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Review

Cadmium sulfide nanoparticles-assisted intimate coupling of microbial and photoelectrochemical processes: Mechanisms and environmental applications

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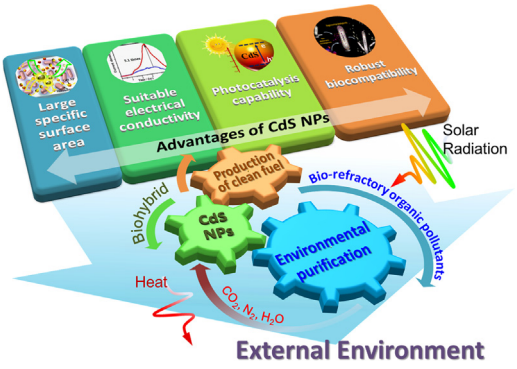
HIGHLIGHTS

- CdS NPs assists hybrid microbial-photoelectrochemical processes.
- CdS NPs display desirable biocompatibility with microorganisms.
- CdS NPs-immobilized biohybrids display a potential for environmental application.

GRAPHICAL ABSTRACT



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ABSTRACT

Intimate coupling of microbial extracellular electron transfer (EET) and photoelectrochemical processes is an emerging research area with great potential to circumvent many disadvantages associated with traditional techniques that depend on independent microbial or photocatalysis treatment. Microbial EET processes involve microorganism oxidation of extracellular electron donors for respiration and synchronous reduction of extracellular electron acceptors to form an integrated respiratory chain. Coupled microbial EET-photoelectrochemical technologies greatly improve energy conversion efficiency providing both economic and environmental benefits. Among substitutes for semiconductor photocatalysts, cadmium sulfide nanoparticles (CdS NPs) possess several attractive properties. Specifically, CdS NPs have suitable electrical conductivity, large specific surface area, visible light-driven photocatalysis capability and robust biocompatibility, enabling them to promote hybrid microbial-photoelectrochemical processes. This review highlights recent advances in intimately coupled CdS NPs-

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Biohybrid
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microbial extracellular electron transfer systems and examines the mechanistic pathways involved in photoelectrochemical transformations. Finally, the prospects for emerging applications utilizing hybrid CdS NPs-based microbial-photoelectrochemical technologies are assessed. As such, this review provides a rigorous fundamental analysis of electron transport dynamics for hybrid CdS NPs-microbial photoelectrochemical processes and explores the applicability of engineered CdS NPs-biohybrids for future applications, such as in environmental remediation and clean-energy production.

Contents

1. Introduction

Microbial extracellular electron transfer (EET) is a process by which microorganisms oxidize extracellular electron donors (*e.g.,* low-molecular-weighted organic carbon) to release electrons for their respiration concomitant with transporting electrons directly to external electron acceptors (Flemming and Wingender, 2010). Previous investigations reported that microbial EET processes were facilitated through direct contact between microorganisms and electron acceptors *via* microbial nanowires or specific *c*-type outer-membrane cytochromes (*e.g.,* OmcB/C, OmcE, OmcZ and OmcS in *Geobacter sulfurreducens*) (Hernandez and Newman, 2001; Li et al., 2020b; Reguera et al., 2005), interactions with exogenous or endogenous electron shuttles (*e.g.,* quinone-containing compounds) (Chen et al., 2017a; Chen et al., 2017b; Li et al., 2019), and reactions with conductive materials (*e.g.,* active carbon, biochar and reduced graphene oxide) (Chen et al., 2018b; Chen et al., 2016; Luo et al., 2019). In spite of these advances, the selectivity of microbial electrocatalysis technology associated with specific genetically encoded expression is still a bottleneck that must be overcome before realizing this technology for practical applications (Liu et al., 2018a). Therefore, optimization of microbial electrocatalysis technology and its integration with effective chemical catalysis technologies are major challenges limiting future advances.

Novel technologies integrating intimate coupling of microbial and photoelectrochemical processes demonstrate promise for several potential applications, such as environmental remediation and clean energy production (Liu et al., 2016; Nichols et al., 2015; Torella et al., 2015; Yu et al., 2020; Zhang, 2015). The "intimate coupling process" is characterized as a coupled reaction process in which electron transport is simultaneously derived from both photocatalysis and microbial EET. For instance, one might employ "sequential treatment" by combining photocatalysis with subsequent biodegradation to realize complete mineralization of recalcitrant organic pollutants (Li et al., 2012a). Hence, if photocatalysis and microbial degradation are intimately coupled, sequential treatment processes can be designed and optimized for specific applications. These coupled processes overcome many of the inefficiencies associated with sequential independent processes to realize enhanced reaction efficacy, particularly by eliminating the uncertainty of photocatalysis intermediates (Xiong et al., 2017; Zhou et al., 2017). Thus, a comprehensive review of the mechanisms involved in electron transfer of hybrid microbial-photoelectrochemical processes is important and timely for providing theoretical guidance to advance future research and development of emerging bioelectrochemical engineering technologies.

Photocatalysts primarily involve special semiconducting materials with specific light absorption characteristics (Fagan et al., 2016; Schultz and Yoon, 2014; Yoon et al., 2010; Zhou et al., 2015). Metal sulfides are a common photocatalysts given their relatively narrow band gap and a suitable conduction band position, which display outstanding visible-light responsiveness (He et al., 2015; Shen et al., 2011). Among a variety of semiconducting materials, CdS nanoparticles (NPs) possess a relatively narrow band gap (2.4 eV) and enhanced performance for visible light absorption compared to those of titanium dioxide NPs (band gap of 3.2 eV that can only absorb ultraviolet light with wavelengths <387 nm) (Cheng et al., 2018). Consequently, CdS NPs are considered the most versatile nano-sized semiconductor photocatalysts among the various sulfides (Hopfner et al., 2002; Koca and Şahin, 2002). Considering their excellent photocatalytic properties and visible-light response, energy conversion derived from coupled CdS NPs-derived photobiocatalysis and microbial EET processes are expected to achieve higher specificity and conversion efficiency than those of biological or chemical pathways alone.

In this review, we synthesize recent advances in understanding the mechanisms mediating intimately coupled microbial EET-photoelectrochemical processes in conjunction with CdS NPs. We then consider the use of CdS NPs in bioelectrochemical engineering approaches to develop technological applications to solve real-world problems. We expect this review to advance the design of novel, stable and highly reactive CdS NPs-based targeting systems,

leading to new applications in environmental remediation and clean fuel production.

2. Electrical conductivity and specific surface area of CdS NPs

Previously, Li and coworkers demonstrated enhanced microbial nitrate reduction and electrical generation in the presence of semiconductor materials (*e.g.*, TiO_2, α-Fe_2O_3 and γ-Fe_2O_3), highlighting the electron transmission mechanism through the conduction band of these semiconductors (Liu et al., 2014; Zhang et al., 2012). Because semiconducting CdS NPs have comparatively low resistance (~$10–10^{-2}$ Ω·cm) (Chen et al., 2013; Seoudi et al., 2012), extracellular electrons are theoretically permitted to transfer across the outer membrane-bound proteins of microbes to the conduction band of CdS NPs (Fig. 1). In terms of electrical conductivity, CdS NPs are superior to several competing semiconductor materials, such as Fe_2O_3 NPs, ZnS NPs and TiO_2 NPs (corresponding resistance of $10^3–10^{-2}$, $10^2–10^{-2}$ and $10^{10}–10^3$ Ω·cm, respectively) (Baek et al., 2019; Soni et al., 2009; Yildiz et al., 2008). Ye et al. (2019) previously demonstrated a promotion of electron transfer resulting from a weaker interfacial resistance derived from CdS NPs supplemented assays (which was only 59% that of non-CdS NPs amended assays). The enhance electron transfer resulted in higher direct carbon dioxide-to-methane conversion by *Methanosarcina barkeri* due to stimulation by CdS NPs. Similarly, for biological removal of nitrate, we found that the average removal rate per unit mass of biomass and semiconductor material was at least 2.3-fold higher for CdS NP-amended *versus* Fe_2O_3 NP-amended assays (Chen et al., 2019a; Liu et al., 2014). These examples highlight the efficacy of CdS NPs for electrical modification of bioelectrochemical systems through decreasing interfacial resistance and promoting charge transfer.

Supplementation of CdS NPs into biosystems also provides abundant contact sites for interactions with microorganisms and electron acceptors due to their large specific surface area (Chen et al., 2013; Li et al., 2008; Zhang et al., 2018b). In general, CdS NPs have large specific surface area with an abundance of surface active sites to facilitate adsorption of reactant molecules, mass transfer and efficient charge transfer. For example, Yu et al. (2012) demonstrated a higher hydrogen production rate (up to 1.21 mM/h) when splitting water with nanosized CdS (surface area = 46 m^2/g) than submicron CdS particles (less 0.35 mM/h for 17 m^2/g). Thus, it is plausible that CdS NPs fill small gaps where microbes and electron acceptors are not in close association to provide long-range electron transfer along biofilms. Herein, CdS NPs

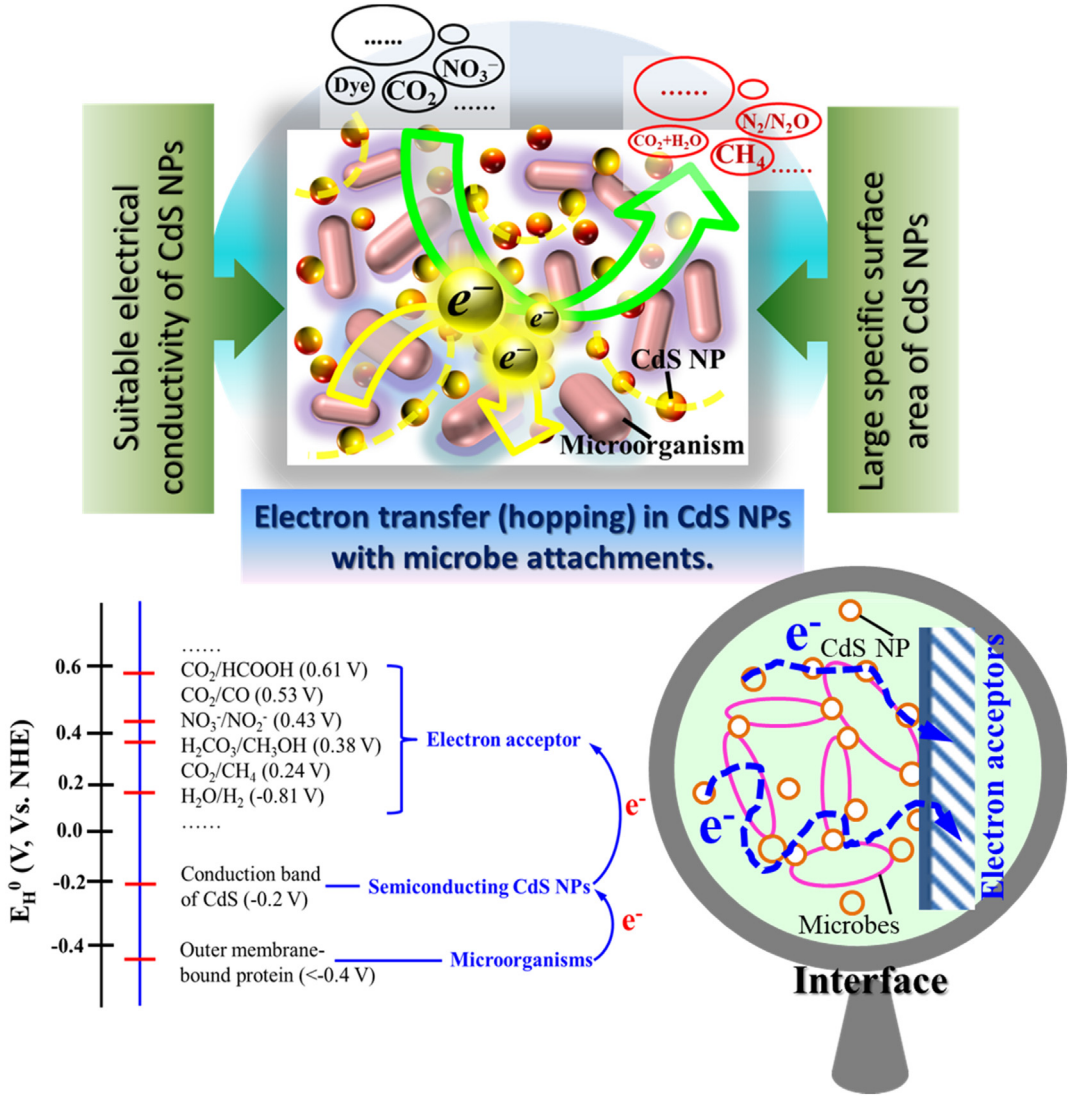

Fig. 1. Physical advantages of CdS NPs in promoting electron transfer at microbe-CdS NPs interfaces. CdS NPs with efficient electrical conductivity gain high recognition with delivered electrons, enabling a direct contact-based EET process. Increased exposure/contact between CdS NPs, microorganisms and electron acceptors enhances overall electron transfer within the system.

enhanced EET performance by means of constructing an enlarged and more continuous artificial conductive network for long-range electron transfer (Chen et al., 2019c).

Owing to the large specific surface area and suitable electrical conductivity of CdS NPs, a direct contact-based EET process is posited for circumstances where microorganisms adhere to the surfaces of CdS NPs (Fig. 1). The low electron transfer resistance at CdS NPs-microbe attachment interfaces facilitates a faster transfer of electrons from microorganisms to electron acceptors. This is especially important when isolated areas exist where electrons are not easily shuttled due to physical disruptions in the conductive network (Zhang et al., 2018b). In this case, semiconducting CdS NPs provide a bridge where hopping electron transfers are enhanced by conductive interfaces between microbes and CdS NPs (Xie et al., 2014).

3. CdS NPs-driven photoelectrochemical processes

A number of investigations report the efficacy of CdS NPs as a promising photosensitizer (Hetsch et al., 2011; Zhang et al., 2010). Considering the narrow band gap of CdS NPs, the superior photosensitivity characteristics of CdS NPs efficiently excite photoelectrons-hole pairs upon solar illumination (Zhang and Guo, 2013). Several studies emphasize the photocatalytic capacity of CdS NPs for production of hydrogen (Ryu et al., 2007; Zong et al., 2010) and hydrocarbon fuels as shown in Fig. 2 (Jin et al., 2015; Yu et al., 2014). To realize hydrogen production by splitting water under visible light irradiation, a semiconductor photocatalyst having suitable conduction and valence band potentials and an appropriate band gap width is required (Cheng et al., 2018). Notably, the oxidation potential of O_2/H_2O is more negative than the top level of the CdS NPs valence band position, and the reduction potential of H^+/H_2 is more positive than the bottom level of the CdS NPs conduction band (Li et al., 2016). This unique property makes CdS NPs an ideal semiconductor photocatalyst for hydrogen production. The electrochemical advantage of CdS NPs is also exhibited in CdS NP-driven photocatalysed reduction of carbon dioxide under visible light irradiation (Cheng et al., 2018). The redox position of carbon dioxide is matched between the potentials of the conduction and valance bands of CdS NPs. Thus, carbon dioxide is effectively reduced by CdS NP-derived photocatalysis into hydrocarbon products (*e.g.,* formic acid, methanol, methane) (Ahmad Beigi et al., 2014; Ijaz et al., 2016; Li et al., 2012b).

Further, the efficacy of CdS NPs-assisted photocatalysis is prominently exhibited in applications targeting the removal and mineralization of bio-refractory organic pollutants. In the aqueous phase, bio-refractory organic pollutants are readily adsorbed to the surface of CdS NPs due to their large and reactive surface area. Under visible light irradiation, CdS NPs absorb photons to produce oxidative photoholes (*e.g.,* reactive oxygen species) that promote photocatalytic degradation of large organic pollutants into low-molecular-weight byproducts and synchronously separate photoelectrons, hindering the recombination of photoelectron-hole pairs (Zhang et al., 2018a). The resulting byproducts are more labile with respect to microbial degradation, resulting in further mineralization to water and carbon dioxide. Photoelectrons generated by photocatalyst also participate in the microbial degradation process through *c*-type cytochromes' delivery (see Section 4). The timely microbial degradation of these byproducts effectively circumvents any adverse effects imposed by unfavorable oxidation conditions and interferences with microbial metabolic processes. Thus, complete removal of bio-refractory organic pollutants in the presence of CdS NPs is ascribed to the synergistic effects of adsorption, photocatalysis and biodegradation resulting from intimate coupling of photocatalysis and microbial degradation. Several examples of intimately coupled degradation processes for mineralization of bio-refractory organic pollutants include tetracycline hydrochloride (Zhu et al., 2019b), reactive dyes (Cui et al., 2018), phenazopyridine (Zyoud et al., 2010) and nitrofurazone (Hou et al., 2020). Intimate coupling of degradation processes, such as these, holds great potential for enhanced wastewater treatment of industrial pollutants. Overall, these studies demonstrated the potential utility for exploiting the excellent photocatalytic efficiency of CdS NPs for applications involving a range of photoelectrochemical transformations.

4. Biocompatibility of CdS NPs and microorganisms

4.1. Membrane-bound protein participation in photoelectron transport chains

Several possible redox proteins involved in electron transfer channels are summarized in Table 1. These membrane-bound proteins

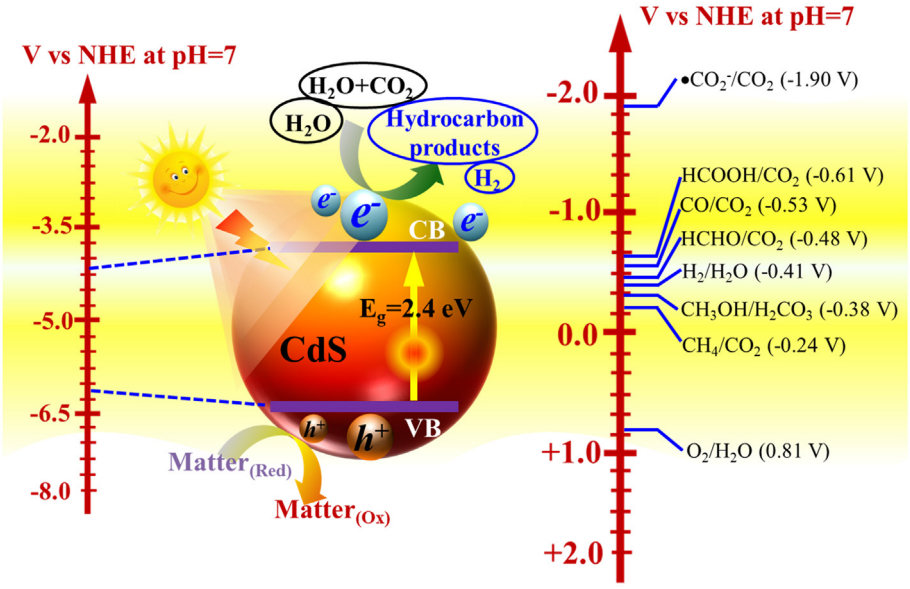

Fig. 2. Schematic representation of CdS NP-derived photocatalysis under visible light irradiation for production of hydrogen and reduction of CO_2 to hydrocarbons.

commonly contain several haems that are electron transfer centers composed of iron atoms and porphyrin rings, or several Fe—S proteins with a high redox potential (Li et al., 2020b; Wang et al., 2019c). Therein, the binding iron atoms of active sites (*i.e.,* haems, iron-sulfur protein and other functional proteins) play a pivotal role in balancing internal electron flow or redox potentials of these proteins through valance regulation (Choi and Sang, 2016; Shi et al., 2016). Additionally, these active sites are densely packed or staggered across membrane-bound redox proteins (*e.g.,* cytochrome and ferredoxin) that are located in outer/inner membranes and periplasmic space, thereby enabling rapid electron transfer through a multistep hopping mechanism. For example, several outer-membrane *c*-cytochromes, such as OmcB/C, OmcE and OmcS in *Geobacter sulfurreducens*, serve as important carriers for transporting electrons or terminal reductase throughout the microbial extracellular respiratory electron transfer chain (depicted in Fig. 3). This enables electron transport from the intracellular reduced NADH electron pool to the outer membrane (Shi et al., 2016). Although existing studies have successfully revealed membrane-bound proteins regulation for the direct transfer of bio-electrons in many gram-negative bacteria, the mechanistic understanding of transmembrane photoelectron transfer at the molecular level remains limited.

Several key membrane-bound proteins are known to serve as critical carriers for delivering electrons during microbial respiration processes as the energy derived from intracellular and extracellular membranes are preferably exchanged at their junctions (Belchik et al., 2011; Li et al., 2020b; Shi et al., 2007). To systematically design hybrid microbial-photochemical systems, knowledge concerning the ability of membrane-bound proteins to facilitate photoelectron transfer is required. For example, Katz et al. (2006) found that the direction and strength of photocurrents generated by photo-illuminated CdS NPs were controlled by *c*-cytochrome activation. The *c*-cytochromes are specialized membrane-bound proteins containing several iron porphyrins or hemes that are responsible for electron transport (Wang et al., 2019c). This work further demonstrated that reproducible *c*-cytochromes-mediated biocatalytic performance was maintained even at high photoactive levels by CdS NPs. Thus, photoelectron transport within biological cells is proceeded with the support and cooperation of membrane-bound proteins at appropriate photoinduction strengths (Brown et al., 2012; Kornienko et al., 2016; Shi et al., 2016; Wilker et al., 2014). Herein, we infer that the activities of functional membrane-bound proteins are positively correlated to participation of CdS NPs-excited photoelectrons in microbial extracellular respiration processes.

Notably, recent research using gene knockout technology successfully confirmed that the membrane-bound protein-mediated mechanism was important for photoelectron transfer in microorganism cells. Huang et al. (2019) demonstrated that the efficiency of methyl orange degradation by an OmcB-deleted mutant (an outer membrane-bound protein) *Geobacter sulfurreducens* was markedly decreased (>20%) compared to that of wild *G. sulfurreducens*. However, methyl orange degradation was promoted upon intermittent illumination of CdS NP-amended samples, indicating that wild *G. sulfurreducens* could directly use extracellular photoelectrons. Similarly, coupled microbial-photoelectrochemical performance was suppressed in CdS NPs-photosensitized mutant strains of *Thiobacillus denitrificans* (Chen et al., 2019a) and *Methanosarcina barkeri* (Ye et al., 2019) in which specific functional membrane-bound proteins were deleted. Therefore, we posit that membrane-associated proteins are essential for photoelectron transport during biotransformation processes.

4.2. Physiological response to stimulation by illuminated CdS NPs in syntrophic systems or mixed strains

In practical bioengineering applications, syntrophic systems and mixed strain cultures are especially important, such as for energy production, wastewater treatment and environmental bioremediation (Park et al., 2017; Tang et al., 2010). Therefore, it might be expected that combinations with CdS NPs and solar illumination could favor interspecies modifications. There is a paucity of information concerning the influence of CdS NPs on physiological stress of microbial syntrophic systems under illumination. A recent study by Chen et al. (2019b) found the growth of *G. metallireducens* and *G. sulfurreducens* in syntrophic systems was repressed under visible light illumination, whereas such inhibition was alleviated when amended with CdS NPs under illumination. In addition, they demonstrated that direct interspecies electron transfer was driven by irradiated CdS NPs that generated photoelectron-hole pairs in conjunction with the Gmet_2896 cytochrome of *G. metallireducens* and the OmcS cytochrome of *G. sulfurreducens*. Further, the energy consumed for biosynthesis of OmcS and Gmet_2896 in the co-cultures of *Geobacter* was lower than that of CdS NP-free assays (Chen et al., 2019b). These findings provide strong evidence for a favorable CdS NP-mediated direct interspecific electron transfer under illumination that can be manipulated through interactions between functional cytochromes and photoelectrons.

It is also important to consider that the photohole produced by CdS NPs under illumination could cause oxidative stress or membrane destruction of microbial cells (Li et al., 2013; Tang et al., 2015). To avoid cell damage from photohole-induced stress, the biocompatibility of CdS NPs in mixed cultures must be considered. Extracellular polymeric substances (EPS) excreted from mixed strain cultures play a critical role in maintaining the stability of bioaggregates (Flemming et al., 2007; Sheng et al., 2010). This is especially important for periphytic biofilms in aquatic ecosystems that display a strong tenacity against photo-stress from CdS NPs by stimulating more EPS production (Zhu et al., 2018; Zhu et al., 2019a). Since EPS is dominated by high-molecular-weight humic substances (which are the potential sacrificial reagent of photoholes) (Tang et al., 2017; Xiao et al., 2017) and electroactive *c*-cytochromes (Ye et al., 2018), such oxidative stress may be alleviated by interactions between biofilms and CdS NPs.

Previous investigations demonstrated that microorganisms harbor EET capabilities that evolve special strategies to adapt their metabolism and survival by optimizing their biotic interactions, habitat affinities and/or microbial physiologies (Barberan et al., 2012). In cultured systems with coexisting mixed strains and CdS NPs, electron transfer mediated by different mechanisms may not be initiated by independent factors. Instead, it is more likely to be instigated by multiple factors in a synergistic manner. As previously mentioned, the productions of *c*-cytochromes and EPS stimulated by CdS NPs favored electron transfer. In addition to EPS containing large amounts of redox-active quinoid groups responsible for accelerating EET (Xiao and Zhao, 2017), restrained electron transfer resulting from unfavorable shifts in microbial community caused by illumination might be correspondingly mitigated (Zhu et al., 2018). For example, charge transfer barriers in conductively isolated areas can be alleviated through interactions with *c*-cytochromes and redox-active moieties contained in EPS (Huang et al., 2018; Xiao and Zhao, 2017). Hence, newly developed mechanistic models for electron transfer between microorganisms and CdS NPs provide a theoretical framework for future bioengineering applications incorporating CdS NPs and solar illumination.

5. Applicability of CdS NPs for promoting hybrid microbial-photochemical processes

5.1. CdS NPs-assisted hybrid microbial-photoelectrochemical systems

In 1992, Shumilin et al. (1992) determined that NADH was photogenerated from NAD-dependent hydrogenase extracted from *Alcaligenes eutrophus* in the presence of semiconducting CdS. Their study provided strong evidence that photoelectrons generated

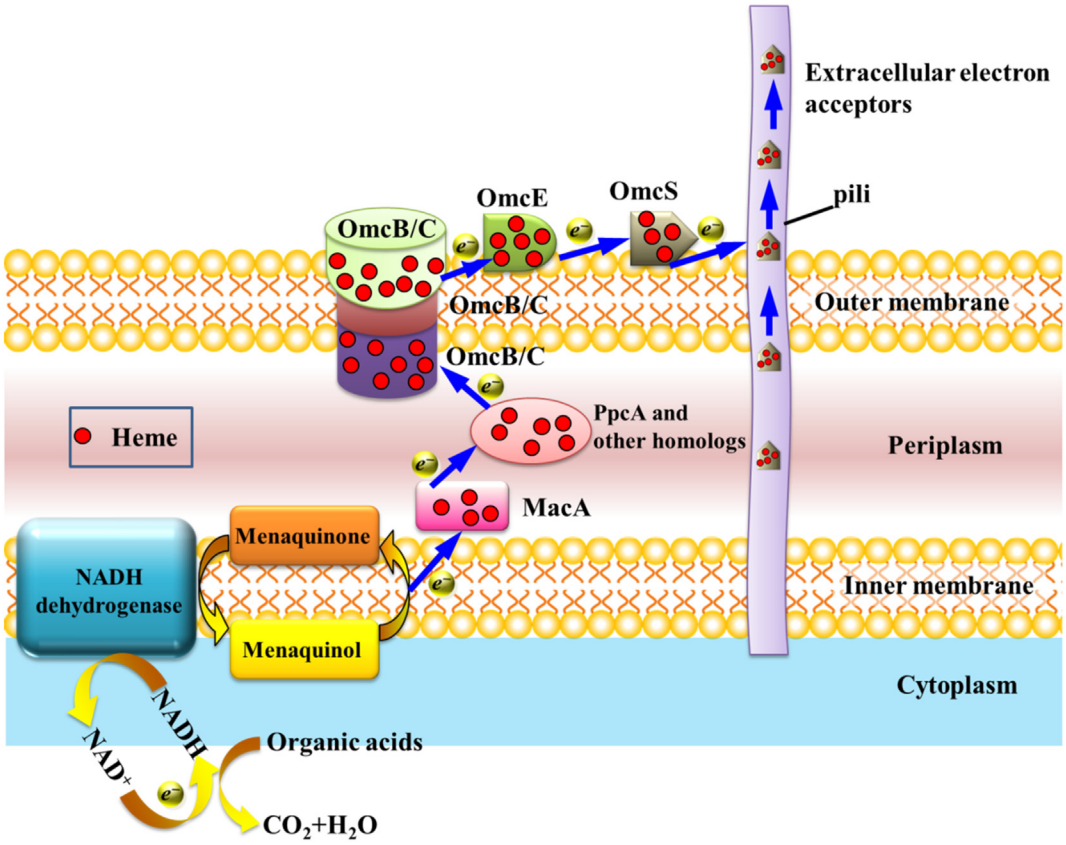

Fig. 3. Proposed transmembrane electron transfer pathway in cell membrane of *G. sulfurreducens*. Electrons produced from intracellular oxidation of organic substrates in cytoplasm transfer to NADH dehydrogenase and quinone pools located in the inner membrane. Electrons are then delivered from periplasm to the outer membrane through multistep hopping pathways involving protein carriers. Herein, a series of homologous proteins containing several haems responsible for electron transfer, located in periplasm (*e.g.,* MacA and PpcA) and the outer membrane (*e.g.,* OmcB/C, OmcE and OmcS), serve as electron carriers.

from illuminated CdS particles participated in microbial intracellular biochemical processes at the molecular level. Since then, several biogeochemical investigations demonstrated that both chemoautotrophic and chemoheterotrophic microorganisms utilize photoelectrons generated from solar energy and semiconducting minerals for their adaptive evolution in the epigeosphere (Lu et al., 2012; Sakimoto et al., 2016a; Tributsch et al., 2003). These previous studies greatly advanced our understanding of the underlying mechanisms for electron transport in the presence of CdS NPs. Thus, elucidating electron transport and new microbial energy metabolism pathways in a ternary "CdS NPs-microorganisms-solar energy" composite system will identify several challenges and opportunities applicable to future environmental applications.

Upon illumination, excited holes in the valence band of CdS NPs may combine with bio-electrons (*i.e.,* produced from microbial degradation of labile organic substrates) or remain scavenged by labile organic substrates to sustain microbial growth. The later hinders the recombination of photoelectron-hole pairs (Lu et al., 2014; Zhou et al., 2015), and increases the probability of photoelectrons participating in hybrid microbial-photoelectrochemical processes. Additionally, because CdS NPs assemble prominent energy level discrepancies, the excited photoelectrons or delivered bio-electrons can jump from the top of the valence band to the bottom of the conduction band of CdS NPs (Seoudi et al., 2012). These electrons are injected into microbial extracellular electron transfer chains. Moreover, since the potentials of highly reductive photoelectrons are commonly more negative than that of most of biological compounds (Yang et al., 2011), the delivered photoelectrons maybe theoretically accepted by specific microorganisms to participate in various biotransformation processes. Recently, this knowledge was employed to construct intimately coupled, CdS NPs-assisted microbial-photoelectrochemical systems that were successfully applied for *in-situ* nitrate removal is wastewaters (Zhu et al., 2018), sustainable bioelectrosynthesis of chemicals from carbon dioxide (Sahoo et al., 2020) and hydrogen production (Wang et al., 2017).

Given that photoelectrons can be used as an alternative electron sources for nonphototrophic microorganisms, this hybrid process has several advantages over other microbial EET processes that rely solely on microbial degradation of organic substrates (*e.g.,* acetate and lactate) as an energy source (Chen et al., 2018a). For instance, integration of photocatalytic reactions from CdS NPs into microbial fuel cells (MFCs) generates a higher cathode potential and greatly improves the overall energy output of the coupled microbial-photoelectrochemical hybrid system. Correspondingly, a dual-chamber-equipped microbial-photoelectrochemical fuel cell could be configured with a photocathode consisting of CdS NPs to harvest solar energy (Zhang et al., 2019). This hybrid system has the advantage of coupling *in situ* anodic biodegradation of organic substrates and cathodic photocatalytic generation of hydrogen into a single integrated reactor (Li et al., 2011; Lu et al., 2017; Ravi et al., 2017). These results collectively substantiate the promising role that CdS NPs-assisted hybrid photoelectrochemical-microbial EET could play in strategies for several environmental engineering applications (Fig. 4). Therein, integration of photoelectrochemical catalytic processes and microbial EET processes maybe achieved to participate in suitable environmental applications.

5.2. Engineered CdS NPs immobilized nonphototrophic microorganism biohybrids

Among various kinds of CdS NPs, semiconducting CdS quantum dots (QDs) are fluorescent nanocrystals with average sizes of 1–20 nm that display distinguished quantum confinement effects (Qin et al., 2018). Photosensitive CdS QDs have high visible light absorption coefficients and strong surface electrostatic properties (Chen et al., 2014; Jaffar et al., 2004). Thus, barriers to charge transfer should be reduced due to their close contact with those microorganisms responsible for specific biotransformation reactions. Research examining the synthesis of CdS QDs-microbial associations confirmed production of a microbial protein capping on the CdS QDs that greatly enhanced the biocompatibility of CdS QDs with the microbial membrane (Chen and Rosenzweig, 2002). This suggests the possibility for photoelectrons to directly interact with both extracellular and intracellular biological processes due to CdS QDs loading across the periplasmic space of microorganism cells. Moreover, because of the positive response of *c*-cytochrome activities to illuminated CdS QDs, specific CdS QDs hybrids were designed for efficient detection of *c*-cytochromes (Bin et al., 2016; Wang et al., 2019d; Yan et al., 2011). Several additional proof-of-concept studies advocate for the construction of targeting systems by *in-situ* self-assembling hybrid precipitating CdS QDs, CdS NPs, CdS@ZnS NPs and other specific CdS NP-based composite materials onto cell surfaces of nonphototrophic microorganisms to target engineered biohybrids for specific environmental applications (Brown et al., 2016; Ding et al., 2019; Guo et al., 2018).

In general, most nonphototrophic microorganisms have a robust capacity for loading on CdS QDs surfaces to construct light-harvesting biohybrids. There is a wide range of environmental applications for CdS QDs-derived biohybrids as summarized in Table 2. For instance, in a CdS QDs-immobilized *T. denitrificans* biohybrid, enzyme metabolism related to denitrification was activated by photoelectron energy derived from illuminated CdS QDs and enrichment of electron transfer chains (depicted in Fig. 5) (Chen et al., 2019a; Wang et al., 2019a; Ye et al., 2019). Additionally, a CdS QDs-immobilized *G. sulfurreducens* biohybrid demonstrated significantly higher light-driven decolorization (*i.e.,* degradation) of methyl orange (Huang et al., 2019). This biohybrid achieved the highest maximum kinetic constant (1.441 h^{-1}) among previously published studies and retained a comparably high catalytic ability (>95% of initial catalytic efficiency) after four repeated reaction cycles (Huang et al., 2019). Overall, previous studies demonstrated that CdS NPs-derived biohybrids have a high capacity for light-harvesting and desirable biocompatibility for hybrid microbial-photoelectrochemical processes, as well as a strong capacity for recycled use. Therefore, CdS QDs-immobilized nonphototrophic microorganism biohybrids provide an attractive and promising tool for a wide variety of biochemical engineering applications.

Because of certain long-range transitivity of photoelectrons (Höfer et al., 1997; Jia et al., 2010), the stagnancy of localized energy delivery and a lag phase for electron transport are likely to be "broken down" in systems with CdS NPs-microbial attachment interfaces. In general, microbial activities and catalytic reactions respond dynamically to fluctuations in their environment and redox mediators to optimize their performance (Liu et al., 2018b). With respect to energy consumption

Fig. 4. Potential environmental applications of hybrid microbial-photoelectrochemical reduction using CdS NPs. Integration of suitable inorganic and organic processes benefit bi-directional exchange of electrons and energy with the external environment, thereby promoting a wide array of applications in environmental purification and clean energy production.

and efficacy, CdS NPs-derived biohybrids commonly display superior performance compared to treatments with specific redox mediators (Holzmeister et al., 2018; Martinez and Alvarez, 2018).

5.3. Carbon dioxide bioelectrosynthesis and nitrogen fixation by engineered CdS NPs-immobilized biohybrids

The tremendous global demand for clean and sustainable energy substitutes (*e.g.,* hydrogen, methane or other hydrocarbon) provides unique challenges and opportunities for CdS NPs-immobilized biohybrids. Global climate change and increased hydrocarbon fuel demand have elevated awareness in the research community to reconsider the use of carbon dioxide in a green and efficient manner to contribute to future energy needs. Several studies utilizing CdS NPs-immobilized biohybrids provide compelling evidence for the ability to produce biofuels in the laboratory environment. For instance, chemical energy in the form of acetic acid was generated by carbon dioxide reduction catalyzed through an integrated enzymatic transformation with CdS NPs photocatalysis in a *Moorella thermoacetica*-CdS NPs biohybrid (Sakimoto et al., 2016a). Under illumination, carbon dioxide-reducing equivalent ([H]) is generated from photoelectrons (either from outside the cell or by direct electron transport to the cell) concomitant with hole oxidation of cysteine into cystine, enabling the effective separation of photoelectron-hole pairs. Subsequently, acetic acid was biosynthesized *via* the acetyl coenzyme A Wood-Lungdahl pathway where [H] and carbon dioxide are reacted (Chiranjeevi et al., 2019). Thus far, there is a paucity of research regarding carbon dioxide conversion to clean fuels using CdS NP-immobilized biohybrids. Several challenges are apparent in the practical application of sustainable bioelectrosynthesis for production of chemicals (*e.g.,* methanol, formic acid/formate) from carbon dioxide with the aid of solar energy. Thus, exploring more carbon dioxide bioelectrosynthesis mechanisms to enhance and optimize enzymatic transformations and reaction conditions using engineered CdS NPs-immobilized biohybrids are warranted.

Table 2
Applications of illuminated engineered CdS NPs-immobilized biohybrids.

Application	Biohybrid	Illumination	Remarkable results	Ref.
Decolorization of methyl orange	*G. sulfurreducens*-CdS QDs biohybrid	LED irradiation 3.07 ± 0.14 mW/cm^2	• The maximum kinetic constant was up to 1.441 h^{-1} • Exhibited favorable catalyzed ability during 4 repeated cycles	Huang et al. (2019)
Conversion of carbon dioxide to methane	*M. barkeri*-CdS QDs biohybrid	Violet LED irradiation 1.0 ± 0.14 mW/cm^2	• Methanogenesis rate (0.19 μmol/h) was comparable to that of plants or algae • Nearly 1.5-fold of *mcrA* gene copies were increased in biohybrid	Ye et al. (2019)
Denitrification of nitrate to generate nitrous oxide	*T. denitrificans*-CdS QDs biohybrid	Violet LED irradiation 3.07 ± 0.14 mW/cm^2	• >72.1% of NO_3^-–N was converted into N_2O–N • >96.4% yield of N_2O–N in final gaseous products (N_2O and N_2)	Chen et al. (2019a)
Hydrogen generation	*E. coli*-CdS QDs biohybrid	Xenon lamp irradiation 200 mW/cm^2	• 1800 μmol of H_2 produced within 3 h under 2000 W/m^2 of visible light irradiation • Higher quantum efficiency (~9.6%) of biohybrid than that of phototrophic bacteria	Wang et al. (2017)
Hydrogen generation	*E. coli*-CdS NPs biohybrid	Xenon lamp irradiation 350 W	• H_2 production was nearly 80-fold of that of *E.coli* alone in dark after 24 h • Continuous H_2 production for 96 h under natural aerobic conditions	Wei et al. (2018)
Dinitrogen reduction to ammonia	Nitrogenase MoFe protein-CdS QDs biohybrid	LED irradiation 3.5 mW/cm^2	• Photocatalysis replaces ATP hydrolysis to drive enzymatic reduction of N_2 into NH_3 • ATP-coupled reaction rate for the nitrogenase complex was up to 63%	Brown et al. (2016)
Synthesis of acetic acid from carbon dioxide	*Moorella thermoacetica*-CdS NPs biohybrid	LED emitter with wavelength of 405 nm	• A number of enzymes are upregulated in the presence of CdS NPs under illumination • Glycolysis, TCA cycle and Wood-Ljungdahl pathway were active in ATP production	Zhang et al. (2020)
Synthesis of acetic acid from carbon dioxide	*Moorella thermoacetica*-CdS NPs biohybrid	Violet LED irradiation with photon flux of 5×10^{18} cm$^{-2}\cdot$ s^{-1}	• Nearly 90% of CO_2 was converted into acetic acid in illuminated biohybrid • 10-fold greater quantum yields than averages determined for plants and algae	Sakimoto et al. (2016a)
Biological nitrogen fixation	*Rhodopseudomonas palustris*-CdS NPs biohybrid	Visible light irradiation 8 mW/cm^2	• Increase of 1.5-fold for solid biomass accumulated in biohybrid compared to control • Outstanding photosynthetic efficiency (6.73%) and malate usage efficiency (0.06 g/h)	Wang et al. (2019b)
Conversion of nitrogen to ammonia-nitrogen	*Rhodopseudomonas palustris*-CdS NPs biohybrid	Microaerobic-light condition 3000 lx	• Cofactors for nitrogenase did not affect cysteine desulfhydrase • Activity of CdS NPs up-regulated alternative nitrogen fixing genes (*vnfG* and *nifH*)	Sakpirom et al. (2019)
Enhanced carbon dioxide reduction and organic chemical production	*Rhodopseudomonas palustris*-CdS NPs biohybrid	Visible light irradiation 8 mW/cm^2	• Production of β-polyhydroxybutyrate (PHB), solid biomass and carotenoids and was increased by 47%, 48% and 22%, respectively • Biohybrid exhibited a survival advantage over its natural counterparts under autotrophic conditions	Wang et al. (2019a)
Oxygenic photosynthesis of acetic acid from carbon dioxide	TiO_2-MnPc + *Moorella thermoacetica*-CdS NPs biohybrid	75 W Xenon lamp (AM1.5G, 5% sun) with a 12 h light/12 h dark cycle	• Coupled hybrid system resulted in >3.0-fold increased production of acetic acid than *Moorella thermoacetica*-CdS NPs biohybrid alone • Biohybrid demonstrated a biomimetic approach to complete oxygenic solar-to-chemical production	Sakimoto et al. (2016b)
Light-driven ethylene and PHB synthesis from carbon dioxide	*Cupriavidus necator*-CdS@ZnS QDs biohybrid	365 nm UV light excitation	• More than 15-fold increase of ethylene production in core-shell biohybrids than that of core biohybrid • Up to 150% the PHB yield of wild-type cells alone in biohybrid	Ding et al. (2019)
Light-driven ammonia and hydrogen synthesis from nitrogen and water	*Azotobacter vinelandii*-CdS@ZnS QDs biohybrid	400 nm UV light excitation	• Nearly 18-fold increase of ammonia and hydrogen production in double ZnS monolayers core-shell derived biohybrid compared to that of none core-shell biohybrid • A maximum quantum yield (13.1%) was obtained for combined ammonia and hydrogen production with CdS@ZnS	Ding et al. (2019)

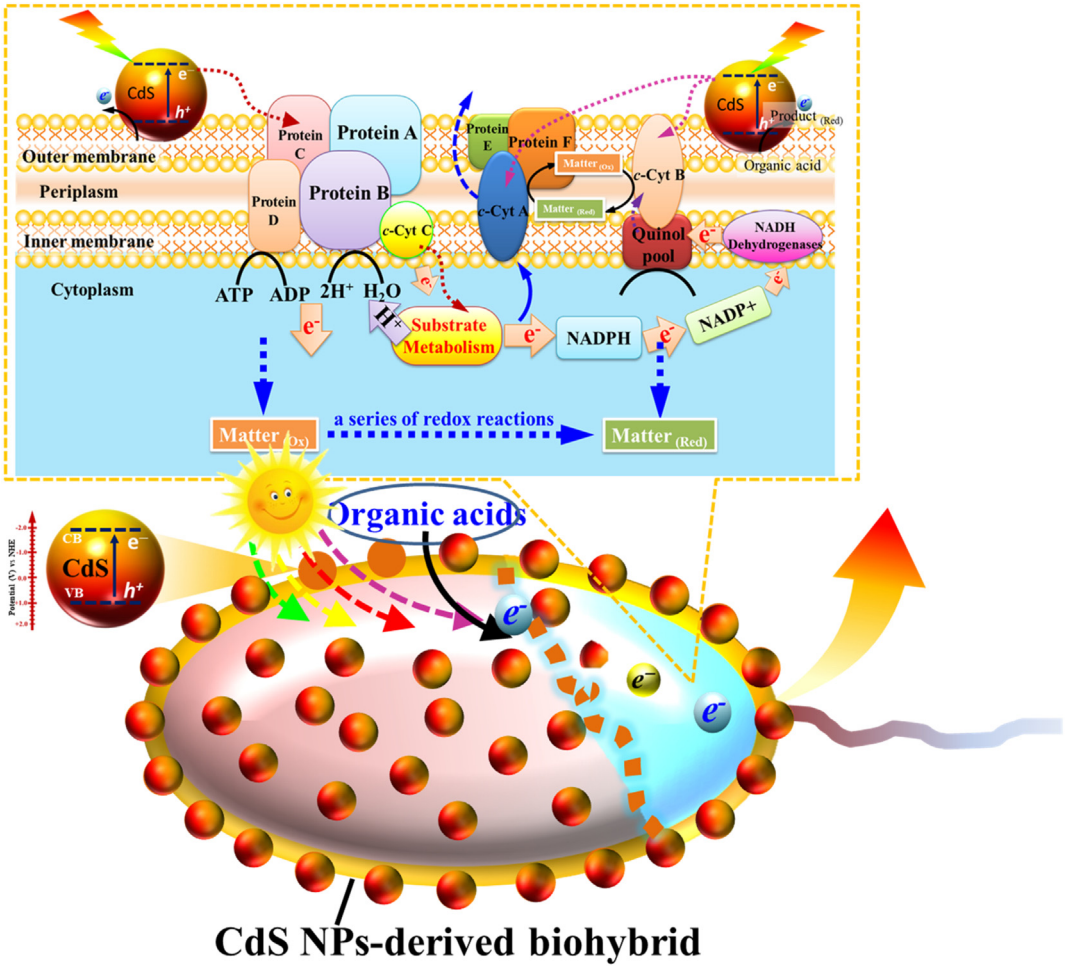

Fig. 5. Schematic representation of light-driven reduction by CdS NPs-immobilized biohybrids (adapted from Chen et al., 2019a; Wang et al., 2019a and Ye et al., 2019). Diagram profiles the pathway of photoelectron flow in association with membrane-bound proteins in CdS NPs-immobilized biohybrids.

Furthermore, engineered CdS NPs-immobilized biohybrids offer a novel approach to synthesize ammonia through sequestrating ambient nitrogen gas for nitrogen fixation. Brown et al. (2016) work on nitrogen gas reduction by coating CdS nanocrystals on the nitrogenase MoFe protein revealed that ATP-coupled reaction rates for the nitrogenase complex was up to 63% under optimal conditions. Subsequently, Wang et al. (2019b) induced the coating of CdS NPs on the surface of *Rhodopseudomonas palustris* for biological nitrogen fixation, and surprisingly found that the final yield of solid biomass was at least 1.5-fold higher in the biohybrid cells than that of natural cells. Sakpirom et al. (2019) confirmed that production of NH_3 up-regulated the expression levels of the V—Fe nitrogenase gene (*vnfG*) and Mo—Fe nitrogenase gene (*nifH*) in the *Rhodopseudomonas palustris*-CdS NPs biohybrid at 2.3- and 2.8-fold changes, respectively. Based on these findings, we posit that several controllable conformational changes in protease or microbes by binding with CdS NPs could be achieved to divert photoelectron flux or support gene expression in engineered CdS NPs-immobilized biohybrid complexes to induce tunable bioelectrosynthesis of ammonia. These studies provide a strategy for future research to optimize visible-light-driven N_2 fixation and solar-to-chemical conversion processes.

To broaden targeted applications of CdS NPs-immobilized biohybrids, selecting suitable microorganisms and identifying their compatibility with CdS NPs, as well as their hybrid catalytic activities are primary challenges. Important future research directions include the following aspects. (1) To improve charge uptake from CdS NPs heterojunction to microbes, the corresponding photocatalytic capabilities of different dimensional CdS NPs for serving as light harvesters and desirable sacrificial reagents for scavenging the holes require additional investigation (Cheng et al., 2018). (2) Considering the cytoprotective effect of the metal-organic framework (MOF) (Ji et al., 2018), CdS NPs-based MOF wrapped biohybrids should be explored to reduce cell damage and thereby upscale their feasible applicability. (3) To promote targeted environmental applications of biohybrids, genetically modified microbes may improve biohybrid performance. For instance, the electron flux could be re-diverted in engineered strains by manipulating genetic circuits (*e.g.,* employing CRISPR [clustered regularly interspaced short palindromic repeats] and CRISPRi [CRISPR interference] technologies) to strengthen the biocompatibility of the biomaterials (Li et al., 2020a; Wu et al., 2020). (4) Further research is warranted to optimize reaction conditions in terms of specific microorganisms, food substrates and the type/amount of immobilized CdS NPs to maximize operational efficiency. (5) Finally, pilot studies must be appropriately scaled to commercial application to fully assess the environmental and economic efficacies of CdS NPs-immobilized biohybrid approaches for energy production.

6. Conclusions and perspectives

This review synthesizes recent advances for CdS NPs application in hybrid microbial-photochemical processes. CdS NPs provide several compelling properties for development of coupled

Table1
Key membrane-bound proteins involved in extracellular electron transfer.

Type	Active sites	Candidate microorganism	Functional proteins responsible for electron transfer in candidate microorganism	Ref.
Cytochrome	Heme protein	*Geobacter sulfurreducens* and *Shewanella oneidensis*	OmcE and OmcS in *Geobacter sulfurreducens*, MtrC and OmcA in *Shewanella oneidensis* MR-1	Li et?al. (2020b); Shi et?al. (2007)
Ferredoxin	Fe-S protein complex	*Clostridium ljungdahlii, Clostridium aceticum, Moorella thermoacetica, Methanothermobacter thermautotrophicus, Methanobacterium palustre* and *Methanococcus maripaludis*	$NAD^{?+}$ oxidoreductase in *Clostridium Ljungdahlii*, electron bifurcating ferredoxin in *Clostridium Ljungdahlii*, and methyltransferase in several methanogens	Chowdhury et?al. (2014); Kracke et?al. (2015); Lane and Martin (2012); Tremblay et?al. (2013)
Rubredoxin	Fe-S protein without acid-labile sulfur	*Desulfovibrio* sp. and *Clostridium* sp.	Specific rubredoxin in *Desulfovibrio vulgaris* and *Clostridium pasteurianum*	Coulter and Kurtz (2001); Lovenberg and Sobel (1965)
Hydrogenase	[Ni—Fe] or [Fe—Fe] or [Fe]-only	*Desulfovibrio* sp. and methanogens	Specific hydrogenase in *Desulfovibrio desulfuricans* and *Methanococcus maripaludis*	da Silva et?al. (2012); Thauer et?al. (2010)
Formate dehydrogenase	Molybdenum or tungsten	*Desulfovibrio* sp.	Specific formate dehydrogenase in *Desulfovibrio desulfuricans*	da Silva et?al. (2012)

microbial-photochemical systems, such as suitable electrical conductivity, large specific surface area and excellent photocatalytic characteristics. Importantly, CdS NPs under light illumination display robust biocompatibility in terms of (1) CdS NPs-excited photoelectrons participating in microbial EET processes with the assistance of several functional membrane-bound proteins, (2) CdS NPs alleviation of photooxidative-stress towards syntrophic strains, and (3) CdS NPs stimulation of EPS secretions that scavenge holes and inhibit the recombination of photoelectron-hole pairs in mixed strain cultures.

There are several advantages of complementing bio-electrons with photoelectrons to enhance microbial transformations. As the potential of photoelectrons are more negative than bio-electrons, the supply of photoelectrons produced by solar illumination of CdS NPs in microbial treatment systems will reduce the cost for the organic substrates consumed by microbes. The efficacy of coupling CdS NPs and microbial EET processes to enhance photoelectrochemical transformations provides several promising opportunities for application in environmental remediation and clean-energy production. Notably, recent findings demonstrated that CdS QDs can be immobilized with several nonphototrophic microorganisms thereby allowing the design of specific biohybrids for a variety of applications. Coupling photocatalysis by CdS NPs and microbial EET processes provide prospects to fulfill specialized environmental remediation applications, as well as the production of clean energy. However, hybrid microbial-photochemical coupling is still in its early stages with a focus on fundamental research. Thus, there is tremendous opportunity for advancing both the fundamental knowledge of biohybrid electron transfer and transformation dynamics, and the application (design/optimization) of biohybrids for specific environmental and clean-energy applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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