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Microbe-engineered nanocatalysts for thermal, photo, and electrocatalytic green transformations: a critical review of structure–activity relationships and performance metrics

Oluwafemi Adebayo Oyewole, *[a] Wasilah Rabi Suleiman, [a]
Majin Emmanuel Nmadu,[a] Innocent Ojeba Musa,[b] Naga Raju Maddela [c]
and Kasim Sakran Abass[d]

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Microbe-engineered nanocatalysts offer a sustainable and adaptable platform for green chemical transformations in thermal, photocatalytic, and electrocatalytic systems. Biological synthesis techniques using bacteria, fungi, yeast, and algae enable the controlled formation of nanoparticles *via* enzymatic reduction, respiratory metal transformation, and photosynthetic redox pathways. However, previous reviews have mostly emphasised biological synthesis pathways, with limited quantitative integration of structure–activity connections and cross-platform catalytic performance measurements. These biogenic nanocatalysts typically have particle sizes ranging from 2 to 100 nm, high defect densities, variable surface functionalisation, and organic capping layers to improve colloidal stability and catalytic selectivity. Quantitative study demonstrates activation energy reductions of 20–60%, turnover frequencies of 0.1–10 s^{-1}, and overpotentials as low as 200–500 mV in electrocatalytic systems. Environmental applications exhibit removal efficiency of over 90% for dyes, heavy metals, and pharmaceutical micropollutants. Energy applications show hydrogen evolution rates of up to 10 mmol g^{-1} h^{-1} and CO_2 conversion selectivity of up to 90%. Despite these performance benchmarks, the field faces significant hurdles in batch-to-batch reproducibility and standardized reporting of metal-normalized activity. Structure–activity relationships suggest that nanoscale defect engineering, active site density, and surface biomolecule interactions all have a significant impact on catalytic performance. This review combines quantitative measures from synthesis, structural characterisation, catalytic mechanisms, and environmental deployment to provide a cohesive framework for rationally designing next-generation bioinspired nanocatalysts for sustainable chemical processes.

1 Introduction

The global trend toward sustainable industrialisation has pushed catalysis to the forefront of the green chemistry revolution. Catalysis accounts for more than 90% of chemical manufacturing processes; yet traditional catalyst production, which commonly employs high-pressure, high-temperature, and toxic chemical reduction procedures, often contradicts the very principles of sustainability this field seeks to promote. This contradiction has fuelled increasing interest in bottom-up microbe-engineered nanocatalysts, which use the metabolic pathways of bacteria, fungi, and algae to create sophisticated metal–organic interfaces under ambient circumstances.[1] Biogenic nanoparticles, unlike their chemically synthesised counterparts, are naturally stabilised by a complex protein corona or bio-capping layer produced from microbial secretomes. This layer does more than just prevent agglomeration; it also creates a distinct chemical microenvironment that alters reactants' mass-transfer coefficient and adsorption energy.[2] The Sabatier principle describes the requirement for optimal adsorption energy between the catalyst surface and reaction intermediates, where binding must be neither too weak (limiting activation) nor too strong (hindering product desorption), thereby enabling efficient catalytic turnover. The morphological and structural diversity of biogenic nanocatalysts is shown in Table 1. While the size- and shape-dependent catalytic trends summarised in Table 1 reflect intrinsic nanoparticle properties, nanoparticle yield in biogenic systems remains highly system-dependent and insufficiently

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[a] Department of Microbiology, Federal University of Technology, P.M.B 65, Minna, Nigeria. E-mail: oa.oyewole@futminna.edu.ng; Tel: +234-8140031875

[b] Department of Microbiology, Skyline University Nigeria, Kano, Kano State, Nigeria

[c] Departamento de Ciencias Biológicas, Facultad de Ciencias de la Salud, Universidad Técnica de Manabí, Portoviejo-130105, Ecuador

[d] Department of Physiology, Biochemistry, and Pharmacology, College of Veterinary Medicine, University of Kirkuk, Kirkuk 36001, Iraq

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Table 1 Particle size distribution of biogenic nanocatalysts

Microbial source	Nanoparticle type	Size range (nm)	Mean size (nm)	Morphology	Reference
Bacteria	Ag	5–50	25	Spherical	3
Bacteria	Pd	5–30	18	Quasi-spherical	4
Shewanella oneidensis MR-1	Fe/Pd	5–25	15	Irregular	4
Fungi	Au	20–100	60	Spherical	3
Fusarium oxysporum	Ag/Au	10–60	35	Variable	5
Yeast	Au	5–40	20	Encapsulated	6
Algae/cyanobacteria	Au/Ag	10–100	55	Variable	7

standardised to be included as a directly comparable parameter.

The morphological diversity of biogenic nanocatalysts, nanoparticle size and shape have a major influence on catalytic efficiency.[8] Smaller nanoparticles (typically in the range of ∼2–10 nm) exhibit enhanced catalytic activity due to a higher density of low-coordinated surface atoms and defect sites.[9] Larger particles (>50 nm) generally show reduced activity due to lower surface-to-volume ratios.[6] In addition to size effects, morphology is equally important; faceted nanostructures expose certain crystallographic planes that can improve reaction selectivity, whilst anisotropic structures may facilitate directional electron transport in photocatalytic and electrocatalytic systems.

To present a more comprehensive structure–activity perspective, Table 2 highlights reported connections between nanoparticle size, shape, and catalytic efficacy, emphasising consistent tendencies across biogenic systems. The trends described in Table 2 show that catalytic activity in biogenic nanocatalysts is not determined by a single parameter, but rather by the interaction of particle size, shape, and surface chemistry, highlighting the necessity of controlled nanoscale design.

Biogenic catalysts provide an adjustable surface chemistry that optimises this intermediate binding energy, especially in complex transformations such as the Oxygen Evolution Reaction (OER) and the breakdown of persistent organic pollutants.[10] Also, combining computational modelling and Density Functional Theory (DFT) has begun to demonstrate how microbial scaffolds can be built with predictable Turnover Frequencies (TOF) and lower activation energies.[17] While the qualitative benefits of green synthesis are well known, the field lacks a standardised quantitative framework for comparing biogenic performance to industrial benchmarks. In this review, the industrial viability and technoeconomic feasibility of microbe-engineered systems as the next generation of high-performance green catalysts by quantifying metrics like Tafel slopes and E-factors is evaluated.[18]

2 Biogenic synthesis of nanocatalysts

The biogenic manufacture of nanocatalysts is a sophisticated bottom-up fabrication strategy in which microorganisms act as specialised nanofactories.[2,19] These organically produced nanoparticles have enormous specific surface areas and hierarchical porosities, which significantly accelerate chemical processes as compared to bulk metal salts.[2] The primary mechanism involves heavy metal sequestration by microorganisms, which is then neutralised *via* metabolic detoxification pathways.[2] Microbes use several distinct proteins and membrane-bound enzymes to convert metal ions into zero-valent or metal-sulfide nanoparticles.[15,20] This enzymatic participation ensures that the resulting particles are smaller, less variable in shape, and have a more uniform size distribution than those produced by conventional chemical precipitation.[20]

In recent years, high-performance nanocatalysts have been successfully created from a diverse spectrum of microscopic species, including bacteria, fungi, yeast, and algae, each having its own metabolic templates for particle nucleation.[11,14] The efficacy of this biological reduction is highly dependent on the presence of specific biomolecules within the microbial secretome, such as organic acids, cofactor reductants (NADH/NADPH), and metal-resistant genes.[15] These biological components facilitate the controlled anchoring of metal atoms onto biomolecular scaffolds, which is essential for the formation of high-loading single-atom catalysts and cluster-based systems.[2]

Beyond simple reduction, proteins and short peptides function as both nucleation templates and natural capping agents.[15,20] These microorganisms aid nanocatalysts in maintaining long-term colloidal stability by providing electro-steric repulsion, which effectively prevents particles from clumping or sintering during high-temperature reactions.[16] The metal core interacts with biological ligands such as carboxyl, amine, and thiol groups to produce a protective bio-corona that controls the catalyst's oxidation state and protects it from environmental leaching.[15,16] The ability to control these microbial habitats by adjusting pH, temperature, and nutrient input allows for precise customisation of catalyst facets, making biogenic synthesis a viable and sustainable option for large-scale industrial applications.[15,21]

2.1 Microbial candidates

Bacteria and other microbes, have been employed to produce nanocatalysts made of various metals or compounds (*e.g.* gold, silver, cadmium, platinum, zinc, and iron oxide) at moderate temperatures and pressures. Microorganisms have the ability to absorb and store metals. They also release several enzymes that aid in the transformation of metal ions. Beyond their synthetic

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Table 2 Influence of nanoparticle size and morphology on catalytic performance

Nanoparticle feature	Size/shape range	Catalytic parameter affected	Trend	Mechanistic basis	Reference(s)
Ultra-small nanoparticles	∼2–10 nm	TOF, activation energy	Higher catalytic activity; reduced activation barriers reported across systems	High density of low-coordinated atoms and defect sites	9 and 10
Small nanoparticles	∼10–50 nm	Surface area, reaction rate	Optimal balance between activity and stability commonly observed	Increased surface-to-volume ratio with improved structural stability	2 and 3
Larger nanoparticles	>50 nm	Catalytic activity	Gradual decrease in activity due to reduced surface exposure	Lower fraction of surface atoms limits active site availability	3
Spherical morphology	Isotropic	General catalytic activity	Moderate, non-selective catalytic behaviour	Uniform surface energy distribution	11
Faceted nanoparticles (cubic, octahedral)	Defined crystal planes	Selectivity, kinetics	Enhanced selectivity and activity depending on exposed facets	Specific crystallographic planes influence adsorption energetics	10 and 12
High-index facet structures	Step/kink-rich surfaces	TOF, adsorption energy	Improved catalytic turnover reported in facet-engineered systems	High density of unsaturated coordination sites	8
Rod-like/anisotropic structures	High aspect ratio	Electron transfer, photocatalysis	Improved charge transport and photocatalytic efficiency	Directional electron mobility and reduced recombination	13 and 14
Porous/hierarchical structures	Micro–mesoporous	Mass transfer, diffusion	Enhanced reaction kinetics due to improved diffusion pathways	Facilitates reactant accessibility and product removal	2 and 11
Bio-capped/core–shell structures	Organic shell (∼1–10 nm)	Stability, selectivity	Improved stability and reusability reported in multiple cycles	Organic capping layer prevents aggregation and modifies adsorption	15 and 16

versatility, an important practical consideration in microbial nanocatalyst production is nanoparticle yield, particularly in the context of scalability. Unlike chemically synthesised nanocatalysts, for which yield trends can often be generalised across morphological categories, microbially produced nanoparticles present a significantly more complex and less predictable yield landscape. Microbial biosynthesis is frequently associated with relatively low production rates, broad particle size distributions, and challenges in standardising protocols across different organisms and cultivation conditions.[15,22]

Reported yields vary widely depending on the microbial system and experimental conditions. For instance, fungal synthesis of silver nanoparticles has been reported at concentrations on the order of $\sim$0.1 g L^{-1} under optimized conditions,[23] while magnetotactic and metal-reducing bacteria have demonstrated yields approaching sub-gram per litre levels in controlled systems.[24] Larger-scale demonstrations are limited but notable; for example, biogenic magnetite production has been achieved at multi-gram to kilogram (wet weight) scales in pilot bioreactor systems while maintaining nanoscale particle characteristics.[25,26] Importantly, these studies also highlight that nanoparticle yield does not always correlate directly with microbial growth, underscoring the complex interplay between metabolic pathways and metal reduction mechanisms. Despite these advances, industrial implementation remains constrained by low production titers, challenges in reproducibility, and difficulties in controlling nanoparticle morphology at scale.[17]

Microbes can produce metal nanoparticles both intracellularly and extracellularly. Intracellular synthesis typically involves enzymatic reduction within the cytoplasm or periplasmic space, leading to confined nanoparticle growth, whereas extracellular synthesis is mediated by secreted biomolecules that facilitate reduction and stabilization in the surrounding medium. These biogenic nanocatalysts exhibit catalytic functionalities comparable to those of conventionally synthesised catalysts. The microorganism utilised determines the nanoparticles' position, size, and form. Nanocatalysts can be produced in both single and multicellular organisms using a variety of ways.[27] Bacteria absorb metal ions and combine them with enzymes to form nanocatalysts of particular sizes. They are grown in nutrient solutions containing the components required to produce nanoparticles. Bacteria can produce nanocatalysts both within and outside of their cells, depending

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Table 3 Microbial systems and reaction conditions for biogenic nanocatalyst synthesis

Microbial system	Synthesis mechanism	Reaction conditions	Nanocatalyst characteristics	Morphology/shape	Reference
Bacteria	Intracellular enzymatic reduction	20–37 °C; pH 6.5–7.5; 0.1–2 mM metal precursor	Spherical nanoparticles, 5–50 nm	Predominantly spherical	3
Bacteria	Extracellular reduction *via* secreted enzymes	Ambient temperature; neutral pH	Protein-capped nanoparticles, 10–80 nm	Spherical to irregular	4
Shewanella oneidensis MR-1	Respiratory metal reduction	Anaerobic; 25–30 °C	Reduced Fe, Pd, Au nanocatalysts, 5–30 nm	Spherical/clustered	4
Fungi	Cell-wall-mediated reduction	25–30 °C; acidic to neutral pH	High-yield nanoparticles, 20–100 nm	Spherical to quasi-spherical	3
Fusarium oxysporum	Intra-/extracellular synthesis	25–30 °C; pH 5–7	Stable Ag/Au nanoparticles, 10–60 nm	Spherical to anisotropic (occasional rods)	5
Yeast	Intracellular biomineralization	28–32 °C	Encapsulated nanoparticles, 5–40 nm	Spherical (intracellularly confined)	5
Algae/cyanobacteria	Photosynthetic reduction (NADPH-mediated)	Light intensity 50–150 μmol m^{-2} s^{-1}	Metal nanoparticles, 10–100 nm	Spherical to irregular	7

on where they reside. Many nanoparticles are confined, altered, and coated while being produced inside cells. Enzyme secretion, bio-reduction, and particle capping are actions that take place outside of cells that help to produce chemicals. Individual enzymes are required for bioreduction because they convert electrons from donors to positively charged metal ions.

A noteworthy example is *Shewanella oneidensis* MR-1's ability to manufacture nanometal catalysts.[28] It is capable of performing the biological reduction of metals process. Different metals (or comparable compounds) are utilised outside the organism in this biological process in order to accept electrons at the conclusion of a reaction.[4] Important metabolites, proteins, enzymes, and other tiny chemicals are released by fungal cells, converting toxic compounds into safer or less toxic ones. Nanocatalysts are made from these products.[29] Under the same conditions, they grow more quickly than bacteria and convert metal salts into tiny metal catalysts with the help of several enzymes.

Nano metal catalysts are produced when fungi's cell walls absorb and reduce metal ions.[5] Due to their ability to collect and handle heavy metals, fungi are becoming crucial in the production of nanometal catalysts. This has been seen in a type of fungus called *Verticillium* and *Fusarium oxysporum*.[29] Although the mechanisms underlying fungal nanoparticle synthesis are yet to be fully understood, fungi are capable of producing nanoparticles both intracellularly and extracellularly.[5] The primary method of forming nanocatalysts is through the production of minerals, which yeast cells can assist with. The ease of use is one advantage of employing yeast cells to transport nanoparticles. No stabilisers are required; all that is needed are yeast cells, water, and a few additional substances. The microscopic particles that make up yeast cells are composed of large molecules.[6] They are covered in β-glucans, glycoproteins, and chitin. They also function as tiny capsules, enclosing and storing a polymer nanocatalyst with the aid of a membrane.[30]

Algae are suitable for producing nanoparticles because they develop quickly and require fewer nutrients than larger plants. The ability of some algae to convert metal ions into metal particles has made the production of microscopic particles from these algae a novel and inventive field of scientific study.[31] Algae convert metal ions through respiration and photosynthesis. In the algae, this mechanism aids in the production of metal nanoparticles. The reduction of small metal particles in cyanobacteria is believed to be aided by the enzyme nitrogenase. Participating in the photosynthetic electron transport system (PETS) and respiratory electron transport system (ETS), which are located on the cell membrane and within the cytoplasm of algae, helps to explain how energy is produced. Metal ions are believed to be converted into small particles in cyanobacteria by substances such as NADPH or enzymes that rely on NADPH. The electron transport system's energy-producing mechanisms, as well as chemical events occurring in the cytoplasm, cell membranes, and thylakoids, are responsible for this.[7] Table 3 summarises the main microbial systems used in biogenic nanocatalyst production, including reduction pathways, reaction conditions, nanoparticle properties, and relevant

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literature sources. A comparative analysis indicates significant disparities amongst microbial platforms. Bacteria-derived nanocatalysts frequently have superior control over particle size and dispersion due to regulated intracellular reduction pathways, whereas fungal systems produce more nanoparticles with larger size ranges due to external enzymatic activities.[32–34] Algal systems present novel photochemical production pathways, which can alter electronic structure and photocatalytic activity.[11] These distinctions highlight the need to select microbial systems based on their intended catalytic application rather than viewing biogenic synthesis as a homogeneous process.[33]

2.2 The bio-catalytic cycle

The majority of bionanotechnology research analyzes microbe-engineered nanocatalysts using heterogeneous kinetic models, which need reactant molecules to be adsorbed on the catalyst surface for a chemical transition to occur.[3] The biogenic interface is distinguished by a protein-rich capping layer that acts as an advanced molecular filter or gatekeeper.[16] This biological shell is proposed to influence substrate accessibility and protect active sites from deactivation, allowing small reactant molecules to diffuse through the organic matrix to the metallic active sites while also preventing larger, bulky macromolecules from damaging or blocking the metal's active components.[15,16] This natural architecture provides selectivity and protection that entirely synthetic catalysts frequently lack, as surface fouling is a typical cause of deactivation.[3] These biogenic particles are thought to have surface flaws and undercoordinated sites, which could lead to enhanced catalytic activity.[20] These distinct active sites may reduce the activation energy required for reaction start, lowering the energetic barrier and allowing the process to run at higher rates.[3]

Beyond the initial catalytic phase, microorganisms provide a robust structural framework, often composed of extracellular polymeric substances (EPS) or cell wall fragments, which keep the individual nanoparticles in a fixed spatial orientation.[11,14] This structural confinement prevents particles from sticking to one another or sintering during the process's heat and mechanical stresses.[16] This unusual stability is the primary reason why biogenic catalysts may be recovered with simple centrifugation or filtration, and they have been demonstrated to retain activity throughout multiple reuse cycles.[3,21] Furthermore, the metallic core's synergistic interaction with biological ligands optimises adsorption–desorption energetics, ensuring that products are released efficiently to refill active sites for the next catalytic event.[15,20]

2.3 Confinement effect

The confinement effect provides a mechanistic basis for understanding nanoparticle nucleation and growth within microbial environments. In this model, microbial cells and their EPS operate as natural nanoreactors.[20,21] These biological scaffolds impose rigid physical templates on forming crystals, thereby limiting particle size distribution and reducing the polydispersity commonly observed in uncontrolled chemical precipitation[19] Confinement within cellular compartments or the EPS matrix significantly impacts nucleation behavior by localizing metal ions at specific biological interfaces.[11,14] This spatial confinement regulates nanoparticle nucleation and growth, suppresses agglomeration, and provides intrinsic stabilisation comparable to synthetic capping agents.[16] These scaffolds can modify local reactant concentrations, gathering and concentrating molecules to influence their interaction with active sites.[15,20] While this geometry fundamentally affects adsorption and catalytic behavior, direct experimental evidence linking microbial confinement to specific catalytic mechanisms remains limited.[3,16]

Within these confined environments, metal ion transformation is governed by multiple biochemical pathways. Enzymatic reduction plays a central role, particularly through NADH-dependent nitrate reductases, which utilise electron shuttle molecules such as anthraquinones and naphthoquinones to facilitate electron transfer. Hydrogenases contribute to the reduction of noble metals such as palladium, while enzymes like cysteine desulfhydrase regulate metal sulfide formation through S^{2-} ion generation.[35,36] In parallel, biomineralisation proteins act as both reducing and stabilising agents; for example, magnetite biomineralisation (Mms) proteins precisely control crystal size and morphology, while surface-bound proteins in organisms such as *Rhizopus oryzae* contribute to nanoparticle stabilisation. Additionally, EPS provide polysaccharide-rich matrices that facilitate biosorption and reduction, with reducing sugars acting as electron donors for metal ion conversion.[36] Nanoparticle formation is often linked to stress-induced microbial defence mechanisms, including efflux systems and enzymatic precipitation that sequester toxic metal ions away from vital cellular components.[35] While synthesis parameters such as pH, temperature, and precursor concentration are known to influence nanoparticle properties, the molecular-level control governing these effects remains insufficiently resolved. In particular, the role of confinement in dictating electronic interactions between metal cores and biological functional groups represents a critical gap in current understanding, highlighting the need for targeted mechanistic and spectroscopic investigations.

3 Characterization and evolution of biogenic nanocatalyst

A comprehensive characterisation approach is required to determine the structure–property correlations that regulate catalytic performance during the transition from a raw microbial secretome to a functionalised nanocatalyst.[16] Unlike many supported or ligand-free heterogeneous catalysts, microbe-engineered nanoparticles feature a complex hybrid architecture with an inorganic crystalline core enclosed within an organic, amorphous bio-shell.[16] A multimodal analytical technique is required to distinguish between the core's physical dimensions and its effective hydrodynamic behaviour in reaction fluid.[16] The primary focus of characterisation is to determine the phase purity, crystallite size, and surface

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Table 4 Stability and reusability of biogenic catalysts

Parameter	Range	Representative value	Units	Interpretation	Reference
Activity retention after 10 cycles	70–95	85	%	Operational stability	17
Structural integrity loss	5–25	12	%	Physical durability	37
Metal leaching	0.1–5	1.2	%	Environmental safety	13
Storage stability	3–12	8	Months	Shelf life	3

functionalisation provided by microbial metabolites, as these characteristics have a direct impact on the system's active site exposure and mass-transfer behaviour.[11]

Beyond simple identification, biogenic nanocatalysts must be described in terms of soft-matter interaction.[16] The organic capping layer, composed of proteins, polysaccharides, and lipids, adds heterogeneity not found in conventional heterogeneous catalysts.[15] This involves the use of microscopic techniques such as high-resolution transmission electron microscopy (HR-TEM) to see the metallic core's lattice fringes, as well as spectroscopic equipment such as Fourier Transform Infrared (FTIR) spectrometer to map the chemical fingerprints of the stabilising ligands.[16] The combination of these techniques allows researchers to quantify the degree of surface functionalization. This is critical, as biogenic capping layers can enhance colloidal stability and chemo-selectivity, but excessive surface ligands may obstruct active sites and reduce overall catalytic turnover. Consequently, optimizing synthesis conditions (such as pH and temperature) is essential to balance surface protection with active site accessibility.[19] The stability and operational durability of biogenic catalysts are illustrated in Table 4. By using a standardised quantitative characterisation technique, the discipline can proceed toward more predictable bio-nanofactory formation over numerous catalytic cycles and under various reaction circumstances.[3]

3.1 Characterization of nanocatalyst

A multimodal characterisation strategy is essential to move beyond simple identification and reveal the species-specific structural and surface features of biogenic nanocatalyst. Techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) are not merely descriptive; they reveal the well-defined, periodic arrangements and diverse morphologies that distinguish microbe-engineered materials.[28,38] High-energy X-ray diffraction, particularly when combined with atomic pair distribution function analysis, has revealed that biogenic catalysts can exhibit species-dependent internal architectures. Unlike the uniform lattices of chemical analogs, biogenic materials exhibit structural diversity dictated by the host organism; for instance, bacterial synthesis may produce birnessite-type layers, while fungal routes yield todorokite-type tunnels.[38] These techniques identify the internal structural integrity and phase evolution of the inorganic core, thereby linking the biological origin of the system to its resulting crystalline phase and catalytic properties.[39,40]

Table 5 shows the surface engineering and physicochemical stabilization of the nanocatalyst. Transmission Electron Microscopy (TEM) provides the direct visual evidence required to analyze the size, shape, and spatial distribution of green-synthesized nanoparticles.[39,41] Beyond simple size measurements, TEM identifies how microbial secretomes, such as those from *Shewanella oneidensis* MR-1, template the formation of complex alloys and metallic sulfide nanoparticles.[28] This allows for a precise correlation between the morphological fingerprint of the catalyst and its performance in electrocatalytic or biocatalytic applications.[28,42]

X-ray Photoelectron Spectroscopy (XPS) serves as the definitive tool for composition analysis, specifically targeting the surface chemistry and electrical characteristics of the bio-interface.[40,43] XPS is critical for determining the elemental composition and oxidation states within biogenic frameworks, revealing how the microbial environment influences the chemical condition of the surface.[39,44] These surface characteristics directly influence catalytic activity, selectivity, and stability by modulating adsorption behaviour and electron transfer processes.[39,45] Compared to chemically synthesised analogues, biogenic nanocatalysts consistently exhibit greater structural heterogeneity and organic–inorganic interfacial complexity, which can enhance catalytic performance but also introduce variability in reproducibility. This distinction

Table 5 Structural and surface properties

Property	Typical range	Representative value	Measurement technique	Catalytic relevance	Reference
Crystallite size (nm)	5–50	22	XRD	Active facet exposure	46
Specific surface area ($m^2\ g^{-1}$)	20–300	150	BET	Adsorption capacity	47
Zeta potential (mV)	−30 to +30	−18	DLS	Colloidal stability	48
Organic capping thickness (nm)	1–10	4	TEM/XPS	Prevents aggregation	37
Defect density	15–50	35	HRTEM/SASA	High-energy active site generation	49

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Table 6 Structural and physicochemical properties of biogenic nanocatalysts

Parameter	Typical range	Reported variability/notes	Characterization technique	Catalytic significance	Reference(s)
Particle size	2–15 nm to 20–100 nm	Varies with synthesis conditions; statistical distribution is typically reported from TEM analysis	TEM/HRTEM	Determines active surface area and density of low-coordinated sites	3 and 9
Crystallite size	5–40 nm	Dependent on XRD peak broadening, variability is influenced by instrumental and sample factors	XRD	Influences crystallinity and charge transfer	46
Specific surface area (SSA)	20–180 $m^2 g^{-1}$	Reported values depend on the adsorption model and measurement conditions	BET	Controls adsorption capacity and mass transfer	47
Zeta potential	−45 to −15 mV	Typically reported as average values; varies with pH and medium	DLS	Indicates colloidal stability	48
Capping layer thickness	1–12 nm	Estimated from imaging/spectroscopy; varies with biological source	TEM/XPS	Governs stability *vs.* accessibility trade-off	19 and 37
Defect density	High	Often qualitatively described rather than quantitatively standardised	HRTEM/Raman	Enhances catalytic active sites	10 and 49
Heteroatom loading	0.5–5.0 wt%	Depends on the synthesis route and precursor concentration	ICP-OES/EDX	Influences the electronic structure	50 and 51
Turnover frequency (TOF)	100–5000 h^{-1}	Reported values vary significantly across studies and conditions	GC/HPLC	Measures intrinsic catalytic activity	5 and 12

highlights both the advantages and challenges associated with biologically derived systems.

Table 6 summarises the important structural and physicochemical properties of biogenic nanocatalysts, relating characterisation techniques to catalytic activity.

3.2 *Operando* techniques of nanocatalysts

Operando and *in situ* methods are required to record the dynamic evolution of the biogenic interface during an active chemical transformation.[16] The hybrid nature of microbe-engineered catalysts, particularly the organic–inorganic interface, is highly responsive to external stimuli such as temperature variations and electrochemical potentials.[16] *Operando* X-ray Absorption Spectroscopy (XAS) and X-ray Absorption Near Edge Structure (XANES) are key approaches for real-time monitoring of the metallic core's oxidation condition and coordination environment.[16] Advanced analytical approaches allow researchers to investigate the coordination environment of metal centers in biogenic systems.[11] Coordination concepts seen in synthetic systems may apply to nitrogen-containing biogenic interfaces.[15] This level of detail is not obtainable through post-mortem testing because the catalyst may undergo structural relaxation or atmospheric oxidation after the reaction is completed.[16]

In situ Fourier-Transform Infrared (FTIR) spectroscopy and Surface-Enhanced Raman Spectroscopy (SERS) provide a molecular-level view of catalytic processes in progress.[16] These methods can track the adsorption of reactants and the subsequent synthesis of intermediates on nanoparticle surfaces.[3] This is especially beneficial for biogenic catalysts since it helps to understand the role of the protein corona. *In situ* data can reveal if specific carboxyl or amine groups benefit in catalytic processes or cause steric effects that affect reaction rates.[15] Environmental Transmission Electron Microscopy (E-TEM) allows for direct visualisation of nanoparticle stability and interactions at the atomic level in reactive environments.[16] Correlating these analytical insights with kinetic data enables researchers to develop comprehensive structure–activity connections.[3] This integrated strategy ensures that future green catalysts are built using an understanding of the material's active state rather than its precursor form, which improves the predictability and efficiency of microbe-mediated conversions.

3.3 Structure–activity relationships (SAR)

Structure–activity nanocatalyst relationships are built on a synergistic merger of biological precision with inorganic functionality (Fig. 1).[3] Unlike traditional chemically synthesised catalysts, bio-inspired catalysts have multi-tiered hierarchical architectures that boost performance.[52] As a result, smaller, well-dispersed particles significantly enhance the number of accessible active sites per gram of catalyst, a key SAR factor.[3] Aside from size effects, organic ligands can significantly influence nanoparticle catalysis.[15] These chemical ligands can effectively regulate substrate selectivity.[16] The SAR in this scenario is primarily governed by two mechanisms: steric hindrance and electronic induction.[16] Ligands can either modify the electron density of the metal core (electronic effect) or physically block specific orientations of a reactant molecule (geometric effect), so strategically directing reaction routes.[16]

Another critical factor is heteroatom incorporation. During the synthesis process, heteroatoms like nitrogen (N), sulphur (S), and phosphorus (P) can be systematically integrated into catalytic structures or carbonised supports.[15] These atoms have a considerable effect on the electronic characteristics of metallic nanocatalysts. Nitrogen doping, for example, can significantly modify the metal's electronic state, optimising reactant adsorption energy.[15] This equilibrium is delicate: if the binding is too strong, the catalyst becomes poisoned, and if it is

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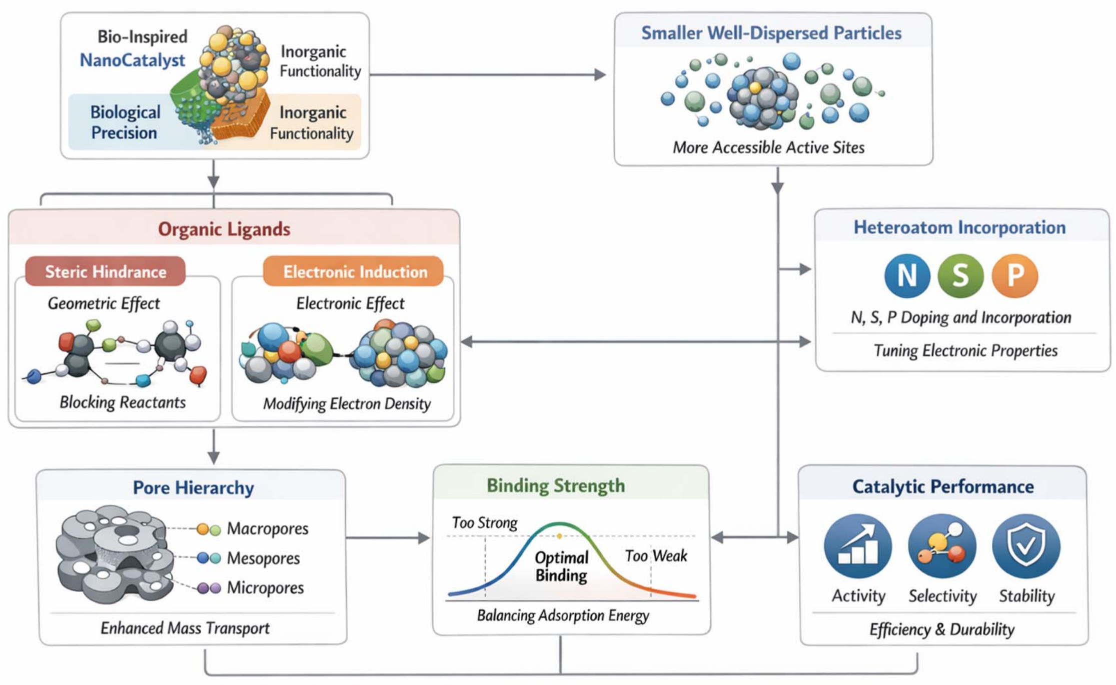

Fig. 1 Structure–activity relationships in nanocatalysts [prepared originally using https://www.biorender.com/].

too weak, the reaction does not begin.[3] The optimal binding strength represents the best balance of catalytic performance.[3] The macrostructure of catalysts determines the final material's pore hierarchy.[11] Mass transport essentially constrains catalytic activity, specifically how rapidly reactants can reach active sites and how effectively products can escape.[3] Well-designed catalyst structures may have hierarchical porosity, with varying pore sizes to increase surface area and diffusion.[11] Research indicates that catalysts with optimised structural designs have improved mass-transfer capabilities, resulting in higher catalytic efficiency.[3] Quantitative criteria for catalytic efficiency and stability prioritise structure–activity interactions across diverse catalytic systems.[3]

Given the complexity of these hierarchical architectures, robust characterization is required to validate structural claims. Studies demonstrate successful detection of heteroatom doping in biogenic nanocatalysts using complementary analytical techniques. X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform infrared (FTIR) spectroscopy are the primary methods for confirming the presence of the elements.[53–55] Advanced direct imaging is achievable through aberration-corrected STEM with electron energy loss spectroscopy.[56] Biogenic sources, including fruit extracts and plant materials, successfully incorporate nitrogen, sulfur, boron, and oxygen dopants.[53,54,57] Importantly, XRD reveals amorphous rather than crystalline structures in doped materials, limiting its utility for lattice distortion analysis.[53] No standardized characterization sequence exists; instead, researchers employ multi-technique approaches tailored to specific materials and detection requirements.[58,59]

Table 7 Catalytic performance and structure–activity relationships

Parameter	Quantitative values	Effect on catalysis	Reference
Activation energy reduction	20–60% Decrease *vs.* uncatalyzed reactions	Accelerates reaction rates	60
Adsorption energy ($\Delta E_{(\text{ads})}$)	-0.2 to -1.5 eV	Determines binding strength of intermediates	10
Current density (electrocatalysis)	10–100 mA cm^{-2}	Indicator of catalytic activity	12
Overpotential	200–500 mV	Lower values indicate better performance	10
Catalyst reuse cycles	10–20 cycles	Stability and durability	61
Turnover frequency	0.1–10 s^{-1}	Intrinsic catalytic activity	2
Mass-transfer characteristics	System-dependent (not directly comparable across studies)	Enhanced diffusion and reactant accessibility in porous and hierarchical structures	9

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Table 7 summarises key catalytic performance characteristics used to evaluate microbe-engineered nanocatalysts, as well as their relevance to SAR. It is important to note that the values presented vary significantly across studies. These disparities are caused by differences in microbial systems, synthesis conditions (such as pH, temperature, and precursor concentration), nanoparticle size and morphology, and experimental procedures used to evaluate performance. As a result, these numbers should not be viewed as globally comparable measurements, but rather as system-specific markers of catalytic activity. This diversity underlines the existing absence of standardised benchmarking techniques in biogenic nanocatalysis, which prevents direct comparisons between investigations.

4 Theoretical modelling

Theoretical modelling is the critical link between experimental observations and molecular-level understanding of biogenic nanocatalysts, the great structural complexity of the organic–inorganic interface is a modelling problem in these hybrid systems.[16] Unlike typical metal-oxide supports, microbial scaffolds present a diverse environment rich in functional groups, necessitating advanced multiscale models to accurately anticipate catalytic behaviour.[15] Theoretical frameworks are generally used to establish the reaction coordinate and the energetic barriers that influence TOF.[3] Beyond simple geometry, theoretical modelling focuses on the electronic effect caused by the microbial secretome.[15]

Computational studies can estimate characteristics such as work function shifts, interfacial charge redistribution, and charge-transfer resistance at the metallic nanoparticle-protein corona interface.[16] Studies on coordination settings show that heteroatom coordination stabilises metal centers under catalytic circumstances. Similar coordination principles may apply to heteroatom-containing biological ligands.[15] Models enable the visualisation of the active site architecture, which demonstrates how orbital interactions between metal and biological ligands might result in a more reactive surface.[3] Furthermore, the inclusion of theoretical techniques in these models allows for the prediction of reaction pathways, offering a blueprint for constructing more efficient biological synthesis systems.[3] By incorporating these theoretical insights, the research shifts from empirical trial-and-error to a rational design approach that can guide catalyst design and identify interesting active-site motifs before experimental validation.[3]

4.1 Density functional theory (DFT) calculations

The complexity of biogenic interfaces necessitates a multi-scale theoretical approach. Computational modeling has evolved from a descriptive tool into a foundational framework for identifying the atomic-scale drivers of catalytic performance.[62] Density Functional Theory (DFT) is widely used to elucidate the electronic structure of biogenic interfaces, particularly in understanding how heteroatoms (*e.g.*, N, S, P) introduced by microbial secretomes influence surface energetics.[15] DFT calculations enable the quantification of key catalytic parameters, including adsorption energies ($\Delta E_{(\mathrm{ads})}$), which govern the binding strength of reaction intermediates in processes such as oxygen reduction (ORR), CO_2 reduction (CO_2RR), and hydrogen peroxide formation.[15,62] In addition, transition state analysis provides activation barriers that determine the kinetic feasibility of reaction pathways on microbially templated surfaces.[3] Also, DFT studies highlight the role of facet-dependent activity, where low-coordinated sites and defect-rich surfaces, commonly observed in biogenic systems, stabilise reactive intermediates and enhance catalytic turnover, features that may not be readily accessible in conventional synthetic systems.[16,62]

4.2 Machine learning

Machine learning (ML) is increasingly used to complement DFT calculations by enabling rapid prediction of catalytic properties across complex compositional and structural spaces.[63] Machine learning models trained on high-throughput DFT datasets, including neural networks, kernel ridge regression, and random forest algorithms, have demonstrated near-DFT accuracy in predicting atomic configurations and catalytic properties.[63,64] These approaches enable predictive screening of complex alloy systems, for example, eXtreme Gradient Boost Regression (XGBR) has been used to evaluate multicomponent catalysts (*e.g.*, NiCoCu) for hydrogen evolution reactions (HER), incorporating variables such as surface coverage and microstructural features.[65] Additionally, active learning frameworks allow models to iteratively identify high-uncertainty regions in the catalytic landscape, guiding targeted experimental validation while reducing the use of costly biological reagents.[17,66]

Despite these advances, a significant gap remains in the application of ML to biogenic nanocatalysts. Most existing models are developed for synthetic alloys and nanomaterials, with limited adaptation to the complex, heteroatom-rich coordination environments characteristic of microbially derived systems. This represents a critical opportunity for the application of generative Artificial Intelligence (AI) and graph-based models to better capture the structural diversity and dynamic behaviour of biological nanocatalysts.

5 Mechanistic pathway of microbe-engineered nanocatalysts

The catalytic process in microbe-engineered systems is a finely coordinated series of physicochemical processes that go beyond simple surface contact (Fig. 2). This process begins with the exterior mass transfer of reactants from the bulk fluid phase to the catalyst's boundary layer, followed by internal diffusion across the diverse biological microenvironments.[3] Unlike synthetic catalysts, the biogenic interface has a protein corona that can modify substrate accessibility and adsorption orientation, specifically, the coordination sites on the nanoparticles' surfaces.[16] Activation happens by chemisorption, in which reactant molecules form chemical bonds with metallic centers, weakening internal molecular bonds.[15]

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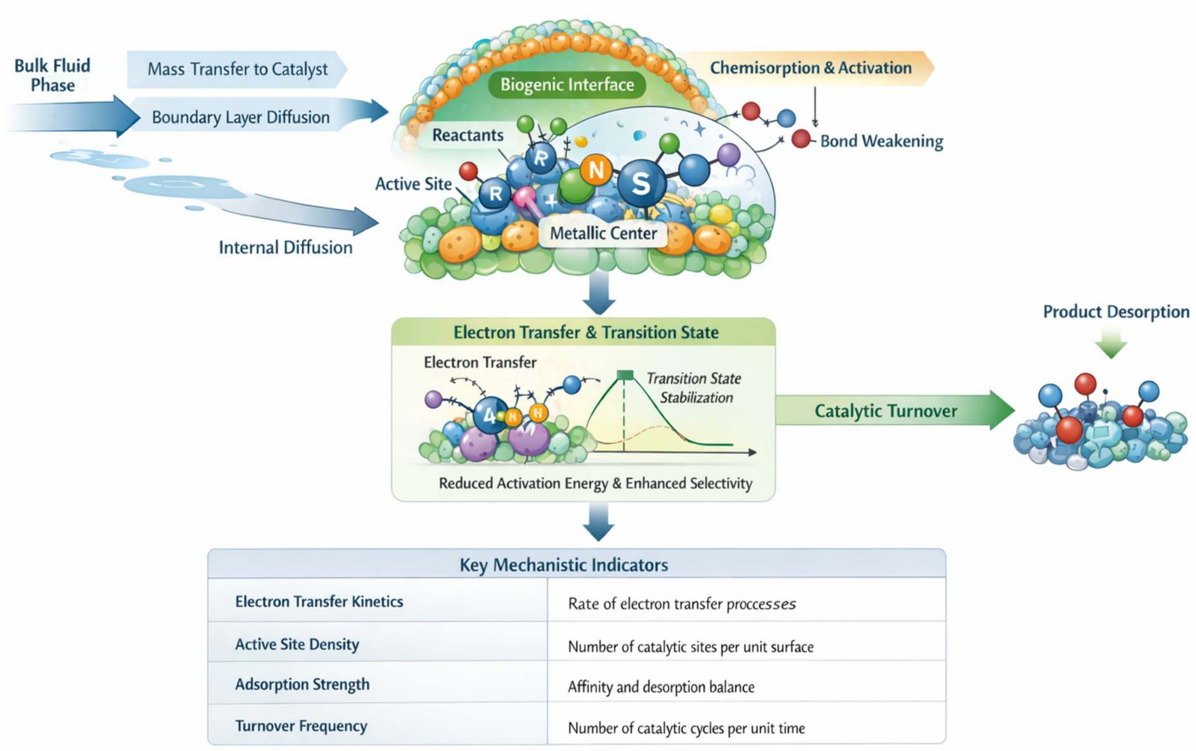

Key Mechanistic Indicators	
Electron Transfer Kinetics	Rate of electron transfer proccesses
Active Site Density	Number of catalytic sites per unit surface
Adsorption Strength	Affinity and desorption balance
Turnover Frequency	Number of catalytic cycles per unit time

Fig. 2 Mechanistic pathway of microbe-engineered nanocatalysts [prepared originally using https://www.biorender.com/].

In these biological systems, heteroatoms from microbial biomass, such as nitrogen (N) and sulphur (S), may be integrated into electron transport pathways.[15] This electronic synergy stabilises high-energy transition states while lowering the activation energy required to start the reaction.[15] The catalytic cycle ends with the description of the product, which must be balanced for maximum catalytic performance.[3] The adsorption must be strong enough to activate the reactant but weak enough to allow the product to exit without contaminating the environment.[3] Biogenic catalysts maintain this equilibrium, allowing for continuous catalytic turnover under favourable reaction circumstances. This mechanistic elegance mimics enzymatic precision, allowing complex green transformations to occur under milder conditions than traditional industrial catalysts. To better understand the mechanistic behaviour of microbe-engineered nanocatalysts, several quantitative parameters are commonly used to describe catalytic pathways and efficiency. These parameters include electron transfer kinetics, active site density, and adsorption characteristics, which collectively determine catalytic performance and selectivity. Table 8 summarises key mechanistic indicators used to evaluate catalytic pathways in biogenic nanocatalytic systems. Selectivity values are highly reaction-dependent and are presented as representative ranges rather than universal constants. Reported electron transfer rates in biogenic and nanostructured catalytic systems are typically derived from time-resolved spectroscopic or electrochemical techniques and vary significantly depending on catalyst composition, reaction environment, and measurement methodology.

5.1 Thermal catalysis

Thermal catalysis is still the foundation of commercial chemical processing, using external caloric energy to overcome the energetic barriers of resistant molecular bonds.[3] The relationships between thermal catalytic kinetics and SAR are illustrated in Table 9. These relationships are derived from reported experimental trends and computational studies, providing a generalised framework for understanding catalytic

Table 8 Mechanistic indicators of catalytic pathways

Mechanistic parameter	Quantitative indicator	Representative value	Units	Mechanistic implication	Reference
Electron transfer rate	10^6–10^9	10^7–10^5 (System-dependent)	s^{-1}	Redox activity	2
Active site density	10^{16}–10^{18}	5×10^{17}	Sites per g	Catalytic capacity	49
Surface coverage	0.2–0.9	0.6	Fraction	Adsorption extent	9
Reaction selectivity	Reaction-specific (typically 40–95% depending on system)	78	%	Product control	67

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Table 9 Thermal catalytic performance metrics

Parameter	Quantitative range	Representative value	Units	Catalytic significance	Reference
Activation energy reduction	20–60	40	%	Reaction acceleration	17
Turnover frequency	0.1–10	3.5	s^{-1}	Intrinsic activity	9
Adsorption energy	−0.2 to −1.5	−0.8	eV	Intermediate binding	10
Catalyst reuse cycles	10–20	15	Cycles	Durability	61
Mass-transfer coefficient	1.5–5× increase	3×	—	Enhanced kinetics	2

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performance. The inherent structural flaws of biogenic nanocatalysts, such as surface vacancies, adatoms, and low-coordinated edges, provide a better landscape for thermal activation.[3] These locations have more surface energy than bulk materials, making them highly reactive. A major difficulty in thermal catalysis is sintering, in which nanoparticles migrate and agglomerate at high temperatures, resulting in a reduction of active surface area. To address this, biogenic catalysts use stabilisation effects, in which heteroatoms such as nitrogen, sulphur, and phosphorus serve as atomic anchors, tying metallic particles to the carbonaceous microbial substrate.[15] This atomic-scale stabilisation ensures that the catalyst retains a high active site density and uniform shape even under extreme temperatures.[3]

Biogenic metal-based catalysts have demonstrated high efficiency in environmental applications, including CO_2 methanation and water–gas shift reactions. The existence of residual biological carbon frequently works as a secondary reducing agent, allowing for continual regeneration of the active metallic state during the reaction.[15] The microbial scaffold's hierarchical pore structure enhances the transformation of gaseous precursors like CO and H_2 into value-added compounds, overcoming mass-transfer limits.[11] Researchers can optimise bio-derived catalytic systems for commercial applications by evaluating the link between temperature input and catalytic performance.[3]

5.2 Photocatalysis

Photocatalysis is a sustainable frontier that directly turns light energy into chemical potential at room temperature.[13] Biogenic nanocatalysts, such as TiO_2 or ZnO_2 absorb photons with energy matching their band gap, promoting an electron from the valence band to the conduction band and leaving a positively charged hole.[11] Table 10 presents how biogenic doping improves photon utilization. The key engineering problem is the quick recombination of electron–hole pairs.[13] Microbe-engineered devices overcome this issue by utilising biological heteroatoms' doping action.[14] Nitrogen and sulphur atoms form mid-gap states that trap photogenerated carriers, enhancing their lifetime and the likelihood of a surface redox reaction.[14]

Recent studies on Single-Atom Catalysts (SACs) have enhanced this by organising individual metal atoms within nitrogen-coordinated microbial frameworks.[52] This band-gap engineering enables biogenic catalysts to act in visible light, increasing the efficiency of solar-driven water splitting and organic pollutant degradation.[13] The organic capping layer can promote substrate adsorption through π–π interactions or hydrogen bonding, depending on the molecular structure of the reactant. This ensures that photogenerated radicals are produced in the immediate vicinity of the substrate.[16] This spatial proximity optimises the quantum yield and overall rate constant of the photocatalytic process, offering a roadmap for the creation of next-generation green photocatalysts.[13]

5.3 Electrocatalysis

The main force for chemical transformation in electrocatalysis is electrical potential, which occurs at the triple-phase boundary between the electrode, electrolyte, and nanocatalyst.[21] The overpotential, the additional voltage required beyond the thermodynamic limit, is used to assess the efficiency of this interface. Table 11 illustrates the overpotential requirements, Tafel slopes, and charge-transfer resistance for single-atom and nanoparticle electrocatalysts. Biogenic electrocatalysts, particularly those with atomically scattered metal sites, function very well due to their distinct coordination environments.[52] Kulkarni *et al.* (2023) have identified single-atom catalysts with coordination motifs as benchmarks for the Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER).[14] Several investigations have found varied intrinsic activity for distinct metal-based locations in biogenic systems.[11] This hierarchy is determined by the adsorption energies of intermediary species on metallic sites. Using the nitrogen-rich microbial scaffold,

Table 10 Photocatalytic properties

Parameter	Range	Representative value	Units	Photocatalytic role	Reference
Band gap energy	1.8–3.2	2.4	eV	Light absorption	68
Quantum efficiency	5–35	18	%	Photon utilization	7
Photodegradation rate constant	0.01–0.12	0.06	min^{-1}	Reaction speed	68
Reactive oxygen species generation	1–10	5	$\mu mol\ L^{-1}$	Oxidation mechanism	1

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Table 11 Electrocatalytic performance

Parameter	Range	Representative value	Units	Significance	Reference
Current density	10–100	45	mA cm^{-2}	Activity indicator	12
Overpotential	200–500	320	mV	Energy efficiency	10
Tafel slope	40–120	75	mV dec^{-1}	Reaction kinetics	12
Charge-transfer resistance	5–50	18	Ω	Electron mobility	10

researchers can tune the electrical characteristics of these metal atoms, improving intermediate binding strength and lowering energy expenditure through heat.[19]

Also, the microbial biomass provides a strong, conductive support that allows for fast electron transfer.[20] The bio-capping layer prevents the catalyst from detaching or leaching during rapid gas evolution.[16] Quantitative measures show that these biogenic systems use efficient electron transport pathways.[21] As we transition to a hydrogen-based economy, the capacity to create high-loading electrocatalysts by microbial fermentation represents a quantum leap in sustainable energy technology.[13]

However, it is important to note that values were not intended to serve as quantitative or universally predictive models, as catalytic performance is highly system-dependent and influenced by variations in synthesis conditions, material properties, and experimental methodologies. Furthermore, reliance on a single characterisation or modelling approach may lead to incomplete interpretations; therefore, integrated multi-technique validation is essential for accurate analysis.

6 Green transformations

Biogenic nanocatalysts represent a paradigm shift in industrial chemistry, enabling "Green Transformations" that prioritise atom economy, waste reduction, and energy intensity minimisation.[3] According to the fundamental principles of sustainable engineering, these procedures prioritise the effective use of raw materials, ensuring that the greatest number of atoms from the starting reagents are absorbed into the final product.[19] This technology's flagship application is the production of green hydrogen by electrochemical water splitting, a carbon-neutral alternative to steam methane reforming.[13] Nanocatalysts produced from microbial biomass have shown remarkable hydrogen evolution performance due to their high surface-to-volume ratios and hierarchical porosity.[11]

Recent studies show that these biogenic systems can consume much less energy throughout the production process than typical metal-oxide catalysts.[14] The manufacture of these catalysts utilising low-energy microbial fermentation has a significantly lower carbon footprint than established processes like chemical vapour deposition or thermal breakdown, which demand high vacuum and caloric input.[52] Microbial synthesis at ambient temperatures eliminates the requirement for toxic reducing agents and organic solvents, lowering the synthesis's environmental impact.[21] Researchers are developing a circular economy in which the catalyst's origin and eventual environmental role are inextricably linked.[15,20]

6.1 Carbon recycling

Carbon recycling is a key method in green transformations, converting carbon dioxide (CO_2) from a waste product into a valuable C1 fuel or chemical feedstock.[13] The CO_2 molecule's great thermodynamic stability and linear geometry make catalytic activation energy-intensive.[3] Nanocatalysts use electrical activation to bend CO_2 molecules, reducing the energy needed for reduction.[21] The initial stage in this recycling pathway is successfully collecting and concentrating CO_2 molecules at the catalyst surface, which is commonly impeded by the low concentration of CO_2 in industrial flue gases.[13] Biogenic catalysts made from nitrogen-rich microbial scaffolds are excellent adsorption platforms, forming weak Lewis acid–base adducts with CO_2 molecules.[15] This intimate association promotes a high local concentration of the reactant, allowing the metallic active sites to work to their full potential.[20] When the surface catches the CO_2, it commences a charge-transfer process that transports electrons into the molecule's antibonding π orbitals, weakening the C=O bonds.[15] This electronic manipulation is critical for recycling carbon at far lower temperatures and pressures than typical industrial methods like the Sabatier process.[19] The capacity of biogenic catalysts to operate well in mild circumstances not only saves energy but also prevents heat degradation of the catalyst, making it a long-term option for large-scale carbon capture and utilisation (CCU) technologies.[11]

6.2 Water remediation

Biogenic nanoparticles help change harmful waste from factories into safer substances by using processes like oxidation, adsorption, and degradation. The textile and printing industries release large amounts of tough dyes into water bodies that are made to be long-lasting and hard to break down. Common examples like methylene blue, methyl orange, and Congo red have complicated ring structures that are difficult to break apart.[69] Biogenic nanocatalysts help Advanced Oxidation Processes (AOPs) by producing very reactive oxygen molecules, called hydroxyl radicals. These molecules can break down complex structures. This process can break down dyes into CO_2, water (H_2O), and simple minerals. This may create less pollution than regular chemical methods.[68] The relationship between biogenic catalyst application and environmental remediation efficiency is synthesized in Table 12. The data demonstrates high removal potential across multiple pollutant classes, with ranges typically spanning 70–99% for dyes and 80–99% for heavy metals. However, as remediation performance is

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Table 12 Environmental remediation performance

Application	Performance metric	Quantitative range	Representative value	Units	Reference
Dye degradation	Removal efficiency	70–99	92	%	1
Advanced oxidation	Mineralization	60–90	82	%	68
Heavy metal removal	Efficiency	80–99	90	%	13
Adsorption capacity	Pollutant uptake	50–400	210	mg g^{-1}	70
Micro pollutant degradation	Removal	70–95	88	%	71

inherently sensitive to experimental conditions, these ranges are best understood through specific benchmarks.

For instance, the upper tier of the 'Dye degradation' range in Table 12 is exemplified by biogenic Pd/Fe nanoparticles (0.5 g L^{-1}), which achieved 96.1% removal of methyl orange (100 mg L^{-1}) within 30 minutes.[3] Also, heavy metal removal, plotted here in the 80–99% range, includes high-performance cases such as the 82% reduction of hexavalent chromium [Cr(VI)] by *Shewanella*-templated catalysts.[28]

Besides organic dyes, water systems often have harmful heavy metals like chromium (Cr), mercury (Hg), and lead (Pb) in them. These metals do not break down and can be very dangerous to people's health. Biogenic catalysts solve this problem using two methods: they attract substances (adsorption) and change them (reduction).[13] The natural groups from the biological process act as spots where metal ions can attach themselves from water. The metal center helps change the state of these metals, like turning the very toxic and water-soluble Cr(VI) into the less toxic and less soluble Cr(III).[13] This two-step method helps remove and settle heavy metal pollutants from dirty water. A new field of interest in water remediation is getting rid of tiny pollutants, like antibiotics, hormones, and pesticides. These substances are found in very small amounts but can still cause serious harm to living things.[71] Biogenic nanocatalysts can bind to the pollutants and convert them to innocuous materials in water, by adsorption or reduction (in the case of heavy metals) or *via* photocatalytic degradation in the case of antibiotics, hormones and pesticides, when exposed to light (Fig. 3). Their special surface helps them stick to complicated organic molecules.[19] Although laboratory studies show good results for different types of pollution, real-world testing and improvement of these systems still need more work.[68]

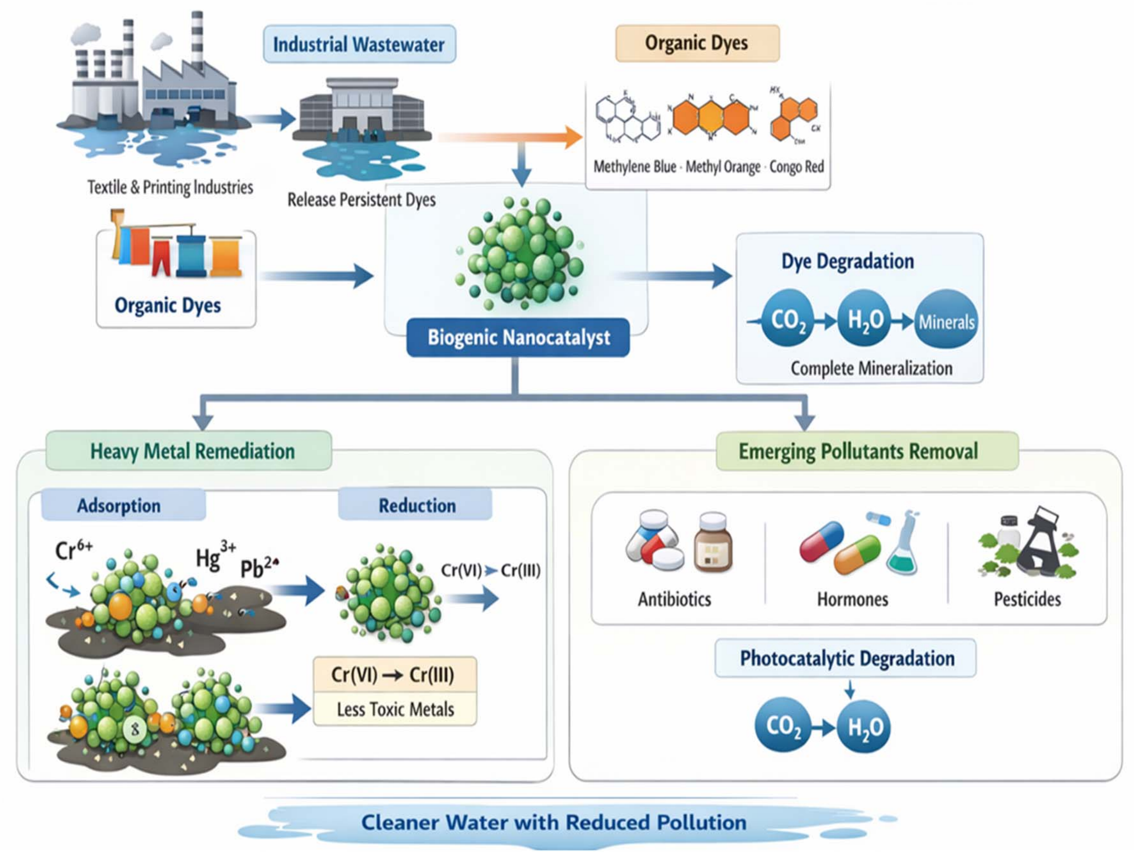

Fig. 3 Remediation of pollutants using microbe-engineered nanocatalysts [prepared originally using https://www.biorender.com/].

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Table 13 Environmental and energy applications of biogenic nanocatalysts

Application	Performance metric	Quantitative outcomes	Reference
Dye degradation	Removal efficiency	70–99% within 30–180 min	1
Advanced oxidation processes	Hydroxyl radical generation	Mineralization efficiency > 80%	68
Heavy metal remediation	Removal efficiency	80–99% for Cr(VI), Pb^{2+}	13
Adsorption capacity	Pollutant uptake	50–400 mg g^{-1}	70
CO_2 capture	Adsorption capacity	0.5–5.0 mmol g^{-1}	70
CO_2 conversion	Product selectivity	40–90%, depending on the catalyst	67
Hydrogen evolution	H_2 production rate	0.1–10 mmol g^{-1} h^{-1}	72
Micropollutant degradation	Removal efficiency	>85% for pharmaceuticals	71

6.3 Waste transformation

Waste transformation refers to the conversion of waste into valuable products.[3] The unique surface of natural nanocatalysts and catalyst abilities suggest they could be used to convert agricultural and other wastes into useful compounds.[13] However, research on this is limited in comparison to how they are used to purify water.[13] Lignocellulosic biomass is derived from scrap wood and plants.[52] It is a rich source of renewable carbon, but its complex structure makes it difficult to convert into usable sugars or fuels.[52] The unique surface chemistry and functional groups that enable biogenic nanocatalysts to effectively clean water may also be useful in biomass processing.[15] Current research provides little information about how well biogenic nanocatalysts work to improve biomass.[16] This is an issue that requires further research.[16] A novel approach is to employ leftover farming products to manufacture parts for catalysts, which are compounds that aid in chemical reactions.[14] This creates a mechanism for converting garbage into usable catalysts.[14]

Waste materials such as rice husks can be converted into biochar to aid in the growth of metal nanoparticles, which is consistent with eco-friendly methods already utilised to produce nanoparticles from biological sources. This technology has the potential to reduce the environmental impact of catalyst production while also addressing other sorts of waste. Biogenic nanocatalysts' environmental and energy applications highlight their potential for a variety of sustainable processes.[3] Table 13 summarises representative environmental applications of microbe-engineered nanocatalysts, as well as their performance parameters.

6.4 Critical evaluation and benchmarking of biogenic nanocatalysts

A critical evaluation of the current landscape reveals that while biogenic synthesis offers a sustainable alternative to traditional methods, the field is characterized by a fragmented approach to performance benchmarking. Robust evaluation frameworks, such as those provided by Roy *et al.* (2021), demonstrate that fungi often provide superior surface area through mycelial structures and enhanced particle uniformity, whereas algal systems excel in synthesis speed.[3] For instance, specific bacterial platforms have demonstrated high efficacy in environmental remediation, achieving up to 83.90% removal of Congo red dye using copper nanoparticles synthesized *via Escherichia* sp.[3] However, these unique properties are often offset by significant challenges in process control, including time-consuming culturing processes and inherent difficulties in regulating nanoparticle shape, size, and distribution across different biological scaffolds.[3]

The primary barrier to establishing biogenic nanocatalysts as a standardized technology is the intrinsic variability of microbiological systems, which complicates the reproducibility of physicochemical characteristics.[22] Synthesis mechanisms differ significantly even within the same species, as parameters such as pH, temperature, and precursor concentration dramatically alter the resulting nanoparticle properties.[73] This lack of protocol standardization undermines the ability to conduct systematic performance comparisons. Furthermore, the literature exhibits major deficiencies in several areas essential for rigorous evaluation: there is a notable absence of quantitative catalytic performance comparisons with conventional catalysts using standardized metrics, a lack of cost-*per*-unit-activity economic benchmarking, and a deficiency in long-term stability studies under actual operational conditions.[3]

Also, the lack of comprehensive lifecycle assessments and standardized testing protocols for catalytic activity assessment prevents a meaningful comparison between biogenic and conventional synthesis routes. While biogenic nanoparticles synthesized without high-temperature treatments or additional chemicals present a real alternative to traditional physical and chemical methods, their evolution from laboratory curiosities to industrial solutions is hindered by underdeveloped catalytic benchmarking.[73] Future advancements in the field necessitate the development of quantitative performance metrics and systematic optimization studies that transcend application-specific data to enable a rigorous assessment of biogenic nanocatalysts against state-of-the-art synthetic alternatives.[3] A further limitation lies in the lack of standardized normalization metrics for catalytic activity. In many studies, performance is reported based on the total mass of the bio-organic composite rather than the actual active metal content or accessible active sites. This complicates direct comparison with conventional catalysts, where activity is typically normalized to metal loading or surface area. Additionally, the presence of the bio-capping layer (protein corona) introduces uncertainties in long-term catalytic stability, as its structural integrity under operational conditions (*e.g.*, elevated temperatures or electrochemical potentials) remains insufficiently characterized. These factors

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Table 14 Comparative overview of biogenic and conventional synthetic nanocatalysts based on reported literature trends

Feature/metric	Biogenic nanocatalysts (bacteria/fungi/algae)	Conventional synthetic nanocatalysts	Representative sources
Synthesis conditions	Typically conducted under ambient temperature and pressure using biological reducing agents; minimal use of toxic chemicals	Often require elevated temperatures, pressures, and chemical reductants	3 and 73
Particle size & morphology control	Strongly influenced by microbial species, metabolic activity, and synthesis conditions; size and morphology may vary across systems	Highly controlled using established physicochemical methods with tunable size and shape	3 and 22
Catalytic performance	Reported to be effective across environmental and energy applications, though performance varies depending on system and conditions	Typically optimized for high activity, selectivity, and stability under controlled conditions	3 and 73
Activity normalization	Often reported based on total catalyst mass or composite material; limited standardization across studies	Commonly normalized to metal loading, surface area, or active site density	General literature trend (discussed in this review)
Reproducibility	Can be affected by biological variability, including strain differences and growth conditions	Generally high due to standardized synthesis protocols and controlled environments	22
Surface functionalization	Naturally capped with biomolecules (*e.g.*, proteins, polysaccharides), influencing stability and selectivity	Typically ligand-engineered or uncapped surfaces depending on application	2 and 15
Stability and durability	Often stable under mild conditions, though long-term stability under harsh catalytic environments remains under investigation	Generally well-characterized and stable under a wide range of operating conditions	2 and 3
Scalability	Scale-up is challenging due to biological process control, downstream processing, and variability	Established large-scale production methods with industrial integration	3 and 22

collectively hinder the ability to conclusively determine whether biogenic catalysts outperform synthetic analogues under equivalent conditions. To provide a balanced comparison, Table 14 summarises key differences between biogenic and conventional synthetic nanocatalysts based on general trends reported in the literature, rather than direct one-to-one quantitative comparisons. The comparisons presented are derived from a synthesis of multiple studies and are intended to highlight general characteristics rather than direct one-to-one quantitative comparisons under identical experimental conditions. Variations may arise due to differences in catalyst composition, synthesis protocols, and testing environments.

7 Process development and technoeconomic scaling

The transition of biogenic nanocatalysis from milligram-scale laboratory synthesis to large-scale industrial production remains a major barrier to commercial deployment.[34] Unlike conventional inorganic synthesis routes, biogenic processes are governed by microbial metabolism, enzymatic activity, and physiological stability, introducing additional complexity in process control.[74] Scaling these systems requires maintaining consistent nanoparticle morphology, surface chemistry, and catalytic performance across increasing production volumes. This necessitates precise control over multiple interdependent parameters, including physicochemical conditions (*e.g.*, pH, dissolved oxygen, and nutrient supply), hydrodynamics and mass transfer (*e.g.*, mixing intensity and shear stress), and biological variability associated with microbial growth and secretome composition.[17,22,34] In particular, achieving reproducibility remains a significant challenge due to polydispersity and variability in bio-capping layers across batches.[22,75]

For biogenic nanocatalysts to compete with established industrial processes, technoeconomic analysis (TEA) is essential. Reported trends in the literature suggest that biogenic synthesis routes can reduce capital expenditure (CAPEX) relative to conventional catalytic systems, primarily due to the elimination of high-temperature, high-pressure reactors and energy-intensive infrastructure.[76] However, operating expenditure (OPEX) remains strongly influenced by the cost of culture media, downstream processing, and bioreactor operation, which can limit large-scale economic feasibility.[22]

From a sustainability perspective, process intensification strategies, particularly the use of continuous-flow bioreactors,

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have been proposed to improve space-time yield and reduce the environmental factor (E-factor). Studies suggest that bio-based catalytic systems may achieve significantly lower E-factors compared to conventional chemical synthesis routes, especially when waste-derived feedstocks such as agricultural residues or industrial effluents are utilised as carbon sources.[15,77] These approaches not only enhance resource efficiency but also align with circular economy principles.

From a market standpoint, the competitiveness of biogenic nanocatalysts is increasingly shaped by environmental regulations, carbon pricing mechanisms, and waste management costs. Reduced reliance on toxic precursors and lower hazardous waste generation may translate into economic advantages under strict regulatory frameworks.[77] However, despite these benefits, current biogenic systems often exhibit lower production throughput and greater variability compared to conventional synthetic catalyst manufacturing, limiting their competitiveness in large-scale applications.

Despite their potential, several technical and economic barriers remain. These include the cost and complexity of downstream processing (*e.g.*, nanoparticle purification and partial removal of bio-capping layers), risks of catalyst poisoning or metal leaching during operation, and challenges in maintaining batch-to-batch consistency.[22,77] Furthermore, microbial systems are highly sensitive to environmental fluctuations, which can affect yield, morphology, and catalytic performance. Addressing these limitations will require integrated strategies, including genetic and metabolic engineering to enhance productivity, as well as process standardisation to improve reproducibility and scalability.[34]

Overall, while biogenic nanocatalysts offer clear environmental advantages and promising economic potential, their industrial implementation will depend on achieving a balance between sustainability benefits, process reliability, and cost-effective large-scale production.

7.1 Life cycle analysis (LCA) and sustainability of biogenic nanocatalysts

The application of LCA to biogenic nanocatalysts represents an emerging research field with promising sustainability outcomes but limited comprehensive studies. Chandra *et al.*, 2026 demonstrated that $NiFe_2O_4$ nanoparticles synthesized *via* hydrothermal methods in microbial electrolysis cells significantly reduced electricity-related emissions and improved environmental sustainability across global warming, acidification, eutrophication, and ozone depletion impact categories.[78] Similarly, biogenic nanoparticles derived from microbial processes offer superior environmental compatibility, low cost, and high efficacy compared to conventional synthesis methods, though their LCA analysis revealed some adverse impacts, including contributions to global warming (27.86%), ozone formation (54.64%), and marine eutrophication (98.24%) from agricultural waste feedstocks.[79] Sierra and Ojeda, 2018 found that green synthesis of silver nanoparticles using plant extracts as reducing agents showed decreased environmental impacts compared to traditional synthesis, despite ethanol and silver nitrate remaining critical environmental contributors.[80] However, the fundamental challenges in applying LCA methodology to engineered nanomaterials include the need for comprehensive inventory data, standardized system boundaries, and adequate impact assessment frameworks.[81] Sustainability metrics beyond LCA, including atom economy, E-factor, and energy intensity, are essential for quantitative analysis of nanomaterial synthesis protocols, noting that the term "green" is often used without considering net ecological impact.[82] The field requires more specific evaluation standards and improved database construction to advance from passive evaluation to active sustainable design strategies.[61]

7.2 Toxicity and environmental safety of biogenic nanocatalysts

Biogenic nanocatalysts have emerged as promising alternatives to conventional physicochemical synthesis methods.[3,83] These green synthesis approaches offer significant advantages, including eco-friendliness, cost-effectiveness, low energy requirements, and reduced use of toxic precursor materials.[84,85] The biological synthesis process is simple and serves as a sustainable alternative that addresses environmental concerns associated with traditional nanocatalyst production.[3]

Despite their green synthesis origins, biogenic nanocatalysts exhibit various toxicity mechanisms that require careful consideration. Nanocatalysts applied in industrial processes demonstrate toxicity in both cell and animal models, with specific molecular mechanisms varying between different nanocatalyst types.[86] The primary toxicity pathway involves oxidative stress through the generation of reactive oxygen species (ROS), which affects ecological receptors and organisms.[83,87] Seabra and Duran 2015 specifically address the nanotoxicology of biogenic metal oxide nanoparticles, noting that while these materials show increasing importance, comprehensive toxicity characterization remains necessary for nanosafety considerations.[88] The toxicity mechanisms include cytotoxicity and genotoxicity, with effects linked to the release of free metal ions, dissolution-enhanced toxicity, and direct intercalation with biological targets.[83]

The environmental behavior of biogenic nanocatalysts significantly influences their toxicity profiles. Nanoparticles undergo substantial physicochemical transformations in environmental conditions, with ionic strength, pH, and surface potential strongly affecting their stability and aggregation.[83] These transformations directly impact bioavailability and aging processes, including surface coating effects and interactions with dissolved organic carbon. There are also concerns regarding the accumulation, translocation, and biotransformation of nanocatalysts in food cycles, particularly affecting plants and fish.[89] This bioaccumulation potential represents a significant environmental risk that must be considered in the deployment of biogenic nanocatalysts for water treatment and environmental remediation applications.[70]

Experimental evidence reveals varying toxicity profiles among different biogenic nanocatalysts. Ghosh *et al.*[89] conducted comprehensive ecotoxicological studies showing that

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silver nanoparticles exhibit phytotoxicity at 100 μg ml^{-1} concentrations during lentil germination, while gold and bimetallic alloy nanoparticles demonstrated non-toxic behavior at equivalent concentrations.[90] This research emphasizes the importance of material-specific safety assessment. Ngcongco *et al.*,[85] 2023 notes that cytotoxic effects of biogenic metallic nanoparticles result from their physicochemical properties, but these effects can be mitigated through the use of appropriate capping agents that serve as reducing and stabilizing agents.[85] This finding suggests potential strategies for designing safer biogenic nanocatalysts.

The field faces several critical challenges that require immediate attention. Key obstacles, including safe solvent selection, process parameter optimization, nanomaterial cytotoxicity assessment, bulk production scaling, morphology control, and knowledge deficiencies that currently trap green synthesis largely in the laboratory phase.[84] Therefore, there is a need for detailed studies to determine possible risks posed by the special physical and chemical properties of engineered nanoparticles, calling for a critical evaluation of challenges and future needs for safe environmental nanotechnology.[87] More studies aimed at better characterizing the potential toxicity of biogenic metal oxide nanoparticles for nanosafety and environmental perspectives are encouraged.[88]

Future research must bridge the gap between laboratory-scale synthesis and industrial application by optimizing synthesis factors while maintaining environmental benefits.[84] Also, the integration of Life Cycle Assessment frameworks will be essential to track the environmental fate of these catalysts from microbial synthesis to end-of-life disposal, ensuring that the green advantages of biogenic production are not offset by unforeseen long-term toxicity.

7.3 Future prospects and limitations

Biogenic nanocatalysis is a new technology; implementing it in industry presents certain problems.[3] We need to increase consistency and provide structural stability.[16] The bio-organic corona's inherent complexity offers both advantages and disadvantages.[16] On the one hand, it prevents particles from sticking together, while on the other, it might obstruct the active areas where reactions occur.[16] This may render it less effective than conventional synthetic catalysts.[3] Changes in pH, temperature, and food levels can all have an impact on microbial metabolism, resulting in variances between batches. This is not appropriate for quality monitoring in large-scale production.[11]

To address these challenges, future biogenic catalysts will most likely employ advanced biological techniques. Researchers can boost the production of enzymes by employing genetic engineering to create cell factories, allowing them to make nanoparticles with precise forms and features.[52] Combining these modified microorganisms with process optimisation approaches such as continuous-flow bioreactors and real-time metabolic monitoring can assist in ensuring product consistency over time.[21] Furthermore, specific norms and detailed safety standards are required to meet bionanomaterials' health and environmental safety requirements.[14] The final step in achieving a truly sustainable chemical economy is to link tiny lab findings with large-scale production.[3]

8 Conclusion

Biogenic nanocatalysis is an effective and sustainable alternative to traditional catalytic technologies. Microbial systems can be used as natural nanofactories to synthesise complex catalytic materials under moderate, environmentally friendly settings with fine structural control. This review demonstrates how advances in structure–activity understanding, combined with computational tools like density functional theory (DFT), enable the rational design of highly efficient catalysts for critical green transformations like CO_2 valorisation, water purification, and waste conversion. However, the field remains constrained by significant variability in reported performance metrics and a lack of standardised evaluation protocols. Differences in synthesis conditions, catalyst composition, and testing methodologies often lead to inconsistencies that complicate direct comparison with conventional synthetic catalysts. Addressing these challenges requires systematic studies that integrate synthesis parameters with catalytic performance, alongside the development of standardised benchmarking frameworks. Although large-scale production and fully understanding the complexity of the bio-inorganic interface are still challenges, emerging strategies that combine synthetic biology, machine learning, and advanced characterisation techniques provide a clear path toward scalable and predictable catalyst development. Collectively, these advancements highlight microbe-engineered nanocatalysts as a promising platform for next-generation sustainable chemical synthesis and environmental remediation.

Author contributions

Oluwafemi Adebayo Oyewole: conceptualization, supervision, review and editing; Suleiman Wasilah Rabi: preparation of original draft; Innocent Ojeba Musa: review and editing; Majin Emmanuel Nmadu: preparation of original draft; Naga Raju Maddela: preparation of original draft, review and editing; Kasim Sakran Abass: review and editing.

Conflicts of interest

The authors have no relevant financial or non-financial interests to disclose.

Data availability

Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

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