-enofuranose), Chromogen III (3-acetamido-5-(1',2'-dihydroxyethyl)furan), 3,6-AGF (2-acetamido-3,6-anhydro-2-deoxy-D-glucufuranose), and 3,6-AMF (2-acetamido-3,6-anhydro-2-deoxy-D-mannofuranose) are having potent biological applications and could be used in medicine and the food industry as additives.¹⁴³ Chromogen I (Chr I) was reported as a major product obtained from the Morgan–Elson reaction initially, and later the alkaline and borate treatment of *N*-acetyl-D-mannosamine (NAM) and NAG has been found to give Chromogen I and III.¹⁴⁴ Ogata and co-workers investigated the synthesis of 3,6-anhydrohexofuranose from NAG.¹⁴⁵ The reaction was carried out using 100 mM NAG solution taken in 250 mL borate buffer (0.4 M, pH 7) and this solution was incubated for 2 h at 100 °C; the reaction mixture was then analyzed using a charcoal–Celite column with a linear gradient of ethanol. 3,6-AGF and 3,6-AMF were formed at 10.2% and 9.8% respectively. The 3,6-anhydrohexofuranoses were then converted to furanodictines using isovaleryl chloride in a single step. Furanodictines represent the pioneer examples of amino sugars possessing an attractive bicyclic bis-tetrahydrofurofuran framework. They exhibit neuronal differentiation activity and can be used as model structures in the invention of novel nerve-rejuvenation drugs.¹⁴³ The intricate structure, combined with their potent biological activity, renders them highly desirable targets for total synthesis.¹⁴⁶ The formation of 3,6-anhydrohexofuranoses from NAG and the structures of furanodictines are given in Scheme 4.

High-temperature water was used as a dehydration medium for the conversion of NAG to chromogens, and is noteworthy for being non-catalytic and greener. This approach takes advantage of the higher ion product constant of water in the

temperature range of 180–220 °C compared with ambient temperatures, which aids in the efficient dehydration of NAG. Osada and co-workers tried the dehydration of NAG, and they were able to obtain Chr I (23%) and Chromogen III (Chr III) (23.1%) in the presence of high-temperature water at 120–220 °C and 250 bar pressure within 39 seconds.¹⁴⁷ In similar conditions the dehydration of a chitin dimer (*N,N'*-diacetylchitobiose) resulted in a poor yield of chromogens.¹⁴⁸ NAG can exist in both its furan ring and open-chain forms when dissolved in water. The epimerisation of NAG to NAM is possible *via* keto–enol tautomerization. Dehydration predominantly occurs from the open-chain (keto) form, facilitated by the electron-withdrawing properties of the *N*-acetyl group, which aids in the removal of a proton (H-2). The subsequent ring closure of the dehydrated open chain leads to the formation of Chr I, which can undergo further dehydration to yield Chr III. Finally, the dehydration of Chr III produces 3A5AF. A probable mechanism for the formation of Chr I, Chr III and 3A5AF from NAG and NAM is given in Scheme 4.

An extended work on the non-catalytic conversion of NAG in high-temperature water by Osada, *et al.* has reported 37% and 34.5% of Chr I and III respectively at 180–280 °C and 250 bar in 5–34 seconds. 3A5AF was also obtained in less than 1% yield from the dehydration of Chr III.¹⁴⁹ The dehydration of Chr III proved to be challenging in the absence of a catalyst, resulting in the lower yield of 3A5AF. The effect of acidic and basic catalysts was studied under similar reaction conditions. Acid catalysts were found to suppress the formation of Chr I while promoting the dehydration of Chr I to Chr III. On the other hand, base catalysts exhibited a negative effect on the reactions. The same research group also explored the direct conversion of chitin to Chr I, using a similar approach. The reaction took place at higher temperatures, specifically



Scheme 4 Probable reaction pathway for the formation of Chromogen I, Chromogen III, 3A5AF and 3,6-anhyrohexofuranoses form NAG.

between 290 and 390 °C, under a pressure of 250 bar, and over a longer duration of 180 minutes.¹⁵⁰ Despite their efforts, the yield of Chr I from chitin was only 2.6%, and the conversion of chitin to chromogens was found to be relatively insignificant. This observation suggests that the non-catalytic conversion of chitin and the associated dehydration reactions are sluggish processes.

In summary, chromogens and 3,6-anhydro sugars are rare *N*-furan derivatives derived from the conversion of chitin or NAG. So far, there are no reported catalytic systems for this conversion, apart from the non-catalytic systems, as mentioned earlier. The mechanism of NAG conversion to these products indicates that designing an effective catalyst poses a significant challenge, as excessive acidity can lead to the formation of 3A5AF or undesirable products. To successfully advance the application of these compounds, proper methods for separation and purification must be devised, especially for Chr I, in order to enable their further transformation into important molecules like furanodictines. A compilation of reports on 3,6-anhydrosugar and chromogen synthesis is given in Table 3.

4.1.3 Other heterocyclic compounds from chitin and chitin derivatives. Nitrogen-containing heterocyclic compounds are an essential part of many bioactive molecules. The formation of heterocycles was found during the pyrolysis of chitin with trivial yields. The direct transformation of chitin to

acetic acid and pyrrole was reported by Yan, *et al.*¹⁵¹ where the reaction was carried out in the presence of copper oxide (CuO) catalyst and sodium hydroxide (NaOH) in the presence of oxygen at 250 to 325 °C. Even though acetic acid and other organic acids were the major products obtained, a few pyrazine and pyridine derivatives were also observed along with pyrrole (2% yield) in the nitrogen-containing product fraction. The use of an external ammonia source increased the pyrrole yield to 6% within a minute by using 1 M NaOH at 325 °C. The proposed reaction mechanism suggests that the dehydration of chitin monomer forms a furanic compound, which on O–N exchange followed by hydrolysis at the side chain led to the formation of pyrrole. When shrimp shell powder was directly used as the starting material, the major product obtained was acetic acid. The formation of pyrazine derivatives like fructosazine (FZ) or 2,5-bis(*D*-arabino-tetrahydroxybutyl)pyrazine and deoxyfructosazine (DFZ) or (2-(arabo-tetrahydroxybutyl)-5-(*erythro*-2,3,4-trihydroxybutyl)-pyrazine) were reported from GA. These compounds are used in therapeutic applications and the food industry as antimicrobial and flavoring agents.¹⁵²

These compounds are naturally produced through the Maillard reaction involving reducing sugars and ammonia-containing compounds. Synthetic pathways for the formation of these compounds from monosaccharides (glucose/fructose) and polysaccharides (cellobiose/inulin) have been established, employing ammonium salts as catalysts in a weak acid

Table 3 Synthesis of chromogens and anhydrosugars from NAG and chitin

Substrate	Reaction conditions				Product (% yield)	Ref.
	Solvent	Temperature (°C)	Time (s)	Pressure (bar)		
NAG	Borate buffer (pH 7)	100	2	—	3,6-AGF (10.2), 3,6-AMF (9.8)	145
NAG	High-temperature water	220	39	250	Chr I (23), Chr III (23.1)	147
NAG	High-temperature water	280	34	250	Chr I (37), Chr III (34.5)	149
Chitin	High-temperature water	390	3600	250	Chr I (2.6)	150

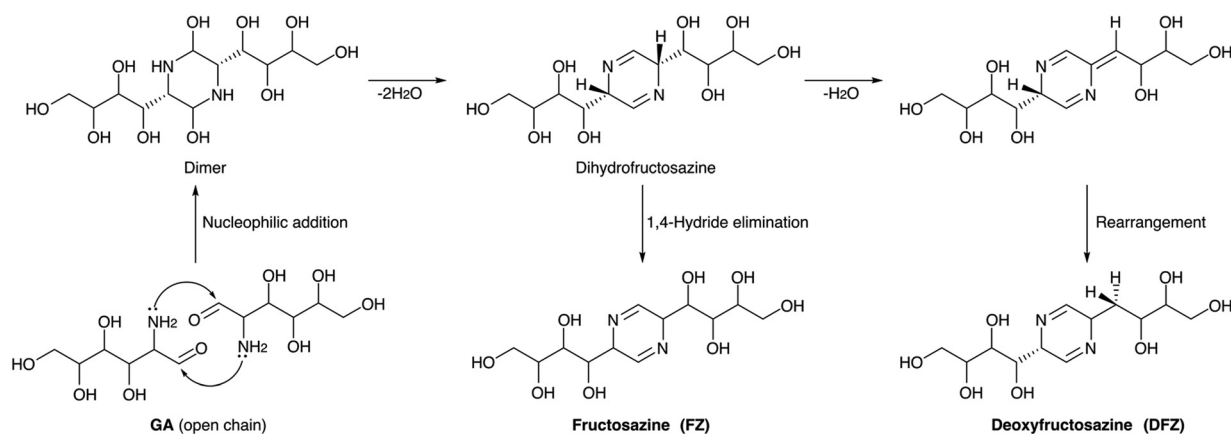
aqueous solution. However, these routes require additional nitrogen resources, which does not comply with green chemistry aspects.

There have been few efforts to make these compounds from GA condensation. In the presence of methanol and sodium methoxide at 70 °C, glucosamine hydrochloride (GA-HCl) and mannosamine hydrochloride (MA-HCl) were converted to FZ within 4 hours, yielding 24.8% and 39.4% respectively.¹⁵³ Candiano *et al.* tried GA condensation in the presence of lysine in water under simulated physiological conditions [100 mM lysine was incubated with 100 mM GA in phosphate buffer (0.02 M, pH 7.4) for 1 week at 37 °C in the dark] and the condensation product formed was FZ (70% yield).¹⁵⁴ This reaction represents the browning process of amino acids and proteins in systems that resemble human blood serum. It also serves as a fundamental tool for studying the circulating and structural proteins in diabetes mellitus and their browning and aging.¹⁵⁴ A unique method for producing DFZ was described, involving a condensation reaction of GA-HCl in the presence of phenylboronic acid and NaOH. Remarkably, this approach yielded a 96% of DFZ after 2 hours of reaction. Comparable results were achieved when using disodium tetraborate, sodium metaborate, or a solution of boric acid in NaOH.¹⁵⁵

Ionic liquid aiding the conversion of GA-HCl was also studied by several groups. The self-condensation of GA-HCl catalysed by an ethanolic solution of a basic ionic liquid, 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH), was reported. The IL was used as both catalyst and solvent, and a mixture of FZ and DFZ (49%) was obtained at 120 °C in 3 h in a DMSO-IL system.¹⁵² Changing the IL to 1-ethyl-3-methylimidazolium acetate ([Emim]OAc) could give a total yield of 37% FZ and DFZ at 100 °C in 1.5 hours.¹⁵⁶ The effectiveness of these ionic liquids stemmed from their strong hydrogen bonding capabilities with amino and hydroxyl groups, facilitating the activation of GA and promoting the dehydration reaction to form the desired products. A detailed mechanism for the formation of FZ and DFZ from GA is presented in Scheme 5. The bifunctional nature of the IL has been antici-

pated in DFT calculations. It was found that the acidity of the cationic component within the IL plays a role in catalyzing the dehydration process, while the basic counter-anion assists in the dehydrogenation step. The formation of an intermediate dihydrofructosazine and the observation of a lower thermodynamic barrier for the formation of DFZ have been corroborated by both computational and experimental findings.¹⁵⁷ Furthermore, the impact of various additives on the condensation of GA into FZ and DFZ was investigated. 40.2% of DFZ was obtained *via* a dehydration process while using the boric acid as additive.¹⁵⁸ The dehydrogenation reaction was enhanced when the oxidizing agent used was H₂O₂ and the major product was FZ (25.3%). Boron coordination helped in a ring-opening and successive dehydration reaction and was favored by both thermodynamic and kinetic factors. Dehydration of the intermediate dihydrofructosazine was fundamental in controlling the complete reaction. A choline chloride (ChCl) based deep eutectic solvent system was also employed for GA condensation as an alternative to ILs. Amino acids were used as cocatalysts, among which arginine was found to be most effective. 13.5% DFZ was obtained at 100 °C and 150 minutes in a choline chloride/urea system.¹⁵⁹ The use of arginine enhanced the yield to 30.1% while FZ was found only in traces. The hydrogen bonding interaction of arginine and the presence of the dihydrofructosazine intermediate was observed from *in situ* NMR studies, suggesting that the mechanism of formation of the products is similar in both cases.

The synthesis of heterocyclic compounds from chitin is a nascent field requiring in-depth exploration. Investigating the diverse synthetic possibilities for various heterocycles derived from chitin and characterizing them is essential. Compounds like FZ and DFZ hold significant value, and their sustainable synthesis from chitin biomass could be a viable avenue in biomass biorefinery. The use of basic ILs in polar aprotic solvents has demonstrated the ability to produce FZ and DFZ; however challenges remain in addressing their separation and purification. The elevated cost of ILs and concerns about the stability¹⁶⁰ of basic ILs add complexity. Separating these compounds from solvents like DMSO is problematic and possesses



Scheme 5 Mechanism of formation of FZ and DFZ from GA condensation.

risks in food industry applications. The use of bio-based DES shows promises due to their tunable properties, cost-effectiveness, and scalability. However, there is a need to explore novel heterogeneous catalytic systems, and effective methods for the separation and purification of these compounds must be developed. Detailed information on the formation of heterocyclic compounds from chitin biomass can be found in Table 4.

4.1.4 Amide polyols and amines from chitin and chitin derivatives. Metal catalysts facilitate the conversion of cellulose and glucose in the presence of hydrogen, forming a variety of polyols, including sorbitol, mannitol, ethylene glycol (EG), and propylene glycol (PG).^{161,162} These polyols hold potential applications in the chemical industry, as they can be directly utilized in various industrial processes or serve as essential building blocks for the production of functional polymers, pharmaceuticals, and clean hydrogen fuel.^{163,164} The hydrogenation of chitin and chitin monomers could form the amino sugar alcohols, similar to the cellulose and glucose hydrogenation products. These N-containing sugar derivatives such as amide polyols can be used for the synthesis of aromatic polyamides. CO₂ absorption of ethanolamine is an instance of another potential application.¹⁶⁵

Yan *et al.* were the first to report the hydrogenation of NAG using noble metal-supported catalyst (Pt/C, Pd/C, Rh/C and Ru/C) in the presence of hydrogen.¹⁶⁶ Ru(1 mol%)/C was found to be effective in converting NAG to 8.7% N-acetylmonoethanolamine (NMEA) under conditions of 180 °C and 40 bar H₂ pressure within 1 hour. 6.1% of C4 polyols, and 71.9% of C6-nitrogen-containing polyols were also obtained. 2-Acetamido-2-deoxy-D-sorbitol (ADS) was the major product, and its selectivity was higher at lower temperatures. At high temperature a yield of C2–C4 polyols was increased due to the breaking of C6-polyols. NMEA and C4-polyols were formed in a single step *via* retro-aldol condensation and the use of NaOH enhanced the yields of the C2 and C4 products. According to the proposed mechanism, four parallel reaction pathways have been elucidated which involve the direct hydrogenation of NAG to ADS, NAG undergoing a retro-aldol reaction followed by hydrogenation to yield NMEA and C4-polyols, deacetylation of NAG to GA and its hydrogenation to form C6-

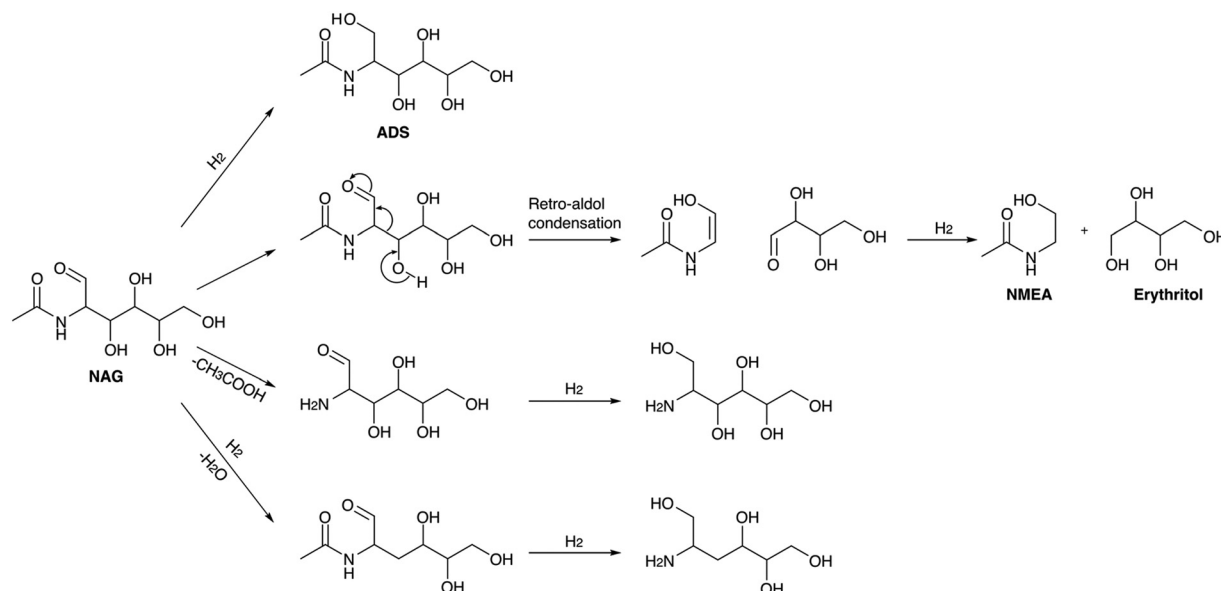
amino sugar alcohols without further breakage to smaller polyols and lastly the dehydration of NAG and its subsequent hydrogenation to form the partially oxygenated C6-amino sugar alcohol. The proposed reaction pathways are outlined in Scheme 6. The catalyst demonstrated recyclability for at least three cycles, with minimal Ru leaching observed at only ppb levels. Reactions using chitin and chitosan as substrates revealed that at elevated temperatures (260 °C), no C6 polyols were detected. Instead, 8% liquid products, including NMEA (from chitin), MEA (from chitosan), ethylene glycol (EG), and acetic acid (AA), were observed, along with 10% gaseous products, primarily methane and carbon dioxide. The generation of gaseous products was attributed to the exceptionally high reaction temperature.

Later Kobayashi and co-workers reported a hydrolytic hydrogenation procedure to obtain ADS directly from chitin.¹⁶⁷

They ball-milled chitin with H₂SO₄, and the resulting chito-oligomeric mixture, along with acid, underwent one-pot hydrogenation using 5 wt% Ru/TiO₂ as the catalyst at 40 bar H₂ pressure. Rapid heating to 200 °C and rapid cooling led to a 25% ADS yield. Improved selectivity and yield were achieved by separating the hydrolysis and hydrogenation steps. The precise control of pH and temperature during hydrolysis (pH 2, 175 °C) and hydrogenation (pH 3–4, 120 °C) was crucial to prevent side reactions under acidic conditions and retro-aldol reactions under basic conditions caused by the Ru catalyst. In a two-step hydrolytic hydrogenation reaction with a maintained pH of 3–4, an overall hydrogenation selectivity of 85% and a 52% ADS yield were obtained. The study indicated ADS stability under the reaction conditions, suggesting that a high-temperature, low pH hydrogenation catalyst holds promise for the rapid and selective conversion of NAG to ADS. Their group also described a method to synthesize acetyl glycine (AG) and NMEA from NAG *via* oxidation and hydrogenation reactions.¹⁶⁸ Using 5 wt% Ru/C as the catalyst with NaHCO₃, NAG underwent a base-catalyzed retro-aldol reaction, forming 2-acetamido-acetaldehyde and erythrose. Subsequently, 2-acetamido-acetaldehyde was hydrogenated to NMEA using the metal catalyst at 40 bar H₂ pressure and 120 °C in 1 hour, yielding 15% NMEA along with other products such as ADS, 2-acetamido-2-deoxymannitol (ADM), 2-acetamido-2,3-dideoxyhexitols, and

Table 4 Formation of heterocyclic compounds from chitin biomass

Substrate	Catalyst	Reaction conditions			Product (% yield)	Ref.
		Solvent	Temperature (°C)	Time (min)		
Chitin	CuO	NaOH	325	35	Pyrrole (6)	151
GA·HCl	NaOMe	MeOH	70	240	FZ (24.8)	153
MA·HCl					FZ (39.4)	
GA	Lysine	Water	37	1 week	FZ (70)	154
GA	Phenylboronic acid + NaOH	Water		120	DFZ (96)	155
GA·HCl	[Bmim]OH ethanolic solution	[(Bmim)OH] + DMSO	120	180	FZ + DFZ (49)	152
GA	[Emim]OAc	DMSO	100	90	FZ + DFZ (37)	156
GA	[Emim]OAc + B(OH) ₃	DMSO	90	180	DFZ (40.2)	158
GA	[Emim]OAc + H ₂ O ₂	DMSO	80	180	FZ (25.3)	
GA	ChCl-urea + arginine	ChCl-urea	100	150	FZ (30.1)	159



Scheme 6 Reaction pathways for the formation of C4, C6 polyols and NMEA from NAG.

acetic acid. The oxidation of the OH group on the NMEA was achieved with the same catalyst in NaHCO_3 solution under 10 bar O_2 pressure at 120 °C for 1 hour, resulting in 21% AG under optimized conditions. The Ru/C catalyst, with Ru species present on the carbon as hydrous RuO_2 with a hydroxo, aqua, μ -hydroxo, and μ -oxo ligand environment, facilitated the oxidation process.

The hydrolysis of NMEA yields ethanolamine (ETA), a versatile component used in CO_2 sequestration, dermatological formulations, cleaning agents, and surfactants. Chowdhury *et al.* explored the hydrogenation of NAG to NMEA using a Ni (10 wt%)/ CeO_2 catalyst.¹⁶⁹ Among the various ceria supports (cubic/rod/polyhedral shaped) employed, cubic CeO_2 demonstrated the highest activity under optimized conditions. With NaHCO_3 as an additive, 42% NMEA was obtained at 120 °C in 8 hours and 40 bar H_2 pressure. Two proposed pathways for NMEA formation involve the retro-aldol condensation of NAG to produce 2-acetamidoacetaldehyde and erythrose, followed by hydrogenation to NMEA over a Ni catalyst. Alternatively, NAG can undergo hydrogenation to ADS, and its subsequent hydrodeoxygenation with C–C cleavage leads to NMEA formation. Control experiments and intermediate compound detection confirm the reaction pathway involving the formation of ADS.

Amine synthesis is crucial for developing pharmaceuticals, materials, and agrochemicals, given the role of amines in biological molecules, drugs, polymers, and pesticides. Amine synthesis from NAG was reported by Lin and co-workers. They have carried out the deoxygenation of NAG using H_2 and a Ru/C catalyst under acidic conditions.¹⁷⁰ The highest total amine yield (47.5 mol%) was achieved at 250 °C with 33 bar H_2 in 2 hours, using a 4.45 molar ratio of H_3PO_4 to NAG. The identified amine products included *n*-butylamine, pyrrolidine,

2-methylpyrrolidine, *n*-amylamine, 2,5-dimethylpyrrolidine, piperidine, 2-methylpiperidine, 3-methylpiperidine, and 1-ethylpiperidine, with cyclic amines prevailing. The hydrogenation environment with Ru/C likely led to the removal of oxygen atoms from the NAG as H_2O and/or CO/CO_2 , generating methane as the primary by-product through the hydrogenation of CO. The *in situ* formation of acetic acid also resulted in the production of ethane. Additionally, various polyol-based side products were detected in the reaction.

Analogous to the conversion of sorbitol to isosorbide, ADS can be converted to 2-acetamido-2-deoxyisobutane. Unlike sugar compounds, ADI's solubility is better due to its sole hydroxyl group, and it could be a potential precursor of nitrogen-containing polymers. Kobayashi *et al.* converted chitin-derived amino sugar alcohol (ADS) to an isosorbide analogue (ADI). NAG to ADS conversion involved a hydrogenation reaction using Ru/C at 1 bar H_2 and 150 °C for 3 hours.¹⁷¹ ADS was then transformed into ADI through acid-catalyzed dehydration, utilizing trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$) under vacuum conditions. $\text{CF}_3\text{SO}_3\text{H}$ ($\text{pK}_a = -15$, $\text{S/C} = 2$) produced the highest ADI yield (33%) under pressures less than 1 bar. Seeking an alternative to the corrosive $\text{CF}_3\text{SO}_3\text{H}$, they employed phosphorous acid (H_3PO_3) for the ADS to ADI conversion through cyclization *via* phosphite ethers.¹⁷² The optimal yield of ADI (25%) was achieved at 130 °C for 3 hours, with H_3PO_3 's reducing property aiding in reducing the humin formation. DFT calculations also supported the reaction proceeding through the formation of phosphite intermediates, lowering the activation energy compared with typical acid-catalyzed dehydration condensation reactions.

Kobayashi *et al.* explored another possible transformation of ADS. They studied the catalytic conversion of ADS to chiral oxazolidinones namely 4-(1,2,3,4-tetrahydroxybutyl)-1,3-oxazo-

lidin-2-one (1,2-OX) and 4-hydroxymethyl-5-(1,2,3-trihydroxypropyl)-1,3-oxazolidin-2-one (2,3-OX). The reaction was done in methanol and dimethyl carbonate (DMC) at 80 °C for 24 h using KHCO_3 and it selectively formed 84% 2,3-OX (5(*S*)-isomer) which is a potential antibiotic agent.¹⁷³ DFT calculations revealed that the inner molecular hydrogen bonds in the transition states facilitated 2,3-OX formation by reducing the energy barrier. Interestingly, the direct conversion of NAG to oxazolidinones did not occur under the same conditions. The addition of $\text{Na}_2\text{B}_4\text{O}_7$ slightly modified the reaction selectivity, increasing the yield of 1,2-OX threefold. Scheme 7 shows the possible transformation of chitin-derived ADS to ADI and oxazolidinones.

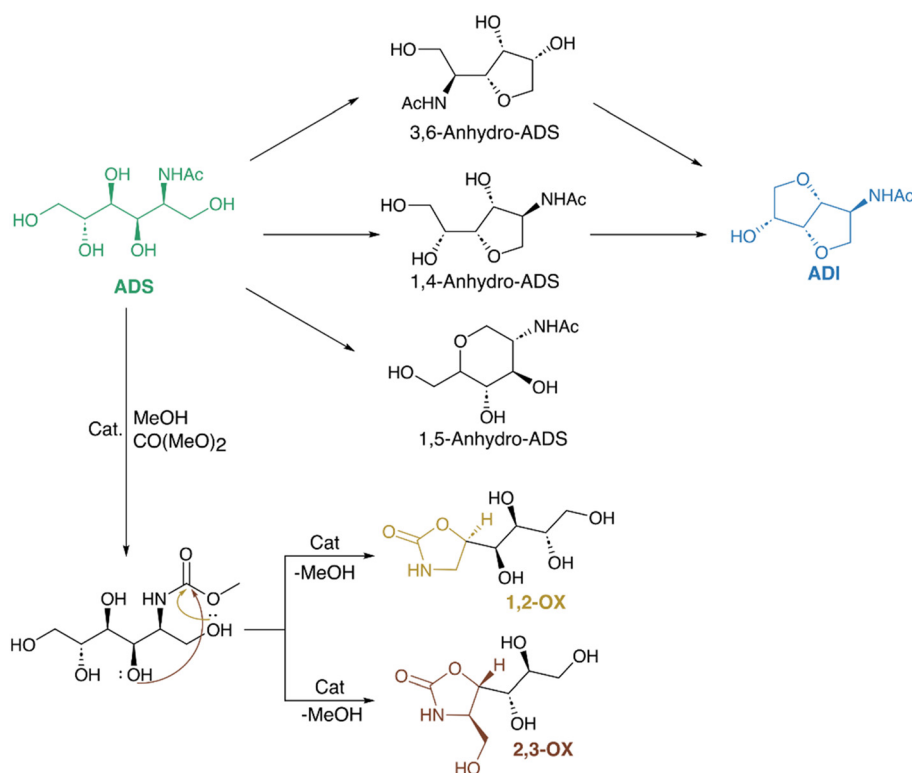
In summary, the hydrogenation of NAG presents a novel avenue for the synthesis of N-containing polyols and amines directly sourced from biomass. While ruthenium-based supported metal catalysts demonstrate superior performance, they all operate under a high hydrogen pressure. Directly hydrogenating chitin proves challenging due to the need for the precise tuning of hydrolysis and hydrogenation conditions to maximize the product yield, making single-step conversion difficult. Exploring low-cost metal catalysts is an alternative, but their selective transformation into specific products remains unexplored. The subsequent upgrading of products, such as ADS to ADI and oxazolidinones, shows potential, with further investigations needed to explore their potential transformations and application. The literature summary of conver-

sion of chitin and chitin-derived chemicals to amide polyols and amines has been listed in Table 5.

4.2 Conversion of chitin to non-nitrogen chemicals

4.2.1 Furan derivatives from chitin.

5-Hydroxymethylfurfural (HMF) stands out as a versatile platform chemical obtained through biomass valorization.¹⁷⁴ Its production from cellulosic biomass materials is widely recognized, and the feasibility of deriving HMF from chitin biomass has also been established. The acid catalysts typically played a catalytic role in the hydrolysis and dehydration reactions involved. Earlier methodologies primarily employed mineral acid catalysts such as HCl, H_2SO_4 , and acetic acid to facilitate the conversion of chitin to furan derivatives such as HMF. Chitin was converted into 5-chloromethylfurfural (CMF) and levulinic acid (LA) in a biphasic system of HCl/dichloroethane (DCE) (1 : 2 v/v) at 150 °C in 3 hours, resulting in a yield of 45% for CMF and 29% for LA.¹⁷⁵ Cellulose exhibited a more favorable transformation, producing 85% CMF. This discrepancy underscored the inherent challenge associated with chitin conversion, attributed to its structural rigidity. Furthermore, CMF displayed facile conversion into HMF through hydrolysis. When subjected to reactions with ethanol and hydrogen, CMF yielded 5-(ethoxymethyl)furfural and 5-methylfurfural, respectively. In a separate HCl-catalyzed conversion of chitosan, microwave irradiation at 200 °C for 30 minutes resulted in a modest 2.2% HMF yield.¹⁷⁶ A low-



Scheme 7 Possible transformation of chitin-derived ADS to ADI and oxazolidinones.

Table 5 Conversion of chitin and chitin derivatives to amide polyols and amines

Substrate	Catalyst	Reaction conditions				Product (% yield)	Ref.
		Solvent	Temperature (°C)	Time (h)	Pressure (bar)		
NAG	Ru(1)/C	Water	180	1	H ₂ (40)	C2–C4 polyol (6.1), C6-polyols with N (71.9), NMEA (8.7)	166
Chitin ^a	Ru(5)/TiO ₂	Water	175 ^b , 120 ^c	2	H ₂ (40)	ADS (52)	167
NAG	Ru(5)/C + NaHCO ₃	Water	120	1	H ₂ (40)	NMEA (15)	168
			120	1	O ₂ (10)	AG (21)	
NAG	Ni(10)/CeO ₂	NaHCO ₃	120	8	H ₂ (40)	NMEA (42)	169
NAG	Ru/C	H ₃ PO ₄	250	2	H ₂ (40)	Amines (47.5)	170
ADS	Ru/C + CF ₃ SO ₃ H	Water	150	3	H ₂ (1)	ADI (33)	171
ADS	H ₃ PO ₃		130	3	—	ADI (25)	172
ADS	KHCO ₃	MeOH + DMC	80	24	—	2,3-OX (84), 1,2-OX (6.9)	173

^a Chitin ball milled with H₂SO₄. ^b Hydrolysis temperature. ^c Hydrogenation temperature.

temperature hydrothermal process involving dilute H₂SO₄ at 174 °C for 36.9 minutes achieved a more substantial 12.1% HMF yield.¹⁷⁷ Notably, under similar conditions, glucosamine (GA) produced only a 1.8% HMF yield in 5 minutes. Levulinic acid (LA), a recurring byproduct of HMF synthesis, was commonly observed in conjunction with HMF formation. Ultrasound-assisted chitosan degradation, utilizing a 0.5% (v/v) acetic acid solution, yielded 12.1% HMF.¹⁰³ Additionally, sonication of chitosan at 40 °C for 30 minutes resulted in a concentrated soluble fraction of chitosan.

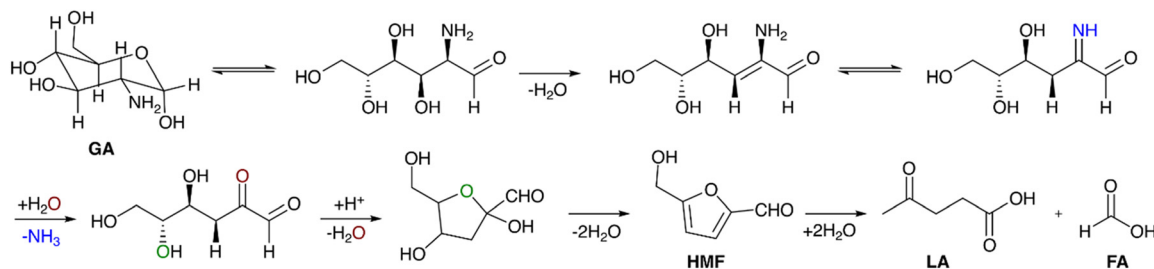
The use of weak acids such as formic acid was also employed for the chitin conversion. During the liquefaction of chitin mediated by formic acid, the formation of 5-(formyloxy-methyl)furfural (FMF) was observed with a yield of up to 35% after an extended reaction time of 168 hours at 80 °C.¹¹² The hydroxyl group undergoes formylation, resulting in the formation of soluble polymeric products. These polymers subsequently undergo hydrolysis, leading to the generation of both monomeric products and rehydrated products. Examining GA conversion in the presence of 0.1 M methanesulfonic acid (MSA) at 160 °C for 40 minutes produced a 2.3% HMF yield, accompanied by LA and formic acid (FA).¹⁷⁸ A parallel study on chitosan conversion with MSA at 200 °C for 15 minutes resulted in a more substantial 15% HMF yield,

employing 2% (w/w) chitosan and 0.2 M MSA as catalyst.¹⁷⁹ Mineral Brønsted acids, while providing ease of operation, often cause by-product formation and non-selective transformation, necessitate costly post-treatment, and their inherent corrosiveness that can contribute to reactor part corrosion. In light of these drawbacks, researchers have explored alternative acid catalysts, such as Lewis acidic catalysts including metal chlorides and ionic liquids, for chitin biomass conversion. Table 6 summarizes reports on the synthesis of HMF through mineral and organic acid catalyzed transformations of chitin biomass. Various metal chloride systems were utilized as catalysts, leveraging their Lewis acidity, in the conversion of chitin biomass. Hydrolysis of chitosan using SnCl₄·5H₂O at 200 °C for 30 minutes under microwave heating was found to produce HMF.¹⁷⁶ In this study, metal-containing catalysts were found to be effective among all those screened. Lower SnCl₄·5H₂O concentrations produced 10 wt% HMF, while higher concentrations yielded 21.6% LA in chitosan hydrolysis. Chitin hydrolysis under similar conditions resulted in 11.5–12.6% LA, and without catalysts or conventional heating, no HMF or LA formed. GA was treated in similar conditions to explain the mechanism of hydrolysis, and under optimised conditions 32 wt% of LA was obtained without HMF formation. The coordination of amino groups with a metal center or proton

Table 6 Chitin biomass transformation to HMF using Brønsted acid catalysts

Substrate	Catalyst	Reaction conditions			Product (% yield)	Ref.
		Solvent	Temperature (°C)	Time (h)		
Chitin	HCl	DCE	150	3	CMF (45)	175
Chitosan	HCl	Water	200 (MW ^a)	0.5	HMF (2.2)	176
Chitosan	H ₂ SO ₄	Water	174	0.6	HMF (12.1)	177
GA				0.08	HMF (1.8)	
Chitosan	CH ₃ COOH	Water	40 (US ^b)	0.5	HMF (12.1)	103
Chitin	HCOOH	HCOOH	80	168	FMF (35)	112
GA	0.1 M MSA	Water	160	0.67	HMF (2.3)	178
Chitosan	0.2 M MSA	Water	200	0.25	HMF (15)	179

^a MW: microwave heating. ^b US: ultrasound.



Scheme 8 Mechanism for HMF and LA production from GA.

aided the cleavage of glycosidic bonds in the chitosan to yield glucosamine which on subsequent dehydration and deamination forms HMF.

Further rehydration by two molecules of water produces LA according to the proposed mechanism (Scheme 8). SnCl_4 often forms SnO_2 and HCl in aqueous solution. The reaction carried out using both SnO_2 and HCl together produced 27.4 wt% LA from chitosan. They have also compared the effect of microwave heating by keeping the same reactions under conventional heating conditions. The formation of 12.08 wt% LA was found after 9 days of conventional heating whereas there was no HMF formation observed. In another work, a 67 wt% aqueous solution of ZnCl_2 was found to catalyse the hydrolysis of chitosan, GA, and NAG to HMF.¹⁸⁰ At 120 °C in 90 minutes, 10.1% of HMF was formed from chitosan, and GA and NAG produced 21.6% and 2.8% of HMF respectively. The yield of HMF and conversion of substrate decreased with a decrease in the ZnCl_2 concentration. Eight Lewis acidic metal chlorides were screened as cocatalysts, out of which H_3BO_3 and AlCl_3 were having promotional effects in HMF formation. The complex formation of Zn^{2+} with amino and hydroxyl groups weakened the polymeric backbone and eased the hydrolysis step to form the monomers. The zinc-monomer complex in pyranose form isomerises into open form and then back into cyclic furanose form unlike in the case of tin chloride catalyst, and further dehydration and deamination led to the formation of HMF. HMF formation from NAG was poor, because the presence of the amino group was essential for the HMF formation.

Zang *et al.* have screened 16 metal salts in a DMSO–water biphasic system for the hydrothermal conversion of chitin biomass.¹⁸¹ $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ showed the best catalytic activity in the conversion of GA, NAG, chitosan, and chitin to HMF. The yield of HMF obtained was 24.5, 37.9 (at 180 °C in 5 h), 26.6, and 19.3 mol% (at 190 °C in 6 h) respectively from GA, NAG, chitosan, and chitin. In Lewis acid catalyzed reactions, it has been observed that the coordination of the Cl^- anions with $-\text{NH}_2$ and $-\text{OH}$ groups plays a key role in breaking the hydrogen bonding network present in chitosan and chitin. Also, metal cation interactions weaken the β -glycosidic bond and promote hydrolysis.

Sulfamic acid, also known as amidosulfonic acid, is considered a safer alternative to other strong acids like HCl or H_2SO_4 in various applications due to its lower corrosivity and higher stability. It possesses several advantageous properties,

including being non-volatile, odorless, non-corrosive, moderately acidic ($\text{p}K_a = 1.0$), non-hygroscopic, and cost-effective. The catalytic properties of sulfamic acid can be attributed to its inherent zwitterionic nature ($\text{H}_3\text{N}^+\text{SO}_3^-$), which arises from its tautomeric structure.¹⁸² Under the conditions of 200 °C and 2 minutes, the conversion of 3% (w/w) chitosan yielded 21.5% HMF in the presence of 0.7 M sulfamic acid.¹⁸³ This marks a notable improvement over previous studies, demonstrating higher HMF yields in a shorter time frame with sulfamic acid as the catalyst. In a related study by the same group, the conversion of GA to LA was explored. Interestingly, at lower sulfamic acid concentrations, the production of HMF was reduced. Specifically, using 0.3 M sulfamic acid at 200 °C for 15 minutes resulted in 0.14 mol% HMF and 33.76 mol% LA.¹⁸²

Polyoxometalates (POMs) were another group of catalysts explored for HMF synthesis. They represent a versatile group of anionic metal–oxygen clusters that encompass a broad range of early transition metals. These clusters exhibit diverse chemical properties, including redox potential, acid–base properties, and solubility in both aqueous and organic media. Remarkably, the chemical characteristics of POMs can be readily and precisely adjusted across a wide range by intentionally manipulating their composition and structure. A microwave-assisted chitin conversion using polyoxometalate (POM) clusters as a catalyst was reported recently.¹⁸⁴ Using silicotungstic acid ($\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$), a 23.1% HMF yield was obtained at 200 °C within 3 minutes where the solvent system used was 67% DMSO–water. The chitin was first ball milled in the presence of H_2SO_4 , which boosted the reduction in crystallinity and resulted in an improvement in the solubility of the chitin. Table 7 shows the literature reports on Lewis acid-catalyzed transformations of chitin biomass to HMF.

Heterogeneous catalysts offer advantages over homogeneous catalysts, primarily in terms of their potential for separation, recovery, and recyclability. Additionally, they tend to be environmentally friendly and do not corrode the reaction equipment. In the area of biomass conversion reactions, various solid acid–base catalysts have been explored. However, the conversion of chitin biomass to HMF using heterogeneous catalysts is a relatively unexplored area, with only a few recent studies addressing this aspect. Recently, H- β -zeolite was used in combination with acetic acid, to produce HMF from chitosan by Dandekar *et al.*¹⁸⁵ Different catalysts were screened

Table 7 Formation of HMF from chitin biomass using Lewis acid catalysts

Substrate	Catalyst	Reaction conditions			HMF (% yield)	Ref.
		Solvent	Temperature (°C)	Time (h)		
Chitosan	SnCl ₄ ·5H ₂ O	Water	200 (MW ^a)	0.5	10	176
Chitosan	ZnCl ₂	Water	120	1.5	10.1	180
NAG					2.8	
GA					21.6	
Chitin	FeCl ₂ ·4H ₂ O	DMSO	190	6	19.3	181
Chitosan			180	5	26.6	
NAG					37.9	
GA					24.5	
GA	0.3 M Sulfamic acid	Water	200	0.25	0.14	182
Chitosan	0.7 M Sulfamic acid	Water	200	0.03	21.5	183
Chitin (BM with H ₂ SO ₄)	H ₄ [SiW ₁₂ O ₄₀]	DMSO + water	200	0.05 (MW)	23.1	184

^a MW: microwave heating.

where H-β-zeolite and Amberlyst-15 were found to have the best performance along with 10% acetic acid as additive. Under the optimized reaction conditions (180 °C and 60 minutes in the presence of a 5% catalyst concentration) chitosan with molecular weight 20 kDa, NAG, and GA·HCl yielded 25.16 ± 0.75%, 12.42 ± 0.25%, and 23.78 ± 0.15% of HMF. In this system, the Lewis acidity of the solid catalyst, coupled with the Brønsted acid sites (hydronium ions) from aqueous acetic acid, facilitates the rapid isomerization of the pyranose ring into furan and its subsequent hydrolysis. The addition of acetic acid, at a concentration of 10% v/v, enhances the surface coverage of the solid acid catalyst with the substrate and product. However, using acetic acid alone resulted in a poor yield of HMF. It was observed that higher acid loading resulted in the poisoning of the H-β-zeolite catalyst and the recovered catalyst gave only 7.43% of HMF.

Later Chung *et al.* reported HMF production from chitosan using Nafion®50 resin in a biphasic solvent system consisting of methyl isobutyl ketone (MIBK) and water (v/v = 2).¹⁸⁶ A 32.6 ± 4.2 mol% of reasonable yield of HMF was obtained as in the case of homogeneous acid systems at 180 °C in 2 h. The catalyst's efficacy in converting chitosan can be attributed to the interactions between the chitosan and the perfluorinated surface of the resin, coupled with its highly acidic characteristics. Unfortunately, the recyclability of the catalyst was not demonstrated. A notable challenge in this process involves the deactivation of catalytic sites (acid) due to the release of ammonia from the acetamido/amino group during the reaction. Hence the development of innovative heterogeneous cata-

lytic systems is crucial for efficient HMF production from chitin biomass. The literature studies on the formation of HMF using heterogeneous catalysts are summarized in Table 8.

Ionic liquids are organic salts characterized by a lower melting point (<100 °C) when compared with conventional inorganic salts. In contrast to traditional organic solvents, they possess minimal vapor pressure. Additionally, they demonstrate a broad liquid temperature range, conductivity, broad electrochemical window, and exceptional dissolving power for most organic, inorganic, and organometallic substances.¹⁸⁷ The various combinations of cation and anion enable the tuning of their properties desirable for task specific applications.^{188–190} Over the last two decades, ionic liquids have played a crucial role as both solvents and catalysts in the dissolution and conversion of biomass.^{191,192} Their extensive use extends to the transformation of lignocellulosic materials, such as cellulose, lignin,¹⁹³ and hemicellulose,¹⁹⁴ into essential platform chemicals. Researchers are actively exploring the use of ILs to depolymerize chitin, leveraging its structural similarity to cellulose. Various attempts have been made to convert chitin biomass specifically into HMF using ILs.

Zang *et al.* reported the conversion of chitosan to HMF under hydrothermal conditions using 5 wt% of 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim]HSO₄) ionic liquid and AlCl₃·6H₂O (100 mol%) as co-catalyst. They could achieve 25.2 mol% of HMF in 5 h at 180 °C.¹⁹⁵ The catalysts were recyclable, and the activity was found to be constant for the first five cycles. Chitosan was converted into HMF using

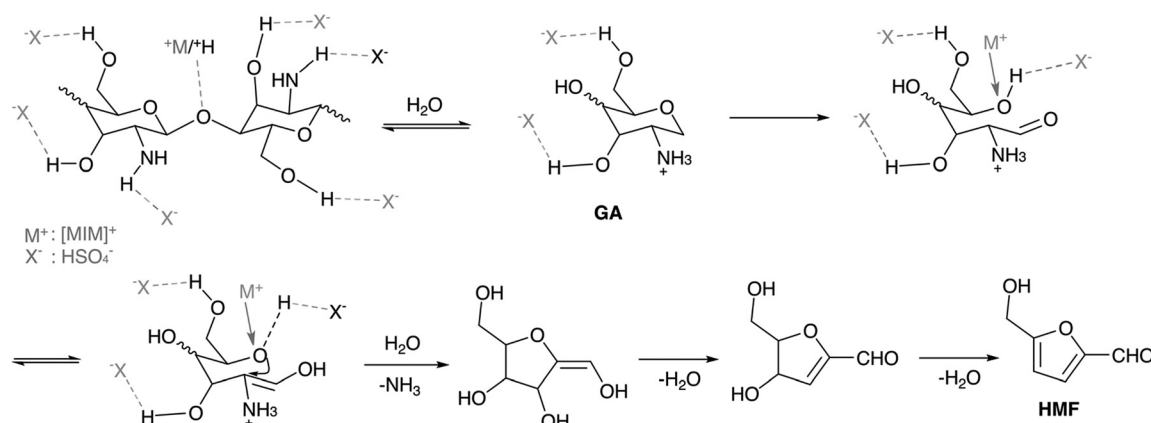
Table 8 Conversion of chitosan and chito-monomers to HMF using heterogeneous acid catalysts

Substrate	Catalyst	Reaction conditions			HMF (% yield)	Ref.
		Solvent	Temperature (°C)	Time (min)		
Chitosan	H-β-zeolite + CH ₃ COOH	Water	180	60	25.2	185
NAG					12	
GA					23.8	
Chitosan	Nafion®50	MIBK + water	180	120	32.6	186

different acidic ionic liquids *via* a hydrothermal reaction by Zang and co-workers.¹⁹⁶ 4 wt% of *N*-methyl imidazolium hydrogen sulfate ([MIM]HSO₄) aqueous solution at 180 °C in 5 h produced 29.5 mol% and 19.3 mol% of HMF from chitosan and chitin, respectively. Among the 9 ILs screened, [MIM]HSO₄ was found to be more efficient. The catalyst demonstrated recoverability through straightforward post-processing and remained recyclable for up to five runs. The IL anions' coordination with hydroxyl and amino groups played a crucial role in disrupting the hydrogen bonding, while the IL cations weakened glycosidic bonding, facilitating monomer formation. The anticipated mechanism involves isomerization, cyclization to furan form, and subsequent dehydration, ultimately leading to HMF formation. Scheme 9 illustrates the anticipated mechanism of HMF formation facilitated by IL. Later, a series of Lewis-Brønsted acidic ionic liquids were employed for the hydrothermal synthesis of HMF from chitosan.¹⁹⁷ A 1.25 wt% aqueous solution of the IL 1-hexyl-3-methylimidazolium hydrogen sulfate along with FeCl₂ ([Hmim][HSO₄]-0.5FeCl₂) produced 44.1% of HMF at 180 °C in 4 h. This IL system showed remarkable activity for the first four catalytic cycles. In the DMSO–water system, NAG was successfully converted to HMF through hydrothermal synthesis at 180 °C for 6 hours. Utilizing the [Hmim]HSO₄ ionic liquid, a notable 64.6 mol% yield of HMF was achieved.¹⁹⁸ Evaluation of various imidazo-

lium and thiazolium cation-based ILs revealed the essential role of the HSO₄[−] anion for higher HMF yields. Under similar conditions, GA, chitosan, and chitin produced 54.9, 34.7, and 25.7 mol% of HMF, respectively. The decreased accessibility of HSO₄[−] anions to chitosan and chitin resulted in lower HMF yields due to reduced polymer hydrolysis. The catalyst, along with the DMSO, was recovered and reused for up to five catalytic cycles, demonstrating reasonable activity. Benzimidazole and NMP-based ionic liquids were also studied for chitosan degradation by the same group. The catalytic efficiency of the ionic liquid benzimidazolium chloride ([Hbim]Cl) was exceptional, yielding 30.8 mol% HMF in a water medium and 34.9 mol% in a 10% DMSO–water system. The addition of DMSO improved the solubility of the chitosan and minimized side-product formation. The catalyst demonstrated reusable capability for five cycles without compromising its effectiveness.

Table 9 presents a summary of studies on the IL-catalyzed conversion of chitin and its derivatives to HMF. Notably, acidic ionic liquids have demonstrated superior performance compared with conventional acid catalysts in terms of yield, conversion, catalyst recovery, and recyclability for HMF production from chitin biomass. The optimization of ionic liquid properties, either independently or along with co-catalysts, holds potential for enhancing catalytic activity. Future endeavors in



Scheme 9 Proposed mechanism of IL-promoted conversion of chitosan to HMF.

Table 9 Ionic liquid catalysed conversion of chitin and chitosan to HMF

Substrate	Catalyst	Reaction conditions				Ref.
		Solvent	Temperature (°C)	Time (h)	HMF (% yield)	
Chitosan	[BMIM][HSO ₄] + AlCl ₃ ·6H ₂ O	Water	180	5	25.2	195
Chitosan	[MIM]HSO ₄	Water	180	5	19.3	196
Chitosan	[Hmim][HSO ₄]-0.5FeCl ₂	Water	180	4	44.1	197
Chitin	[Hmim]HSO ₄	Water + DMSO	180	6	25.7	198
Chitosan					34.7	
NAG					64.6	
GA					54.9	
Chitosan	[Hbim]Cl	Water + DMSO	180	3	34.9	199

this research area should focus on conducting reactions at lower temperatures, with attention given to the specific choice of reaction solvents due to concerns about IL and product separation.

4.2.2 Organic acids from chitin biomass. Levulinic acid or 4-oxopentanoic acid is a potent platform chemical, which is formed as a by-product in the conversion of C6-sugars to HMF.²⁰⁰ HMF undergoes rehydration under elevated temperatures and acidic conditions to yield levulinic acid (LA) and formic acid (FA). The formation of LA is commonly observed alongside HMF in many reactions discussed in the preceding section. Similar to HMF synthesis, various acid catalysts, including mineral acids, organic acids, metal chlorides, ILs, and solid acid catalysts, are employed for the production of levulinic acid.

In the context of reports on mineral acid-catalyzed chitin conversion to LA, a microwave-assisted hydrothermal process using 2 M H₂SO₄ at 190 °C for 30 minutes resulted in a yield of 37.8 mol% of LA.²⁰¹ Similarly, employing HCl under comparable conditions yielded 32.7 mol% of LA. This approach was extended to GA, NAG, and various chitosan samples, where 19.3 to 37 mol% of LA was observed with both HCl and H₂SO₄ within 10 to 30 minutes. In a separate study, 4 wt% of H₂SO₄ successfully converted GA into LA (25.3 wt%) at 188 °C in 49 minutes.²⁰² Methanesulfonic acid (MSA) is an environmentally benign and green catalyst. Even though it is a strong acid (pK_a = −1.9), it is non-oxidizing, non-foaming, less corrosive and bio-degradable compared with other mineral acids. In a hydrothermal conversion of GA at 200 °C using 0.5 M MSA, 49.9% LA and 50.8% FA was formed in 30 min.¹⁷⁸ Under the same reaction conditions 28.2% of LA was formed from 2% chitosan when 0.2 M MSA was used.¹⁷⁹

When Lewis acids such as SnCl₄·5H₂O were used in the hydrothermal conversion of chitosan at 200 °C under microwave irradiation, in 30 minutes 23.9% LA was formed and the conversion of chitin produced 11.5% LA.¹⁷⁶ The poor yield of LA from chitin polymer is due to its structural rigidity, intensive network of hydrogen bonding and crystallinity. A very low yield of LA (0.48%) was obtained in a 0.7 M sulfamic acid catalysed hydrothermal degradation of chitosan at 200 °C within 2 min.¹⁸³ At the same temperature the 0.3 M sulfamic acid catalysed hydrolysis of GA yielded 33.76 mol% of LA within 15 min. 39.03 mol% FA and 26.48 wt% humins (insoluble products) were also detected.¹⁸² Zirconium oxychloride (ZrOCl₂) was able to catalyse the hydrothermal degradation of chitosan. At 200 °C and 20 min 21.3 mol% of LA was obtained from 5 wt% chitosan using 15 mol% catalyst.²⁰³ Solid acid Amberlyst-15 was able to transform GA into 36.9% LA at 180 °C in 60 minutes.²⁰⁴

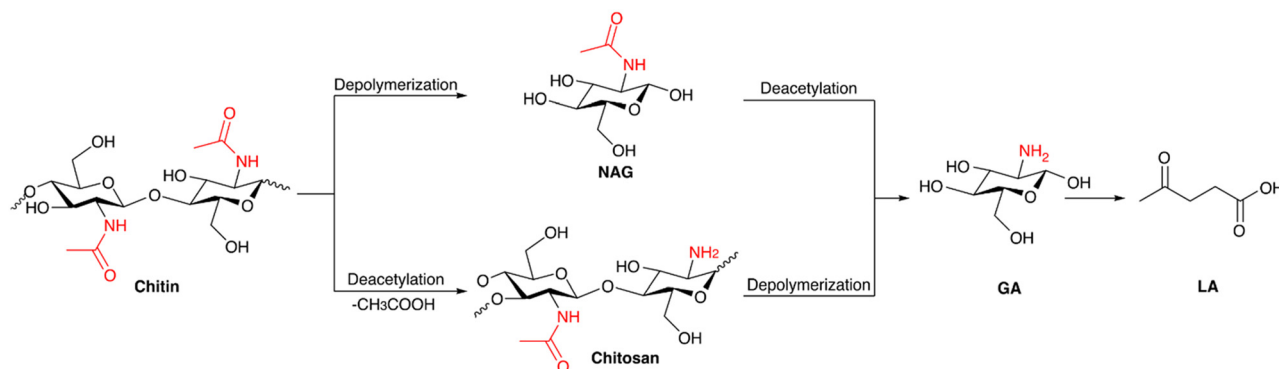
Sulfonic acid-functionalized imidazolium ionic liquids were used for the transformation of chitosan to LA, and various anion combinations were tried by keeping the cation the same. Among them 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulphate ionic liquid ([C₃SO₃Hmim]HSO₄) showed the best activity. At 170 °C and 5 h, 1 g of the catalyst was able to convert 250 mg of chitosan in water (4 g) to 49% LA.²⁰⁵ The

presence of water played a pivotal role in the reaction, as the absence of water led to a decrease in LA yield and the formation of a significant amount of humins. Reducing the substrate amount to 50 mg increased the LA yield to 64%, indicating a dilution effect. The increased selectivity for LA was attributed to the highly acidic nature of the IL. According to the proposed mechanism, chitosan underwent quaternization and depolymerization, forming the glucosammonium salt. This salt then underwent dehydration and deamination to produce HMF. Subsequent rehydration resulted in the formation of LA. However, the catalytic activity of the IL decreased after two cycles due to a reduction in acidity caused by ammonia released during the reaction. The researchers quantified the amount of NH₄⁺ ion in the reaction mixture using ion chromatography analysis. Remarkably, the catalyst was found to be reusable for up to five catalytic cycles when 1 equivalent of H₂SO₄ was added after recovery.

Liu *et al.* have recently reported the direct conversion of chitin to LA using the acidic ionic liquid [C₃SO₃Hmim]HSO₄.²⁰⁶ The effect of the structural properties of IL on the chitin conversion and the role of the acetlamino group was investigated in detail. At 180 °C and 5 h, 56.5 mol% of LA was obtained from 3.4 wt% of chitin. A significant increase in LA yield (67 mol%) was observed when 0.7 wt% of chitin was used. [C₃SO₃Hmim]Cl was found to have remarkable efficiency in LA (54 mol%) formation despite its lower acidity compared with [C₃SO₃Hmim]HSO₄. However, the catalyst's activity decreased in recycling experiments, with the LA yield reaching 34 mol% in the fifth catalytic cycle, likely due to a decline in acidity resulting from an interaction with NH₃ released during the reaction. The addition of 1 equivalent of H₂SO₄ as a supplement maintained a consistent catalytic activity. A two-way approach to the depolymerization and formation of LA was proposed by the investigators (Scheme 10). It can be either *via* deacetylation followed by depolymerization to GA and LA or by direct depolymerization to NAG and its conversion to GA and LA.

In another study, they presented a highly selective one-step method for synthesizing LA from raw crab shells using [C₃SO₃Hmim]HSO₄.²⁰⁷ They achieved a notable 77.9% LA yield at 180 °C in a 5 hour reaction. The acidity and hydrogen-bonding ability of the IL played a crucial role in the catalytic activity.

Monitoring the degree of acetylation at various time intervals provided insight into the reaction's mechanism, revealing that direct depolymerization and successive deacetylation or depolymerization occurring on the outer surface of the chitin while the inner crystalline structure remained inert were viable pathways. However, the catalytic activity of the IL diminished within the first three cycles due to the deamination of NAG and the CaCO₃ component in crab shells. The addition of H₂SO₄ during recycling proved effective in restoring the activity. Theoretical investigations on chitin to LA conversion also appeared in recent literature. Tian *et al.* investigated the impact of −SO₃H functionalized ionic liquids on chitin conversion to LA through a comprehensive analysis using DFT



Scheme 10 Proposed mechanism of formation of LA from chitin.

studies. In their research, the relative catalytic activity of the IL was predicted by calculating the LUMO–HOMO band gap of the most stable complexes of IL–NAG. Imidazolium-based ILs exhibited the highest activity, followed by pyridinium cation- and ammonium cation-based ILs. Through ^1H NMR and DFT analysis, $[\text{C}_4\text{SO}_3\text{Hmim}]\text{HSO}_4$ was identified as the catalyst of choice for converting chitin to LA. Under reaction conditions of 190 °C for 5 hours, utilizing 1 g of chitin with a catalyst amount of 1.5 g in 6 g of water, $[\text{C}_4\text{SO}_3\text{Hmim}]\text{HSO}_4$ showed a remarkable LA yield of 74.7%.²⁰⁸

Table 10 summarizes literature findings on converting chitin biomass into LA. These data reveal that for LA synthesis, a catalyst with higher acidity is essential with control of acidity to minimize humin formation. MSA and acid-functionalized ionic liquids exhibited a superior performance among all the catalysts. Although ILs required longer reaction times, they proved to be effective for the direct conversion of raw shell waste. However, challenges arise due to the deactivation of acid catalysts in the presence of minerals in shell waste and the removal of acetamido groups in the form of NH_3 . Also, the

separation and purification of products remain unresolved in the current solvent and catalytic systems. This complexity underscores the need for designing an efficient, recyclable, cost-effective, and environmentally friendly catalyst for the chitin to LA conversion process.

Acetic acid (AA) is another important organic acid that can be obtained from chitin. The production of acetic acid is more practical from chitin biomass in comparison with lignocellulosic biomass. This is due to the fact that the hydrolysis of the acetamido group in chitin invariably results in the simultaneous removal of acetic acid. Yan and co-workers have demonstrated the hydrothermal oxidation of raw shrimp shells and chitin to produce AA and pyrrole in a single-step transformation.¹⁵¹ 100 mg of chitin in 5 mL of 2 M NaOH solution was converted into 23.5% of AA without any oxidant and metal oxide additives at 300 °C in 35 min, while the use of ball milled CuO and 5 bar oxygen enhanced the AA yield up to 38.1% and 47.9% of AA was obtained from crude shrimp shell waste, under similar conditions. Along with AA, other acid products such as LA, FA, oxalic acid (OxA), glycolic acid (GlyA),

Table 10 Levulinic acid formation from chitin biomass

Substrate	Catalyst	Reaction conditions			LA (% yield)	Ref.
		Solvent	Temperature (°C)	Time (h)		
Chitosan	HCl	Water	190 (MW ^a)	0.5	32.7	201
	H ₂ SO ₄				37.8	
GA	H ₂ SO ₄	Water	188	0.82	25.3	202
Chitin	HCl	DCE	150	3	29	
GA	0.5 M MSA	Water	200	0.5	49.9	178
Chitosan	0.2 M MSA	Water	200	0.5	28.2	179
Chitosan	SnCl ₄ ·5H ₂ O	Water	200 (MW ^a)	0.5	23.9	176
Chitin					11.5	
Chitosan	Sulfamic acid	Water	200	0.25	33.8	182
Chitosan	ZrOCl ₂	Water	200	0.3	21.3	203
GA	Amberlyst-15	Water	180	1	36.9	204
Chitosan	$[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$	Water	170	5	49	205
Chitin	$[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$	Water	180	5	56.5	206
	$[\text{C}_3\text{SO}_3\text{Hmim}]\text{Cl}$				54	
Crab shell	$[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$	Water	180	5	77.9	207
Chitin	$[\text{C}_4\text{SO}_3\text{Hmim}]\text{HSO}_4$	Water	190	5	74.7	208

^a MW: microwave heating.

and various other C4–C6 acids containing hydroxyl groups were also identified and quantified using GC-MS, GC-FID and TOC (total organic carbon) analyses. Using ^{13}C -labeled acetamido groups in NAG, the relative ratio of AA formed from the pyranose ring and the sidechain acetamido group was determined *via* GC-MS. The analysis revealed that 60% of AA formation resulted from acetamido group hydrolysis, while the remaining 40% originated from pyranose ring decomposition and oxidation. The proposed mechanism involves chitin deacetylation and depolymerization to GA and AA, with subsequent deamination leading to C6-sugars. Parallel reactions were evidenced by the presence of unstable intermediates, ultimately converting into various stable organic acids. Untreated tiger shrimp shell powder, utilized under similar conditions, yielded 47.9% AA, suggesting the protein content in shrimp shells contributes to AA formation.

2-Amino-2-deoxy-D-gluconic acid or glucosaminic acid (AGA) is an α -amino acid which is having potential applications as a starting material in synthetic chemistry and used in various biomedical applications.²⁰⁹ GA can be converted into AGA by the oxidative cleavage of the O–C bond in the pyranose form of GA. While numerous enzymatic and microbial methods exist for this conversion, the literature reports only a limited number of chemo-catalytic approaches for the transformation of GA to AGA. In 1915 oxidation of GA to AGA was tried with HgO and H_2S but the process was not well considered due to environmental concern and lack of consistency in the activity, and also the mercuric sulphide left in the reaction was not separable easily.²¹⁰ Later an active charcoal-supported Pd–Bi bimetallic catalyst in the presence of molecular oxygen was found to oxidize GA to form AGA at 30 °C.²¹¹ 70% of the AGA was achieved in the reaction in pure form. The mechanism was proposed to be the oxidative dehydrogenation of glucosamine hydrochloride. The role of Bi was as the co-catalyst, and it reduced the over-oxidation of the Pd surface during the reaction. The catalyst was recyclable for eight cycles. Tominaga and colleagues introduced an electrocatalytic method for oxidizing glucosamine (GA) in both basic and neutral pH environments.²¹² They utilized a carbon electrode modified with 2 nm-sized gold nanoparticles and a gold plate

electrode. In an alkaline solution, the conversion to AGA achieved a remarkable current efficiency of 100% at -0.2 V , while in a neutral pH, AGA was detected with an approximate current efficiency of 70% at 0.4 V .

Ebitani *et al.* investigated the air oxidation of GA-HCl and its derivatives in a base-free environment using gold (Au) particles supported on heterogeneous basic supports.²¹³ Various supports were examined, with Au/HT (hydrotalcite) and Au/MgO catalysts showing the best activity. At 40 °C and 3 hours under O_2 flow, Au (2 wt%)/HT and Au (0.9 wt%)/MgO produced 89% and 93% of AGA, respectively. Other amino sugars such as NAG and NAM were also oxidized to yield the corresponding acids at approximately 90% under similar conditions. However, Au/HT exhibited reduced activity in successive cycles, with an agglomeration of Au particles in the spent catalyst. Conversely, the high basicity of MgO prevented Au particle growth, maintaining high catalytic activity during the first and second reuses. Furthermore, Yan *et al.* developed a two-step process for the transformation of chitosan salts to form AGA using an Au/MgO catalyst system.²¹⁴ Initially, mineral/organic acid-treated chitosan underwent hydrolysis with the solid acid catalyst Amberlyst-15. Subsequently, oxidation using Au/MgO yielded AGA. A monomer yield of 58% was achieved when chitosan treated with H_2SO_4 was utilized as the substrate at 160 °C in 2 hours. However, the presence of polymeric material and humins during hydrolysis impeded the oxidation catalyst's activity, limiting the AGA yield to 17%. The introduction of a detoxification method using activated carbon for the hydrolyzed product, followed by oxidation, significantly increased the AGA yield to 63% under 5 bar O_2 pressure at 40 °C in 3 hours.

Recently Chen *et al.* reported the conversion of chitin-derived NAG into organic acids. The reaction employed 0.1 M NAG and 0.5 M NaOH at 35 °C for 48 hours, utilizing various oxidants.²¹⁵ Under ambient air, the total yield of organic acid products reached 72.3%, encompassing acetic acid (AA), formic acid (FA), and glyceric acid (GlycA). Product selectivity was influenced by the choice of oxidants, with a predominant formation of FA (57.1%) observed when hydrogen peroxide (H_2O_2) was utilized. Conversely, the use of oxygen favored the production of AA and GlycA, constituting 41.2% of the major

Table 11 Formation of other organic acids from chitin biomass

Substrate	Catalyst	Reaction conditions				Product (% yield)	Ref.
		Solvent	Temperature (°C)	Time (h)	O_2 (bar)		
Chitin	CuO	NaOH	300	0.58	5	AA (38.1)	151
Shrimp shell						AA (47.9)	
GA	Pd–Bi/C + KHCO_3	Water	30	6	Bubbled O_2	AGA (70)	211
GA	Au on carbon electrode	Alkaline water	—	—		AGA (100)	212
GA	Au(0.9)/MgO	Water	40	3	1	AGA (93)	213
	Au(2)/HT					AGA (89)	
Chitosan– H_2SO_4	Amberlyst-15 + Au/MgO	Water	40	3	5	AGA (63)	214
NAG	NaOH + H_2O_2	Water	35	48	—	FA (57.1)	215
	NaOH	Water	35	48	5	AA + GlycA (41.2)	
Chitin	MgO	Water	260	6	—	LcA (10.8)	216
GA						LcA (23.3)	
NAG						LcA (7.7)	

products. Following this, various metal oxide catalysts were assessed for the direct oxidation of chitin itself, with MgO exhibiting the most efficient catalytic activity, resulting in a significant yield of 10.8% lactic acid (LcA) as the major product at 260 °C in a 6 hour reaction.²¹⁶ The conversion of GA and NAG under similar reaction conditions showed LcA yields of 23.3% and 7.7%, respectively. While the catalyst demonstrated recyclability for the initial three runs, the first recycling revealed 15% Mg leaching. The accelerated leaching of Mg was attributed to the formation of acidic products.

Table 11 summarizes literature reports on organic acids obtained from chitin biomass oxidation reactions. Given the limited number of studies conducted on the oxidation of chitin biomass, there exists a significant scope for exploring various catalytic systems in this reaction.

The incorporation of a base or basic support is crucial in oxidation reactions and designing a suitable catalyst for achieving the selective formation of acids, such as AGA and LcA, is highly desirable. Additionally, addressing the challenge of separating the various acids formed during the reaction underscores the importance of research focused on selectivity.

5 SWOT analysis

A SWOT analysis for the conversion of chitin to value-added chemicals can help to identify the strengths, weaknesses, opportunities, and threats associated with this process. As the drive toward eco-friendly and sustainable solutions gains momentum, understanding the potential and constraints of this process becomes vital. A SWOT analysis diagram for the production of chemicals from chitin is given in Fig. 6.

5.1 Strengths

Chitin is the second most abundant biopolymer, making it an excellent resource for the production of renewable chemicals.

Chitin is primarily derived from crustacean shells, a byproduct of fisheries and marine aquaculture, ensuring its continued production in the future. The production of nitrogen-containing chemicals from renewable resources, which does not require ammonia synthesized from the energetically inefficient Haber process, is expected to play a vital role in achieving net zero emissions and sustainable development goals. In this context, chitin, as the only nitrogen-containing renewable resource, is invaluable as a feedstock. Furthermore, the use of shell waste would decrease environmental pollution and waste management costs.

5.2 Weaknesses

The main weakness is that basic research on chitin as a feedstock is still in its early stages. The major advances in chitin chemistry have been made by drawing parallels with cellulose chemistry due to structural similarities. The general principles of chitin chemistry are not well understood. Furthermore, there is no techno-economic analysis done so far in the field of production of chemicals from the catalytic conversion of chitin biomass to determine the industrial viability of the associated process. Another issue is that commercial chitin extraction methods are not environmentally friendly, as most of the processes focus solely on chitin extraction, while the other components of shell waste are not properly utilized.

5.3 Opportunities

The abovementioned weakness creates significant opportunities. More systematic research is needed in the field to determine a chitin extraction process that focuses on utilizing the protein, lipid, and mineral components of shell waste in addition to chitin, as the co-production of all the components would reduce costs. Understanding the reaction mechanism provides ample opportunities for rationally designing catalytic active sites for chitin conversion to chemicals. Because chitin-

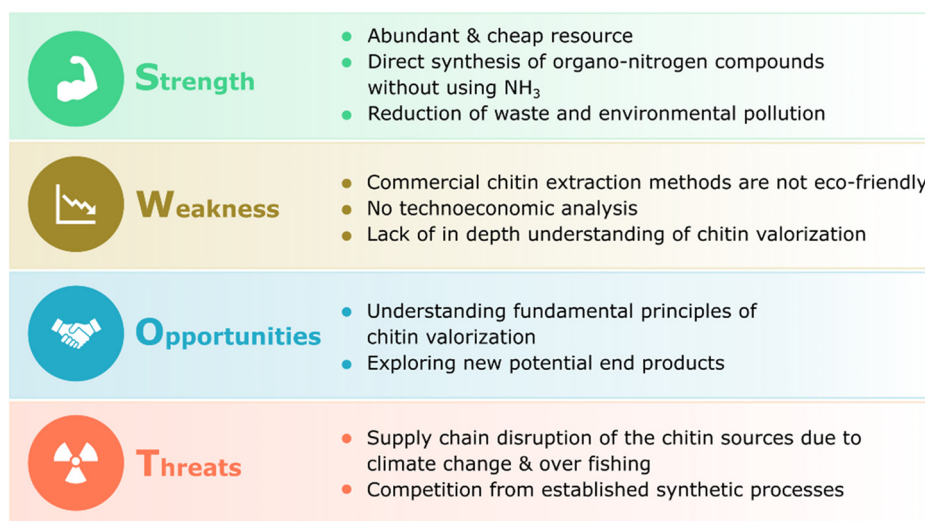


Fig. 6 SWOT analysis for the production of chemicals from chitin biomass.

derived chemicals have a wide range of applications in the polymer and pharmaceutical industries, also the new end products can be compared with existing related products. For example, the properties of polymers that can be synthesized from chitin-derived monomers should be investigated, as this will aid in identifying important monomers and providing researchers with a meaningful goal for the development of catalytic reactions.

5.4 Threats

Despite these opportunities, several threats loom over the process. The most serious threat to the process is likely to be the cost competitiveness of the end products. The main competition would come from existing similar products. Furthermore, the industrialization of chitin-based end products may necessitate a different infrastructure than what is currently in place, which could serve as a bottleneck. On the other hand, shell waste supply chain disruptions may occur as a result of rapid climate change, overfishing, or other causes.

Overall, the establishment of a chitin-based bio-refinery would require more careful fundamental research and careful governance and policies.

6 Analysis of products in chitin chemistry

As we have discussed in the previous sections there are a reasonable number of studies on the valorization of chitin and chitosan to yield various chemicals with or without nitrogen. However, it is observed from the literature that the reported analytical methods can detect and quantify either oligomer or monomer or furan derivatives. The polarity of amino sugars and sugar derivatives are very close to each other and mostly soluble in water, and that is why they are hard to separate. Moreover, due to lack of optimum analytical conditions, a few products were not separated, and some were undetected. From the literature, it was seen that chitin/chitosan-derived compounds can be separated and quantified by various analytical methods like chromatographic (gas chromatography (GC),^{111,186,217} column chromatography, high-performance liquid chromatography (HPLC)^{181,186,218}), chemical (Fehling's test, gravimetric analysis)²¹⁹ and colorimetric methods (DNS method).^{181,195,218,220}

In our work, firstly, the properties (*e.g.*, kinetic diameter, melting point, boiling point, degradation temperature, solubility, molecular weight) of chitin-derived compounds (mainly acid-catalysed depolymerization and degradation products of chitin biomass such as GA, NAG and HMF) were examined, which is very essential before starting the analytical method development.²²¹ The study suggested that the compounds may not be separated only on the basis of their polarities since they are mostly polar in nature, which was evidenced from their higher solubility in water compared with methanol. The size-based separation of these compounds is not possible as they have very minimal differences in their size (kinetic diameter of

GA, NAG and HMF is 6.954 Å, 7.460 Å, and 6.186 Å respectively). The amino sugar compounds GA and NAG cannot be analyzed by gas chromatography as they degrade at the higher temperatures used to vaporize the samples. A TLC (thin layer chromatography) experiment was conducted to understand the trend in polarity of these compounds and R_f (retention factor) values. It was realized that the polarity trend follows the order GA > NAG > HMF. Considering all these factors, we have presumed that HPLC is the easiest, most convenient, rapid, and sensitive technique to separate chitin-derived chemicals which are both water soluble and organic. Researchers have extensively employed HPLC as a primary analytical technique for chitin/chitosan valorization chemistry. However, there is a lack of prior reports on the simultaneous separation and quantification of all the compounds derived from chitin/chitosan during the reaction. This is primarily due to the limited research conducted in selecting suitable analytical techniques capable of effectively separating and quantifying these compounds.^{108,186,221}

After a thorough literature survey on the analysis of chitin/chitosan-derived products, our group has worked towards the investigation and optimization of various HPLC parameters which can simultaneously separate and quantify various chitin-derived compounds.²²¹ Initially, the mixture of GA, NAG, and HMF was analyzed using a previously reported HPLC method employed in chitin chemistry for HMF analysis. In this analysis, an C18 column (non-polar), a mobile phase consisting of methanol and water (2.3/7.7 v/v), and a UV detector set at a wavelength of 284 nm were used.¹⁸¹ However, only HMF was detected, and no peaks corresponding to GA and NAG were observed. From the UV-Visible absorption study of the compounds, we have observed that the $\lambda_{\max}$ (maximum absorption wavelength) value for amino sugars was at 195 nm. This indicates that the UV wavelength on the detector should be set at 195 nm to effectively detect these compounds. In the previously reported literature, a UV detector with a wavelength of 284 nm was employed, resulting in the detection of only HMF ($\lambda_{\max}$ = 284 nm). As a consequence, compounds that do not exhibit UV activity below 284 nm could not be analyzed using this method.

In our study, setting the UV wavelength to 195 nm allowed the detection of all the compounds, based on the understanding that higher energy is associated with lower wavelengths, effectively exciting electrons in all the compounds. Another challenge that arose was the selection of the VWD wavelength when using a methanol/water mobile phase. It was crucial to set the wavelength above 205 nm due to methanol's UV cut-off at that value. According to the literature, the measurement wavelength should be higher than the UV cut-off of the mobile phase to prevent any contribution from the mobile phase in the measured absorbance.²²²

To address the limitations posed by methanol's UV cut-off, we replaced it with acetonitrile, which has a lower UV cut-off (<190 nm). The use of acetonitrile led to less difference in the retention times of the compounds compared with methanol, owing to the different polarity index of acetonitrile. Our ana-

lysis was conducted with a C18 column, utilizing an acetonitrile/water ratio of 2.3/7.7 v/v and a VWD wavelength of 195 nm. To further enhance the compound separation, we introduced a more polar solvent, specifically water, into the mobile phase. By varying the acetonitrile-to-water ratio, we explored different combinations. After evaluating all the possible ratios, we found that a 1/9 v/v ratio of acetonitrile to water provided the best separation of GA, NAG, and HMF. This optimized condition allowed us to achieve improved resolution and differentiation between the compounds.

During our investigation, we also examined the effect of column length on compound separation. It was determined that longer columns are more effective in separating compounds as they allow for a greater interaction time with the stationary phase, minimizing the chance of peak merging. However, when utilizing a non-polar C18 column for analyzing other sugars and chitin valorized products, the retention times showed only minimal differences, making it difficult to achieve distinct peaks. In an attempt to improve the separation, we opted to use a polar column (amino column) since

polar compounds are expected to exhibit strong interactions with a polar stationary phase. However, the chromatogram obtained using the polar column showed peak tailing, suggesting that the compounds were strongly retained on the stationary phase due to strong interactions. This finding led us to conclude that polar columns are not suitable for separating these polar compounds, as they tend to exhibit tailing and peak merging, resulting in undesirable separation. Based on our previous experimental observations, it became clear that the stationary phase should possess an optimum polarity to facilitate the rapid adsorption-desorption of the compounds on the stationary phase. Then we carried out the experiments on an ion-exchange column (monosaccharide lead (Pb^{2+}) column). In this column the stationary phase is composed of sulfonated styrene divinyl benzene polymer with Pb^{2+} exchanged cations and offering medium polarity. A suitable separation was observed when water was used as the mobile phase (0.5 mL min⁻¹ flow rate), a column temperature of 80 °C, and a VWD wavelength of 195 nm. In addition to this, other sugars and chitin-derived compounds showed clear separation with this column and the abovementioned analysis conditions. A schematic representation of the separation of various amino sugars and chitin-derived chemicals using Pb^{2+} is given in Fig. 7. Method validation was done by ensuring precision, day to day variations and repeatability and proved to be accurate and sensitive.

In order to accomplish effective separation of chitin/chitosan-derived compounds, we evaluated various columns with different properties, including polarity, length, and stationary phase, together with mobile phases of varying polarity. Through our experimental study, we discovered that both the C18 (non-polar) column and the cation exchange Pb^{2+} column (medium polar) was suitable for the detection and separation of amino sugar monomers and dimers, other N-containing compounds, and furan derivatives. Although the non-polar C18 column exhibited better separation compared with the polar amino column, it struggled to separate sugars with

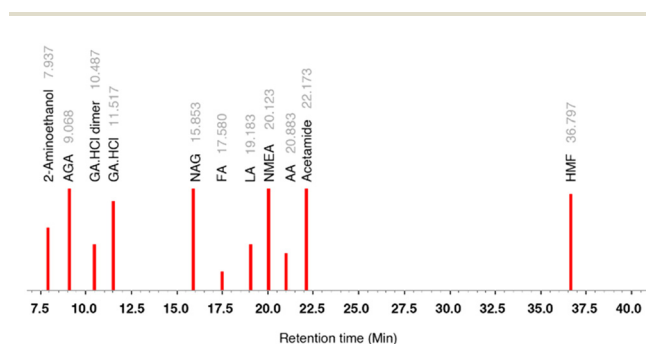


Fig. 7 Separation of various chitin-derived chemicals by HPLC on a Pb^{2+} monosaccharide column (analysis conditions: column temperature: 80 °C, mobile phase: water, flow rate: 0.5 mL min⁻¹, VWD wavelength: 195 nm).

Table 12 Summary of the separation of different compounds using various columns, and analysis conditions using HPLC

Column	Polarity, phase, (length × internal diameter in mm, matrix, particle size in μm, pH range)	Analysis conditions (mobile phase, flowrate, column temperature, VWD wavelength)	Remarks on separation [compounds (RT in minutes)]
C18	Non-polar, reverse (250 × 4.6, octadecylsilane, 5, 2–9)	Acetonitrile : water (1 : 9 v/v), 0.5 mL min ⁻¹ , 25 °C, 195 nm	Good separation of GA (4.037), NAG (5.582) and HMF (9.735) but retention times of other products were merging [AA (5.983), NAG (5.582)], [GA-HCl dimer (3.994), GA (4.037), AGA (4.126)]
	Non-polar, reverse (100 × 4.6, octadecylsilane, 5, 2–9)	Acetonitrile : water (1 : 9 v/v), 0.5 mL min ⁻¹ , 25 °C, 195 nm	Peaks of GA and NAG were merged as compounds got less interaction time with the stationary phase
Amino	Polar, normal (250 × 4.6, silica, 2–8)	Acetonitrile : water (8 : 2 v/v), 0.5 mL min ⁻¹ , 30 °C, 195 nm	Tailing of peaks due to strong interaction; peaks of HMF (7.130), acetamide (7.990) and AGA (7.493) were merged due to peak tailing
Monosaccharide Pb^{2+}	Medium polar, reverse (300 × 7.8, sulfonated styrene divinyl benzene, 8, 7)	Water, 0.5 mL min ⁻¹ , 80 °C, 195 nm	Very good separation of GA (11.517), NAG (15.853) and HMF (36.797). Separations of other products were also good [AGA (9.068), GA-HCl dimer (10.487), LA (19.183), AA (20.883), acetamide (22.173)]

similar functionality and polarity, while the cation exchange Pb^{2+} column was able to effectively separate most of the compounds due to its optimum polarity. A summary of the HPLC analysis parameters and separation of compounds is given in Table 12. With the developed HPLC method, we achieved separation of amino sugars and HMF within 39 minutes and observed a strong linear relationship as indicated by the regression analysis. As a result, we have successfully established a simple, quick, accurate, and precise HPLC method that enables the separation and quantification of chitin/chitosan-derived products.

7 Conclusions

1. In this review, we described various methods of fractionating shell waste into different components. We have described in detail the various products obtained so far from the catalytic conversion of chitin and chitin derivatives to N-containing furan compounds, amino sugars, heterocyclic compounds such as pyrazines and pyrrole, amino acids, amines, amino sugar alcohols, and 5-hydroxymethylfurfural, levulinic acid, acetic acid, and glucosaminic acid, among others.

2. Even though shell waste is inexpensive, the current fractionation methods require a higher price for high-purity chitin. New fractionation techniques that are inexpensive, environmentally friendly, and efficient must be developed to obtain chitin without compromising the product purity or resulting in the loss of other valuable components.

3. The direct transformation of chitin is difficult due to the recalcitrant structure of chitin, while the products were easily attainable from low molecular weight chitosan and monomeric compounds.

4. In the hydrolysis and dehydration reactions of chitin biomass, while homogeneous acid and base catalysts exhibit efficiency in achieving reasonable conversion, their drawbacks, including corrosiveness, poor recovery and reusability, and the loss of nitrogen atoms from product molecules pose significant challenges. Conversely, ionic liquid catalytic systems demonstrate promising performance in terms of product selectivity.

5. Due to the significant risk of catalytic site poisoning by ammonia during dehydration reactions, prioritizing the production of nitrogen-containing furan derivatives or other heterocycles over the synthesis of HMF and LA from chitin is recommended. This preference is based on the potential transformations of these nitrogen-containing compounds, underscoring the crucial importance of preserving the amino/acetamido group intact during the catalytic processes.

6. Given the environmentally benign nature and ease of separation, there is a strong inclination towards employing heterogeneous catalysts in chitin biomass conversion. While recent attempts have utilized heterogeneous catalysts for chitin valorization, there remains massive potential for exploration and

innovation in the realm of heterogeneous catalytic systems for this purpose.

7. The vast potential of hydrogenation and oxidation reactions remains largely unexplored. There is a need for extensive research into various catalytic systems to selectively produce desired products. Additionally, the exploration of potential upgrades for hydrogenation products represents a promising avenue that has yet to be thoroughly investigated.

8. It is crucial to comprehend both the potential and constraints of chitin valorization to propel this research area into a commercially viable process. Conducting a SWOT analysis enabled us to do a comprehensive exploration of the strengths, weaknesses, opportunities, and threats associated with chitin valorization, thereby enhancing the current scope of this review.

9. Future research in this field is expected to focus on several key directions. First, there will be efforts to develop efficient methods for extracting high-purity chitin from shell waste, optimizing the process to maximize yield and minimize waste and production cost.

10. Another area of interest will be the synthesis of nitrogen-containing chemicals from chitin. Researchers may explore novel approaches and reaction pathways to convert chitin into valuable nitrogen-based compounds, such as amino acids, amines, and other nitrogen-containing derivatives.

11. Designing suitable catalysts for the chemical transformation of chitin biomass will also be a priority. Catalyst development can enable more efficient and selective reactions, leading to improved yields and reduced energy consumption in chitin valorization processes. The designing of the catalysts should also consider the structural rigidity and the features of the target chemicals.

12. Moreover, conducting a thorough examination of reaction mixtures through the utilization of suitable analytical tools should be essential. Employing advanced analytical techniques to characterize reaction intermediates, by-products, and end products will offer profound insights into the intricacies of reaction mechanisms, reaction kinetics, catalyst impact, and the optimization of reaction conditions. This acquired knowledge will play a pivotal role in enhancing the precision and optimization of chitin valorization processes in the future.

13. The separation of the products and their purification is another area which is lacking in the studies of chitin biomass valorization. Devising these protocols is mandatory for commercial viability of the end products. Developing efficient separation techniques, such as chromatography or membrane-based processes, will enable the extraction as well as purification of target compounds from complex reaction mixtures.

14. Detailed investigations are required to make this valorization process economically viable on a large scale in future.

15. Combining the process of chitin extraction from shell waste and its conversion into various value-added products is highly recommended in terms of industrial upscaling of the valorization of raw shell waste.

16. Awareness about the possibilities of shell waste applications should be passed on to the fisheries sector. Also, establishing industries on fisheries sites for the production of chitin and shell waste fractionation could be beneficial in terms of the commercial production of chitin.

17. Research efforts for making cascade processes for the direct conversion of shell waste to value-added chemicals have to be considered and the potential of this conversion process has to be acknowledged and emphasized properly to build a foundation for shell waste-based shell-biorefinery.

Author contributions

Lavanya K: conceptualization, data curation, visualization, writing – original draft, and writing – review & editing, Neha Ghosh: writing – review & editing, Paresh L Dhepe: supervision and writing – review & editing.

Conflicts of interest

The authors declare no conflicts of interest.

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