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Cross-scale design of abiotic–biotic interfaces for semi-artificial photosynthesis

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By coupling semiconductor nanomaterials with living microbes, nanomaterial–microorganism hybrid systems (NMHSs) create powerful biohybrids that unlock new routes for efficient and sustainable solar-to-chemical conversion. Central to the performance of this system is the biotic–abiotic interface, where photoelectrons must efficiently traverse from inorganic materials into complex cellular redox networks. This review highlights recent progress in understanding and engineering these interfaces across three dimensions: material architecture, microbial electron-handling machinery, and interfacial construction strategies. By dissecting how composition, size, and morphology of photosensitizers align with extracellular matrices, transmembrane conduits, and intracellular compounds, we reveal principles for minimizing interfacial resistance and maximizing charge transfer. We further classify interface communication modes into extracellular wiring, transmembrane bridging, and intracellular embedding, and evaluate corresponding construction approaches. By drawing connections between interfacial features and electron-transfer performance, we propose a multidimensional framework that integrates material engineering, microbial adaptation, and interface optimization. This perspective emphasizes the synergistic co-design of both abiotic and biotic components to achieve efficient and stable solar-to-chemical conversion, offering new opportunities for rational design of high-performance NMHSs.

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1 Introduction

In the face of a deepening energy crisis and mounting environmental pressures, efficiently capturing and converting clean resources—especially solar energy—has become paramount for sustainable development.[1–3] Yet, in the life sciences, leveraging light to power microbial metabolism remains a formidable challenge: natural photosynthetic microbes convert under 3% of solar energy into biomass, while industrially optimized strains lack any inherent light-harvesting capability.[4] Semiconductor nanomaterials, prized for their exceptional photon-capture prowess, can drive redox reactions under illumination to emulate natural photosynthesis.[5–7] However, their limited catalytic selectivity constrains both product diversity and value.[2]

To surmount the inherent limitations of both natural and artificial photosynthesis, the NMHSs has emerged by incorporating microbial cells with semiconductor materials, with light-harvesting materials capture photons to generate charge carriers, while microbial metabolisms channel those electrons into value-added chemical production.[8,9] For discussion on NMHSs involving in various solar energy conversion applications, we direct the reader to additional comprehensive reviews.[10,11]

Despite these advances, most NMHSs remain proof-of-concept demonstrations under tightly controlled conditions and deliver overall low solar-to-chemical efficiencies.[12] A major contributor to this performance gap is the biotic–abiotic interface, where the transfer of photoelectrons from the material to cellular metabolism undergoes substantial losses.[13] Although state-of-the-art photosensitizers can convert ~80% of absorbed photons into free carriers,[14] typically fewer than 10% of those electrons ultimately reach intracellular enzymes.[15] This indicates that the dominant losses occur at the interface rather than in light capture. An efficient interface directs photoelectrons into target biological pathways rather than dissipation as recombination or side reactions. Besides, the interface must reconcile the divergent physicochemical needs of the two components, maintaining catalyst stability and favorable charge energetics while preserving cell viability and membrane integrity.[2,16] Taken together, these constraints underscore that

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the interface is not a passive boundary but the central design element that controls the fate of photoelectrons and ultimately dictates the performance ceiling of NMHSs. Consequently, a comprehensive review that systematically elucidates the biotic–abiotic interface is essential for guiding the rational design of semi-artificial photosynthesis systems (SAPSs).

Recently, several insightful reviews have begun to address aspects of the NMHS interface. Our previously published review analyzed the solar-energy flow for NMHSs, discussing light capture, energy transport and conversion process.[10] Although it briefly touched on interfacial electron transfer within the broader context of energy flow, its emphasis remained on system-level energetics rather than the fundamental nature of the interface. Other excellent reviews have highlighted more specialized dimensions of NMHSs operation. For example, one review provided an elegant overview of strategies for coupling materials with the native electron-uptake machinery of electroactive microbes;[17] however, its focus on a specific class of electroactive microorganisms naturally limits the broader applicability of NMHSs, and the crucial influence of material properties design on interfacial behavior was not extensively discussed. Likewise, a recent electron transfer related perspective offered a comprehensive survey of biological, physicochemical, and electrochemical characterization tools, especially advances in spatiotemporal imaging at the single-cell level, yet focused primarily on measurement techniques rather than mechanistic determinants of interface structure and function.[18] Reviews centered on quantum-efficiency analysis have also contributed valuable insights by quantifying the role of interfacial processes in overall energy-conversion efficiency,[19] though these discussions largely address performance metrics rather than the underlying architectural and mechanistic basis of the interface itself. Together, these works have significantly advanced the field, each illuminating a particular facet of NMHSs interfacial behavior. Nevertheless, a unified and cross-scale framework that connects material architecture, microbial electron-handling pathways, and the design principles that govern biotic–abiotic coupling remains missing.

The communication of materials and cells involves the physical contact form and photoelectrons transfer behavior, which originated from the material physico-chemical structure and the microbial electron-handling machinery. Realizing efficient electron flow demands co-design on both material and microbial fronts. On the material side, photosensitizer composition (metal-based semiconductors, MOFs, quantum dots), size (quantum *vs.* meso *vs.* micro),[20–24] and morphology (nanoparticles, sheets, layers, porous scaffolds) govern light absorption, carrier mobility,[25–27] and physical contact with cells.[28,29] On the biological side, extracellular polymeric substances (EPS),[30,31] conductive appendages (*e.g.*, OmcS and OmcZ),[32,33] transmembrane complexes (such as the Mtr cytochromes),[34,35] and intracellular redox cofactors create multistep electron-relay pathways or coupling effect with nanomaterials.[36–38] Beyond the bandgap effects covered in previous reviews, efficiently aligning a material's photophysicochemical properties with microbial binding motifs and electron-shuttle pathways shortens charge-transfer distances and lowers interfacial resistance, thereby maximizing electron-transfer efficiency at the material–cell interface. To date, the relationships between specific semiconductor–microbe interfacial features and their corresponding electron transfer rates remain poorly understood. Unraveling these underlying mechanisms will enable the rational design of NHMSs systems for efficient solar-to-chemical conversion.

In this review, we develop a cross-scale framework for revealing interface design in NMHSs by examining three interwoven dimensions: material architecture, microbial structure, and interfacial construction strategies. First, the influence of photosensitizer composition, size, and morphology—from quantum-confined dots to macro structure—affect cell coupling and charge delivery (Sections 1.1–1.3) were systematically discussed. Next, we dissect microbial electron-handling mechanisms as well as on biohybrid coupling and electrons transfer—extracellular EPS networks, transmembrane conduits, periplasmic relays, and intracellular cofactors—and their structural determinants (Sections 2.1–2.6). Finally, we analyze the above two parts on material and cell communication modes, and classified interface construction and electron transfer modes into extracellular wiring, transmembrane bridging, and intracellular embedding of photosensitizers (Sections 3.1–3.6), comparing physical adsorption, electrostatic/hydrogen binding, and biomineralization approaches. Drawing these threads together, we propose a multidimensional synergistic optimization strategy—combining topology, tailored surface chemistry, and enhanced bio-affinity—to guide the rational design of high-performance NMHSs interfaces.

2 Synergizing material geometry with charge transfer at the interface

In NMHSs, photocatalytic materials generate electron–hole pairs upon exposing to light irradiation. Photoelectrons are subsequently conveyed across the biohybrid interface into microbial cells, enabling intracellular metabolic pathways for the selective production of target molecules.[39,40] Optimizing materials is essential for enhancing charge carrier transport and impacting the system's stability and energy conversion efficiency. Photocatalytic materials function as light-harvesting elements in NMHSs, similar to chlorophyll and other pigments in natural photosynthesis, by absorbing solar energy and transferring it into photogenerated charge carriers. The photoelectrochemical properties of these materials substantially affect the efficacy of solar-to-chemical energy conversion. Effective photocatalysts must exhibit excellent photon absorption and excited-state charge carriers generation ability.[41] Ideal light-harvesting materials should have broad spectrum absorption and high absorption coefficients, enhancing light usage and promoting the generation of excited-state electrons. Inefficient light absorption leads to an initial energy loss that cannot be mitigated by enhanced downstream electron transfer and catalytic mechanisms. If the material components of NMHSs demonstrate inadequate absorption at certain wavelengths, the associated portion of solar energy is not fully

utilized, consequently diminishing the overall light-to-energy conversion efficiency at the interface.[28] Besides, the photostability of these materials is also essential for preserving energy transfer at the interface. Photocatalysts that degrade or undergo structural alterations upon exposure to light may see a gradual decrease in energy capture efficiency, thereby impacting the long-term stability and operational efficacy of the system.[42] Therefore, these characteristics of photocatalysts determine the theoretical maximum for solar-to-chemical energy conversion efficiency at the material–biological interface in NMHSs.

The influence of photoelectrical properties of materials, including photocurrent density, bandgap, and charge carrier mobility on photoelectron generation and subsequent transfer efficiency, have been thoroughly reviewed.[43–47] However, the underlying mechanisms that shape these properties have received far less attention. In particular, how material size and structural characteristics modulate intrinsic photoelectrical behavior and, in turn, dictate the modes by which materials interface with microorganisms remains insufficiently understood. These factors are key determinants of both the resulting photoelectrochemical performance and the efficiency of interfacial electron transfer. This study systematically examines the size (from quantum-scale to mesoscale and microscale) and morphology (including particulate, sheet-like, and layered structures) of photocatalytic materials. It clarifies how their spatial compatibility, contact modes, and mass transport architectures collectively influence interfacial electron transfer networks. Rational interface design that leverages the intrinsic dimensions and structural characteristics of materials is essential for attaining multiscale compatibility and synchronized functionality among modules, thus potentially resolving current efficiency constraints. Consequently, comprehensive analysis and targeted optimization of materials are crucial for advancing NMHSs from theoretical models to practical applications, as well as for attaining efficient and sustainable solar energy conversion. This section will focus on the dimensional and structural parameters of light-harvesting materials, examine their effects on overall system performance, and suggest strategies for enhancing interfacial electrons transfer efficiency.

2.1 Classification of material dimensions and their interfacial characteristics

The solar-to-chemical energy conversion efficiency hinges on two physical parameters: (i) band gap determining spectral utilization and driving force, and (ii) electron transfer efficiency governing carrier utilization at bio–abiotic interfaces.[10] Material size and structure play a crucial role in regulating both parameters. The size scale of materials has a significant impact on their physical properties, interface interaction modes, and electron transfer efficiency. As material dimensions shift from the quantum to the nanoscale, notable changes arise in both physical and chemical properties, observable in several critical domains: quantum-scale materials exhibit pronounced quantum confinement effects. When the dimensions of a semiconductor approach the exciton Bohr radius, the continuous band structure transitions to discrete energy levels. This feature enables precise modulation of the bandgap through size control, thus enhancing light absorption characteristics and electronic structure. Therefore, materials of different sizes exhibit distinct properties in the generation, separation, and transport of photogenerated charge carriers. Material size also has a significant impact on the interactions occurring at the material–biological interface. Quantum-scale materials possess a high specific surface area and numerous surface-active sites, enhancing interfacial interactions with biological components and thereby improving electron transfer efficiency. Minimally small sizes can jeopardize interfacial stability and lead to unwanted side reactions. An increase in particle size results in a decrease in specific surface area, potentially reducing spatial coordination with biological partners. The variations in photoelectrochemical properties and integration modes directly affect the efficiency of photoelectrons transfer at the interface, thus determining the overall performance of solar-to-chemical energy conversion within the system. This section examines how materials of different dimensions, ranging from quantum-scale (<10 nm) to mesoscale (10–100 nm) and macroscale (>100 nm), modulate interfacial electron-transfer behavior during the construction of nanomaterial–microorganism hybrid systems. It highlights how dimensionality governs charge-generation, transport, and coupling modes within the hybrid light-harvesting module.

2.1.1 Quantum-scale materials (<10 nm). Materials at the quantum scale are characterized by dimensions under 10 nm, typical examples such as quantum dots. Quantum confinement effects lead to distinctive electronic and optical properties in these materials, defined by discrete energy level structures and adjustable absorption and emission spectra.[48] In NMHSs, insufficient light-to-energy conversion remains a critical limitation on product yield. Quantum-scale materials exhibit exceptional capabilities in light harvesting and conversion, leading to their extensive application as critical elements in light-harvesting modules. As shown in Table 1, the quantum-scale materials offer distinct advantages in optimizing light absorption and energetic alignment. For instance, CdSe quantum dots (QDs) allow for precise modulation of the bandgap through dimensional control, enabling emission tuning across the visible to near-infrared spectrum to significantly improve solar energy capture.[49] Unlike bulk transition metal oxides, these nanoscale materials can exhibit enhanced redox potentials and increased active site density through surface modification and size tuning, which are critical for driving demanding catalytic reactions.[50] Beyond spectral properties, the dimension of materials profoundly influences charge carrier dynamics. When QD dimensions approach the exciton Bohr radius, photogenerated electrons must travel only nanometer-scale distances to reach the surface, effectively extending charge carrier lifetimes from the nanosecond to the microsecond scale. Furthermore, specific QDs can generate multiple excitons *via* high-energy photon excitation. This "multiple exciton generation" process enables electron multiplication from a single-photon input, significantly improving

Table 1 Classification of material dimensions and their interfacial characteristics

Classification	Material type	Advantages	Binding mechanisms	Ref.
Quantum-scale materials (<10 nm)	QDs	Quantum confinement effect, ultrasmall dimensions, facile surface functionalization	Intracellular self-assembly, internalization/active uptake	52 and 53
	Photosensitizer molecules	High membrane permeability, excellent lipophilicity	Free diffusion	54–56
Mesoscale materials (10–100 nm)	Non-metallic compounds	Size-tunable visible-light response, biosynthetic compatibility	Biomineralization, surface display	13 and 57
	Metallic compounds	Bandgap engineering for enhanced light harvesting & charge separation, carrier design balances catalytic activity and biosafety	Adsorption *via* carrier micropores, electrostatic adsorption, covalent bonding	15 and 58–61
	Metal nanoparticles	Surface plasmon resonance effect enabling photothermal-catalytic synergy	Internalization/active uptake	62–64
Micrometer-scale materials (>100 nm)	MOFs	Tunable porous architecture enabling compartmentalized encapsulation of semiconductors/microbes	*In situ* self-assembly, electrostatic adsorption, covalent bonding	65–68
	Carbon-based composites	Exceptional biocompatibility and environmental sustainability	Electrostatic adsorption, covalent bonding	69–71
	Conjugated organic polymers	Inherent multiple electron donor–acceptor units, strong membrane affinity *via* hydrophobic/π–π interactions	Surface self-assembly, electrostatic adsorption	72–74

photocurrent densities when integrated into biohybrid systems.[51]

Previous studies have synthesized various core–shell QDs with tunable band gaps, leveraging the unique properties of quantum-scale materials, and spanning excitation energies from ultraviolet to near-infrared ranges. QDs were coupled with targeted enzyme sites in bacteria *via* chemical bonding and self-assembly. Upon exposure to light, photoelectrons from QDs are transferred to bacteria, which subsequently utilize substrates including carbon dioxide, nitrogen, and water to synthesize valuable products such as isopropanol, 2,3-butanediol, and methyl ketones.[75] The benefits of quantum-scale materials in surface redox reactions have been extensively utilized in battery technologies. The modification of graphene using carbon QDs enhances the specific capacity of lithium and sodium-ion batteries, leading to improved performance compared to conventional graphene-based batteries.[76] NMHSs leverage the electronic properties of quantum-scale materials, facilitating the rapid transfer of photoelectrons to low-potential biological catalytic centers, thereby improving the efficiency of light-harvesting modules.

Besides, the small size of quantum-scale materials shortens the distance for electron delivery to biological catalytic sites, enabling their internalization by bacteria and allowing direct interaction with intracellular electron-transfer chains (such as hydrogenase active centers). Such dimensions not only facilitate physical proximity but also enhance quantum confinement effects, which can increase charge-carrier density and improve the driving force for photoelectron injection into biological redox cofactors. For example, the design of gold nanocluster/organic semiconductor heterostructures (AuNC@OFTF) provides dimensions suitable for penetrating bacterial cells and interacting directly with the thylakoid membrane. The resulting efficient photoelectron injection into photosystem II leads to markedly enhanced photocurrent relative to conventional systems.[62] Similar strategies have been demonstrated using CdS@ZnS quantum dots for specifically binding to the nitrogenase in the *Azotobacter vinelandii* and *Cupriavidus necator* bacteria.[75] These particles establish close contact with intracellular redox centers of PSI/PSII components and metabolic enzymes, thereby enabling multistep intracellular photoreducing cascades and improving solar-to-chemical conversion efficiencies.

Despite their potential, the inherent limitations of quantum-scale materials—including aggregation, structural instability, and cytotoxicity constrain their broader applicability in hybrid systems.[77] The extremely small size of QDs also makes them prone to aggregation, which decreases the availability of active sites and compromises the long-term stability and performance of the hybrid system. In addition, many QDs contain heavy metal components, and the gradual release of metal ions can induce cytotoxic effects, including oxidative stress, cell-cycle arrest, and even cell death.[20] While surface modification has been employed to enhance the dispersion of QDs in aqueous solutions to inhibit aggregation, the ligand and penetration of cell membrane is also toxic to bacteria.[54] Future research will focus on the development of core–shell materials to enhance biocompatibility, reduce biological toxicity, and further

optimize quantum dot dispersion through more biocompatible surface modification techniques. The challenges associated with quantum-scale materials underscore the importance of exploring other material classes. Mesoscale materials, with greater structural stability, provide a natural next step for enhancing hybrid system performance.

2.1.2 Mesoscale materials (10–100 nm). Mesoscale materials refer to those with dimensions ranging from 10 to 100 nm. Inorganic substances (like CdS and InP), metal oxides (like TiO_2, ZnO, and Fe_3O_4), and metallic nanoparticles (like Au, Ag, and Cu) are a few examples. These mesoscale materials strike a balance between the structural stability of microscale materials and the high surface area of nanomaterials, enabling both biocompatibility and efficient light harvesting, which underpins their widespread application in NMHSs.[13,78,79] For example, mesoscale gold nanoparticles exhibit significant surface plasmon resonance (SPR) effects, enhancing local electromagnetic fields and substantially improving light absorption, particularly within the visible to near-infrared spectrum (*e.g.*, 520–800 nm). This characteristic can markedly enhance overall light-to-energy conversion when integrated with NMHSs.[80] This benefit also presents drawbacks, as SPR may induce local warming under intense light, potentially detrimental to microbial activity. To mitigate this issue, integrated thermal dissipation structures may be necessary. To achieve broadband absorption and efficient charge separation, strategies such as heterojunction engineering (*e.g.*, $BiVO_4/WO_3$) and multilevel pore architectures (*e.g.*, mesoporous TiO_2) are commonly utilized.[2] Integrating these materials with microorganisms further shortens electron transport pathways and enhances charge separation efficiency.[81,82] As illustrated in Table 1, these materials significantly enhance charge carrier mobility by promoting long-range electron transport through conductive networks or crystalline grain boundaries within their frameworks. The surfaces of these porous structures often exhibit a high density of defect states, such as oxygen vacancies in TiO_2, which can facilitate electron injection into biological receptors *via* tunneling effects and serve as electron traps, resulting in significantly enhanced tunneling efficiencies compared to microscale structures. Dopants such as carbon or nitrogen can enhance their activity within the visible spectrum, despite their intrinsic light absorption typically being confined to the ultraviolet range (below approximately 380 nm).[83] Additionally, typical mesoscale CdS nanosheets possess a moderate bandgap of ~2.4 eV, allowing efficient absorption of visible light. Their high carrier mobility facilitates rapid photoelectron transport, enhancing overall photoelectron generation efficiency. Furthermore, the increased surface area at the mesoscale provides a greater number of active sites for interfacial charge transfer. Studies have shown that acetate-producing bacteria can self-photosensitize by biomineralizing CdS on their surfaces. Upon light exposure, the activated CdS generates photoelectrons, which are transferred into the bacterial cells to drive the conversion of carbon dioxide into acetic acid.[11] In this regard, mesoscale materials are more appropriate for scalable applications compared to quantum-scale materials due to their advanced synthesis methods, cost-effectiveness, and superior light-harvesting efficiency relative to microscale materials.[21]

Despite their broad potential, mesoscale materials used in NMHSs face several intrinsic challenges that constrain stability and solar-to-chemical conversion efficiency. First, photostability remains a key bottleneck. Metal-based semiconductors such as CdS are prone to photocorrosion under illumination, leading to the release of metal ions that can cause biological toxicity and disrupt long-term operation. Second, the rapid recombination of photoelectron–hole pairs limits carrier availability for microbial uptake, fundamentally restricting the energy conversion efficiency of NMHSs.[84] Mesoporous heterojunctions (*e.g.*, $BiVO_4/WO_3$) illustrate enhanced coupling light harvesting, charge separation, and transport within a spatially coordinated architecture promote directional electron flow toward microbial redox proteins such as cytochromes.[85] We refer to this enzymatic example because molecular-level electron-transfer pathways are more explicitly resolved in enzyme–nanoparticle systems, providing mechanistic insights that are directly translatable to the design of biotic–abiotic interfaces in whole-cell NMHSs. This indicates the heterojunctions architecture facilitates directional electron flow toward biological membrane receptors, including cytochrome c6, driven by the interfacial potential difference. Limitations arise from synthesis precision, structural instability, and mismatches between pore sizes and biomolecules or whole cells, which can restrict reactions to surface interactions. Moreover, high specific surface areas often introduce surface defects, such as dangling bonds, that reduce catalytic activity or accelerate charge carrier recombination (*e.g.*, *via* surface states in TiO_2).[86]

Addressing these issues requires material designs that provide stable, well-defined heterojunctions and pore structures compatible with biological components, providing a pathway to more effective integration with mesoscale materials in NMHSs. Additionally, efforts could be directed towards refining the design of the material–biological interface to optimize electron transfer pathways, such as used the redox mediator for facilitating the interfacial electron transfer. Furthermore, surface passivation, interface engineering, and defect regulation can suppress recombination and improve biocompatibility.[10,87] More broadly, integrating mesoscopic architectures with quantum-scale sensitizers or microscale porous networks may enable multiscale complementarity, enhancing charge generation, separation, and utilization across the biotic–abiotic interface.

2.1.3 Micrometer-scale materials (>100 nm). Materials sized from a few hundred nanometers to tens of micrometers (0.1–100 μm) are commonly classified as micrometer-scale materials. Classical continuum mechanics primarily dictates their physical properties. Nonetheless, these materials can exhibit unique functional properties through deliberate micro/nano structural design.[88] Micrometer-scale materials are commonly employed in NMHSs due to their enhanced mechanical stability, structural uniformity, and potential for large-scale production. Biological systems receive robust physical support from these materials, which exhibit greater

resistance to microbial metabolite degradation compared to those at quantum and mesoscopic scales, thereby extending the system robustness.[89] Mechanical stability is a critical metric that maintain its structural and functional integrity under external stresses, which is crucial for the long-term and efficient energy conversion in interfacial energy transfer systems. Enhanced atomic connections within the material at the micrometer scale reduce performance degradation by improving structural resilience to physical stress, thermal variations, and chemical disturbances.[90,91] Moreover, the enhanced structural homogeneity of micrometer-scale materials reduces the effects of surface defect randomness and quantum confinement. Traditional synthesis techniques enable precise control over size, shape, and surface properties, ensuring uniform light absorption, charge separation, and catalytic performance. This significantly enhances the stability and reproducibility of the system.[92] Furthermore, micrometer-scale materials exhibit enhanced spatial assembly capabilities. Hierarchical structures that facilitate light harvesting, optimize mass transfer, and coordinate reaction site spatial arrangement can be constructed through advanced microfabrication techniques. Quantum and mesoscopic materials are constrained in their integration into multifunctional modules due to their small size, which increases susceptibility to aggregation, and the challenges associated with precise spatial organization.[93] The macroscopic characteristics of materials at the micrometer scale provide distinct advantages in the context of material–biological interactions. Cyanobacteria and other microorganisms can be accommodated by their large pore structures (100–500 nm), facilitating three-dimensional encapsulation with porous silicon microspheres.[94] The imitation of natural photosynthetic membranes with enhanced light-scattering properties significantly enhances light absorption efficiency.

In NMHSs, these advantages of micrometer-scale materials are exemplified across a variety of widely used photocatalysts, including carbon-based composites, MOFs, perovskite microcrystals, and semiconductor microspheres. For instance, MOFs-constructed from the self-assembly of metal ions or clusters with organic ligands—possess abundant surface oxygen vacancies that enhance photon capture and facilitate electron transport, while their micrometer-scale frameworks provide superior mechanical robustness against environmental perturbations.[95] Similarly, strengthened interlayer interactions in micrometer-scale g-C_3N_4 improve its structural integrity and photostability.[96] InP, another representative photosensitizer, benefit from inhibited aggregation and sustained long-term performance when uniformly dispersed within larger host matrices.[97] Collectively, these examples highlight how micrometer-scale architecture not only enhances mechanical stability and defect tolerance but also enables more reliable optical and catalytic performance, reinforcing their essential role in constructing durable and high-efficiency NMHSs. Notably, the processability of micrometer-scale materials makes them suitable for large-scale industrial production, offering a significant advantage for the practical implementation of micrometer-scale materials based NHMSs. In industrial manufacturing, such systems often require uniform coverage across extensive carrier surfaces. Micrometer-scale materials can be evenly deposited onto diverse substrates through simple and efficient techniques such as spin-coating, spray-coating, and doctor-blading, thereby forming continuous functional coatings. For example, solution-based spin coating can be employed to produce NMHSs utilizing conjugated polymers like PPy/PFP/PDI, resulting in large-area uniform films. These coatings enhance overall light-to-energy conversion efficiency by closely integrating with biological processes while also offering remarkable mechanical strength and flexibility.[72–74] The conjugated polymer chains contain multiple electron donor and acceptor units, which generate excited states that enhance charge separation and transport upon photoexcitation.

However, the application of micrometer-scale materials in NMHSs still presents several non-negligible limitations. The significantly reduced specific surface area presents a substantial challenge. The surface area is a significant factor influencing the interaction between catalysts and reactants. In NMHSs, an increased surface area leads to a higher number of active sites for charge transfer, thereby enhancing photocatalytic activity. As shown in Table 1, the proportion of surface atoms decreases with increasing material size into the micrometer range, resulting in a significant number of atoms being located in the bulk phase and thereby reducing the availability of accessible active sites for charge transfer. SiO_2@MoS_2 composites exhibit numerous surface-active sites at the quantum and mesoscopic scales; however, their activity diminishes at the micrometer scale due to a reduced availability of surface atoms.[11] Extended charge transport distances represent a significant limitation. The reduced photocatalytic effectiveness is attributed to the increased distance that photogenerated carriers must traverse to reach the surface, thereby elevating the likelihood of recombination at defect or impurity sites.[98] Direct electron transfer with intracellular receptors is often impractical because of size limitations, typically necessitating the involvement of redox mediators.

To overcome these limitations, multilevel porous structural designs can be employed for further optimization. Hierarchical porous structures refer to material systems that simultaneously contain micropores, mesopores, and macropores, and their rational design serves as an important strategy to enhance light-harvesting capabilities and improve photocatalytic efficiency. For example, in MOF-based NMHSs, hierarchical MOFs can be obtained by tuning synthetic conditions. Macropores function as transport channels for bulk reactant molecules and can also host photosensitizers such as porphyrin derivatives, thereby facilitating rapid diffusion of reactants into the mesoporous and microporous regions where catalytic active sites are located. In addition, the multiple scattering and reflection of light within hierarchical pores significantly strengthen the light-harvesting capacity of MOFs, promoting the generation and separation of photogenerated charge carriers and ultimately enhancing photocatalytic performance.[99–101] Employing conductive biofilms to construct electron "highways" represents another important optimization strategy. Conductive biofilms, which are secreted by microorganisms and possess intrinsic electrical conductivity, can efficiently transport electrons and

reduce the recombination probability of photogenerated charge carriers.[102] Integrating conductive biofilms with microscale photocatalysts can provide efficient pathways for photogenerated electron transport. For photocatalysts such as PFP/PDI conjugated polymers and rRO, coupling with conductive biofilms significantly enhances their charge-transfer performance and overcomes the inherent limitation of long charge-migration distances at the microscale, thereby improving the overall efficiency.[22–24] Together, these strategies enhance both mass diffusion and electron transport, thereby reinforcing the overall efficiency and robustness of micrometer-scale materials based NMHSs.

2.2 Material architecture and interfacial properties

Recent studies highlight that the three-dimensional (3D) topology of materials strongly affects photogenerated charge carrier dynamics, including separation, transport, and recombination. Quantum confinement and surface state distributions largely govern these effects. Material topology also influences the spatial organization and metabolic activity of biological components. This influence is mediated by interfacial chemical features (*e.g.*, functional group type, charge distribution) and physical morphology (*e.g.*, pore size, surface roughness).[29] The structural parameters collectively influence the overall energy conversion efficiency of NMHSs. Hierarchically porous MOFs featuring integrated micro-, meso-, and macropores enhance light absorption *via* confinement effects. Additionally, surface-exposed carboxyl groups facilitate site-specific immobilization of carbon fixation enzymes, thereby significantly improving the coupling efficiency of CO_2 reduction pathways.[103] While this study was conducted on enzyme–nanoparticle hybrids, the underlying principle of utilizing surface carboxyl moieties to anchor catalytic proteins provides a valuable design strategy for NMHSs, potentially facilitating the binding of microbial outer membrane proteins to reduce interfacial transfer resistance. This section systematically examines how material morphology influences electron transfer across the material–biological interface, building on the previous analysis of size-dependent effects and interfacial structure in nanomaterials. We propose a multidimensional co-optimization framework that integrates recent research advances, coordinating topological design, surface chemistry, and biological compatibility to improve light-to-energy transduction in NMHSs.

2.2.1 Particulate architectures. Particulate materials, such as nanoparticles (NPs), TiO_2, and QDs, are widely employed for light-harvesting in NMHSs due to their high dispersibility, tunable sizes, and pronounced surface effects. Their structural scale closely matches that of biological macromolecules, including enzymes and membrane proteins (Fig. 1). This enables two key interactions: effective anchoring to microbial membrane *via* surface functional groups (carboxyl, amino, *etc.*) or intracellular internalization of microorganism. This specific positioning minimizes electron-transfer distances to the nanometer scale. Additionally, the increased specific surface area of the particles enhances the density of active sites for interaction with redox compounds, thereby facilitating an efficient pathway for photoelectrons to biological partners. Gold nanoparticles (Au NPs) exhibit a localized surface plasmon resonance (LSPR) phenomenon that significantly enhances light absorption and hot electron generation within the visible to near-infrared spectrum. By attaching Au NPs to intracellular engineered protein condensates (functioning as artificial membranelles organelles within living bacteria) through engineered protein tags, the system enables the direct transfer of photoelectrons to proximal hydrogenases. This intracellular spatial organization significantly enhances solar-driven hydrogen synthesis in whole-cell hybrid systems.[104] Particulate materials can also establish efficient interfaces with microbes through diverse coupling strategies. QDs, for instance, can be internalized by cells *via* endocytosis, enabling precise modulation of microbial metabolism. For example, $CuInS_2$/ZnS QDs into the cytoplasm of electroactive bacteria, have successfully achieved hydrogen generation under visible light.[105] Similarly, hydrothermally synthesized iodine-doped carbon materials featuring negatively charged surfaces exhibit strong adhesion to microbial surfaces *via* electrostatic interactions.[70] This "plug-in" hybrid system reduces interfacial contact resistance and enables non-photosynthetic microorganisms to generate hydrogen with high quantum efficiency.

However, particulate architectures also present distinct challenges. Due to their irregular shape, attaching or uptake of particles can induce changes in membrane permeability, potentially leading to metabolic disturbances or cell cycle arrest.[106,107] Additionally, the high surface energy of particles makes them prone to aggregation; for example, Au NPs tend to spontaneously aggregate into micron-scale clusters in solution, which significantly reduces the density of active sites for charge transfer.[108] Therefore, surface chemical modifications and dispersion optimization are critical to ensuring the long-term stability and biocompatibility of particulate NMHSs. Certain researchers have employed protective coatings, such as SiO_2 or polydopamine, on particulate structures to form core–shell structures, thereby addressing their limitations. The design of heterointerfaces and shell encapsulation effectively addresses issues related to aggregation, toxicity, and inadequate photostability commonly observed in traditional particles. Core–shell CdS@TPPA nanospheres were synthesized through the *in situ* growth of a covalent organic framework (COF) shell layer on the surface of CdS nanospheres. The confinement effect of the porous shell facilitates precise regulation of reactant transport pathways, thereby enhancing photocatalytic selectivity.[109] In NMHSs, composite materials such as CdS@Mn_3O_4 are formed through the deposition of Mn_3O_4 onto the surface of CdS. Co-assembly with *Thiobacillus denitrificans* resulted in superior nitrogen fixation under light conditions. The Mn_3O_4 shell acts as a protective buffer layer, preventing photodegradation of the photocatalyst and mitigating the effects of reactive oxygen species (ROS) generated on the CdS surface. This significantly reduces oxidative damage and improves long-term system stability.[25] The fabrication of core–shell structures typically requires careful multi-step management, and interfacial defects can increase charge carrier recombination rates. Additionally, excessively thick shells can hinder mass diffusion and light

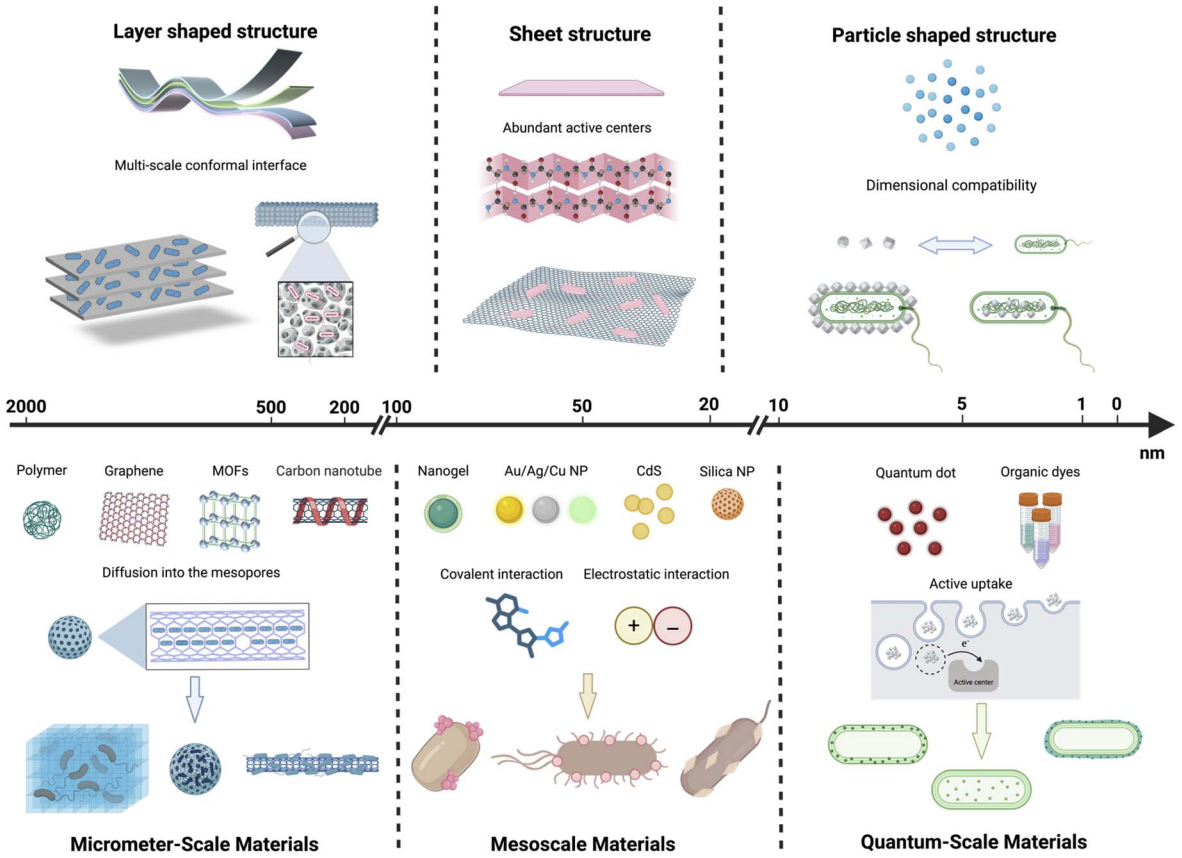

Fig. 1 Material architecture and interfacial properties. Based on the material dimensions, this figure illustrates the binding modes between materials and microorganisms categorized by scales (>100 μm for micro-scale, 10–100 nm for mesoscale, and <10 nm for quantum-scale). It also compares the structural advantages of different material shapes when combined with microorganisms, accompanied by schematic diagrams showing materials bound to bacteria.

penetration. Improving shell porosity is essential to balance protective effects with mass transfer requirements. Future applications of dynamic self-assembly methods may enable the development of adaptive core–shell interfaces, enhancing both material stability and energy transfer efficiency at the material–biological interface.

2.2.2 Sheet-like architectures. Two-dimensional (2D) sheet-like materials, including graphene nanosheets, bulk MoS_2, and black phosphorus, exhibit significant potential in NMHSs owing to their distinctive planar structures. The materials possess ultra-high specific surface areas that provide numerous catalytic sites, and their atomic-level thickness enhances charge carrier mobility, thereby promoting efficient separation and transport of photoelectron–hole pairs.[110] The planar extension of 2D materials at the material–biological interface offers a low-resistance pathway for lateral electron migration, thereby minimizing carrier transport distances and improving overall electron transfer efficiency. As shown in Fig. 1, semiconducting nanosheets like MoS_2 and WS_2, characterized by tunable band structures and numerous edge-active sites, are commonly utilized in the development of biohybrid platforms. MoS_2 can establish strong interactions with microbial membrane proteins through sulfur vacancies, facilitating direct and efficient electron transfer.[10] Edge defects directly engage in proton-coupled electron transfer, thereby enhancing light-driven metabolic reactions. Graphene nanosheets can anchor photosensitizers, such as porphyrins, *via* π–π conjugation, facilitating high-efficiency hydrogen evolution under visible light. In addition, the sulfur edges of MoS_2 serve as active sites for charge transfer, and their combination with nitrogenase markedly increases the rate of photoelectronic nitrogen fixation.[111,112] Graphitic g-C_3N_4 nanosheets possess atomically flat surfaces and in-plane conjugated structures, which facilitate directional charge transport and interlayer electron transfer. The lateral dimensions of 2D sheets, exceeding 10 μm, align well with the size of microbial cells, which range from 1 to 10 μm, thereby providing significant spatial compatibility.[113] Additionally, stacked 2D layers create multidimensional porous networks that enhance metabolite diffusion and replicate biological membranes, thereby offering a continuous matrix for the transport of photogenerated charges.[114] This design sustains microbial viability and preserves long-term interfacial cooperation. A multilayered MoS_2 nanosheet structure was synthesized on the surface of *Raoultella planticola*, yielding a biohybrid system that exhibits improved microbial metabolism and electron transfer capacity, which resulted in a notable enhancement in the biodegradation efficiency of methyl orange dye.[115] Besides, the multilayered structure enhanced surface area,

facilitated light scattering, and improved light-trapping efficiency, thereby extending the optical path and increasing light absorption. These factors collectively diminished charge transfer resistance, improved electron migration efficiency.

Excessive epitaxial growth of 2D sheets may decrease the density of edge-active sites, thereby reducing the capacity for enzyme or bacterial loading. As shown in Fig. 1, robust interlayer van der Waals interactions frequently lead to aggregation, thereby constraining the effective surface area.[116] This challenge can be addressed through surface functionalization, such as carboxylation, or intercalation strategies, including the introduction of carbon QDs to inhibit restacking.[26] For example, graphene/MoS_2 heterojunctions have been developed to address the low density of planar active sites, combining the high conductivity of graphene with the catalytic properties of MoS_2.[117] These combinations increase carrier lifetime while enhancing both efficiency and stability. Another promising method involves defect engineering, specifically the introduction of nitrogen-vacancy through plasma treatment, which enhances the density of edge-active sites and improves the catalytic performance of 2D materials.[118] Besides, mechanical fragility presents a significant issue; ultrathin layers are vulnerable to structural damage during prolonged operation, and certain materials are prone to oxidative degradation in humid conditions.

2.2.3 Layered architectures. Layered materials, including two-dimensional metal–organic layers (MOLs), layered perovskites, and layered double hydroxides (LDHs), have garnered considerable interest in NMHSs owing to their distinctive multiscale structural compatibility with microorganisms. The materials exhibit nanometer-scale thickness for each layer and micrometer-scale lateral extension, facilitating accurate interface engineering. Their single-layer thickness aligns with biomolecules like cytochrome c_6, facilitating interlayer gaps that can anchor enzyme active sites and create biomimetic electron transfer channels. As shown in Fig. 1, their lateral dimensions create multiscale contact interfaces that diminish interfacial shear stress through layer-by-layer flexible attachment. The micropores between MOLs have been shown to selectively confine enzymes in hybrid catalysts, resulting in a 'light harvesting–catalysis' integrated interface.[119] For NMHSs, this confinement strategy offers a blueprint for designing interfaces that can stabilize and electrically connect microbial extracellular redox enzymes or nanowires within layered material scaffolds.

Layered perovskites utilize organic cations, such as phenylethylamine, to adjust interlayer spacing, which enhances carrier transport and reduces the recombination of photogenerated charges.[120] LDHs feature positively charged layers that electrostatically adsorb negatively charged microbial membranes, thereby facilitating direct extracellular electron injection into the microbial photosynthetic chain and promoting efficient coupling of light-driven CO_2 reduction with microbial metabolism.[121] A representative study involved the construction of a Z-scheme NMHSs utilizing Mo-doped $BiVO_4$ modified with RuO_2 ($BiVO_4$:Mo|RuO_2) as the light-absorbing component, combined with hydrogenase or formate dehydrogenase.[105] The system effectively accomplished overall water splitting and CO_2 reduction under light irradiation. The stepwise energy band alignment markedly improved interfacial electron transfer and decreased the time necessary for electron delivery into microbial cells. Materials with high biocompatibility, such as polydopamine (PDA), have also been utilized to improve the stability of material–biological interfaces. The catechol moieties of PDA demonstrate a specific binding affinity for microbial exopolysaccharides, resulting in the formation of a controllable bio-adhesive layer. NiO nanosheets coated with PDA (NiO@PDA) exhibit strong adhesion to nitrogen-fixing bacteria (*Azotobacter vinelandii*), facilitating uniform bacterial immobilization.[122] This biohybrid system utilizes the PDA layer as a bioadhesive, charge transport channel, and protective barrier, thereby preserving microbial viability in complex reaction environments, capabilities seldom realized with single-function materials. An electroconductive biofilm was developed through the genetic modification of *Escherichia coli* to secrete extracellular matrix components, which acted as a scaffold for the *in situ* oxidative polymerization of PPy.[123] A self-supporting Z-scheme photocatalytic system was constructed by depositing photocatalysts onto glass substrates and conducting thermal annealing, thereby effectively integrating biological and inorganic components *via* a stable and conductive interface.

Despite their structural benefits, layered materials present significant implementation challenges. From a synthesis perspective, precise control over interlayer chemical bonding is often required, resulting in complex and costly fabrication processes. Operational stability is another concern; for example, layered perovskites tend to delaminate or undergo structural collapse when exposed to high humidity (>60%) or prolonged illumination. Therefore, developing effective surface passivation strategies is essential for improving their durability in aqueous biological environments.[124] In addition to stability issues, mass transport and active site accessibility often restrict the performance of layered architectures. Excessive layer thickness in conjugated polymers (*e.g.*, PPy, PFP) can inhibit microbial activity and undermine system stability, while tight interlayer stacking may limit substrate access to catalytic sites. For instance, the utilization efficiency of edge sites in LDHs is often less than 30%.[125] To overcome these limitations, strategies such as intercalation, exfoliation, or biomimetic mineralization, which dynamically modulates interlayer spacing using biological molecules, have been proposed to maintain structural integrity while enhancing charge transfer at the material–biological interface.[27]

2.3 Research status and challenges

The energy transfer chain in NMHSs, which includes light harvesting, transmembrane transport, and metabolic conversion, demonstrates notable efficiency losses at the material–biological interface. In standard systems, the quantum efficiency of light capture can surpass 80%; however, the efficiency of transmembrane electron transfer significantly declines to only 15–30%, with the ultimate metabolic conversion efficiency frequently dropping below 10%.[126] The energy loss cascade is

mainly due to charge recombination at the material–biological interface. During the material synthesis process, gradient band engineering strategies, such as $ZnO/TiO_2/CdS$ heterojunctions, can significantly decrease interfacial charge recombination rates by 2–3 orders of magnitude.[127] However, there is still no guidance for the rational design of cross-species electron transfer pathways to mitigate energy loss. Unlike enzyme-based hybrids where active sites are exposed and defined, whole-cell NMHSs face greater challenges due to the insulating nature of cell membranes and the complexity of transmembrane electron transport, necessitating more robust interface engineering strategies.

From a materials-design perspective, the transition from quantum-scale to microscale structures introduces additional limitations. Enlarged particle size causes an exponential decline in specific surface area and active contact area, resulting in reduced light absorption, extended charge-carrier transport distances, and weakened interfacial coupling. For instance, QDs exhibit specific surface areas ranging from 300 to 500 $m^2 g^{-1}$, whereas micron-sized MOFs generally have surface areas under 100 $m^2 g^{-1}$.[128] The diminished material–microbe contact area further impairs electron-transfer efficiency and increases interfacial impedance.[129] To address these challenges, multiscale material-engineering strategies including hierarchical pore design and surface nano structuring, such as decorating micron-sized particles with quantum dot arrays, which partially compensate for surface area loss through mesoscopic-scale engineering.[130] Nevertheless, such composite structures may introduce new issues, including additional interfacial defects and enhanced carrier recombination. Future efforts must integrate cross-scale simulations with dynamic interface engineering to rationally regulate the spatial distribution of active sites while ensuring mechanical robustness and manufacturing feasibility. Beyond these structural considerations, NMHSs also face significant cost and stability constraints. High-efficiency solar-assisted photoelectrochemical systems still rely predominantly on noble-metal-based light-harvesting components, where precious metal catalysts account for 60–80% of the total system cost. In terms of durability, NMHSs synthesized by solution-phase methods often exhibit marked performance degradation after 100 hours of continuous operation.[131] Although techniques such as atomic layer deposition (ALD) can generate uniform protective coatings that mitigate photocorrosion, their complex fabrication procedures may increase device costs by a factor of 4–5.[132] Achieving a balanced integration of material stability, microbial viability, and scalable manufacturing therefore remains a major bottleneck to industrial deployment.

Despite these advances in multiscale material design, achieving a balanced integration of stability, microbial compatibility, and scalable manufacturing remains a central barrier to the practical deployment of NMHSs. These limitations highlight that improvements in material architecture alone are insufficient; rather, coordinated progress on both the materials and biological fronts is essential for further enhancing system performance. The synergistic integration of material engineering and microbial genetic engineering, involving the coordinated modulation of material composition, structural hierarchy, and interfacial organization, has already enabled certain NMHSs to achieve solar-to-chemical conversion efficiencies of 3–5%, representing a substantial improvement over the historical benchmark of ~1%.[11] Reaching efficiencies comparable to natural photosynthesis, however, requires breakthroughs in three key areas: (1) elucidating and engineering charge-transfer dynamics at the material–biological interface with atomic-scale precision, supported by cross-scale energy-transfer models; (2) developing photosensitizers that couple biomimetic functionality with environmental safety to overcome efficiency—toxicity trade-offs; and (3) establishing integrated R&D platforms that combine computational design, automated synthesis, and *in situ* characterization for the precise co-optimization of materials and living systems. Moving forward, the convergence of synthetic biology and artificial intelligence will require NMHSs research to transcend traditional structure–property paradigms. Future optimization frameworks must operate across quantum, mesoscopic, and microscale dimensions, while integrating knowledge from synthetic biology, computational materials science, and systems-level modeling. Such multidisciplinary strategies will be crucial for advancing NMHSs toward high efficiency, long-term durability, and scalable industrial application.

3 Microbial structural characteristics determine the efficiency of photoelectron utilization

Photoelectron generation is a crucial characteristic of photocatalytic materials; however, their effective utilization is significantly influenced by the capacity of microorganisms to capture and convert these electrons. In heterologous systems that include photocatalysts and microorganisms, photoelectrons must surmount several barriers prior to being effectively acquired and utilized by microbial cells.[19,133] This process is affected by various factors, such as the transfer efficiency of photoelectrons,[134] the electron transport properties of microbial surfaces,[135] and the intracellular capacity for exogenous electron assimilation *via* metabolic pathways.[136] Variations in interfacial formation, electron transfer mechanisms, and metabolic conversion capabilities primarily account for the differences among microbial species in their ability to utilize photoelectrons. The characteristics offer essential theoretical foundations for the design of NMHSs. An in-depth comprehension of the structural characteristics of various microbial types can inspire the optimization of transfer pathways and enhance energy conversion efficiency substantially.

In the construction of heterojunction electron transfer interfaces, microbial extracellular components and transmembrane structures exhibit synergistic roles that fundamentally affect the binding affinity between microbes and materials, along with the efficiency of interfacial electron transfer. Extracellular structures, including EPS, flagella, and outer membrane proteins, enhance microbial adhesion to material surfaces, facilitate the construction of stable conductive

networks, and modulate the local microenvironment, thereby promoting sustained and efficient extracellular electron transfer. Functional groups in EPS, including hydroxyl, carboxyl, and amine moieties, are capable of forming hydrogen bonds, electrostatic interactions, or covalent bonds with material surfaces, which enhances the efficiency of cross-interface electron transfer.[137–140] Transmembrane structures, including the Mtr complex (an outer-membrane cytochrome complex involved in extracellular electron transfer in *Shewanella* species), outer membrane vesicles (OMVs), and specific ion or metal transport channels, are crucial for facilitating efficient electron transfer across cellular membranes while preserving the electrochemical stability of the cells.[141–143] Active transport processes (*e.g.*, substrate uptake and secretion systems) and metal ion transport mechanisms can enhance microbial responsiveness to material stimuli and may facilitate the *in situ* synthesis of nanomaterials or the stabilization of heterogeneous interfaces. The interaction between extracellular and transmembrane mechanisms creates a functionally diverse and biologically adaptable material–biological hybrid interface, presenting a promising approach to improve photo-electronic coupling efficiency in NMHSs.

Heterologous electron transfer across the interface can be categorized into five distinct functional pathways: extracellular, transmembrane, periplasmic, inner membrane, and intracellular pathways. Each pathway has a specific function in electron transport and energy utilization, characterized by varying transfer potentials. The extracellular pathway primarily entails direct electron transfer (DET) or mediated electron transfer (MET) to enable electron export, with notable electroactive bacteria like *Geobacter sulfurreducens* and *Shewanella oneidensis* demonstrating exceptional performance.[144,145] The transmembrane pathway relies on membrane-associated conductive complexes, such as MtrCAB cytochromes system, to facilitate electron transport across the membrane, thereby supporting respiration and maintaining the extracellular electron transfer chain. The periplasmic pathway, prevalent in Gram-negative bacteria, serves as an intermediary between the inner and outer membranes, utilizing cytochromes and other redox-active proteins to facilitate electron transfer.[146] The inner membrane pathway encompasses essential reaction systems, including the respiratory chain and the photosynthetic electron transfer chain, which function as the metabolic engine for energy conversion.[147] Finally, the intracellular pathway facilitates terminal reduction reactions essential for CO_2 fixation, nitrogen cycling, and other assimilatory processes, allowing microorganisms to perform functional outputs. The efficiency of transfer and the mechanistic characteristics of each pathway dictate the ability of microbes to capture, transport, and utilize photoelectrons. A systematic understanding and regulation of electron transfer routes benefits to optimize electron flow between microbes and materials, enhancing energy conversion efficiency and operational stability in NMHSs.

3.1 Electron transfer carriers in the extracellular pathway

The electron transfer capabilities of various microorganisms in the extracellular pathway are significantly affected by their external structural features. EPS and flagella contribute to the performance of NMHSs through complementary mechanisms. EPS matrixes, often rich in redox mediators, can serve as the medium for electron exchange,[139] whereas flagella facilitate the initial adhesion and subsequent biofilm stabilization on material surfaces *via* motility and scaffolding effects, rather than participating directly in electron conduction.[148,149]

3.1.1 Extracellular polymeric substances. EPS serves as a crucial outer layer barrier for microorganisms, playing a significant role in the capture and transfer of photoelectrons. EPS not only protect microbial cells from environmental stress but also function as essential mediators of electron transfer, attributed to their distinctive chemical structures and electrochemical properties. Redox-active molecular components, conductive network architectures, and varied physicochemical properties of EPS enable electron exchange between microorganisms and their environment, rendering them essential in microbial electron transfer systems. EPS consist of high molecular weight organic compounds, including polysaccharides, proteins, lipids, and nucleic acids.[150] Their production capacity, compositional profile, and functional characteristics differ markedly among microbial species.[151] Gram-negative bacteria frequently secrete substantial amounts of EPS, predominantly consisting of polysaccharides such as glucans and mannans, along with proteins.[152] Conversely, EPS derived from Gram-positive bacteria generally exhibit elevated concentrations of glucans and fructus, in addition to moderate levels of proteins and lipids.[153] Eukaryotic microorganisms typically generate more intricate EPS characterized by highly branched glycan structures, thereby improving their interactions with material surfaces.[154] Cyanobacterial EPS are notably abundant in polysaccharides and specialized metabolites, including phycobiliproteins and lipids. As shown in Fig. 2, the polysaccharide components frequently possess sulfated or carboxylated modifications, which enhance their electrochemical activity considerably. Additionally, EPS containing aromatic residues can establish conjugated electron networks through π–π stacking, facilitating swift electron transport.[155] Numerous EPS possess metal-binding sites that facilitate periodic oxidation–reduction reactions of redox-active metal ions, thereby enabling long-range electron transfer *via* a "redox hopping" mechanism.[30,31] The significant compositional variations in microbial EPS directly affect their electron-conducting properties. EPS that are rich in quinone-like substances, polyphenolic compounds, or small redox shuttles generally enhance efficient electron transfer. In contrast, EPS predominantly made up of inert polysaccharides with limited functional groups usually demonstrate low electronic conductivity and primarily fulfill structural or protective functions.[139] In NMHSs, the composition and chemical properties of EPS influence the efficiency of microorganisms in capturing photoelectrons and determine their interaction dynamics with photocatalytic materials. The interactions govern the efficiency of electron transfer processes and significantly affect the solar energy conversion performance of the system.

3.1.2 Flagella and conductive appendages. Flagella function as the primary motility organelles, enabling chemotactic or

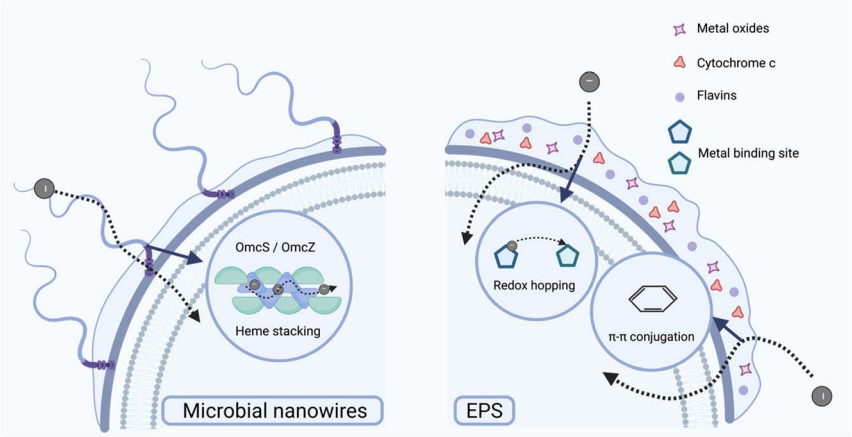

Fig. 2 Electron transfer carriers in the extracellular pathway. The figure on the left shows a schematic diagram illustrating the role of conductive pili in extracellular electron transfer. The figure on the right shows a schematic diagram illustrating the role of EPS in extracellular electron transfer, highlighting the main substances involved and the transfer mechanism.

phototactic migration toward photocatalytic materials. Beyond motility, flagella act as essential structural scaffolds during the initial stages of biofilm formation. For instance, in *Geobacter sulfurreducens*, flagella filaments facilitate the anchoring of cells to solid surfaces and stabilize the biofilm matrix, creating a dense spatial arrangement that favors short-range electron hopping.[156] However, contrary to earlier assumptions, flagella themselves are generally not considered electrically conductive pathways. Conductive appendages, often termed "microbial nanowires" are the true conduits for long-range electron transport. These filaments can extend micrometers from the cell surface, bridging the gap between the cell membrane and external electron acceptors (*e.g.*, metal oxides or electrodes). The exact composition and conduction mechanism of these nanowires have been a subject of intense debate. As shown in Fig. 2, early studies proposed that type IV pili (T4P) composed of the PilA protein conducted electrons *via* the π–π stacking of aromatic amino acids.[149] However, recent work demonstrates that the highly conductive filaments in *G. sulfurreducens* are composed of polymerized multi-heme cytochromes such as OmcS and OmcZ, whose closely stacked hemes form continuous molecular wires capable of rapid micrometer-scale electron transport.[32,33] Moreover, structural analyses reveal that PilA-based pili behave primarily as secretory or periplasmic structures rather than extracellular conductive nanowires, exhibiting conductivities orders of magnitude lower than OmcZ filaments.[157] Additional cryo-EM structures further show that *Geobacter* produces multiple cytochrome-based nanowire types, including OmcE filaments featuring tetra-heme packing, supporting a unified model in which long-range EET is mediated by diverse cytochrome filaments rather than T4P.[158] Collectively, these conductive appendages drastically reduce interfacial charge-transfer resistance and are essential for "wiring" microbes to photocatalysts in NMHSs.[159]

3.2 Transmembrane electron transfer pathways

Extracellular interactions, along with the structural characteristics of microbial cells, significantly affect their response to environmental stimuli. The cell membrane is particularly crucial in regulating mass transport and facilitating extracellular electron transfer (EET).[160] The cell membrane, consisting of a phospholipid bilayer with embedded transmembrane proteins, demonstrates selective permeability that regulates the exchange of ions, small molecules, and macromolecules.[161] Extracellular electrons must cross the membrane *via* specific mechanisms during electron transfer processes before engaging in intracellular metabolic pathways. The process relies on the coordinated function of conductive proteins, transmembrane transfer proteins, and redox-active electron carriers.

3.2.1 Redox protein complex. Transmembrane electron transfer involves various microbial species utilizing redox protein complex and electron carriers to establish electron-conducting pathways across the membrane (Fig. 3). These structures are essential for the transport of photoelectrons and demonstrate a range of functional capabilities. Redox protein complexes mainly consist of membrane-integrated cytochrome assemblies and transmembrane redox enzymes, which collectively facilitate the translocation of electrons across distinct cellular compartments. In *Shewanella* spp., the Mtr complex, which includes the membrane-associated cytochromes MtrA, MtrB, and MtrC, facilitates electron transport from the inner membrane, traverses the periplasm, and ultimately transfers electrons to extracellular electron acceptors through the outer membrane, as shown in Fig. 3.[34,35] Other bacteria, including *Geobacter* spp., have developed efficient transmembrane electron pathways. Membrane-bound cytochromes, including ImcH and CbcL, situated in the inner membrane, collaborate with extracellular redox protein complex such as OmcS and OmcZ to transfer electrons from the terminal respiratory chain to external metal oxides or electrodes.[162,163] Together, these examples illustrate that redox protein complexes constitute the core machinery enabling microorganisms to bridge intracellular metabolic electron flow with extracellular electron acceptors. Despite species-specific variations in protein composition and architectural organization, these membrane-spanning

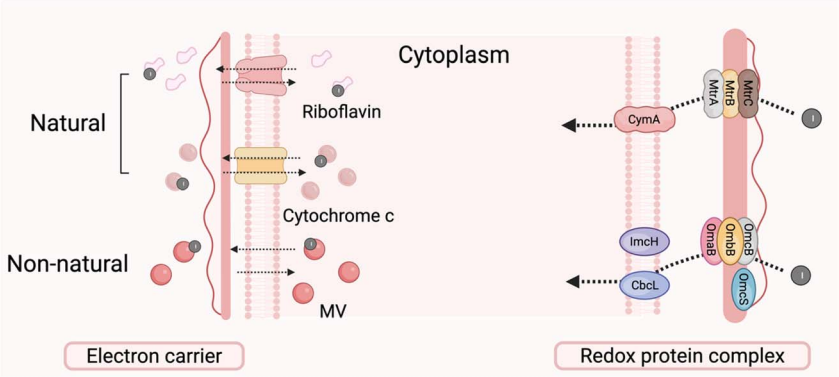

Fig. 3 Transmembrane electron transfer pathways. Left: a schematic diagram of transmembrane electron transfer *via* electron carriers. The upper part illustrates the process of electron transfer by natural electron carriers, while the lower part illustrates the process by non-natural electron carriers. Right: a schematic diagram of electron transfer by redox protein complex related to electroactive bacteria.

conduits share a unifying role: establishing continuous, directionally controlled electron pathways that support respiration, redox balancing, and interactions with external materials. Such mechanistic insights highlight the fundamental importance of redox protein complexes in mediating transmembrane electron transfer and lay the foundation for engineering more efficient biohybrid systems.

3.2.2 Redox mediators in transmembrane electron transfer. Electron carriers are essential components of microbial electron transport chains (ETCs), significantly influencing the efficiency and directionality of transmembrane electron flow. Redox molecules that occur naturally, including flavins like riboflavin, FMN, and FAD,[164] are produced endogenously during microbial metabolism and enable continuous electron flow in both intra- and extracellular redox cycles (Fig. 3). Artificial synthetic redox mediators, including neutral red and methyl viologen,[60,165] provide adjustable redox potentials and adaptability to diverse reaction conditions, thereby enhancing control over microbial electron transfer processes. In prokaryotes, electron transfer relies on a variety of redox-active molecules, including flavins, ferredoxins, quinones, and cytochromes that support both intracellular energy conversion and extracellular electron flow. For example, in *Rhodopseudomonas palustris*, flavin-based molecules enable electron transfer between intra- and extracellular compartments;[166] while in *S. oneidensis*, soluble quinones facilitate electron transport across the membrane, supporting bioenergetic processes.[167] In eukaryotic microorganisms, electron transfer predominantly takes place within mitochondria, and their transmembrane electron transport abilities are relatively restricted. In cyanobacteria, transmembrane electron transfer is closely linked to photosynthetic activity. High-energy electrons produced by PSI and PSII are partially transferred to extracellular acceptors, with flavin molecules serving as essential mediators for interfacial electron transport.[168] IET usually utilizes diffusible redox mediators to shuttle electrons between intracellular and extracellular environments, in contrast to DET, which necessitates direct physical contact between microorganisms and electron acceptors. IET typically demonstrates lower efficiency compared to DET; however, the low toxicity and high metabolic compatibility of natural redox carriers, combined with the tunability of synthetic mediators, present promising opportunities for improving transmembrane photoelectron transport in NMHSs.

3.3 Periplasmic electron transfer relay pathways

The periplasmic space, unique to Gram-negative bacteria, functions as an essential electron transfer center located between the inner and outer membranes. It enables the uptake of extracellular electrons, mediates the linkage between transmembrane electron transport chains, and directs electrons into intracellular metabolic networks.[169,170] This pathway involves various redox-active molecules, such as cytochromes and hydrogenases, which are essential for photoelectron transfer, providing a range of functional capabilities and potential applications.

3.3.1 Cytochromes and iron–sulphur proteins. Cytochrome c proteins in the periplasm serve as critical electron shuttles, connecting transmembrane complexes with outer membrane electron transfer proteins. An exemplary case is the small tetraheme cytochrome (STC) found in *Shewanella* spp., which effectively transfers electrons from extracellular sources or photoinduced systems into intracellular metabolic pathways.[171] Iron–sulfur (Fe–S) proteins function as essential electron carriers in the periplasmic space. These proteins can quickly respond to variations in the redox potential of electron donors, serving as temporary storage and intermediate transfer points for electrons during photoelectron flow. Their involvement improves the stability and continuity of inter-pathway electron transmission.[172] In photosynthetic bacteria and cyanobacteria, Fe–S proteins are closely associated with PSI, directly participating in electron transport.

3.3.2 Hydrogenases. Hydrogenases are essential enzymes in microbial energy metabolism, facilitating the reversible oxidation of molecular hydrogen and serving a pivotal function in the transformation of photoelectrons into chemical energy.[173] This transformation enhances the efficiency of electron utilization and serves as an additional energy source for cellular

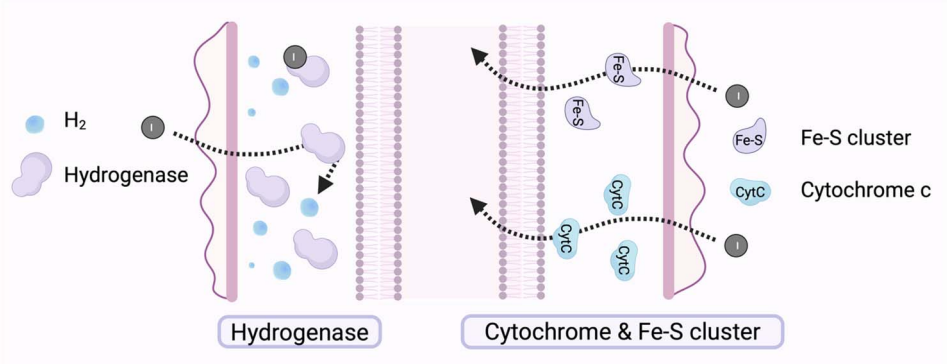

Fig. 4 Periplasmic electron transfer relay pathways. The figure on the left shows a schematic diagram of hydrogenase accepting electrons and carrying out its function in the periplasm. The figure on the right shows iron clusters and cytochrome c in the periplasm mediating electron transfer.

metabolism. Hydrogenases in Gram-negative bacteria are prevalent in the periplasm and play a crucial role in energy metabolism by facilitating proton reduction or hydrogen oxidation reactions, which are essential for ATP synthesis or the generation of reducing equivalents.[174–176] As illustrated in Fig. 4, the localization and maturation of hydrogenases in the periplasm depend on the twin-arginine translocation (Tat) pathway (Tat pathway denotes a protein export route that translocate fully folded proteins across the bacterial inner membrane), which facilitates the export of fully folded enzymes from the cytoplasm to the periplasm.[105,177,178] In eukaryotic microorganisms, hydrogenases are predominantly found in specialized organelles called hydrogenosomes, where they play a role in the fermentative metabolism of energy substrates like pyruvate.[179] Cyanobacteria express hydrogenases that are found in both the intracellular membrane and the periplasm. These enzymes are involved in photosynthetic hydrogen metabolism and play a role in energy conversion under light-driven conditions.[180] The distribution of hydrogenases among microbial taxa is variable, and their mechanisms for responding to photoelectrons are diverse, including proton reduction, hydrogen oxidation, and regulation of redox homeostasis.[181,182] Microorganisms utilize complex intra- and extracellular mechanisms to effectively harness photoelectrons, optimize energy conversion, and exhibit significant adaptability in natural environments. In NMHSs, periplasmic electron transfer pathways and their related redox-active molecules are crucial for connecting extracellular electron harvesting with intracellular energy metabolism. The combined functions of cytochromes, Fe–S proteins, and hydrogenases improve transmembrane electron transfer efficiency and optimize electron flow distribution for metabolic processes. An enhanced comprehension of the functions and regulatory mechanisms of these redox components will facilitate the rational design of more efficient electron transfer networks, thus improving the overall energy conversion efficiency of NMHSs.

3.4 Electron transfer *via* the inner membrane pathway

The inner membrane pathway involves various microbial oxidation–reduction chains and rhodopsins that are essential for photoelectron transfer, demonstrating significant application potential. The oxidation–reduction respiratory chain serves as the primary electron transfer system within microbial inner membranes, prevalent in both aerobic and anaerobic microorganisms. The components create an electron flow chain associated with proton pumps, establishing a transmembrane proton gradient that facilitates ATP synthesis.[183] Rhodopsins act as light-driven proton pumps, absorbing photon energy and causing conformational changes that facilitate the transport of protons from the cytoplasm to the extracellular space, thereby creating membrane potential and proton gradients.[184] By selecting or engineering microorganisms with effective oxidation–reduction chain components and proton pump activity-such as cyanobacteria, photosynthetic bacteria, and halophilic archaea-it is feasible to enhance the efficiency of photoelectron transfer and energy conversion, thereby supporting NMHSs.

3.4.1 Electron transfer chain. Prokaryotic microorganisms typically contain ETC within their inner membranes. These microorganisms employ electron transport chains for redox reactions, producing a proton motive force that facilitates ATP synthesis, such as *E. coli* and *Pseudomonas* spp.[185,186] The terminal electron acceptors in microbial electron transport chains can be dynamically adjusted according to environmental conditions and the characteristics of the microbial chassis. Under oxygen-limited or anaerobic conditions, certain microorganisms switch to alternative electron acceptors, such as fumarate, to adapt to changing redox environments,[187] thereby adapting to varying redox conditions. Depending on the species and niche, microbes may also utilize oxygen, nitrate, or various metal ions as terminal electron acceptors, enabling them to maintain intracellular redox balance, as illustrated in Fig. 5.[188,189] Certain iron-oxidizing bacteria, including *Acidithiobacillus ferrooxidans*, possess specialized transmembrane electron transfer systems. Proteins such as Cyc_2 and Rus create membrane-spanning complexes that enable the influx of electrons from Fe^{2+} into the cell, thereby supporting energy metabolism.[190] Unlike prokaryotes, the electron transport chain in eukaryotic organisms, such as yeast and fungi, is predominantly situated in the inner mitochondrial membrane rather than the cytoplasmic membrane.[191] The mitochondrial

respiratory chain complexes are complex and specialized structures that transfer electrons from NADH or $FADH_2$ to terminal acceptors, such as O_2, while coupled proton pumps generate a proton motive force to facilitate ATP synthesis. Eukaryotic and prokaryotic ETC exhibit structural similarities; however, their spatial distribution and functional regulation mechanisms are more sophisticated, highlighting evolutionary advancements in energy conversion within eukaryotic cells. Cyanobacteria possess ETC and photosynthetic electron transport chain on both their cytoplasmic and thylakoid membranes, which play a role in photosynthesis. Transmembrane protein complexes, including photosystem I (PSI), photosystem II (PSII), plastoquinone (PQ), and the cytochrome b6f complex, are integrated within the thylakoid membrane of photosynthetic bacteria and cyanobacteria. These complexes facilitate light-induced electron excitation and cascade transfer, resulting in the establishment of a proton gradient that drives ATP synthesis.[192,193] The electron transport chains on the cytoplasmic membrane primarily facilitate respiratory metabolism, whereas those on the thylakoid membrane are integral to light-driven electron transfer. The two systems operate together to provide metabolic flexibility in cyanobacteria.[147] The regulatory capacity of ETCs in various microorganisms allows for adaptation to complex redox environments, which improves the stability and energy conversion efficiency of NMHSs. Investigating and refining the composition and regulatory mechanisms of microbial ETCs will enhance the performance of these systems and facilitate more efficient conversion and utilization of light energy.

3.4.2 Rhodopsins. Rhodopsins are light-sensitive receptors situated on the cell membrane that induce conformational changes in retinal following photon absorption. This leads to the transfer of electrons and protons, which drives proton pumps and facilitates ATP synthesis, thereby playing a crucial role in biological energy conversion and cellular signaling.[184] Rhodopsins exhibit a broad distribution among various organisms, yet their functions differ across species. In prokaryotes, rhodopsins primarily function in light-driven ion pumping, supplying energy for the cell.[194] In algae, they contribute to light signal sensing and facilitate energy conversion.[195] The core mechanism of rhodopsins, despite variations in function and distribution among organisms, involves light-induced charge separation, which is essential for biological energy conversion. In NMHSs, rhodopsins function as essential elements for light-driven electron and proton transfer, thereby facilitating ATP synthesis and energy storage (Fig. 5). Their capacity to respond to light signals can optimize electron transfer pathways, thereby improving the system's efficient use of light energy. The strategic application of rhodopsins' light-sensitive characteristics shows potential for enhancing energy conversion efficiency in NMHSs and broadening their use in bioelectronics and renewable energy sectors.

3.5 Intracellular electron transport pathway

The intracellular environment of microorganism functions as a central hub for biochemical reactions, with its material composition and structural characteristics influencing pathways for exogenous electron transfer and utilization. In biologically mediated photoelectron reactions, the binding sites of intracellular materials and their chemical properties are essential for determining the pathways of electron transfer. Microorganisms contain multiple potential electron-binding sites, including redox compounds,[196] protein complexes,[58] intracellular membrane-associated systems,[197] and soluble electron carriers.[164] Together, these sites form heterogeneous intracellular pathways for electron transfer. The electron affinity, redox potential, and spatial arrangement of these pathways determine how photoelectrons are utilized once they

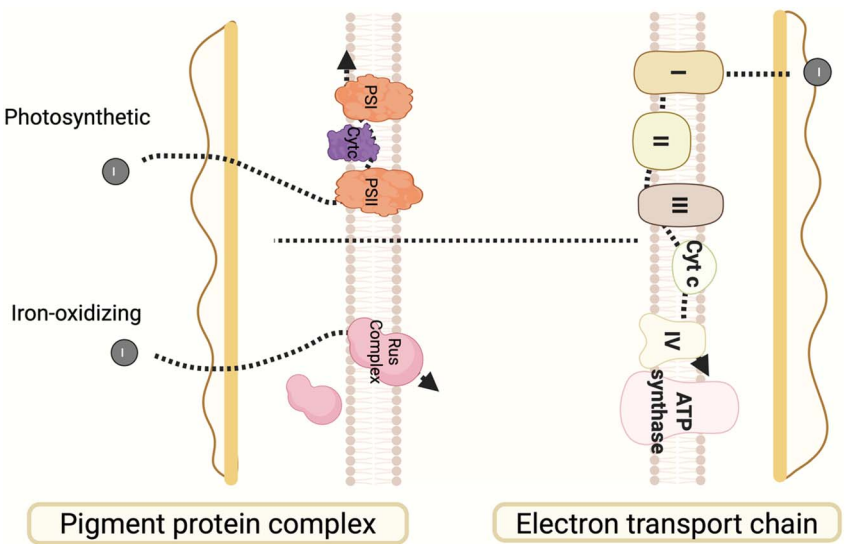

Fig. 5 Electron transfer *via* the inner membrane pathway. The figure on the left shows a schematic diagram of the potential electron utilization mechanism of pigment protein complex in the inner membrane of photosynthetic and iron-oxidizing microorganisms. The figure on the right shows a schematic diagram of the potential electron utilization mechanism of the oxidative respiratory chain in the inner membrane.

enter the cell. Analyzing the characteristics of intracellular electron acceptors, optimizing electron transfer pathways, and modulating the redox environment can enhance the potential for photoelectron applications in biocatalysis and artificial photosynthesis.

3.5.1 Cytoplasmic redox compounds. As illustrated in Fig. 6, intracellular redox compounds such as NAD(P)H, iron–sulfur proteins, flavoproteins, coenzyme Q, and FAD serve as essential carriers in electron transfer and energy metabolism in cells. These compounds facilitate the distribution and transfer of electrons within the metabolic network following the entry of photoelectrons into the cell. NAD(P)H serves as a crucial electron donor, supplying electrons for reductive reactions in processes including carbon fixation, hydrogen metabolism, and biosynthesis.[36,37] Fe–S proteins and flavoproteins, prevalent in photosynthetic bacteria and cyanobacteria, are involved in the transfer of electrons from photosystem I to the carbon fixation pathway. They can also interact with enzymes like hydrogenase and nitrate reductase, thereby regulating the final electron flow.[173] The content, redox potential, and dynamic balance of intracellular redox compounds in NMHSs directly influence the efficiency of photoelectron utilization and the selectivity of product synthesis pathways. Glutathione (GSH) is a significant intracellular tripeptide characterized by its unique reducing properties and potent antioxidant capacity, essential for maintaining intracellular redox homeostasis.[198] GSH preserves intracellular redox balance, scavenges ROS, stabilizes metalloproteins, and regulates the expression of electron transport proteins, thereby indirectly facilitating the efficient functioning of the microbial electron transfer chain and the stability of light and respiration energy metabolism.[38] GSH generation and utilization influence intracellular energy flow and are crucial for protecting against oxidative damage. The regulation of intracellular redox compounds is crucial for optimizing electron utilization and energy distribution. The effective transfer of electron carriers, including NAD(P)H and iron–sulfur proteins, influences the pathway of photoelectrons in biosynthesis and metabolic networks. Modulating the content and activity of redox molecules can improve electron transfer efficiency, enhance system adaptability to complex environments, and ultimately boost the performance of NMHSs.

3.5.2 Compartmentalized organelles. Compartmentalized organelles of microorganisms significantly influence the efficiency of photoelectron utilization. Prokaryotes, despite the absence of complex membrane-bound organelles, exhibit unique compartmentalization that offers specific advantages in the capture and utilization of photoelectrons. The thylakoid membranes of cyanobacteria serve as essential locations for the generation and initial transfer of photoelectrons, housing PSII, PSI, and related components of the electron transfer chain, thereby effectively converting light energy into chemical energy.[199] Certain bacteria contain subcellular structures known as carboxysomes, which enhance the concentration of pertinent enzymes and substrates *via* phase separation, thereby improving biocatalytic efficiency.[200,201] Eukaryotic microorganisms exhibit greater compartmentalization, enhancing the efficiency of photoelectron utilization. In green microalgae, chloroplasts serve as the primary sites of photosynthesis, containing thylakoid membranes that house photosystems and electron transfer chains, while also facilitating precise localization and efficient pathways for photoelectron transfer.[202] Eukaryotic organelles, including mitochondria, peroxisomes, and the endoplasmic reticulum, are essential in regulating intracellular energy flow and redox balance, thereby facilitating multi-pathway distribution and utilization of photoelectrons.[203] Utilizing the potential of eukaryotic compartmentalized organelles allows for the targeted delivery of exogenous materials into specific organelles, thereby enhancing the efficiency of photoelectron generation and capture. Microorganisms demonstrate significant diversity and adaptability in electron transfer and energy metabolism. Microorganisms efficiently respond to the transfer and utilization of photoelectrons by regulating their intracellular and extracellular environments, compartmentalized structures, and essential molecular

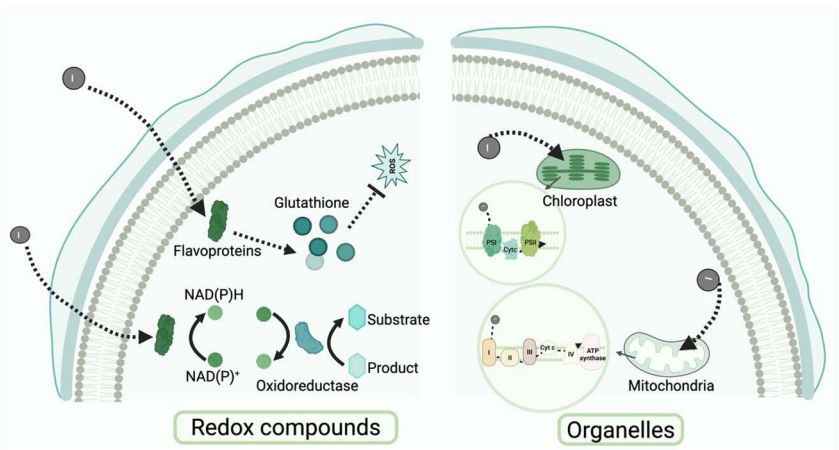

Fig. 6 Intracellular electron transport pathway. The figure on the left shows a schematic diagram of the mechanism by which intracellular redox compounds and coenzymes utilize electrons, including in processes such as antioxidant stress and metabolic product synthesis. The figure on the right shows a schematic diagram of the mechanism by which eukaryotic subcellular structures utilize electrons.

functions (Fig. 6). In NMHSs, the compartmentalization of microorganisms can enhance electron transfer pathways and increase energy conversion efficiency. Compartmentalized structures, including cyanobacterial thylakoid membranes and eukaryotic chloroplasts, create optimal microenvironments for effective electron capture and distribution. Additionally, the collaborative functions of mitochondria and other organelles enhance the variety of electron utilization. By precisely modulating compartmentalized characteristics and electron transfer pathways, the stability and light energy conversion capacity of NMHSs can be enhanced, offering new strategies for constructing efficient bio-material composite systems.

3.6 Research status and challenges

The rapid advancement of bioengineering and materials science has positioned the integration of microorganisms with exogenous materials and the optimization of photoelectron utilization pathways as critical research areas in solar energy conversion and biocatalysis. Prokaryotes and eukaryotes exhibit differences in cell structure, metabolic pathways, and engineering plasticity, providing unique research platforms for the capture, transfer, and utilization of photoelectrons.[10] Cell surface engineering in prokaryotes can markedly improve the interaction between microorganisms and materials. For instance, microorganisms can precisely position photocatalytic nanomaterials or conductive polymers on their surfaces by expressing specific proteins or peptides, such as those that anchor to metal oxide surfaces, thus constructing efficient electron transfer pathway.[204] This method enhances the binding capacity between microorganisms and materials while also improving the efficiency of photoelectron transfer. Eukaryotic microorganisms demonstrate distinct advantages in the utilization of photoelectrons and material binding. Their intricate intracellular structures and varied metabolic pathways facilitate the multi-pathway use of photoelectrons. The cell walls and membrane structures of eukaryotic microorganisms offer increased potential for material binding. Modifying surface proteins, such as by enhancing their affinity for metal ions or nanomaterials, allows functionalized materials to be targeted for anchoring at specific extracellular or intracellular locations. This method demonstrates significant potential for enhancing the capture and transfer efficiency of photoelectrons, especially through the targeted incorporation of light-active materials, such as QDs, into microalgae cells.[205] The intricate metabolic networks of eukaryotes facilitate the distribution of photoelectrons across multiple pathways. For example, genetically engineering heterologous metabolic pathways allows for more efficient participation of photoelectrons in intracellular synthesis processes, such as the production of shikimic acid.[206] This adaptable metabolic regulation increases the capabilities of eukaryotic microorganisms in photobiocatalysis and synthetic metabolism.

Photosynthetic bacteria, such as *Rhodobacter sphaeroides*, are extensively utilized in NMHSs for solar energy conversion and the production of high-value-added compounds.[207] Cyanobacteria, such as *Synechococcus*, engage in photosynthesis and contribute to system functionality *via* nitrogen fixation.[63] Although these microorganisms possess significant potential for genetic manipulation, their capacity to adapt to environmental fluctuations necessitates further enhancement. Conversely, electroactive bacteria such as *G. sulfurreducens* and *Sporomusa ovata* exhibit the capability to efficiently accept electrons and interface with photoelectrodes, thereby utilizing photoelectrons for the reduction of CO_2 or the synthesis of organic compounds, including acetic acid.[208,209] Furthermore, the introduction of exogenous metabolic pathways has enabled engineered microorganisms, such as *E. coli*, to achieve photo-driven synthesis of chemicals, including lysine.[66] Eukaryotic microorganisms, including *Saccharomyces cerevisiae* and green algae, can effectively produce hydrogen and other high-value products when integrated with photocatalytic materials.[206,210] The microbial species utilized in NMHSs are transitioning from individual photosynthetic organisms to engineered, multi-species collaborations and interdisciplinary integrations. Future advancements will depend on interdisciplinary innovations in synthetic biology, materials science, and systems engineering to realize efficient, stable, and scalable clean energy production. These advancements will significantly enhance the application of microorganisms in energy conversion and environmental remediation.

4 Interface construction determines electron transfer efficiency and system compatibility

The interaction between microorganisms and materials governs energy and mass exchange in NMHSs and thus directly influences system efficiency. In these biohybrid systems, photoactive materials convert and supply energy, whereas microorganisms execute metabolic transformations. A poorly engineered interface can lead to photoelectron loss, mass-transfer inefficiencies, or biological incompatibility, highlighting the critical importance of rational interface design.[18,19]

Effective interface engineering must consider several essential factors: the physiochemical properties of materials on separation and migration of photogenerated charges as well as cell coupling, the pathways for photoelectron utilization, and the physiological and metabolic characteristics of the microbial chassis. Microbial extracellular structures, including EPS, cell walls, and membrane-associated redox proteins, interact with material surfaces through physical adsorption, electrostatic interactions, and ligand-specific binding, thereby shaping the formation, stability, and conductivity of electron-transfer interfaces. For example, EPS widely mediates microbial adhesion and sorption, and can modulate the aggregation, mobility, and bioavailability of nanoparticles within biofilms.[150,211] These interactions ultimately influence the chemical and electronic microenvironment at the abiotic–biotic interface and are therefore highly relevant to NMHSs design. Moreover, in systems where microorganisms and materials co-exist, EPS has been shown to mediate interaction with NPs: EPS can adsorb NPs, modulate their distribution and diffusion inside the

biofilm matrix, and affect NP bioavailability and toxicity.[212,213] These findings imply that EPS-material interactions can significantly modulate the stability and electronic/chemical environment at the biotic–abiotic interface, which is relevant for NMHSs design. On the other hand, the size, morphology, and surface chemistry of materials also critically determine the type and performance of the interface. Materials at different scales-quantum, mesoscopic, or micron-sized-and with diverse morphologies (*e.g.*, particulate, layered, sheet-like) establish distinct spatial relationships with cells and consequently differ in their modes of electron delivery and biological compatibility. Accordingly, NMHSs interfaces can be broadly classified as extracellular, transmembrane, or intracellular, each exhibiting unique structural constraints, coupling strengths, and regulatory opportunities for optimizing photoelectron separation and utilization.

Given these material- and microbe-dependent constraints, selecting an appropriate strategy for constructing the abiotic–biotic interface becomes essential for achieving effective photoelectron delivery. Depending on the targeted interface type (extracellular, transmembrane, or intracellular) and the required level of electronic coupling, different assembly approaches can be employed to control material–cell proximity, adhesion strength, and electron-conduction continuity. Among these strategies, the most widely used and experimentally accessible method is the direct co-dispersion of microorganisms with photosensitizer materials. This approach is experimentally simple and requires minimal pretreatment, but weak adhesion between materials and cells can limit electron transfer efficiency. Many photocatalytic materials possess or can be modified with surface functional groups (*e.g.*, $-NH_2$, –OH) that engage in hydrogen bonding or electrostatic interactions with microbial surfaces, partially improving contact.[214,215] Conductive additives or pathways formed by microbial redox proteins can further construct "electron highways" that enhance the transfer of photogenerated electrons to the cell surface. However, for many non-electroactive or eukaryotic microorganisms, achieving high-efficiency photoelectron transfer through surface contact alone remains difficult.

As an alternative, some studies have explored EPS-mediated synthesis and stabilization of metal nanoparticles by microorganisms, whereby EPS acts as a template or capping agent for particle formation/stabilization, altering material–microbe interactions and providing a route for material integration.[211,216] Another approach involves facilitating the penetration of particles through the cell wall and membrane to shorten the electron transport distance. However, direct internalization of particles remains highly challenging, physical intrusion can disrupt membrane integrity and trigger intracellular ROS generation, both of which compromise cellular viability and long-term system stability.[10,212] Overall, the construction of material–microbe interfaces is fundamentally shaped by material physicochemical properties and microbial electron-handling mechanisms. Understanding their interplay enables the rational selection of interface types and engineering strategies that maximize electron-transfer efficiency while maintaining system compatibility.

4.1 Synergistic interface construction between biological structures and multiscale materials

Microbial extracellular and transmembrane structures collectively enable adaptive, multiscale coupling with diverse material morphologies, forming the physical and electrochemical foundation for heterogeneous electron transfer in NMHSs. Through synergistic interactions involving EPS, membrane-bound proteins, vesicle secretion, and ion channels, microbes dynamically modulate material adhesion, electron transfer efficiency, and interfacial stability.[129,141,213] Rationally engineering these bio-interfaces in coordination with material design unlocks new potential for constructing robust and efficient NMHSs.

4.1.1 Scale-dependent coupling between microbial extracellular structures and materials. In the construction of heterogeneous electron transfer pathways, the interaction between microbial extracellular structures and material interfaces is a key determinant of electron transfer efficiency and interfacial stability.[129] In EET pathways, microbial structural components, including EPS, cell wall constituents, and outer membrane proteins, play a dynamic role in modulating the formation and functional expression of heterogeneous interfaces. EPS provide significant adhesion properties, facilitating microbial attachment to electrodes or solid surfaces, while also incorporating conductive molecules or cytochromes, functioning as a "soft conductor" for electron transport.[217,218] As shown in Fig. 7, this is particularly suitable for quantum- or mesoscale particulate materials. Their high specific surface areas allow them to be thoroughly enveloped by the highly viscoelastic EPS matrix, which traps the particles to form stable composite interfaces.[219] This encapsulation not only immobilizes the photosensitizers near the cell surface but also protects them from detachment, ensuring sustained interfacial coupling. Moreover, functional groups such as hydroxyl, carboxyl, and amino moieties within EPS can interact with material surface functionalities through hydrogen bonding, electrostatic attraction, or covalent bonding.[137,220–222] These interactions are particularly strong for carbon-based or metal oxide materials rich in oxygen-containing groups, providing a chemical basis for the robust adsorption of nanomaterials onto the microbial surface. When materials exhibit sheet-like or layered morphologies (*e.g.*, graphene, layered double hydroxides, or 2D semiconductors), EPS tend to spread across the surface, forming uniform coating layers. This layered encapsulation reduces electron leakage, stabilizes local electric fields, and increases interfacial charge density, thereby enhancing overall electron transfer performance. EPS can modulate local ion concentrations and diffusion behavior at the microscale, thereby creating microenvironments that are conducive to electron transport.[139] The surface charge properties, roughness, and heterogeneity of the microbial cell wall directly affect adsorption behavior across materials of different scales.[223] In mesoscopic or porous particulate materials, the irregular structure of the microbial cell wall facilitates physical embedding within material pores, thereby enhancing mechanical interlocking and electronic coupling. The degree of exposure of

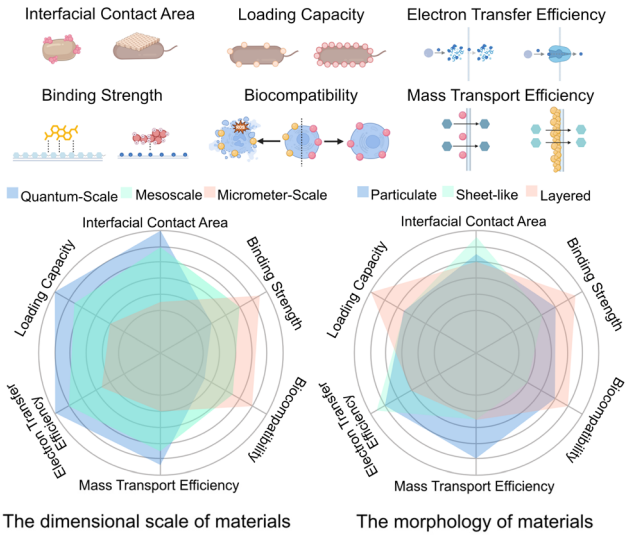

Fig. 7 Synergistic interface construction between biological structures and multiscale materials. Advantages and differences of interface construction with microorganisms using materials of different scales (left) and morphologies (right) in terms of interfacial contact area, binding strength, biocompatibility, mass transfer efficiency, electron transfer efficiency, and binding density.

redox protein complex, such as extracellular cytochromes, on the outer membrane significantly influences the efficiency of outward electron transport and the establishment of low-resistance electron pathways with materials.[224] Flagella, characterized by their extensive surface area, flexibility, and dynamic behavior, significantly contribute to interface formation. They facilitate the initial reversible adhesion to complex material morphologies, including particle edges and sheet boundaries, and enable chemotactic migration toward favorable microenvironments.[225] These physical interactions enhance the frequency and stability of the material–biological contact, providing a robust structural foundation for subsequent electron transfer processes. Various microbial extracellular structures demonstrate multiscale adaptability when interacting with materials of specific sizes and morphologies. These interactions regulate the self-assembly of heterogeneous interfaces, the development of conductive networks, and the establishment of electron transfer routes, thereby providing the structural basis for efficient and stable electron pathways in NMHSs.

4.1.2 Transmembrane structures and multiscale material interface coupling mechanisms. Transmembrane structures play a crucial role in the development of effective material–biological interfaces in heterogeneous electron transfer pathways. Membrane-integrated redox complexes (*e.g.*, Mtr system), cytochrome-rich extracellular filaments/nanowires, and outer-membrane extensions/OMV-derived structures have been shown to participate in early-stage extracellular electron exchange, thereby facilitating stable microbial integration with conductive materials.[141,226,227] These transmembrane systems exhibit strong interfacial compatibility with materials of diverse morphologies, such as sheet-like 2D materials, layered metal oxides, and quantum dots. As shown in Fig. 7, in meso- or quantum-scale particles, elevated surface curvature and reactivity promote dense protein adsorption, resulting in low-resistance electron transfer nodes. Endocytosis and exocytosis are generally restricted in prokaryotes; however, certain strains, such as OMV-producing Gram-negative bacteria, can release vesicles that transport signaling molecules and conductive factors, thereby regulating the interfacial microenvironment and initiating material responses. In eukaryotic microbes, the processes of endocytosis and exocytosis exhibit greater complexity and facilitate the active uptake or expulsion of conductive particles. This method is particularly effective for the targeted adsorption and spatial fixation of microscale or spherical materials, thereby enhancing directional control over electron transfer. Cyanobacteria, though prokaryotic, exhibit pseudo-eukaryotic functionality in material deposition and interfacial activity regulation due to their capacity to secrete membrane vesicles.[143] Moreover, specific ion channels located in cell membranes are crucial for maintaining electrochemical balance and facilitating material transport.[228–230] Heavy metal ion transporters selectively mediate the uptake of Cd^{2+} and other metal ions,[231–233] thereby facilitating controlled intracellular nanoparticle formation. The channels demonstrate size-dependent compatibility with materials: large-pore membrane proteins preferentially interact with micro-layered materials to establish stable "encapsulation–exchange" interfaces, while QDs or ultrasmall particles depend on highly selective and tightly regulated transport mechanisms. The interaction of microbial transmembrane structures, vesicle trafficking, and membrane channel activity influences the efficiency of electron and mass exchange between microorganisms and materials. Biological components interact synergistically with the structural scale and surface morphology of materials. The integration of these interactions with nanomaterial design strategies presents significant potential for enhancing the efficiency and stability of cross-interface electron transfer, thereby improving the energy conversion performance and environmental adaptability of NMHSs.

4.2 Construction and characteristics of extracellular interfaces

To complement the intracellular nanomaterial internalization pathways discussed above, it is equally essential to recognize that many NMHSs do not rely on materials entering the cytosol to achieve efficient electron or metabolite exchange. Instead, the majority of functional interactions occur at the extracellular material–cell interface, where microbes maintain intact membrane structures while receiving photoelectrons, metabolites, or signaling cues from externally associated materials. Therefore, beyond understanding cellular uptake routes, it becomes critical to examine how engineered extracellular interfaces are constructed and regulated to mediate selective adhesion, directional charge transfer, and stable yet reversible coupling between materials and microorganisms. The construction of extracellular interfaces in NMHSs is a crucial strategy in interface design, marked by the relative independence of materials and microbes at the individual level, without

creating an inseparable entity. Interfaces are generally formed *via* physical or chemical interactions, including electrostatic forces, hydrogen bonding, or covalent bonding, to enable the transfer of matter and energy between photocatalytic materials and microorganisms, which typically divided into four types of interfaces: dispersed, tightly bound, biomineralization and surface display, and biofilm interfaces.

4.2.1 Dispersed interfaces. The dispersed interface represents the fundamental configuration of interfaces in NMHSs. A prevalent method entails the direct incorporation of semiconductor photosensitizers into the culture medium throughout microbial cultivation or fermentation. This strategy involves merely the mixing of photosensitizers and microbes without the formation of stable bonds, resulting in no stringent limitations regarding the size or type of materials utilized. In these systems, photoelectrons are generally transferred to microbial cells through electron mediators, such as flavins and methyl viologen. The mediators initially accept the photoelectrons and are reduced to their active forms, subsequently being transported into the cells *via* membrane transport proteins or passive diffusion. Upon entering the cells, the reduced mediators act as electron donors, facilitating microbial metabolism and markedly elevating intracellular NAD(P)H levels, which in turn supports the production of high-value-added chemicals. Co-cultivation of graphitic carbon nitride with *Phaffia rhodozyma* resulted in increased astaxanthin production.[234] As illustrated in Fig. 8, in systems where materials and microbes are spatially separated, electron transfer is significantly dependent on mediators. The efficiency of energy utilization is affected by the reduction efficiency of the mediators as well as the transport efficiency of their reduced forms.[235,236] This was evidenced by the complete separation of photocatalytic materials from microbes. The findings indicated that rhodopsin and its related light-responsive proton pumps, along with decreased flavin, significantly increased intracellular NAD(P)H levels, thereby promoting biomass accumulation.[235]

The dispersed interface strategy facilitates large-scale preparation and application by eliminating the need for complex stable binding interactions. The lack of stringent specifications regarding material size allows for the utilization of diverse photocatalysts, including micron-sized materials. In these systems, the naturally occurring pores among particles offer both physical protection and effective energy acquisition routes. For example, microbes like *S. ovata*, which depend on specific electron donors, benefit from large pores that protect them from intense light while sustaining hydrogen utilization, leading to improved biocatalytic activity.[208]

Despite these advantages, the absence of stable contact between photocatalytic materials and cells constitutes a significant limitation. Electron transfer from photocatalytic materials to the microbial cytoplasm in dispersed systems relies heavily on diffusion, making the process susceptible to physical disturbances such as fluid flow and microbial motility. Consequently, this can lead to fluctuating transfer efficiencies and reduced overall system performance compared to tightly bound interfaces.

4.2.2 Tightly bound interfaces. As previously indicated, short-distance energy transfer effectively minimizes energy loss, highlighting the necessity of constructing tightly bound interfaces between materials and microorganisms. Interface design utilizing intermolecular interactions can facilitate stable attachment between the two entities. As illustrated in Fig. 8, electrostatic interaction is a fundamental force frequently observed between biological and photocatalytic material surfaces. This interaction can be utilized to enhance adhesion by leveraging variations in surface charge polarity. $Zn_xCd_{(1-x)}S$ photosensitizers material demonstrate a positive zeta potential attributed to Zn incorporation, facilitating stable attachment to negatively charged microbial surfaces through electrostatic attraction.[237] Microorganisms that can perform direct electron transfer benefit from these binding strategies, which improve the efficiency of electron mediator utilization and facilitate the direct use of photoelectrons. For example, *S. ovata* facilitates electron transfer *via* cytochrome c, Fe–S proteins, and ferredoxins, thus enhancing the Wood-Ljungdahl pathway. This facilitates effective acetate accumulation and CO_2 fixation in the

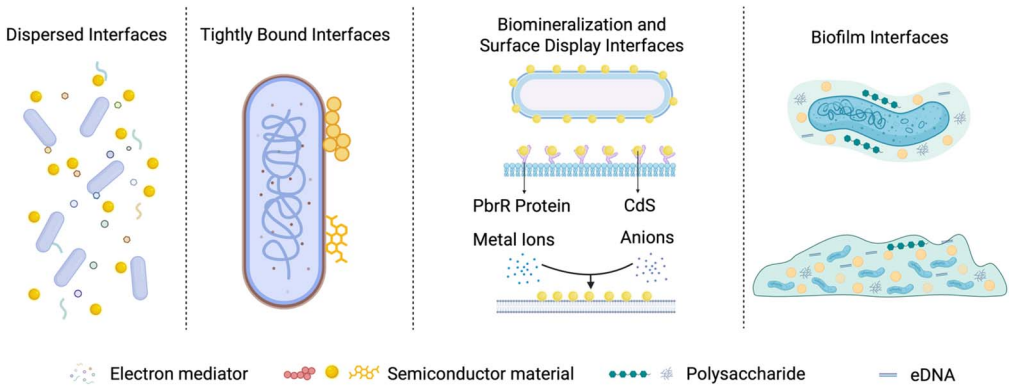

Fig. 8 Construction and characteristics of extracellular interfaces. Each part of bio–abiotic interface represents its combinative mechanism, including unstable connection interface, materials combining with microorganisms by physical or chemical interaction force, protein capture and *in situ* biomineralization, and electron transporting from materials to microorganisms through mediator secreted from microorganism in the biofilm net.

absence of an external hydrogen supply.[237,238] Moreover, many MOFs demonstrate excellent photocatalytic performance and can form robust biohybrid structures with microorganisms *via* electrostatic interaction, thereby improving energy transfer efficiency between the material and microbial partners. For example, PCN-222 possesses a high density of surface functional groups, including C═O, C═N–H, and N–H moieties, which facilitate efficient energy transfer to associated microbes. Leveraging this property, a recent study incorporated *E. coli* into a PCN-222-based NMHSs, resulting in a threefold increase in lysine production.[66]

Additionally, hydrogen bonding is another commonly utilized in contemporary research as a method for creating tightly bound interfaces (Fig. 8). Microbial cell walls are predominantly composed of peptidoglycan or glucan, resulting in surfaces abundant in functional groups (*e.g.*, $-NH_2$ and –CHO) capable of forming hydrogen bonds with specific compounds, including natural polyphenols and organic ligands of MOFs.[239,240] Compounds containing –OH and –COOH groups typically exhibit negative charges in aqueous solutions because of their ability to donate protons, which facilitates coordination with metal ions and the formation of stable complexes.[241] Natural polyphenols, such as tea polyphenols, tannic acid, and terephthalic acid, can function as broad-spectrum biological adhesives for the construction of material–biological interfaces. Tannic acid can form stable complexes with iron ions in alkaline conditions (pH > 8). Its abundant –OH groups enable the formation of hydrogen bonds with polysaccharides and proteins on biological surfaces, resulting in a dense coating layer that provides microbial protection.[242–244] Additionally, metal-centered photocatalytic materials demonstrate effective binding to polyphenol complexes. A study utilized InP as photosensitizers material, which was applied to a tannic acid–iron coating layer, resulting in the development of a yeast-based NMHSs that markedly increased intracellular NADPH levels and enhanced product yields.[206] Similarly, Zr-based MOFs demonstrate exceptional performance in interfacing with bacteria. Constructed *via* the coordination of $Zr(OH)_4$ with 1,3,5-benzenetribenzoate (BTB), these frameworks bind tightly to *M. thermoacetica*, primarily anchored by the formation of (Zr)–O–P bonds with the phosphate moieties of teichoic acid on the bacterial cell wall. Furthermore, the dense architecture of the Zr-based MOF creates a protective barrier that effectively shields the anaerobic bacteria from oxygen exposure.[68]

Interfaces constructed *via* electrostatic interactions and hydrogen bonding offer several notable advantages. By promoting stable adhesion between materials and microbial surfaces, these interactions ensure close spatial proximity, which facilitates efficient electron and energy transfer while minimizing energy loss. At the same time, such non-covalent interactions preserve the integrity of the microbial cell envelope, avoiding the cytotoxic effects or structural disruption that might occur with direct internalization of photocatalytic particles. The resulting interfaces are generally robust, enabling sustained material–microbe coupling under moderate environmental fluctuations.

Despite these benefits, this strategy also has inherent limitations. The predominance of negatively charged microbial surfaces restricts the range of compatible materials to those with complementary surface charges or functional groups, limiting material diversity. Strong electrostatic or hydrogen-bonding interactions can also promote microbial aggregation, which may reduce interface uniformity and light penetration, ultimately affecting energy transfer efficiency and system stability. Careful optimization of material surface properties and functional group density is therefore necessary to maximize interface performance while minimizing adverse impacts on microbial physiology.

4.2.3 Biomineralization and surface display interfaces. In natural environments, specific microorganisms capture metal ions through metabolic processes and surface proteins, leading to the formation of mineral layers on their surfaces, a phenomenon termed biomineralization.[245] As shown in Fig. 8, regulating suitable concentrations of Cd^{2+} and providing an additional sulfur source, such as cysteine, can induce the formation of biomineralized CdS particles on microbial surfaces.[246] The particles strongly adhere to the microbial surface and facilitate the transfer of photoelectrons into the cells, thus improving the efficiency of electron utilization. For instance, CdS was mineralized onto the surface of *Moorella thermoacetica*, and a comparable approach was utilized with *R. palustris*, both resulting in high quantum efficiencies.[13,247] The weak specificity of microbial surface proteins in selecting metal ions necessitates consideration of the strategy proposed, which optimizes ion types and concentrations for constructing heterojunction photocatalysts on biological surfaces through biomineralization.[84] Genetic engineering enhances the loading capacity of individual cells for photocatalytic materials and allows for precise regulation of material types to satisfy various application requirements. As shown in Fig. 8, expressing PbrR proteins on the surface of *E. coli* significantly enhanced hydrogen production efficiency under aerobic conditions.[204] Another approach involved engineering *E. coli* to express curli (adhesive fimbriae), significantly enhancing its capacity to load CdS.[22] Additionally, the design of an outer membrane protein A fused with an Ag-binding domain facilitated the stable anchoring of Ag_2S on the surface of *E. coli*, resulting in effective degradation of environmental pollutants.[248]

This biomineralization-based interface strategy leverages the intrinsic metabolic capabilities of microorganisms to autonomously generate photocatalytic materials, enabling the formation of robust, tightly coupled material–microbe interfaces with high biocompatibility. Such self-assembled interfaces enhance electron transfer efficiency by ensuring close spatial proximity and strong material–cell interactions without compromising cell integrity. However, the spontaneous nature of biomineralization poses challenges for precise control over material composition, size, and uniformity. In addition, the toxicity of certain metal ions can adversely affect microbial viability, limiting the range of usable ions and necessitating careful optimization of ion concentrations. Strategies to improve microbial tolerance and stabilize biomineralized

biohybrid systems are therefore critical for achieving consistent performance and long-term operational stability.

4.2.4 Biofilm interfaces. Besides artificially constructed coatings, specific microorganisms, including *S. oneidensis* and *Pseudomonas aeruginosa*, are capable of naturally forming biofilms *via* the secretion of extracellular substances.[249,250] Biofilms generally comprise extracellular polysaccharides, small-molecule secretions, and extracellular DNA (eDNA). Small-molecule secretions, such as riboflavin and quinones, along with eDNA, are crucial in facilitating extracellular electron transfer processes.[249–252] Biofilms provide significant biocompatibility and function as efficient platforms for the development of electron transfer interfaces between materials and microorganisms. The biofilm-forming capability of *S. oneidensis* was employed to construct CdS–*S. oneidensis* biohybrids, resulting in rapid polylactic acid decomposition and hydrogen production (Fig. 8).[249] In addition to natural biofilms, artificial biofilms can be developed through the integration of genetic engineering and polymer material technologies. Natural polyphenols and conductive polymers, such as polypyrrole, possess a high density of N–H bonds and can establish compact conductive networks with favorable biocompatibility, rendering them suitable for the construction of artificial biofilms. Additionally, genetic modification strategies, including the enhancement of flagellar expression and the regulation of adhesive protein synthesis, can enhance the compatibility and binding strength between artificial biofilms and microorganisms.[22,253] The integration of artificial biofilms with engineered microorganisms and photocatalytic materials results in systems that demonstrate improved stability. Additionally, utilizing their film-forming properties facilitates multimodal energy input, product selectivity, and accurate shaping of living materials, thereby enhancing the versatility of NMHSs.[22,97]

While biofilm-based interfaces provide high biocompatibility, facilitate stable material–microbe coupling, and enable efficient extracellular electron transfer, they also present certain challenges. The dense matrix of extracellular polymeric substances can impede mass transport and limit light penetration, potentially reducing electron transfer efficiency and metabolic activity in the deeper layers of the biofilm. Additionally, the heterogeneity of biofilm formation and variability in thickness across cells can lead to inconsistent interface performance. Careful control of biofilm architecture, combined with material and microbial engineering strategies, is therefore essential to optimize energy transfer and maintain system stability in NMHSs.

In summary, the separation of photoelectrons and their transfer into microbial cells are critical factors in extracellular interface design. Non-electroactive microorganisms or those without transmembrane electron transfer chains, such as cytochrome complexes, can benefit from the addition of external electron mediators like methylene blue or neutral red, which significantly improve electron transfer efficiency.[56,254,255] Furthermore, through the rational design of material types and microstructures, optimization of active sites on microbial surfaces, and utilization of microbial physiological and ecological characteristics, one can effectively reduce the transport distance of photoelectrons or electron mediators into the cells, thus enhancing the energy conversion efficiency of the NMHSs.

4.3 Construction and characteristics of transmembrane interfaces

As the distance increases during the transfer of photoelectrons or electron mediators, the loss of electrons escalates. Thus, it is essential to complete electron transport *via* the most direct route. A feasible approach involves enabling photosensitizers materials to traverse the cell membrane and reach the target enzymatic sites directly. Recent research has investigated various approaches for the development of transmembrane interfaces, such as membrane intercalation, intracellular biomineralization, and the free diffusion of QDs. The following sections elaborate on these approaches.

4.3.1 Intercalated interfaces. Maintaining cellular integrity in NMHSs is crucial for ensuring high viability and optimal functional capacity. Under controlled conditions, the introduction of materials with specific micro-geometries into cells through regulated physical perturbation can improve system efficiency. Carbon nanotubes, recognized for their superior biocompatibility and high conductivity, were effectively integrated into cyanobacterial cells, establishing a rapid electron transfer pathway, as shown in Fig. 9.[256] A different intercalation strategy utilizes the fluidity and amphiphilic characteristics of the cell membrane. Designing organic photosensitizers with functional groups and long hydrophobic alkyl chains analogous to those of the membrane allows these molecules to integrate into the membrane through the principle of "like dissolves like". This integration facilitates direct channels for photoelectrons to enter the cell, thereby improving interfacial electron and energy transfer efficiency. For instance, analogous organic photosensitizers have been developed independently, such as a diamine-structured fluorene–phenylene polymer (PDI/PFP) and an amphiphilic organic photosensitizer (COE-IC) synthesized from 2,2′-bithiophene and 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile. The materials were hybridized with *M. thermoacetica* and *A. vinelandii* to create membrane-intercalated NMHSs, as shown in Fig. 9. In the case of COE-IC, 2,2′-bithiophene served as the electron donor unit, while 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile functioned as the electron acceptor. This configuration facilitated the vibration of photoelectrons along the carbon backbone of the material and their transmembrane delivery into the cell, resulting in efficient fixation of CO_2 and N_2.[72,257] Furthermore, amphiphilic organic photosensitizers can undergo modifications to improve their photocatalytic efficiency. The surface of an amphiphilic organic photosensitizer was functionalized with Au to enhance its electron extraction efficiency. The integration of the membrane intercalation strategy led to the effective development of a highly efficient electron transfer interface.[62]

Membrane-intercalated interfaces offer significant advantages by enabling direct and rapid electron transfer into microbial cells. The close integration of materials with the lipid bilayer facilitates efficient energy and electron delivery,

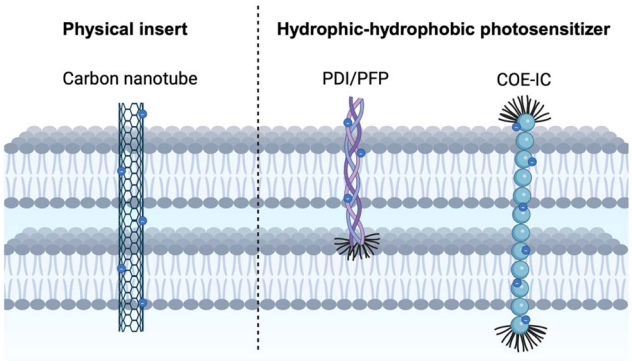

Fig. 9 Construction and characteristics of transmembrane interfaces. Two types of transmembrane materials, including physical insert and hydrophilic–hydrophobic photosensitizer which its hydrophobic side can insert into microbial membrane and another side can generate photo-electron then transport into inside cells through material bone. The arrow represents the flow of photogeneration electrons.

enhances metabolic activity. Additionally, the use of amphiphilic or functionalized photosensitizers allows fine-tuning of electron transfer pathways and photocatalytic efficiency. However, this strategy also presents limitations. The introduction of foreign materials into the membrane can potentially disrupt membrane fluidity or local protein function if not carefully optimized, and the design of compatible materials requires precise control over chemical structure, hydrophobicity, and amphiphilicity. Furthermore, material internalization may be restricted by cell type or size, limiting the general applicability of this approach across diverse microbial species.

4.4 Construction and characteristics of intracellular interfaces

4.4.1 Periplasmic interface. Intracellular or periplasmic interfaces enable precise localization of photosensitizer materials near specific enzymatic sites, thereby improving electron transfer efficiency and minimizing energy loss. By targeting materials to regions such as the periplasmic space, electrons can be delivered directly to key enzymes, such as hydrogenases, without excessive diffusion through the cytoplasm. This spatial control can be achieved using genetically encoded targeting motifs, metal-binding proteins, or amino acid chains that guide photocatalytic nanoparticles to desired intracellular locations. For example, cysteine desulfurase facilitates the removal of thiol groups from intracellular cysteine, mediated by the signal peptide PelB, resulting in the production of hydrogen sulfide (H_2S). This H_2S subsequently reacts with Cd associated with the metal-binding protein A7, leading to the formation of CdS in the periplasmic space. The specific binding of His-tagged proteins to Zn serves as a targeting mechanism. Genetic engineering facilitates the co-expression of molybdenum–iron nitrogenase reductase with His-tag proteins, which enables specific binding to the reductase.[136,258,259] This approach allows for precise targeting with similarly designed metal-based photocatalysts. $CuInS_2$/ZnS QDs were engineered for diffusion into *S. oneidensis* cells. The Zn component exhibits strong binding with the Fe–S cluster subunits of hydrogenase, facilitating transport through the Tat pathway to the periplasmic space, thereby enabling targeted energy delivery to the designated site.[105,177,178]

The periplasmic interfaces minimize energy loss and reduce unintended interactions, such as ROS generation in cytoplasmic space, thereby preserving cellular integrity and enhancing metabolic activity. However, these interfaces also present challenges. The engineering of precise targeting mechanisms requires sophisticated genetic or chemical modifications, which may be strain-specific and difficult to generalize. Additionally, excessive accumulation of materials or reactive species in confined cellular compartments could potentially disrupt local homeostasis or impair enzymatic function, necessitating careful optimization to balance efficiency and cellular health.

4.4.2 Cytoplasmic interfaces. Cytoplasmic interfaces represent a strategy in which photosensitizer materials are localized within cytoplasmic cells to facilitate direct electron and energy transfer to intracellular enzymatic sites. Alongside physical embedding methods, researchers have explored direct intracellular delivery and *in situ* self-assembly of photocatalytic materials. In addition to the previously discussed microbial biomineralization at the cell surface, certain microbes are also capable of intracellular biomineralization, enabling the formation of functional photocatalytic materials within cellular compartments.[245] This strategy entails the careful selection of metal ions, their transport into cells through metal ion channels, and the utilization of endogenous small molecules, such as glutathione and L-cysteine, to facilitate the formation of photocatalytic materials. This method eliminates the requirement for photoelectrons to traverse the cell membrane and wall, which is particularly beneficial in the development of NMHSs for eukaryotic microbes, thereby improving electron utilization efficiency, as shown in Fig. 10. For instance, the introduction of Cd^{2+} and S^{2-} to *S. cerevisiae* facilitates the self-assembly of CdS QDs within the cell, leading to a notable increase in hydrogen production by lactate dehydrogenase.[260] Glutathione, an intracellular antioxidant, can reduce precursors or serve as a sacrificial agent to fill photogenerated holes. Intracellular glutathione in *E. coli* was used to reduce SeO_3^{2-} precursors, leading to the synthesis of CdS_xSe_{1-x} QDs.[261]

Compartmentalization can similarly establish defined cytoplasmic interfaces by creating distinct functional regions within the cell through liquid–liquid phase separation. This process generates microenvironments that differ from the cytoplasm, thereby locally increasing the concentrations of substrates and enzymes.[262–264] Liquid–liquid phase separation is influenced by local concentration gradients resulting from intrinsically disordered proteins and RNA. Modification of photocatalytic materials with peptide functionalities enables the achievement of cell-organelle-like compartmentalization driven by the materials themselves.[265] This strategy facilitated the construction of a CdS-based compartmentalized structure in *E. coli*, which enhances the degradation of environmental pollutants.[264]

Cytoplasmic interfaces offer the advantage of bringing photosensitizers materials into close proximity with

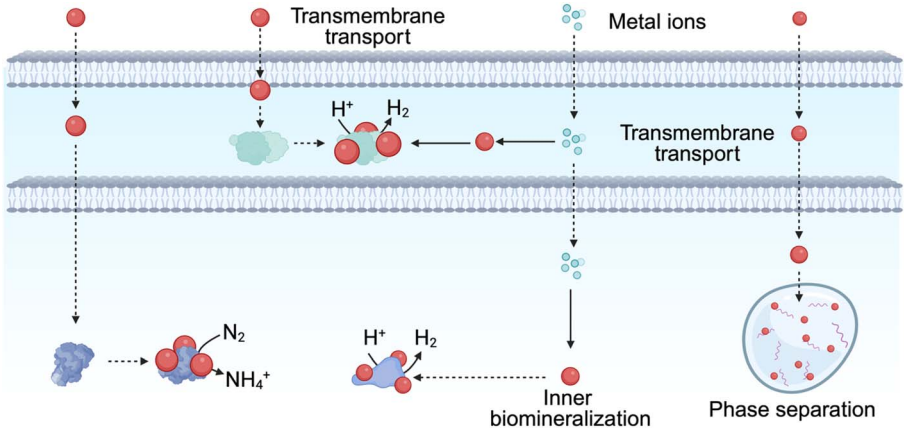

Fig. 10 Construction and characteristics of intracellular interfaces. Two types of materials locate in periplasmic space are demonstrated in the left part of the pattern, including enzyme transportation pathway and quantum dot cross cell membrane. Mechanisms of intracellular location through inner biomineralization and phase separation are demonstrated in the right part of the graph.

intracellular enzymes, thereby enabling highly efficient electron and energy transfer without the need to cross the cell membrane. This spatial precision enhances reaction specificity, local substrate concentrations, and metabolic efficiency, while also allowing the formation of microenvironments tailored for particular biochemical processes. Furthermore, the use of endogenous molecules and liquid–liquid phase separation can facilitate controlled material assembly and mimic organelle-like compartmentalization. However, these strategies also present challenges, the introduction or *in situ* formation of materials within the cytoplasm may disrupt cellular homeostasis or organelle function, and excessive accumulation of photocatalytic materials or reactive species could induce cytotoxicity. Achieving consistent intracellular distribution and maintaining long-term cellular viability thus require careful optimization of material properties, delivery methods, and metabolic conditions.

4.5 Intracellular functional modular interfaces based on genetic engineering

The engineering of intracellular functional interfaces in NMHSs relies on the direct modification of microbial cells at the genetic level. By integrating natural light-responsive systems, such as rhodopsins or chloroplast components, non-photosynthetic microorganisms can be endowed with the ability to capture and convert light energy.[266] For example, exogenous expression of rhodopsin in *E. coli* facilitated ATP synthesis rates.[267] Beyond single-gene integration, more complex strategies involve incorporating entire photosynthetic microorganisms, such as cyanobacteria, into non-photosynthetic hosts *via* cell fusion, mimicking the symbiotic relationship between chloroplasts and mitochondria. These approaches, combined with the reconstruction of metabolic networks, enable the establishment of stable intracellular energy-metabolism interfaces. Research has explored such symbiotic systems using model chassis organisms, including *S. cerevisiae* and cyanobacteria.[268,269]

Genetically engineered intracellular interfaces provide precise control over energy capture and metabolic flux by integrating light-responsive modules directly into microbial cells. This approach enables non-photosynthetic organisms to harness solar energy, improve ATP generation, and establish stable intracellular energy-metabolism pathways, effectively converting them into functional NMHSs. However, such strategies also present challenges: the introduction of exogenous photosystems or metabolic modules may impose a metabolic burden, disrupt native cellular regulation, or provoke unintended interactions between engineered and endogenous pathways. Careful optimization of gene expression levels, module compatibility, and host physiology is therefore essential to maximize energy conversion efficiency while maintaining cell viability.

4.6 Current status and challenges

The material–biological interface in NMHSs is a significant element that has garnered considerable interest from researchers. Current research emphasizes the development of stable and efficient interfaces for long-term energy–matter exchange, utilizing the distinct physical, chemical, and metabolic characteristics of catalysts and microbial surfaces. This necessitates a comprehensive understanding of the catalytic mechanisms of photocatalysts, microbial metabolic pathways, and their interfacial interactions. Current technical limitations present numerous challenges in the study of such interfaces.

The mechanism of "information communication" at the interface, specifically the pathways for signal and energy exchange from electron transfer to molecular interactions, is not well understood. Direct visual evidence concerning alterations in the redox state of intermediates and the behavior of redox protein complex during electron transfer is insufficient. Generally, electron transfer occurs *via* two main routes: the direct EET pathway, where photogenerated electrons from semiconductors are transferred directly to bacterial redox-active proteins (*e.g.*, cytochromes and hydrogenases); and the indirect EET pathway, where electrons are shuttled into bacterial cells *via* soluble redox mediators (*e.g.*, flavins or hydrogen). These pathways, along with the key proteins involved, have been

comprehensively discussed in a recent review.[18] Future advancements may involve the use of *in situ* techniques, including X-ray absorption spectroscopy (XAS), transient absorption spectroscopy (TAS) and other real-time observation methods, to monitor the dynamic process of photoelectron transfer from materials to biological interfaces. Furthermore, fluorescently labeled proteins—which emit specific signals when excited by appropriate wavelengths (*e.g.*, 405 nm for PAmC1, 514 nm for mVenus, 561 nm for mC/PAmC1)—enable the precise tracking of electron transfer events. Notably, recent advances combining multi-channel fluorescence imaging with photoelectrochemical measurements have allowed for the real-time visualization of electron transport at the single-cell level. This integrated approach permits the simultaneous monitoring of protein spatiotemporal dynamics and photocurrent responses from individual cells. Utilizing this platform, *Ralstonia eutropha* was demonstrated to possess direct EET capability mediated by both soluble and membrane-bound hydrogenases, complementing its well-established H_2 mediated indirect electron uptake mechanism.[270]

Secondly, in contrast to biological systems, photocatalytic materials lack the ability to self-replicate. Moreover, ongoing materials results in material degradation. Achieving long-term stability of material–biological interfaces presents a considerable challenge. A potential solution involves establishing microbial reliance on the energy supply from materials and facilitating microbial perception and regulation of abiotic interfaces. Through the screening of various precursor materials and the application of genetic engineering to the biological host, microorganisms can be engineered to detect precursor molecules in their environment and autonomously construct material–biological interfaces as required. This approach facilitates dynamic interface assembly while ensuring long-term stability.

Efficient interfacial electron transfer constitutes a significant limitation in NMHSs. Microorganisms have a comprehensive and self-regulating energy transfer and metabolic network, complicating the precise direction of external energy inputs to specific target sites. Through the application of genetic engineering, adaptive evolution, and machine learning in the design of materials and microbial chassis, it is feasible to create and manage material–biological interfaces that facilitate unidirectional intracellular energy flow. Furthermore, the development of "interface switches" that are inactive under standard conditions but can be activated by specific stimuli (*e.g.*, temperature, pH, current, or light) may facilitate the regulated activation of NMHSs. This enables microbes to transition from natural growth modes to "production worker" states, facilitating efficient, high-yield, and customizable conversion of solar energy into high-value products.

5 Summary and outlook

NHMSs offer a promising blueprint for solar-to-chemical energy conversion by bridging synthetic materials with living organisms. As a biohybrid platform at the intersection of materials science and microbiology, their performance critically depends on the rational integration of components across scales and functions. Central to this integration is the design of the material–cell interface, which underpins both the stability and the efficiency of the system. Material properties such as size, morphology and surface chemistry dictate how interfaces are assembled, while cellular structures and metabolic capabilities govern interfacial electron transfer dynamics. The spatial configuration and mutual compatibility of materials and microbes collectively determine electron transport routes and, in turn, the yield of desired products. Maximizing the potential of these systems requires a bottom-up design strategy, in which materials and microorganisms are selected and tailored according to the functional demands of the hybrid construct. This entails not only matching interfacial properties but also coordinating the interaction landscape to support efficient and sustained energy flow.

To address the complexity of interface engineering, a multi-dimensional optimization framework is essential. Key strategies include: (1) hierarchical assembly to establish efficient charge and mass transport pathways; (2) dynamic interfaces that respond adaptively to environmental cues; (3) biocompatible designs that preserve microbial activity and viability over time; (4) data-driven approaches, such as AI-assisted optimization, to accelerate the discovery and integration of functional material–microbe pairs; and (5) techno-economic analysis for practical application, considering the full energy chain from light harvesting to product formation. Together, these approaches form a roadmap toward constructing robust and high-performing NMHSs, paving the way for scalable and sustainable biohybrid technologies.

5.1 Precision assembly of hierarchical structures

For interface design, a progressive, integrated assembly strategy from photocatalytic materials to microorganisms can be employed, wherein the synergistic interaction between functionalized materials and specific microbes enables *in situ* energy supply and dynamic organization, thereby precisely regulating energy flow and enhancing the conversion efficiency of target products. Within this framework, the hierarchical design and optimization of materials play a pivotal role. For instance, wavelength-tunable quantum dots encapsulated within the pores of MOFs can achieve full-spectrum light harvesting from ultraviolet to near-infrared (300–850 nm), while the confinement effect of the MOFs matrix improves charge separation efficiency of the photocatalytic components.[271] This strategy not only broadens the range of usable solar energy but also significantly enhances photocatalytic activity. Recent studies demonstrate that constructing atomic-level electron bridges at material–microbe interfaces can markedly enhance charge separation and reduce interfacial transfer barriers. For instance, in a C_3N_4/Ru–*Shewanella* hybrid, a single-atom Ru–N_4 motif enables over a tenfold increase in direct electron uptake and leads to more than an order-of-magnitude improvement in solar-driven H_2 production. This illustrates a precise hierarchical strategy in interface engineering governs energy flow and boosts conversion efficiency.[272] Besides, applying this

hierarchical assembly principle to NMHSs, future designs could utilize similar frameworks to co-localize distinct microbial strains or to couple microbial surface catalysts with photosensitizers, effectively reducing ROS damage and optimizing electron transfer pathways.

Beyond material design, the photosynthetic performance of microorganisms is also strongly influenced by their structural distribution. By regulating microbial community composition, metabolic pathways, and cell surface properties, NMHSs can be further optimized. For instance, genetic engineering can be used to control the expression of surface proteins, enabling microorganisms to spontaneously form stable multilevel architectures that improve light utilization efficiency. Moreover, tuning extracellular matrix secretion can enhance microbial immobilization within defined spatial domains, thereby improving system stability and catalytic performance.[273] In summary, by coupling material optimization for enhanced light capture and charge separation with microbial engineering strategies for controlled self-assembly and improved robustness, more efficient energy conversion can be achieved in NMHSs.

5.2 Design of stimuli-responsive interfaces

Stimuli-responsive materials have attracted growing attention in photocatalysis, bioelectronics, and artificial photosynthesis due to their inherent environmental adaptability and dynamic tunability.[274] These materials are capable of undergoing reversible physical or chemical changes upon exposure to external stimuli such as light, heat, or pH. A prominent example is azobenzene derivatives, which undergo reversible *trans–cis* isomerization under ultraviolet irradiation or thermal activation. Leveraging this property, photo-responsive azobenzene units have been widely integrated into polymers, MOFs, and other nanostructured materials.[275] In the context of NMHSs, introducing such dynamic materials into the light-harvesting module enables the real-time modulation of surface properties. For instance, light-induced conformational switching of azobenzene moieties can dynamically alter the surface zeta potential of the material, which may in turn influence the contact angle at the cell membrane interface. This tunability provides a mechanism for stimulus-triggered activation of electron transport pathways, enhancing transmembrane electron flux and thus improving energy conversion efficiency.

Microorganisms inherently possess environmental sensing capabilities, enabling them to reprogram metabolic activity *via* signal transduction networks. Synthetic biology offers powerful tools to augment this capacity, allowing for the design of intelligent microbial chassis that dynamically adjust metabolic pathways in response to cues such as light intensity, nutrient availability, or redox state. For example, genetically encoded redox-sensitive switches can be used to activate photosynthetic pathways under specific intracellular redox conditions, thereby enhancing overall energy conversion efficiency.[276] Specifically, redox-switchable polymer shells have been used to dynamically modulate the conductivity of microbe–semiconductor junctions, thereby optimizing intracellular electron allocation under variable illumination. At the interface level, genetic and metabolic engineering can rewire microbial behavior to preferentially utilize solar energy under light while maintaining viability in the absence of light. Simultaneously, light-responsive catalytic materials can be engineered to sense and respond to changes in the local photonic environment, enabling spatiotemporal control over material–microbe interactions. The integration of stimuli-responsive materials with synthetic biology strategies thus provides a versatile platform for the precise regulation of hybrid photosynthetic systems, offering enhanced control over electron transfer dynamics and energy conversion processes. This dynamic regulation strategy not only improves the stability and responsiveness of NMHSs but also lays the groundwork for future developments in sustainable bioenergy and programmable biohybrid technologies.

5.3 Innovative design of biocompatible interfaces

The selection and design of photocatalytic materials are central to achieving efficient energy conversion. However, many high-performance photocatalysts, such as CdS and CdTe quantum dots as well as organic dyes, while exhibiting excellent light absorption and charge separation capabilities, often suffer from intrinsic biotoxicity, which severely limits their applications in biological contexts. Under illumination, these materials may release toxic metal ions or generate ROS, thereby damaging microbial cells and compromising system stability and long-term functionality. Consequently, enhancing the biocompatibility of photocatalytic materials while maintaining their catalytic efficiency has emerged as a key challenge in this field. Various strategies such as surface modification and interfacial engineering can significantly reduce their adverse effects on microorganisms. For example, coating photocatalysts with biocompatible layers such as polydopamine, silica, or biomacromolecules not only minimizes direct contact with cells but also improves stability and reduces toxicity. Alternatively, modification with EPS secreted by microbes can further enhance material–microbe compatibility, decreasing membrane disruption and alleviating host rejection of foreign materials, thereby improving system robustness.[22,277]

Strengthening microbial adaptability through genetic and metabolic engineering is crucial for the stability of NMHSs. For example, enhancing the expression of antioxidant enzymes can significantly reduce cellular damage caused by ROS generated during photocatalysis. Furthermore, engineering membrane proteins to display specific binding motifs can facilitate the efficient anchoring of photosensitizers, thereby improving electron transfer efficiency at the cellular boundary.[204] Complementary to genetic modifications, structural and ecological strategies can further reinforce system robustness. Optimizing microbial community interactions—such as co-culturing strains with complementary metabolic functions—can establish cooperative networks that boost both efficiency and long-term stability.[278] Additionally, physical encapsulation strategies can create protective microenvironments that shield microbes from harsh reaction conditions. Similarly, biocompatibility-oriented material engineering, such as

introducing lipid-mimetic surface groups onto carbon nitride nanosheets, has also been proven effective in reducing membrane perturbation while sustaining long-term microbial activity. Therefore, integrating approaches such as material surface engineering, microbial adaptability enhancement, and synergistic community design holds great promise for simultaneously improving photocatalytic efficiency and reducing biotoxicity, thereby supporting the long-term stability of NMHSs. This not only expands the applicability of photocatalytic materials in biological contexts but also provides important theoretical and practical foundations for optimizing bio-material interfaces.

5.4 Artificial intelligence for rational design and dynamic control

Advances in computational power and big data analytics have catalyzed the rapid integration of artificial intelligence (AI) into interdisciplinary fields such as synthetic biology and materials science. In the context of NMHSs, AI is evolving from optimizing individual components to enabling end-to-end system-level design. For example, machine learning algorithms can be used to predict the compatibility between material band structures and microbial metabolic networks, or to identify optimal material–microbe pairings *via* high-throughput screening platforms.[279] Data-driven high-throughput simulation methods are emerging as powerful tools in materials discovery, accelerating the selection of efficient photosensitizer–catalyst combinations. In a recent study, Xiong *et al.* employed a machine learning-assisted screening strategy to develop a high-efficiency molecular artificial photocatalytic system.[280] Their approach used key descriptors-including CO_2 adsorption energy, photosensitizer lifetime, and electronic coupling induced by intrinsic transition dipoles-to rapidly identify promising catalyst–photosensitizer pairs from thousands of potential combinations. Looking forward, the integration of modular synthetic biology with AI-powered dynamic control could enable real-time optimization of electron transfer pathways, facilitating the transition of NMHSs from laboratory prototypes to scalable applications.[281] In microbial optimization, AI can support genome editing strategies, refine metabolic regulation models, and fine-tune culture conditions. By analyzing genomic and metabolomic datasets, machine learning models can predict microbial growth performance and photosynthetic output under defined conditions, enabling the selection of high-performing strains. Moreover, computational simulations-when coupled with synthetic biology tools-can direct metabolic rewiring to enhance light-to-chemical energy conversion efficiency.[282]

AI also holds promise for real-time monitoring and feedback control of microbial consortia. By dynamically adjusting cultivation parameters in response to population-level fluctuations, AI can help maintain long-term system stability and performance. These capabilities not only enhance the compatibility between biological and material components, but also accelerate dynamic system optimization across time and environmental conditions. The deep integration of AI and synthetic biology is poised to expand the functional landscape of NMHSs, offering new strategies for renewable energy production and environmental remediation. For example, AI-guided structural analysis of target proteins can inform the design of materials that selectively interact with catalytic active sites. Combined with machine learning-based high-throughput evaluation of system compatibility, this approach could enable the efficient and low-cost construction of next-generation biohybrid photosynthetic platforms.

5.5 Techno-economic analysis for practical application

Evaluating the techno-economic potential of NMHSs is critical for assessing their scalability and real-world applicability. Techno-economic analysis (TEA) provides a systematic framework to quantify energy input, material costs, and product yields across the entire biohybrid workflow, from light harvesting to target chemical formation. By integrating data on material synthesis, microbial cultivation, and system assembly, TEA can identify cost-intensive steps, energy losses, and bottlenecks in electron and mass transport pathways. The practical potential of NMHSs can be further illustrated by recent examples of scalable solar-to-chemical biohybrids. In one study, semiconductor–microbe hybrids were constructed *in situ* by introducing an aerobic sulfate reduction pathway into *Vibrio natriegens*, enabling the utilization of heavy metal ions, sulfate, and organics in wastewater to biosynthesize functional semiconductor nanoparticles. The resulting biohybrids supported efficient solar-driven conversion of organics to 2,3-butanediol, achieving a titer of 13.09 g L^{-1} in a 5 L illuminated fermenter. Life-cycle assessment confirmed substantial sustainability gains relative to conventional production routes, highlighting both the scalability and environmental benefits of this approach.[283]

The rational design of NMHSs should incorporate TEA to guide their potential practical application. Specifically, when materials were designed to enhance light capture and charge separation, their fabrication costs and long-term stability directly influence the overall economic feasibility. Similarly, microbial engineering strategies that improve self-assembly or metabolic efficiency must be balanced against cultivation complexity and operational expenses. Through iterative TEA-guided design, NMHSs can be optimized not only for maximum photocatalytic performance but also for energy- and cost-efficient implementation, thereby bridging the gap between laboratory-scale demonstrations and large-scale industrial or environmental applications.

Therefore, the future development of NMHSs will no longer be confined to single-dimensional performance enhancement, but will instead advance through precise multilevel structural assembly, dynamic regulation of intelligent responsive interfaces, continuous optimization of biocompatibility, and deep empowerment by artificial intelligence, driving the system toward greater complexity, adaptability, and sustainability. Hierarchical structural design not only maximizes full-spectrum solar energy capture and utilization, but also enables efficient coupling of solar-to-chemical conversion through self-organization and microbial community

engineering. Intelligent responsive interfaces endow the system with dynamic "sensing–regulation–feedback" capabilities, maintaining optimal operation under diverse environmental conditions. Continuous breakthroughs in biocompatibility are expected to overcome the dual bottlenecks of material toxicity and microbial tolerance, thereby ensuring long-term stability and ecological safety. Moreover, the integration of artificial intelligence provides a new paradigm for system optimization, enabling data-driven predictions and control from the molecular to the community scale with unprecedented efficiency and precision. Importantly, evaluating system-level energy efficiency and economic viability—including catalyst cost, material scalability, and operational energy inputs—will be crucial for translating NMHSs from academic demonstrations to industrial deployment. Collectively, these cutting-edge strategies lay the scientific foundation for building more efficient, stable, and controllable hybrid systems.

A growing body of studies offers concrete examples of how these strategies can be operationalized. For hierarchical assembly, porphyrinic MOFs such as PCN-222 have been co-engineered with *E. coli* to form multiscale architectures in which macropores enhance photocarrier generation and directional electron delivery.[66] In the domain of intelligent–responsive interfaces, redox-switchable polymer shells have been used to dynamically modulate the conductivity of microbe–semiconductor junctions, thereby optimizing intracellular electron allocation under variable illumination. Together, these representative cases illustrate practical routes for implementing the proposed multidimensional optimization framework.

With further progress, NMHSs are expected to bridge the critical energy-integration gap between modern photovoltaics, photoelectrocatalysis, and biomanufacturing, thereby achieving efficient delivery of exogenous energy into microbial cells, significantly improving the utilization efficiency of one-carbon resources (*e.g.*, CO_2, methanol, formate) in microbial factories, and accelerating the establishment of a third-generation green biomanufacturing paradigm. Beyond enabling the efficient transformation of "non-food resources" into "high-value products" under the carbon-neutrality framework, these systems also show broad potential in environmental remediation (CO_2 capture and valorization), agricultural enhancement (light-driven biosynthesis of natural products), biomedicine (precise synthesis of pharmaceutical precursors), and intelligent materials (construction of living functional materials), thereby opening new pathways for cross-disciplinary applications. With deeper interdisciplinary collaboration and continuous integration of emerging technologies, NMHSs now stand at a pivotal transition from laboratory research to large-scale application, and are poised to become a key technological driver for green energy development and ecological civilization.

Author contributions

Hao Wang: writing – -original draft, writing – review & editing. Jialu Li: validation, writing – review & editing. Yuhua Feng: validation, writing – review & editing. Donghao He: validation. Xiaolei Fan: conceptualization. Bo Wang: conceptualization, formal analysis, validation. Zhonghua Cai: conceptualization, funding acquisition. Cuiping Zeng: conceptualization, funding acquisition. Kemeng Xiao: conceptualization, visualization, project administration, funding acquisition, writing – original draft, writing – review & editing, supervision.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review. All figures in this review were redrawn by the authors and therefore do not require permission from any journals.

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