Summary of the thesis

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Design and Fabrication of Functional Metal Nanocomposites for Advanced Catalytic Applications

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The Thesis will be presented in the form of the following chapters:

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Chapter 1

Introduction

Metal Nanocomposites as Heterogeneous catalysts

Heterogeneous catalysts exhibiting high activity, long-term stability, and efficient recyclability are crucial for enabling a broad range of organic transformations in an effective and environmentally responsible manner [1,2]. Such catalysts support cleaner chemical processes by reducing waste generation, simplifying separation, and enabling repeated use, making them indispensable in modern chemical manufacturing. Depending on the specific reaction requirements, sustainable heterogeneous catalysts can be rationally engineered through the selection of suitable metal nanocomposites that provide appropriate active sites, mechanical integrity, and tunable surface characteristics [3,4]. Among various catalyst systems, metal nanocomposites are particularly attractive due to the synergistic interactions between metal or metal oxide nanoparticles and their supporting matrices, which enhance catalytic performance while suppressing nanoparticle aggregation and deactivation [5,6]. Key industrial transformations such as reduction, hydrogenation, and transesterification demand catalysts that operate efficiently under mild conditions while delivering high turnover numbers, excellent selectivity, and tolerance toward diverse reaction environments. Although numerous catalytic systems have been reported, the development of greener, economically viable, and highly efficient catalysts remains a major research focus. Recent advances in materials design, especially in metal nanocomposite systems, have enabled the creation of catalysts that integrate sustainability, high activity, and reusability, which are essential for both laboratory-scale synthesis and large-scale industrial processes [7]. Owing to their tunable surface properties, improved structural stability, and reduced metal leaching, metal nanocomposites represent a promising route toward next-generation catalytic technologies.

Metal nanocomposites are hybrid materials in which metal or metal oxide nanoparticles are uniformly dispersed within suitable host matrices such as polyphenols [8], polymers [4], metal–organic frameworks, and covalent organic frameworks [9]. Incorporation of nanoparticles within these structured supports effectively limits aggregation while enhancing the mechanical and chemical stability of the catalytic system. These materials typically exhibit high surface areas, abundant exposed active sites, and adjustable physicochemical properties that can be tailored through judicious selection of both the metal component and the supporting matrix. Such attributes promote enhanced catalytic efficiency, improved electron transfer, and broad functional versatility across applications including hydrogenation, oxidation, chemical sensing, antibacterial activity, and environmental remediation. Due to their robust architecture, strong metal support interactions, and design flexibility, metal nanocomposites have emerged as advanced functional materials that outperform standalone nanoparticles and bulk catalysts. These features further enable their application in energy conversion, sensing technologies, catalysis, antimicrobial systems, and drug delivery platforms.

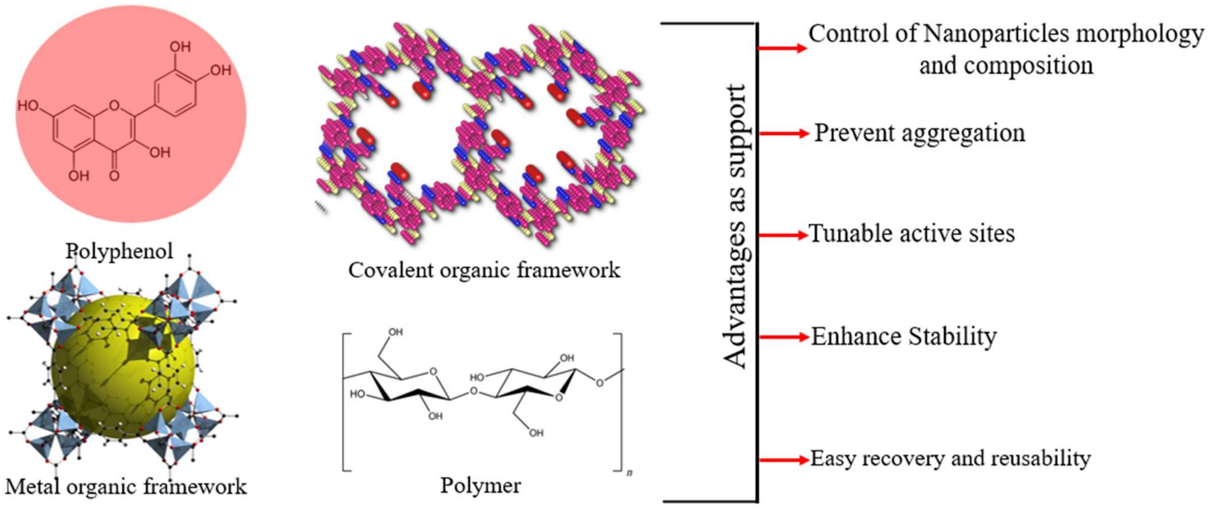


Figure 1: Different supports for metal nanoparticle stabilization and their advantages

The supporting matrix plays a critical role in regulating nanoparticle size, morphology, and stability while preventing aggregation. Bioactive compounds such as polyphenols, flavonoids, terpenoids, proteins, and sugars possess intrinsic reducing capability, facilitating the formation of metal nanoparticles [10,11]. In addition, these biomolecules act as stabilizing and capping agents, effectively inhibiting particle agglomeration. This green synthesis strategy eliminates the need for strong mineral reducing agents, hazardous organic solvents, and toxic capping chemicals, enabling more environmentally benign and potentially scalable catalyst preparation. Bio-capped metal nanoparticles have therefore found extensive application in catalytic processes such as nitroaromatic reduction, cross-coupling reactions, oxidation, hydrogenation, and multicomponent condensation reactions.

Polymeric materials function as stabilizing, structuring, and often functional matrices for metal nanoparticles, allowing precise control over particle size, dispersion, and accessibility while facilitating catalyst recovery and reuse. Chitosan, a cationic polysaccharide derived from the deacetylation of chitin, is widely utilized as a functional biopolymer in materials science, biomedical applications, and nanotechnology [12,13]. It serves as an eco-friendly stabilizer, reducing agent, and size- and shape-directing template in the synthesis of metal nanoparticles such as silver, copper, gold, and palladium, often yielding well-dispersed and biocompatible nanocomposites. The cationic backbone of chitosan effectively chelates metal ions, controls nucleation, and prevents agglomeration, making it particularly valuable for catalytic, antimicrobial, sensing, and biomedical applications.

Porous organic polymers such as covalent organic frameworks are crystalline, highly ordered materials that act as rigid and tunable supports for metal nanoparticle immobilization, producing well-defined heterogeneous catalysts with high surface area, accessible pore networks, and engineered metal support interactions [14]. COFs possess periodically arranged nanochannels with low density and high porosity, allowing metal nanoparticles to be anchored within their pores or on their surfaces while retaining accessibility to reactant molecules. Furthermore, COF backbones can be deliberately designed with donor atoms such as nitrogen, oxygen, sulfur, or phosphorus, as well as chelating functional groups including imine, triazine, pyridine, and phosphine units. These functionalities strongly coordinate metal species, leading to improved dispersion, resistance to sintering, and enhanced stability under demanding catalytic conditions.

The primary aim of this research is to design and fabricate functional metal and metal oxide–based nanocomposites for advanced catalytic applications using sustainable, scalable, and controllable synthesis strategies. Emphasis is placed on immobilizing nanoscale active species within suitable organic, inorganic, and biopolymeric supports to achieve precise control over particle size, morphology, dispersion, and surface functionality. The study systematically investigates the role of support materials, metal–support interactions, and surface functional groups in governing catalytic activity, selectivity, stability, and recyclability. The synthesized nanocomposites are comprehensively characterized and evaluated in representative catalytic systems relevant to environmental remediation, chemical transformations, and enzyme-mimetic reactions, with particular focus on catalytic efficiency, durability, and reuse potential.

The central hypothesis of this work is that coupling metal or metal oxide nanostructures with functional supports such as biogenic capping agents, biopolymers, and covalent organic frameworks (COFs) can markedly enhance catalytic performance while improving sustainability. Biogenic capping and polymeric matrices are expected to promote uniform nanoparticle dispersion, surface stabilization, and enhanced accessibility of active sites, thereby facilitating efficient electron transfer in reduction and enzyme-mimetic processes. In contrast, COF-based supports are anticipated to provide high surface area, ordered porosity, and confinement effects that favour improved activity and selectivity in transesterification and hydrogenation reactions. The synergistic interaction between the metal phase and the supporting matrix is proposed to suppress agglomeration, enhance long-term stability, and enable efficient catalyst recovery, establishing these nanocomposites as robust and environmentally friendly alternatives to conventional catalytic systems.

1. Biosynthesized Copper Oxide Nanocomposite for the Reduction of Nitroaromatics

Biocapped CuO nanocomposites were synthesized using *Euphorbia tirucalli* stem extract through an eco-friendly and sustainable route that exploits the plant's rich phytochemical content, including polyphenols, flavonoids, and related bioactive compounds. These constituents function simultaneously as reducing, stabilizing, and capping agents, eliminating the need for toxic reagents and harsh synthesis conditions. This bio-mediated approach not only offers a cost-effective and environmentally benign alternative to conventional methods but also introduces naturally derived surface functionalities onto the nanocomposite. The resulting biofunctionalized CuO nanocomposite was employed as a heterogeneous catalyst for the reduction of nitroaromatic compounds to their corresponding amines, a transformation of considerable importance in the synthesis of pharmaceuticals, dyes, and fine chemicals. The presence of surface-bound bioactive ligands enhances substrate adsorption and promotes efficient electron transfer during the reduction process, enabling high catalytic activity under mild conditions. Furthermore, the heterogeneous nature of the catalyst allows facile separation and reuse, contributing to waste minimization and improved sustainability. Overall, the integration of plant-derived biomolecules with CuO nanostructures presents a versatile, low-cost, and green catalytic platform for the reduction of industrially relevant nitroaromatic compounds.

2. Chitosan–Copper Nanocomposite as an Efficient Peroxidase-Mimic Catalyst for Glucose Sensing

A copper-based nanocomposite (Cu@CIF) was synthesized using scrap copper wire via a simple, economical, and sustainable approach, demonstrating an effective upcycling strategy that transforms waste material into a value-added functional nanomaterial. The synthesis avoids complex processing steps and costly precursors, making it attractive for large-scale and environmentally responsible production.

The synthesized Cu@CIF nanocomposite was explored as a nanozyme exhibiting peroxidase-like activity for the colorimetric detection of hydrogen peroxide and glucose. Compared to natural enzymes, such nanozyme systems offer superior stability, resistance to harsh environmental conditions, ease of storage, and reduced production costs. The copper nanocomposite provides a robust and biocompatible platform suitable for sensing applications in biological media, enabling reliable glucose monitoring and peroxide detection relevant to clinical diagnostics. Additionally, the heterogeneous nature of the material allows repeated use without significant loss of activity, supporting sustainable and practical implementation. This work highlights the potential of upcycled copper-based nanocomposites as low-cost, stable, and efficient alternatives to natural enzymes for next-generation diagnostic and point-of-care glucose sensing applications.

3. Copper Oxide Nanoparticles Confined within Amine-Functionalized, Pore-Engineered Covalent Organic Frameworks for Transesterification

CuO nanoparticles confined within a pore-engineered, amine-functionalized urethane-linked covalent organic framework (COF) were synthesized using a rational design strategy to integrate catalytically active metal oxide sites with a chemically stable and highly porous organic scaffold. This approach enables uniform dispersion and confinement of CuO nanoparticles within the COF pores, effectively preventing aggregation while maximizing exposure of active sites.

The incorporation of amine functionalities and urethane linkages imparts intrinsic basicity, enhanced structural integrity, and strong metal–support interactions, while the embedded CuO nanoparticles further increase surface basicity and introduce additional catalytic interfaces. The resulting hybrid material functions as an efficient heterogeneous solid-base catalyst for transesterification reactions, which are central to the production of value-added esters and biodiesel. High surface area, improved accessibility of active sites, and excellent structural stability contribute to superior catalytic performance. The catalyst can be readily recovered and reused, minimizing metal leaching and secondary contamination. Beyond model reactions, the system demonstrates applicability in biodiesel synthesis from renewable feedstocks such as castor oil, underscoring its relevance to sustainable energy technologies. Overall, the CuO-confined, pore-engineered COF represents a promising, reusable, and environmentally benign catalytic platform for green transesterification and esterification processes.

4. Nickel Nanoparticle-Doped COF-Derived Porous Carbon for the Hydrogenation of Levulinic Acid

A highly active carbon-based catalyst was developed via a framework-derived strategy employing a urethane-linked covalent organic framework synthesized from bio-derived ellagic acid and phenylene isocyanate. This approach offers a sustainable, cost-effective, and scalable route to advanced catalytic materials. Post-synthetic incorporation of nickel nanoparticles followed by controlled carbonization resulted in uniformly dispersed metallic active sites embedded within a conductive porous carbon matrix, which promotes efficient electron transfer during catalytic reactions.

The resulting Ni-doped carbon catalyst was applied to the hydrogenation of levulinic acid, a key biomass-derived platform molecule, using formic acid as a green, in situ hydrogen source under solvent-free conditions. This strategy eliminates the requirement for external high-pressure hydrogen, thereby enhancing operational safety and sustainability. Strong metal–support interactions suppress nanoparticle aggregation and leaching, imparting excellent catalyst stability and recyclability. The use of earth-abundant nickel in place of noble metals further reduces cost, while the combination of renewable COF precursors, green hydrogen donors, and scalable synthesis underscores the potential of this system for biomass valorization. This work demonstrates the promise of COF-derived carbon–metal composites as efficient and sustainable catalysts for industrially relevant hydrogenation processes.

Chapter 2

Biosynthesized copper oxide nanocomposite for reduction of Nitroaromatics

In this work, a CuO nanocomposite was synthesized using *Euphorbia tirucalli* stem extract as a supporting matrix to stabilize the nanoparticles. The as-prepared nanocomposite was thoroughly characterized using a range of advanced analytical techniques. Its catalytic performance was investigated using the reduction of 4-nitrophenol as a model reaction. Key reaction parameters were systematically optimized, and the progress of the reaction was monitored by UV–Visible spectroscopy. Kinetic analysis was carried out to evaluate the reaction rate and determine the reaction order. Catalyst reusability was examined through recycling studies over eight consecutive cycles. In addition, substrate scope was explored by extending the optimized reaction conditions to the reduction of other nitroaromatic compounds, including 2-nitrophenol, 2,4-dinitrophenol, and various nitroanilines.

Synthesis: Extraction of bioactive components from the stem of *Euphorbia tirucalli* stem done by standard decoction method. The extract was diluted 10 times and added to an aqueous solution of $CuSO_4$. The bioactive components, majorly polyphenols act as reducing and capping agent for the formation of bio-capped copper oxide nanocomposite (ET@CuO NC).

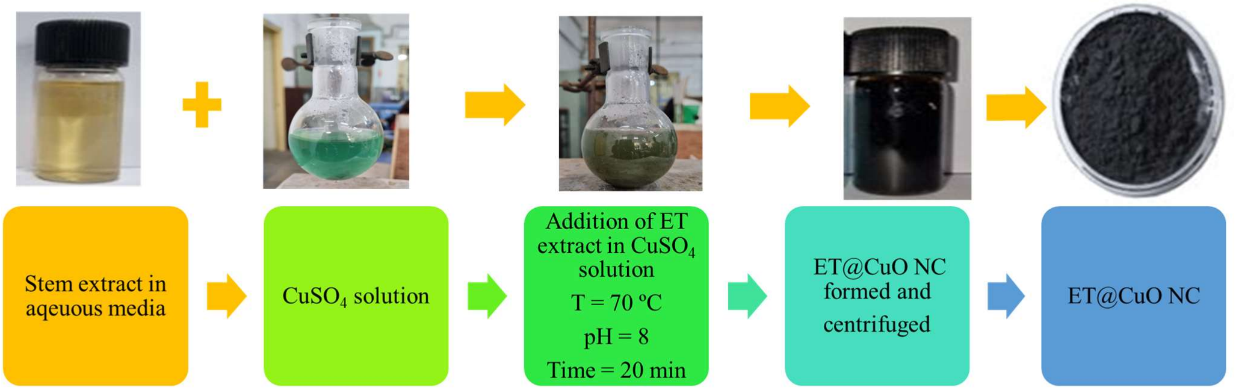


Figure 2: Synthetic route of bio-capped copper oxide nanocomposite

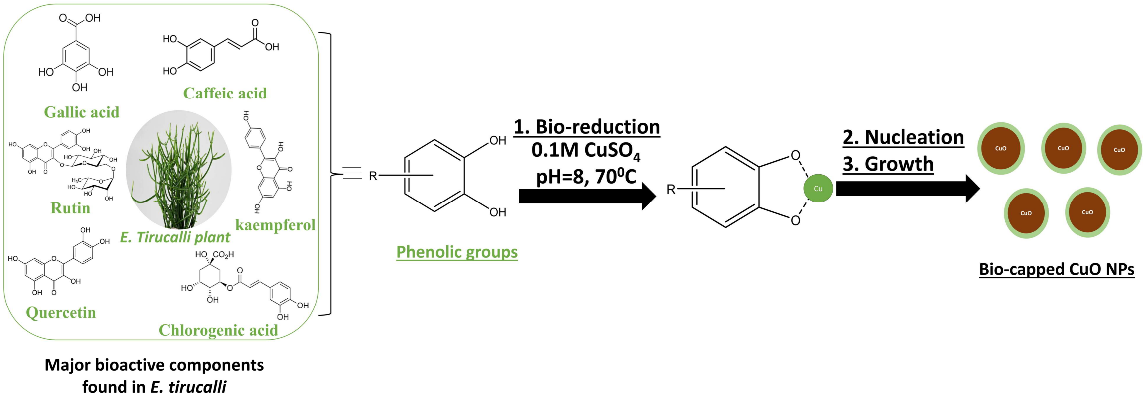


Figure 3: Plausible mechanism for the formation of ET@CuO NC

Characterization: The characterization of ET@CuO NC were carried out using various sophisticated instruments. These techniques proved the successful capping of bioactive components on the surface of nanoparticles to form nanocomposite. The absorption bands of E. tirucalli at 3421, 1549, 1406, 1045 cm^{-1} are due to the O–H (strong and broad band due to the presence of phenolic groups), C = C (stretching), C–H (deformation), C-O (stretching) respectively. The peaks at 1549, 1406, and 1045 cm^{-1} disappeared after the utilization of bioactive components from the plant extract. The absorption bands at 622 cm^{-1} can be assigned to the presence of Cu-O bond. The XRD and RAMAN indicates the presence of Cu in +2 oxidation state with crystalline nature. The TEM and FESEM indicates the rod-shaped morphology with average size of 47 nm. The EDAX indicates elemental composition of the nanocomposite.

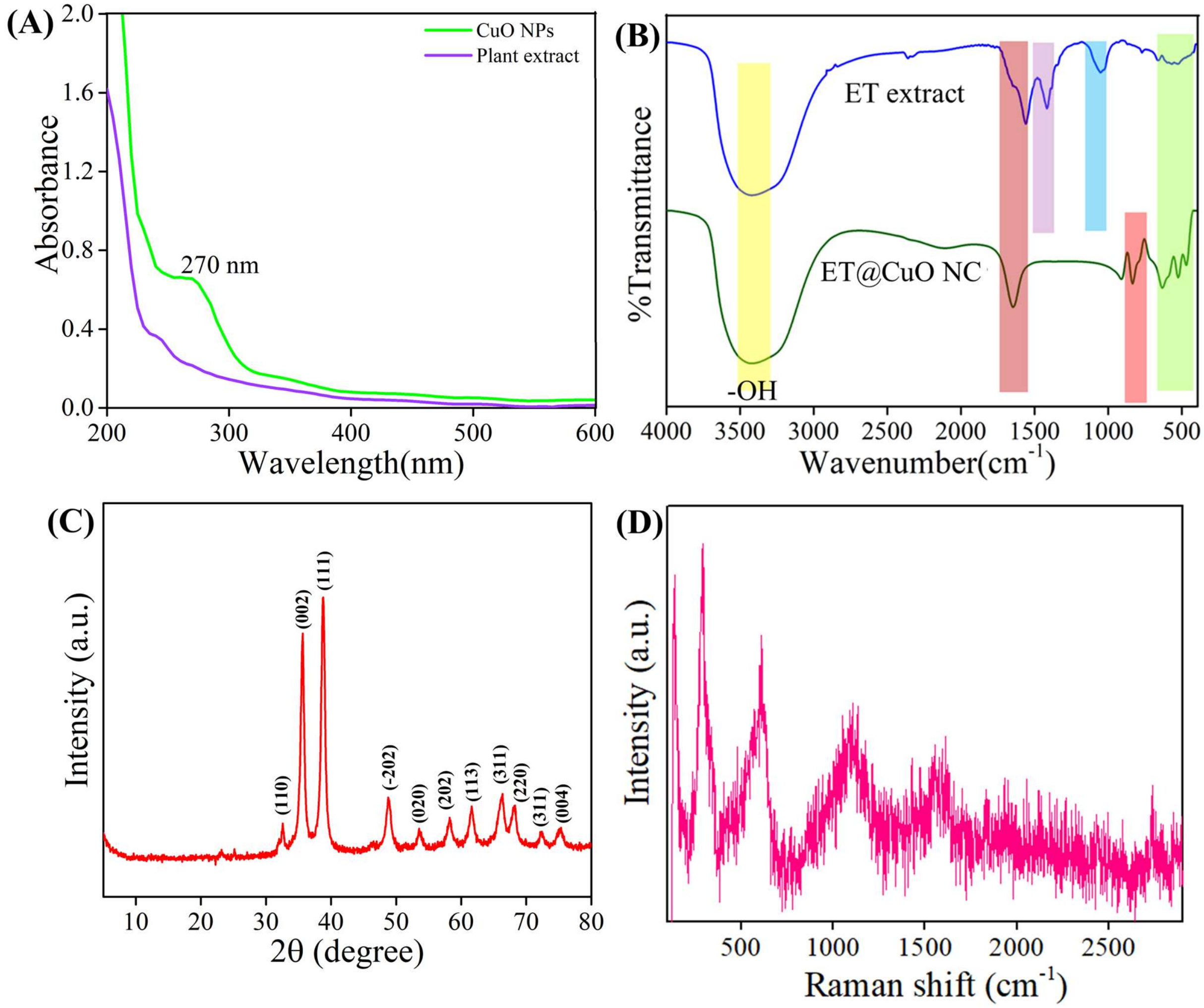
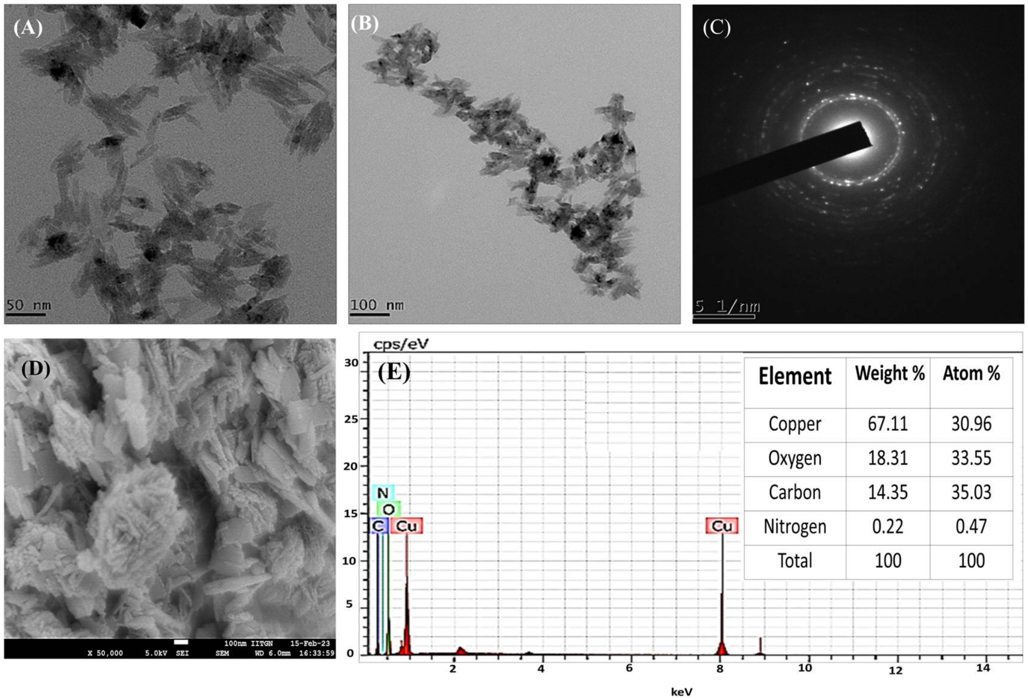


Figure 4: **(A)** UV–Visible spectra of ET extract and ET@CuO NC (b) FTIR spectra of E. tirucalli extract and ET@CuO NC **(C)** XRD spectrum **(D)** Raman spectrum of ET@CuO-NC



Element	Weight %	Atom %
Copper	67.11	30.96
Oxygen	18.31	33.55
Carbon	14.35	35.03
Nitrogen	0.22	0.47
Total	100	100

Figure 5: **(A)** and **(B)**TEM image of ET@CuO NC at different resolutions **(C)** SAED pattern, **(D)** FESEM image **(E)** EDAX pattern

Catalytic Reduction of Nitroaromatic Compounds : The catalytic activity of nanocomposite was determined by reduction of 4- nitrophenol as a model reaction and the reaction was monitored using UV-Visible spectroscopy. The absorbance peak of 4-nitrophenol was observed at 400 nm, which tends to decrease after the addition of catalyst and sodium borohydride. A new absorbance peak is observed at 300 nm indicating the formation of 4- aminophenol. The complete reduction is indicated by the disappearance of the absorbance at 400 nm indicating the conversion of 4- nitrophenol to 4-amino phenol. The reaction parameters like catalyst amount and sodium borohydride concentration were varied. Under the optimised reaction conditions, followed the complete reduction in 6 minutes with conversion efficiency of 96%. The reaction follows pseudo first order kinetic with rate constant 7.02×10^{-2} min^{-1}. The catalyst could be recycled for about 8 cycles without significant change in their efficiency. Scope of the catalyst was extended for the reduction of other nitroaromatic compounds.

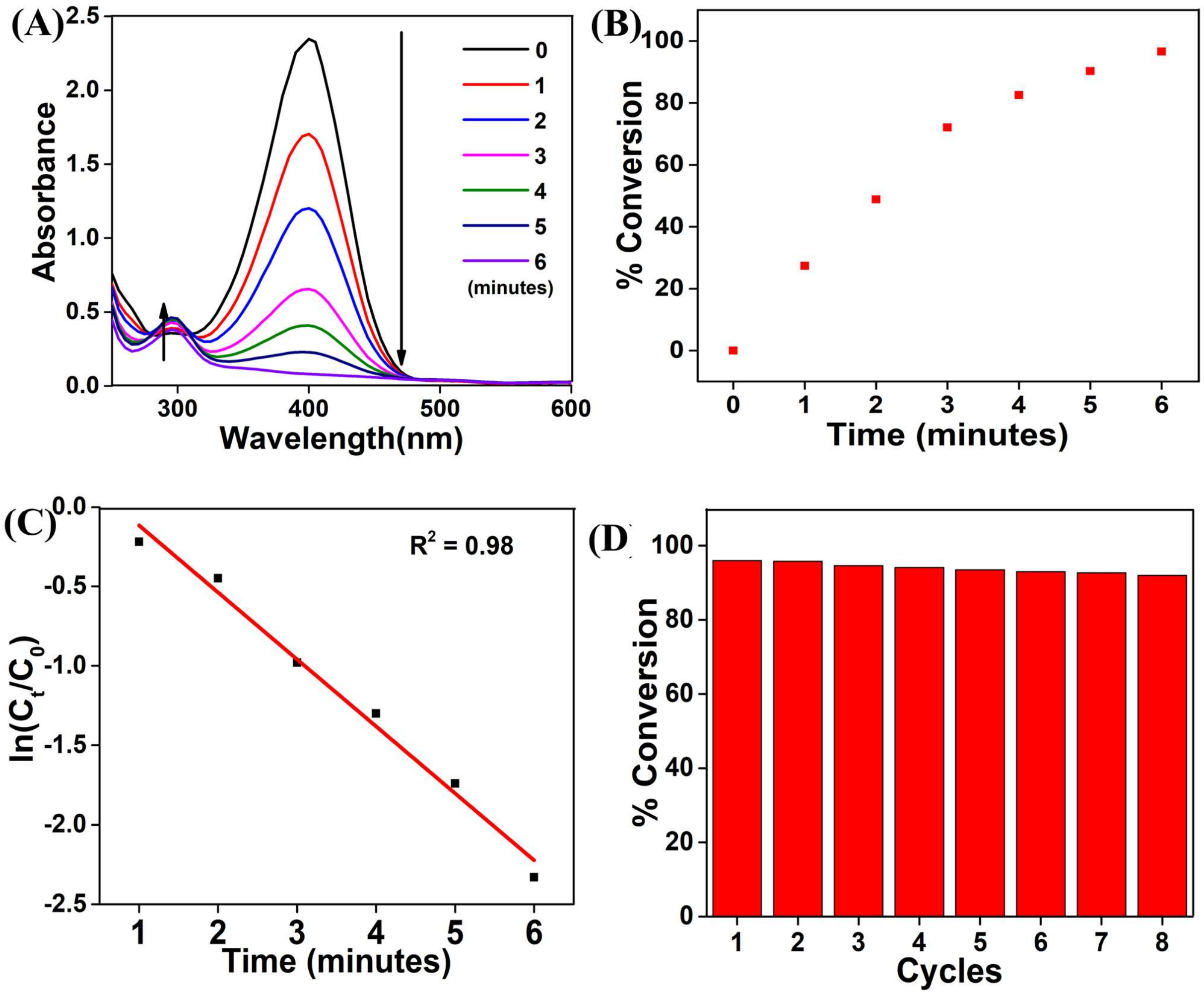


Figure 6: **(A)**The time dependent UV–Visible absorption spectra of 4-NP reduction **(B)** The plot of conversion of 4-NP with time **(C)** The dependence of ln(C/Co) versus time plot for the pseudo-first-order reaction kinetics in the presence of catalyst and $NaBH_4$ **(D)** Recycling performance of catalyst in catalytic reduction of 4-NP

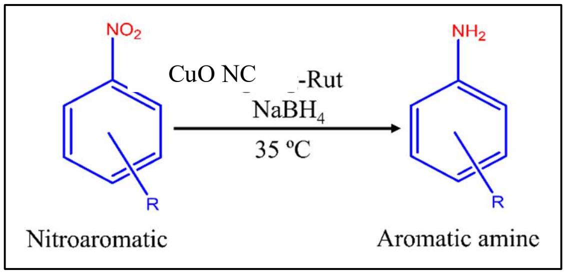


Figure 7: Schematic Illustration for reduction of Nitroaromatics

Chapter 3

Chitosan-Copper Nanocomposite as Potent Peroxidase Mimic catalyst for glucose sensing

We synthesized a copper nanocomposite by crosslinking chitosan with formylated isosorbide followed by doping with copper nanoparticles. The presence of abundant functional groups in formylated isosorbide enhances crosslinking and prevents nanoparticle aggregation, ensuring better stability and dispersion within the chitosan matrix. This design provides a robust platform for catalytic applications. Instead of relying on unstable and costly natural enzymes for radical generation from hydrogen peroxide, the synthesized copper nanocomposite offers an efficient alternative. It is cost-effective, biocompatible, exhibits strong peroxidase-mimicking activity, remains stable over extended periods, and can be easily recycled, making it a practical and sustainable catalyst system.

Synthesis: The upcycled copper salt was obtained from scrap copper wires for the formation of copper nanocomposite.

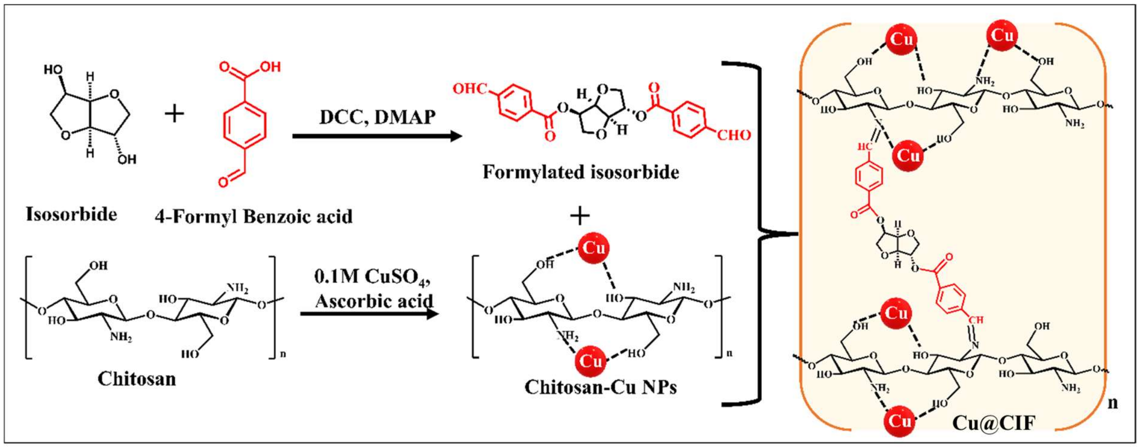


Figure 8: Synthesis of Chitosan-Cu nanocomposite (Cu@CIF)

Characterization: The stability, strength and efficiency of copper nanocomposite was checked using various sophisticated analytical techniques. Spectroscopic analyses (UV-Vis, FTIR, XPS, NMR) confirmed zero-valent copper nanoparticle formation with proper chemical bonding. Morphological studies (SEM, HRTEM) revealed spherical nanoparticles (60 nm average size) with a porous network structure, while XRD validated the crystalline copper structure. Physical characterization showed uniform size distribution (DLS: 107 nm, PDI 0.12) and good colloidal stability (zeta potential +11.5 mV). The nanozyme demonstrated excellent thermal stability (up to 330°C by TGA) and minimal leaching (<1 ppm Cu by ICP), ensuring reusability. ESR spectroscopy confirmed peroxidase-mimicking activity through hydroxyl radical generation. These results collectively validated the nanozyme structural integrity and functional suitability for glucose sensing applications.

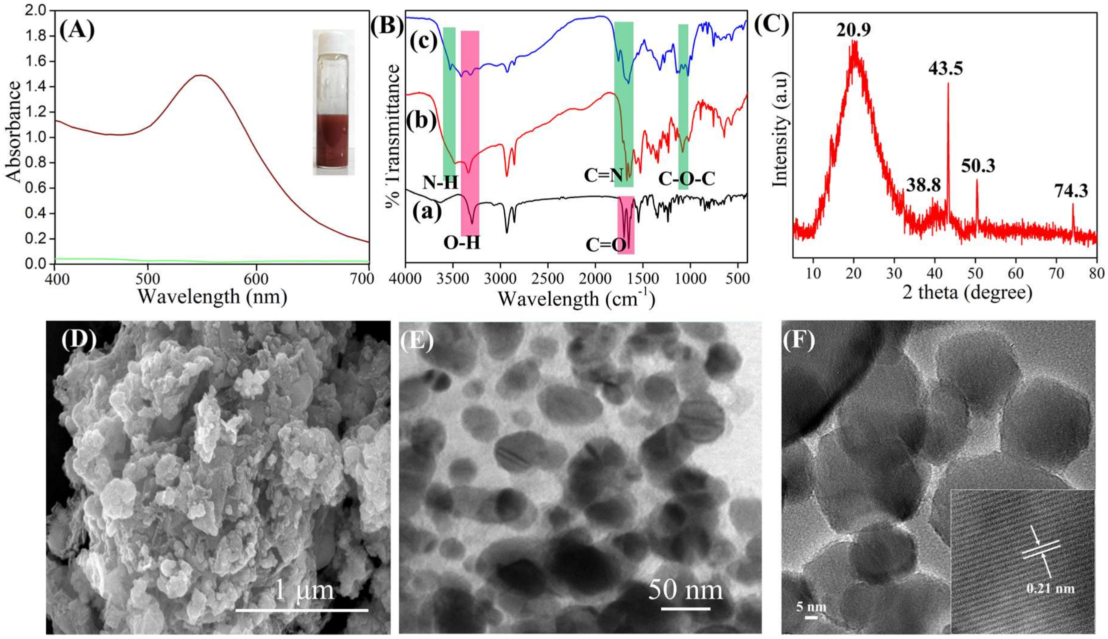


Figure 9: (A) UV–Visible spectrum of Cu nanoparticles formation **(B)** FT-IR spectra of **(a)** FI **(b)** CIF **(c)** Cu@CIF **(C)** XRD pattern **(D)** SEM image **(E)** TEM image **(F)** HRTEM image of Cu@CIF

<u>Catalytic Activity/ Peroxide Mimic for detection of glucose</u>:

Cu@CIF demonstrates excellent peroxidase-mimicking activity, efficiently catalyzing the breakdown of hydrogen peroxide into hydroxyl radicals that oxidize TMB to a distinct blue product. This strong catalytic behaviour, reflected in its low K_m value and high affinity toward H_2O_2, enables sensitive and rapid detection of peroxide. When integrated with glucose oxidase, Cu@CIF becomes an effective colorimetric glucose sensor, where the H_2O_2 produced from glucose oxidation is quantitatively converted into a measurable signal. The system shows a low detection limit (0.87 µM), a linear response in the 1–100 µM range, and high selectivity against other sugars, making it reliable for practical applications. Moreover, its stability, recyclability, and successful performance in artificial sweat and diluted human serum highlight its potential as a cost-effective, robust nanozyme for glucose monitoring in real-world diagnostic settings.

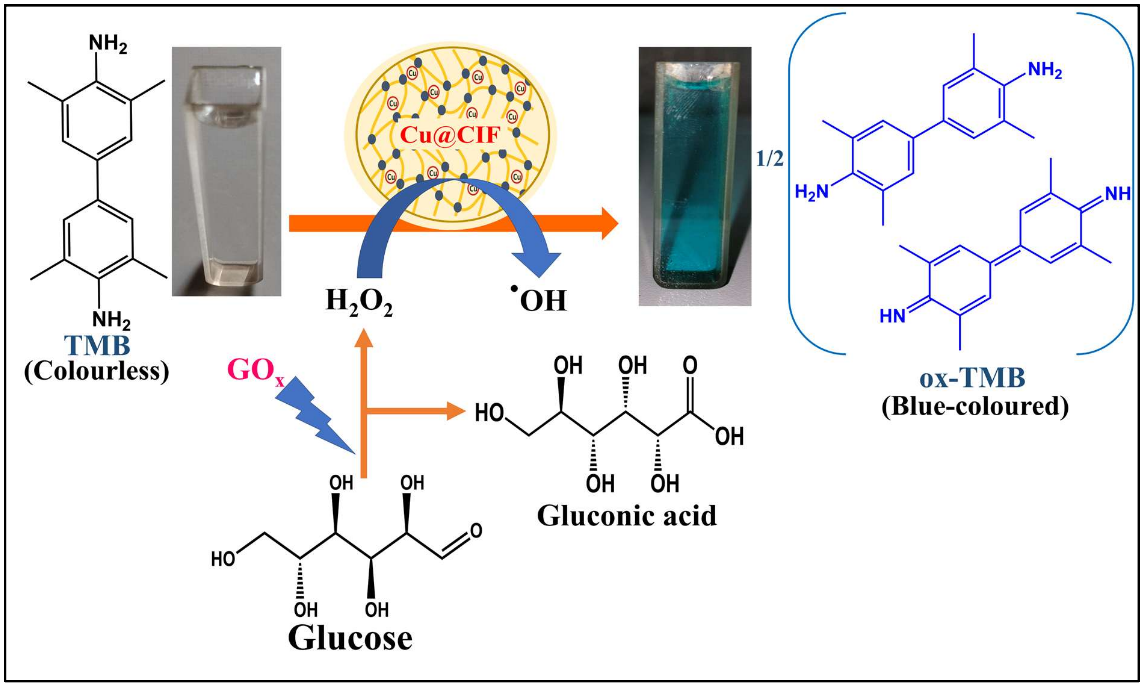


Figure 10: Mechanism of peroxidase activity by Cu@CIF for Glucose detection

<u>Conclusion</u>: Copper nanocomposite (Cu@CIF) was synthesized via simple and cost-effective method using scrap copper wire for its application as nanozyme for peroxide (H_2O_2) and glucose sensing. This nanozyme was characterized using sophisticated techniques which indicated its long- term stability and high dispersibility. Cu@CIF proved to be sensitive peroxidase-mimic for detection of H_2O_2 and glucose in the wide range of 0.25 to 400 µM and 0.5 to 100 µM. The values of $K_m = 0.322$ mM and $V_{max} = 29.73 \times 10^{-9}$ Ms^{-1} which indicated its strong affinity towards H_2O_2. Recyclability of nanozyme up to 5 cycles for colorimetric detection of glucose. The composite was utilized for detecting glucose levels in both diabetic and non-diabetic blood serum samples proving its efficacy as a reliable sensor. The copper nanocomposite demonstrates significant potential as an advanced glucose sensing material, validating the proposed hypothesis. The results also suggest its capability to sense H_2O_2 and glucose levels is less than 1 µM surpassing the traditional glucose sensors detection limits. Furthermore, the biocompatibility and stability of the composite ensure its applicability in real-world biological environments. The feasibility of upcycled nanocopper which mimic natural peroxidase enzyme can be utilized to develop diagnostic kits for detection of glucose in real samples.

Chapter 4

Copper Oxide Nanoparticles confined amine functionalized pore engineered covalent organic framework for Transesterification

We have synthesized copper oxide nanoparticle confined covalent organic framework (COF) for transesterification of triacetin. From literature studies, it was concluded that there are no reports on metal confined COF for this reaction. A urethane linked COF was synthesized and then functionalized with amine groups to bind with metal nanoparticle. This metal confined pore engineered COF was used as solid base catalyst for transesterification reaction.

Synthesis: The UCOF was synthesized using a previously reported solvothermal method. Post synthetic modification was performed using ethylene diamine to obtain UCOF-NH2 with free -NH_2 group to introduce basicity through pore engineering, for transesterification reaction. Further, CuO NPs were incorporated to obtain CuO@UCOF-NH2. The pendent -NH_2 groups will stabilize and prevent agglomeration of NPs. Here, the lattice oxygen atoms (O^{2-}) present in CuO NPs offer Lewis basicity by donating an electron pair or deprotonation of alcohol along with the COF.

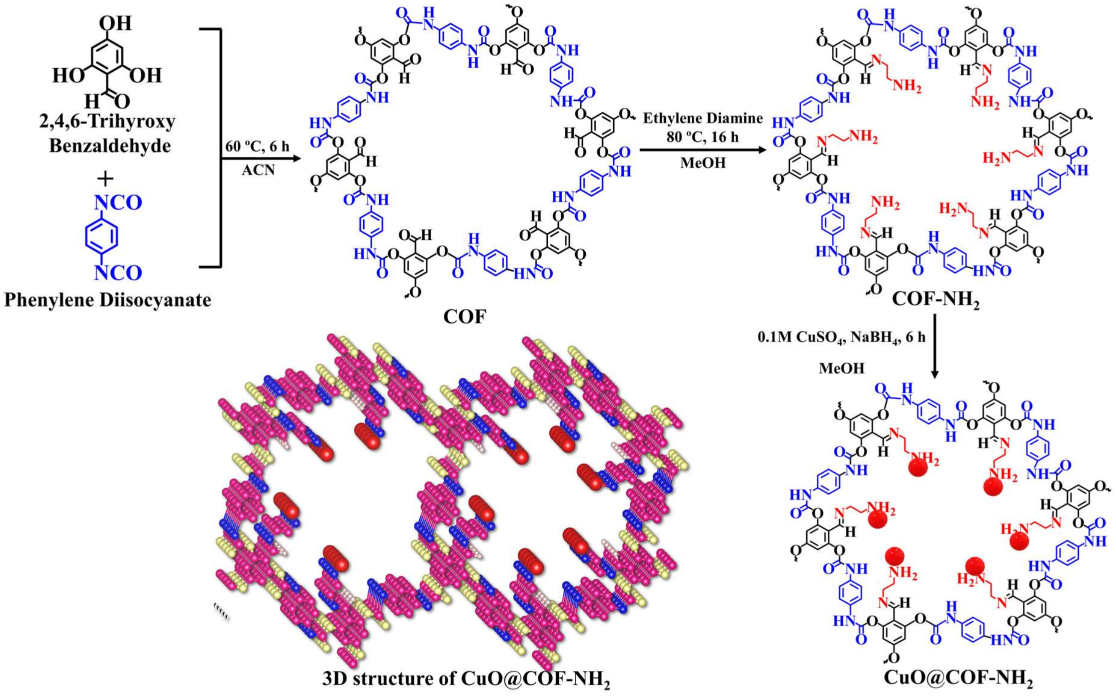


Figure 11: Synthesis of CuO@UCOF-NH_2

Characterization: The CuO NPs confinement and pore engineering in COF was confirmed by various sophisticated techniques. The FTIR analysis confirms the presence of free amine group and CuO NPs confinement in CuO@COF-NH_2. The morphology was studied by HRTEM and FESEM analysis. The crystalline nature and +2 oxidation of Cu was confirmed by XRD analysis and surface area and pore volume known by BET analysis. The XPS analysis gives the oxidation state and the interaction of metal and binding with other functional groups.

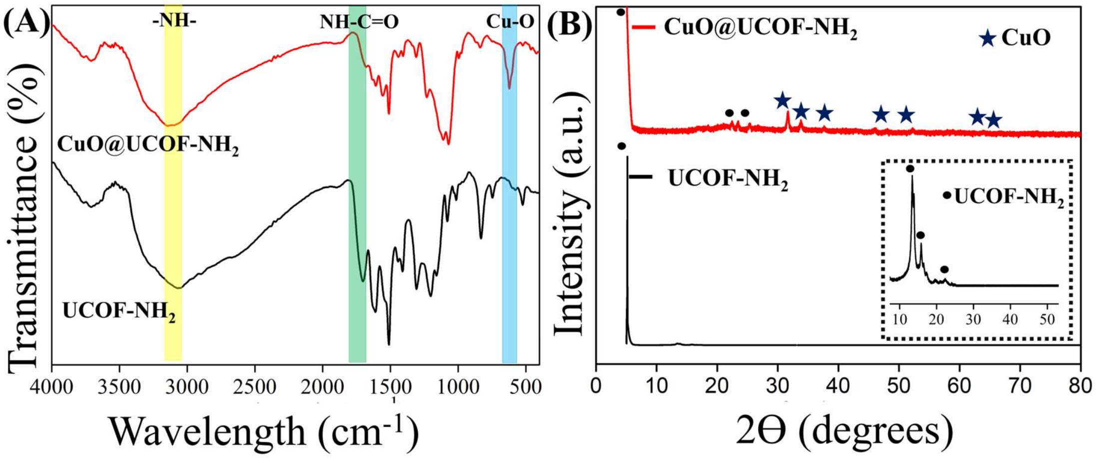


Figure 13: (A) FTIR **(B)** XRD of COF-NH_2 and CuO@COF-NH_2

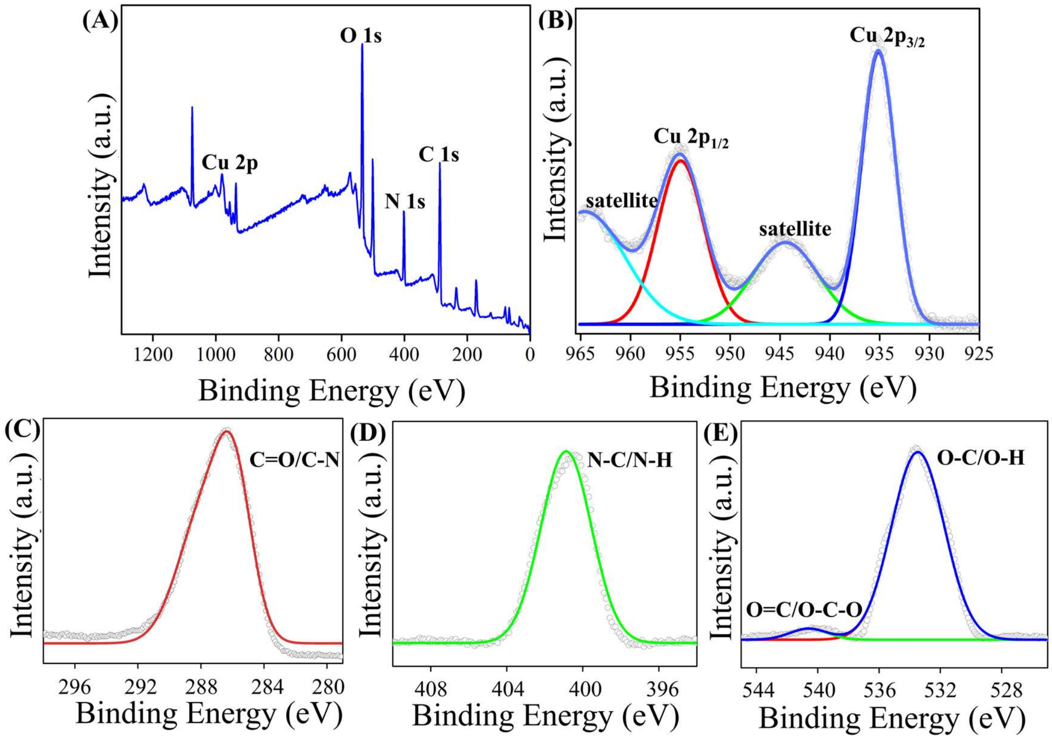
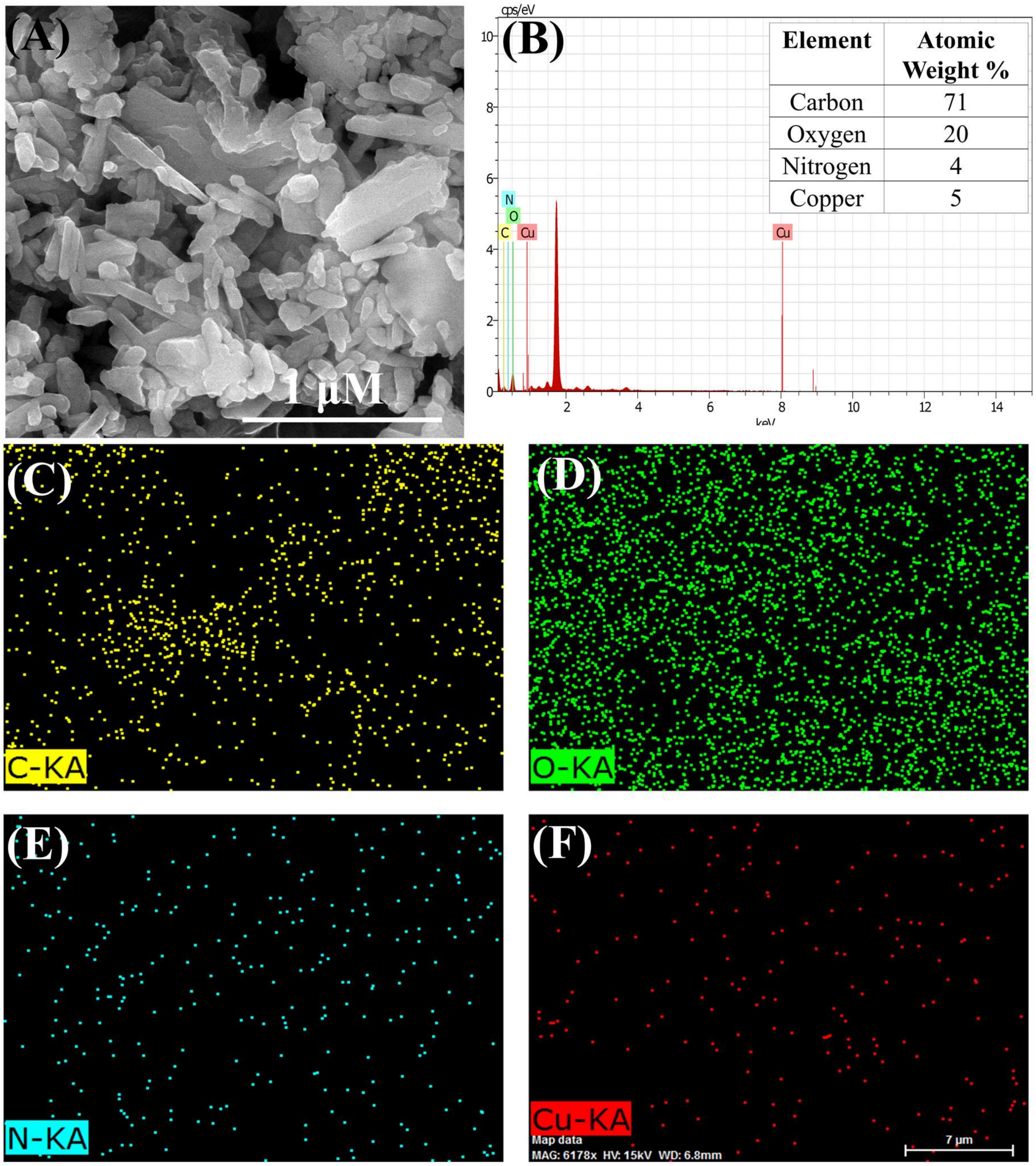


Figure 14: XPS of CuO@COF-NH2showing deconvolution of each element



Element	Atomic Weight %
Carbon	71
Oxygen	20
Nitrogen	4
Copper	5

Figure 15: (A) FESEM **(B)** EDAX **(C-F)** Elemental mapping of CuO@COF-NH$_2$

<u>**Transesterification Reaction**</u>**:** The CuO@COF-NH$_2$ was used as a catalyst for transesterification of triacetin to methyl acetate. The reaction was monitored by thin layer chromatography (TLC) and the % conversion was confirmed by ^{1}H NMR. Various process parameters such as triacetin: methanol ratio, temperature, amount of catalyst and time were optimised to get the complete conversion of triacetin to

methyl acetate. Reaction kinetics were studied and rate constant as well as activation energy were determined. The reaction was optimised for castor oil esterification to get biodiesel.

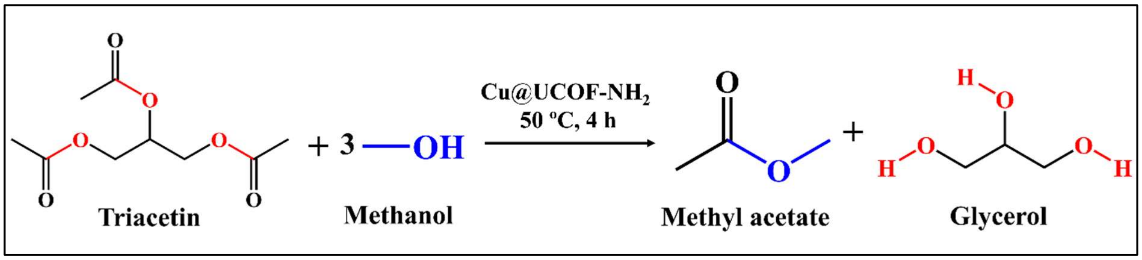


Figure 16 Transesterification reaction of Triacetin with methanol

<u>Conclusion</u>: The CuO-NP-confined, amine-functionalized urethane-linked COF proved to be an efficient solid base catalyst for the transesterification of triacetin and castor oil, owing to the enhanced basicity and increased accessible surface area introduced by CuO nanoparticles. Under optimized conditions (50 °C, 1:29 triacetin: methanol), the catalyst delivered >99% methyl acetate within 4 h and maintained its activity over seven cycles with negligible Cu leaching (<1 ppm), confirming its stability. Its applicability was further demonstrated in biodiesel synthesis from castor oil, yielding fatty acid methyl esters as verified by ^{1}H NMR and GC–MS analyses. Overall, this study highlights the pore-engineered CuO@COF as a robust and recyclable solid base catalyst with significant potential for sustainable biodiesel production.

Chapter 5

Designing nickel nanoparticle doped porous carbon using covalent organic framework for hydrogenation of levulinic acid, a bioplatform molecule

In this work we have synthesized U-COF using ellagic acid and phenylene diisocyanide under environmentally benign conditions without any toxic solvents at room temperature. To increase the catalytic properties, calcination and metal doping was carried out. The catalyst was utilized for hydrogenation of levulinic acid to gamma valerolactone. Formic acid was used as a green hydrogen source. Ellagic acid is a naturally abundant polyphenol, imparts thermal stability to the COF allowing reactions at elevated temperatures.

Synthesis: The UCOF was synthesized using ellagic acid and 1,4-phenylene diisocyanate as precursor and loaded with Ni nanoparticles. Further, pyrolysis of Ni-doped U-COF was carried out under inert atmosphere to obtain porous carbon with active catalytic sites preserving the elemental composition. The nitrogen and oxygen species provide sites for stabilizing nickel nanoparticles in a well dispersed form.

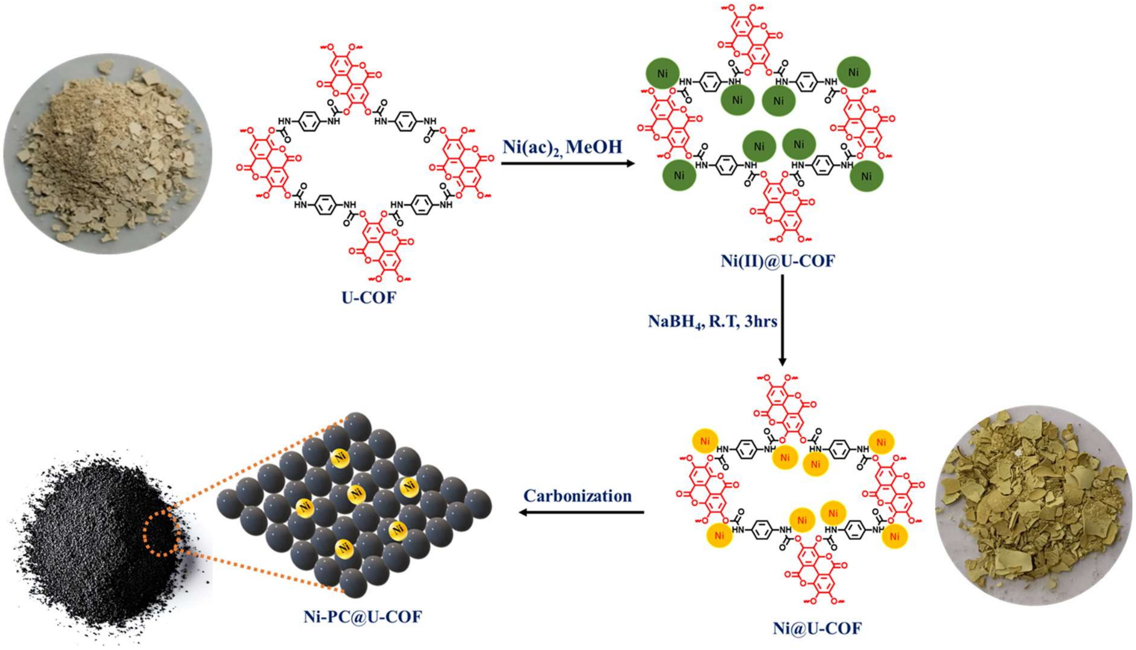


Figure 17: Synthetic route for the formation of Ni-doped U-COF and its carbonization

Characterization: The catalyst was well characterized for determining the active sites and morphology. The TEM image shows the presence of 7nm nickel nanoparticle dispersed within the matrix i.e., porous carbon obtained from carbonization. The XRD and XPS analysis confirmed the presence of Ni is zero oxidation state as well as crystalline nature and the bonding of Ni with other elements. The EDAX analysis presents the elemental composition, also thermal stability obtained from TGA analysis.

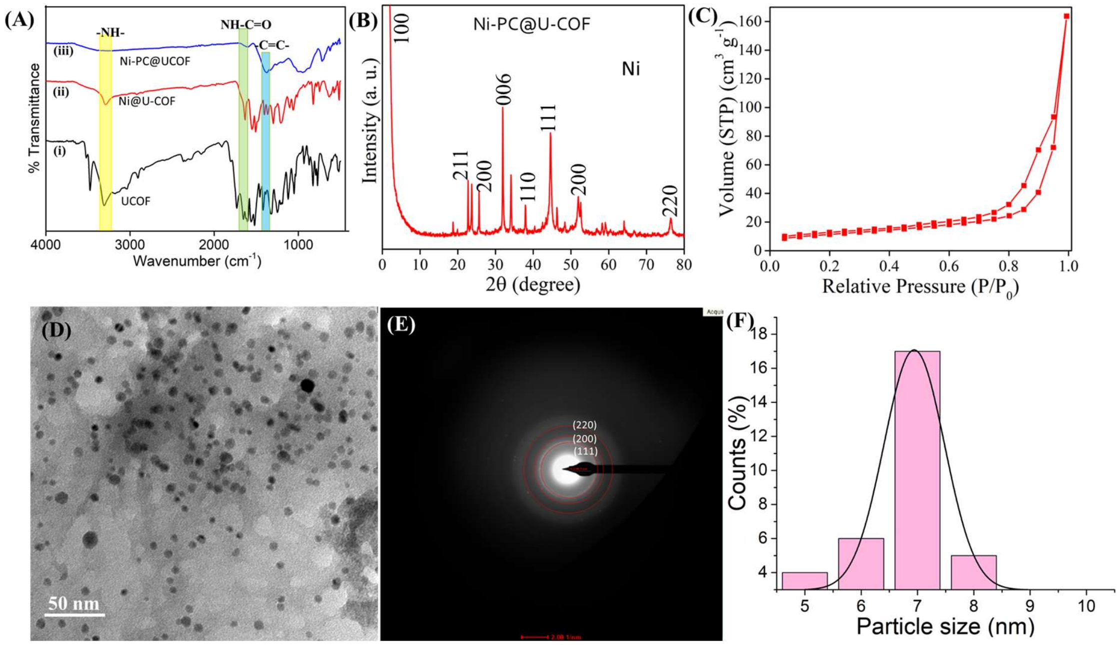


Figure 18: (A) FTIR **(B)** XRD **(C)** N_2 adsorption-desorption isotherm **(D)** TEM **(E)**SAED pattern **(F)**Particle size distribution

Catalysis: Hydrogenation of Levulinic Acid: The synthesized catalyst Ni-PC@U-COF has been investigated for the hydrogenation of levulinic acid where formic acid is utilized as a sustainable hydrogen source. Various reaction parameters like catalyst amount, reaction time, temperature, and mole ratio of levulinic: formic acid were optimized to obtain the highest possible conversion with better selectivity towards ϒ-valerolactone.

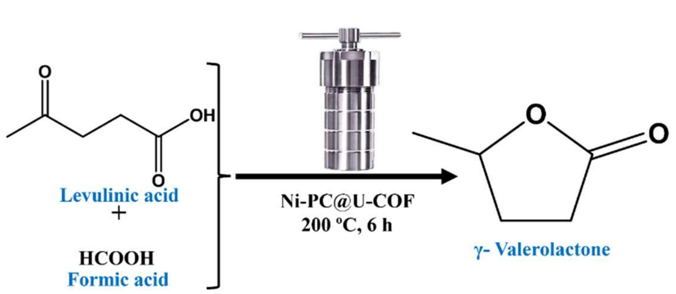


Figure 18: Scheme for the hydrogenation reaction under optimised conditions in a hydrothermal reactor

Conclusion: This work presents the first demonstration of a highly active carbonaceous catalyst derived from a urethane linked ellagic acid–phenylene diisocyanate COF for the hydrogenation of levulinic acid, offering a cost-effective and environmentally benign route for biomass valorization. The U-COF was post-synthetically modified by incorporating nickel nanoparticles followed by carbonization, generating abundant active sites suitable for catalytic hydrogenation. The resulting carbon matrix exhibited excellent dispersion of Ni nanoparticles, as confirmed by TEM and SEM analyses showing uniform 7 nm particles, which facilitates efficient electron transfer during the reaction. Using formic acid as a green hydrogen donor under solvent-free conditions, the catalyst achieved 82.4% conversion of levulinic acid with 91.1% selectivity toward γ-valerolactone within 6 hours. The catalytic performance, reflected in a TON of 26.97 and TOF of 4.49 h^{-1}, surpasses many reported nickel and noble metal based systems. By enabling efficient GVL production, a key platform molecule for biofuels and green chemicals, this study highlights the potential of Ni doped COF derived carbon as a sustainable hydrogenation catalyst. This inexpensive yet highly effective catalyst, operating with a benign hydrogen source without high-pressure requirements, holds promise for broader application in diverse hydrogenation processes at an industrial scale.

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LIST OF Publications

1. **S. Samal**, M. Patel, A. Rohilla, K. Chandodwala, S. Thakore, Sustainable synthesis of multifaceted copper oxide nanoparticles from *Euphorbia tirucalli*: Unveiling antimicrobial and catalytic potential, Material Science and Engineering B, **2024**, 310, 117718
2. **S. Samal**, T. Kikani, S. Thakore, Turning trash to tech: Upcycled copper nanozyme as potent peroxidase mimic for glucose sensing in clinical samples, Chemical Engineering Journal, **2025**, 520, 166313
3. **S. Samal**, Muskan Memon, Soyeb Pathan, Sonal Thakore, Designing nickel nanoparticle-doped porous carbon using bio-based covalent organic framework for hydrogenation of levulinic acid: A sustainable approach towards upgradation of a bioplatform molecule, Journal of Environment and Chemical Engineering, **2025**, 13, 5, 117883
4. S. S. M. Ali, A. M. A. Dawale, **S. Samal**, P. Robin, S. Thakore, *Barleria Grandiflora* Leaf Extract-Driven Silver Nanoparticles: Assessment of Their Antibacterial, Cytotoxicity, and Catalysis, Chemistry Select, **2025**, 10, 31, e00765

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