Review

Photocatalytic Material-Microorganism Hybrid System and Its Application—A Review

Jiaao Song, Huichao Lin, Gaozhen Zhao and Xiaowen Huang*

State Key Laboratory of Biobased Material and Green Papermaking, Department of Bioengineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250300, China; songjiaao0419@126.com (J.S.); linhuichao2020@gmail.com (H.L.); zhaogaozhen2021@126.com (G.Z.)
* Correspondence: huangxiaowen2013@gmail.com

Abstract: The photocatalytic material-microorganism hybrid system is an interdisciplinary research field. It has the potential to synthesize various biocompounds by using solar energy, which brings new hope for sustainable green energy development. Many valuable reviews have been published in this field. However, few reviews have comprehensively summarized the combination methods of various photocatalytic materials and microorganisms. In this critical review, we classified the biohybrid designs of photocatalytic materials and microorganisms, and we summarized the advantages and disadvantages of various photocatalytic material/microorganism combination systems. Moreover, we introduced their possible applications, future challenges, and an outlook for future developments.

Keywords: hybrid photocatalysis; synthetic biohybrid; photoenzymatic synthesis

1. Introduction

With the growth of population and economy, as well as the improvement of living standards, the consumption of energy rises sharply. Alongside the continuous consumption of non-renewable energy sources, resulting problems such as environmental pollution and food shortages are becoming more severe, making green and renewable energy technology development a global research priority [1–3]. One hour of solar energy is equivalent to the entire amount of energy that is used by humanity in a year [4,5]. Hence, the conversion, transportation, and storage of solar energy is of significant concern to scientists [6]. Natural photosynthesis is the most common mechanism of solar energy conversion. Plants, algae, and photosynthetic bacteria can absorb solar energy into chemical energy [7–10]. However, the efficiency of natural photosynthesis is quickly saturated. Excessive sunlight can lead to photodamage. Repairing photodamage requires energy consumption, resulting in an even lower conversion of solar energy [11,12]. The conversion rate only reaches 7%, and the storage efficiency does not exceed 1% under optimal conditions [13–15]. Artificial photosynthesis mimics natural photosynthesis by using semiconductor photocatalytic materials to capture light energy. It has greater designability and a more comprehensive range of wavelength utilization, but it does not have the selective catalytic capabilities. The combination of artificial photosynthesis and natural biocatalytic systems efficiently creates high value-added products. This approach can improve solar energy conversion and storage, and so biocatalysis and artificial component catalysis cannot be performed independently [16,17]. Existing systems, in which photocatalysts such as TiO2 [18], CdS [19], and g-C3N4 [20] can be combined with specific microorganisms to form heterogeneous systems, have become a research hotspot. In this review, we mainly summarize the construction methods and application fields of hybrid systems, discuss the challenges and opportunities for their future development, and provide references for researchers in this field.
2. Photocatalytic Materials—Microbial Hybrid System

The hybrid photocatalytic material-microorganism system combines the strength of photocatalytic material and microorganisms. The self-replication, self-healing, and intracellular metabolic pathways of microbial cells provide potential stability and scalability to cell-based systems [21]. Photocatalytic materials act as light absorbers and generate photogenerated electrons. Microorganisms use these electrons to participate in metabolic pathways for the targeted synthesis of complex products [22]. Nowadays, semiconductors, dyes/polymers, and electrodes can be combined with microorganisms to prepare hybrid photocatalytic material-microorganism systems (Table 1) [23,24].

Table 1. The typical photocatalytic material-microbe hybrid system.

| Build Method | Microorganism | Photocatalytic Material | Composite Method | Function | Efficiency | Ref. |
|--------------|---------------|-------------------------|------------------|----------|------------|-----|
|             | *M. thermoacetica* | CdS NPs | Extracellular deposition | Synthesis acetic acid | 1.43 mM per 12 h | [25] |
|             | *M. thermoacetica* | AuNCs | Intracellular suspension | Synthetic acetic acid | 6.01 mmol/g per week | [26] |
|             | *C. zofingiensis* | Au NPs | Intracellular suspension | Synthetic carotenoids | 10.7 ± 1.2 mg/L | [27] |
|             | *S. cerevisiae ADzwfI* | InP | Extracellular surface modification | Synthetic shikimic acid | 48.5 ± 2.1 mg/L | [28] |
| Semicontactor material-microorganism hybrid system | *E. coli* | CdS NPs | Extracellular deposition | Hydrogen production | 81.80 ± 7.39 μmol per 24 h | [30] |
|             | *E. coli* | CdS NPs | Extracellular surface modification | Hydrogen production | 0.71 mM/h | [31] |
|             | *G. sulfurreducens* | CdS | Extracellular deposition | Methyl orange reduction | 100% removal rate at 3 h | [32] |
|             | *E. coli* | AgInS2/In2S3 | Extracellular surface modification | Hydrogen production | 487 μmol/h | [33] |
|             | *Shewanella oneidensis MR-1* | CuO/RGO | Cell anchoring | Hydrogen production | 322.0 μmol/g Cu2O of H2 in 4 h | [34] |
|             | *C. pyrenoidosa* | PBF | Extracellular surface modification | Promote O2, NADPH, and ATP synthesis | Respectively, up 120%, 97%, and 76% | [35] |
| Dye/polymer-microbial hybrid system | *Synechococcus sp. PCC7942, Syne* | PFP | Extracellular surface modification | Promote O2, NADPH, and ATP synthesis | Respectively, up 52.8%, 47.9%, and 27.2%. | [36] |
|             | *M. thermoacetica* | PFP/PDI | Extracellular surface modification | Synthetic acetic acid | Accumulated 0.63 mM in 3 days | [37] |
|             | *C. pyrenoidosa* | PPE | In situ modification of cell surface | Synthesize ATP | 500 μM monomer improved 115% after 30 min of light | [38] |
|             | *S. ovata* | Silicon nanowire | Integrated combination | Synthetic acetic acid | 1200 mg/L/d | [39] |
| Electrode-Microbial Hybrid System | *S. ovata* | Silicon nanowire | Integrated combination | Synthetic acetic acid | 0.3 g/L/d | [40] |
|             | *X. autotrophicus* | CoP-CoPi | Distributed combination | Synthetic biomass | To 6.2% biomass in 24 h | [41] |
R. eutropha  
**CoPi-NiMoZn**  
Distributed combination  
Synthetic biomass  
Up to 216 ± 17 mg/L  
[42]

R. eutropha  
**Co-P alloy-CoPi**  
Distributed combination  
Synthetic biomass and fusel alcohols  
CO₂ reduction energy efficiency of ~50%  
[43]

*S. ovata*  
**CoP-CoPi**  
Distributed combination  
Synthetic acetic acid  
1.1 mM/h  
[44]

Methanogens  
**TiO₂/CdS**  
Distributed combination  
Synthesis of CH₄  
1925 mL/m²/d  
[45]

### 2.1. Semiconductor Material-Microorganism Hybrid System

In semiconductor material-microbe hybrid systems, semiconductor materials are commonly distributed outside of the microbial cell, on the cell membrane, and inside the cell (Figure 1). Light excites the semiconductor material to generate electron-hole pairs. Photogenerated electrons are then transferred to the microorganism to provide energy for intracellular metabolic pathways, and the target products are selectively synthesized.

![Figure 1](image_url)  
**Figure 1.** In material-microbe hybrids, the material can be distributed outside the cell. (A) On the cell membrane; (B) Inside the cell; (C) The photogenerated electrons generated by the material will enter the microbial cell that supplies energy for intracellular metabolism.

When the material is extracellular, it needs to use an electronic medium to transfer electrons. Honda et al. developed a hybrid system of TiO₂, methylviologen (MV), and recombinant *E. coli* to realize highly efficient light-driven H₂ production mediated via MV [46]. Rowe et al. gained access to a varied and selective set of visible light-driven chemical syntheses without enzyme purification, via the use of MV to transfer photoenergized electrons to the corresponding enzymes in *Shewanella oneidensis*. However, MV is toxic and poorly biocompatible, leading to cell death after the reaction [47]. Photogenerated electrons cross the cell membrane to participate in intracellular metabolic pathways when the material is on the cell surface. In this field, the research results of Yang’s team are of milestone significance. To enable it to function as a light harvester, they precipitated cadmium sulfide nanoparticles on the surface of a nonphotosynthetic bacteria. The collected energy fueled cellular metabolism, resulting in acetic acid production [25]. Guo et al. attached light-harvesting indium phosphide nanoparticles (InP) to the surface of *Saccharomyces cerevisiae* (*S. cerevisiae*). Photogenerated electrons pass through the cell membrane to drive the reduction of cellular NADPH in yeast, which can facilitate the production of shikimic acid [28]. The hybrid system, which was composed of *Moorella thermoacetica*-CdS + TiO₂-MnPc, adopted the Z scheme strategy, in which MnPc selectively reduces cysteine (CySS) with a higher redox efficiency and a longer acetic acid synthesis time [48]. When the material is inside the cell, photogenerated electrons are generated intracellularly, and they are directly involved in intracellular metabolic pathways. Yang’s group replaced cadmium sulfide (CdS) nanoparticles with gold nanoclusters (Au NCs), which had a better biocompatibility and a smaller size. Au NCs could enter the cell, and they further improved the charge transfer rate of the photosensitizer, such that it could achieve a 33%
increase in quantum efficiency for continuous CO₂ fixation [26]. CdS NPs as photocatalytic materials could be used in addition to M. thermoaccia, and microorganisms such as M. barkeri [49], R. palustris [50], T. denitrificans, T. thioparus [51,52], G.thioreducens [32], and D. desulfuricans [53] could construct hybrid systems to achieve solar energy conversion.

Based on the above studies, we found that the charge transfer between photocatalytic materials and microorganisms is essential for studying heterogeneous systems. The electron transfer mode and its efficiency in different distribution systems was not well studied, and the conversion efficiency and the value of the final product were relatively low.

2.2. Dye/Polymer-Microorganism Hybrid System

Dye and polymer are also a class of photosensitizers that provide photogenerated electrons, and they can be used in the form of free molecules. It can compound with cells by electrostatic force, van der Waals force, or physical action, which facilitates the formation of well-contacted hybrids. Park’s group used eosin Y (EY) as a photosensitizer to enter the E. coli cell membrane and it was bound specifically to the heme structural domain of P450. In the absence of cofactors and redox partners, the photoactivated P450 catalytic cycle was realized [54]. Wang Shu’s group has developed a series of polymer photosensitive materials. They have designed a hybrid system through the electrostatic recombination of a photoactive cationic poly(ﬂuorene-co-phenylene) derivative (PFP) and cyanobacterium (Synechococcus sp. PCC7942, Syne). PFP increased the efficiency of light utility and electron transport rate by amplifying the absorption zone of Syne [36]. Gai et al. coated perylene diimide derivatives (PDI) and poly(ﬂuorene-co-phenylene) (PFP) as photosensitizers onto the bacterial surface to form a PN heterojunction (PFP/PDI) layer, providing higher hole/electron separation efficiency, and fixed CO₂ to synthesize acetic acid through the Wood-Ljungdahl pathway [37]. Zhou et al. identified synthetic light-capturing polymers with green light absorption, and found that far-red emission poly(boron-dipyromethene-co-ﬂuorene) (PBF) could enhance the PSI activity of the alga Chlorella Vulgaris, which further upgraded and enhanced the PSII activity of natural photosynthesis, and increased oxygen, ATP, and NADPH production [35]. From Qi et al., bio-palladium catalysts were found to synthesize photoactive polystyrene (PPE) on the surface of C. pyrenoidosa cells. It could expand light absorption and accelerate the cyclic electron transport, thus increasing the synthesis of ATP [38].

There are relatively few studies on dye/polymer-microorganism hybrid systems. The main reason for this may be that compared to solid semiconductor materials, dyes are firstly prone to photobleaching, challenging to adjust, and provide a weak reduction potential. Secondly, the energy bands of polymeric photosensitizers are regulated by functional group modifications and controlled polymerization. However, the products are mixtures and they have poor reproducibility. Finally, the dye/polymer photosensitizer is poorly biocompatible and environmentally toxic.

2.3. Electrode-Microbial Hybrid System

In the electrode-microbe hybrid system, the photoelectrodes provide electrons, H₂ or redox mediators as cytoreductive equivalents that are transferred to cellular metabolic pathways for chemical transformation. The electrode-microbial hybrid system has better adjustability and operability. The systems can be divided into integrated and decentralized systems according to the interaction between the electrodes and the microorganisms.

The integrated system requires the electrode to be in close contact with the microorganisms, and the electrons generated by the electrodes are directly transferred to the organisms [55,56]. A representative study is that Yang’s research group proposed the use of no light, microorganisms and silicon nanoarrays as cathodes, and titanium dioxide nanoarrays as anodes. The nanoarrays act as a light collector, which provides a large surface area, and then acetic acid is synthesized using the Wood-Ljungdahl pathway to fix CO₂ without an auxiliary medium [39]. Due to insufficient interaction between the
The applied overpotential and reduction efficiency of CO\(_2\) was relatively low. To improve this, Yang’s group adjusted the pH value of the electrolyte to increase buffering capacity, then fabricated a closely packed nanowire—S. ovata cathode formation that enhanced the reduction of CO\(_2\) with an electric current density of 0.65 mA cm\(^{-2}\) (Figure 2A) [40]. Chen et al. created a 3D-printed library of micro-pillar arrays of electrodes with different heights and surface features, and investigated the energy/electron transfer process across the bioelectrode interface, which was ultimately almost twice the photocurrent of an advanced porous structure with the same height [57].

The decentralized system involves the insertion of an electrode into a microbial suspension. The electrodes’ electrons are required to couple with hydrogen or the redox medium before the microorganisms can use them. Nichols et al. constructed a hybrid system with TiO\(_2\) as the photoanode and p-InP/Pt as the photocathode, compounded with Methanosarcina barkeri, using H\(_2\) as the reduction equivalent, to convert CO\(_2\) to CH\(_4\) with a total Faraday efficiency of up to 86% [58]. Nocera’s group constructed an electrode hybrid system by combining R. eutropha with a cobalt phosphate (CoPi) anode and a nickel-molybdenum-zinc (NiMoZn) cathode to convert CO\(_2\) into biomass and fusel efficiently (Figure 2B) [42]. However, the O\(_2\) generated by the anode accumulated active oxygen radicals in the system, and the electrode was easily corroded and released toxic metal ions during the reaction process. Based on this, Liu et al. used CoPi as the anode and Co-P as the cathode, and compounded this with Raistonia eutropha. The H\(_2\) produced by the cathode promoted CO\(_2\) reduction to synthesize biomass, fuel, or other chemical products [43]. In addition to carbon sequestration, his group used the aforementioned with an electrode combination of Xanthobacter autotrophicus to fix atmospheric nitrogen in NH\(_3\) or soluble biomass with high flux and energy efficiency [41]. The low dissolution rate of H\(_2\) in aqueous solutions limited the energy transfer efficiency. Rodrigues, R.M. et al. used biocompatible perfluorocarbon nanoemulsion as H\(_2\) carriers. Both the available H\(_2\) concentration and the efficiency of acetic acid synthesis were improved [44].

**Figure 2.** Typical samples of integrated and dispersed systems for electrode-microbial hybrid systems. (A) Integrated system. Construction of a hybrid system using tightly packed silicon nanowires and S. ovata to achieve a 3.6% solar energy conversion efficiency in 1 week. (© 2022 Elsevier Inc.) (B) Decentralized system. Wild-type and engineered NiMoZn hybrid systems generate biomass and isopropanol, respectively.

The slow charge transfer efficiency limits the conversion efficiency of the electrode-microbe hybrid system within the interface between the photoelectrode and the bacteria. The conversion efficiency and the product values remain low, even if the reaction possesses a high degree of selectivity. Although increasing the light intensity can effectively improve electron transfer efficiency, it adversely affects microorganisms and electrodes. Consequently, research on the chemical stability, biocompatibility, electrical conductivity, and surface chemistry of microorganisms that have been integrated into the electrode needs to be enhanced.
3. Application of the Photocatalytic Material-Microbe Hybrid System

3.1. Synthesis of Green Energy

With rapid modernization and the rise in energy consumption, the burning of fossil energy generates a large amount of greenhouse gases such as CO₂. Thus, green energy is receiving increasing attention. The use of microorganisms to fix solar energy to generate green fuels not only solves the problems of non-renewable fossil fuels and environmental pollution, but also provides the possibility for establishing a clean and sustainable energy conversion and storage platform [59]. In recent years, a hybrid system constructed with photocatalytic materials and microorganisms has been significantly able to enhance the utilization efficiency of solar energy by microorganisms. The sustainable conversion of CO₂ into fuel is considered to be an effective method for mitigating climate change and alleviating energy depletion [60–64].

Sakimoto et al. used a semiconductor light collector and M. barkeri to construct a hybrid system that reduced CO₂ to CH₄ [65]. Ye et al. developed a biological hybrid composed of CdS nanoparticles and non-phototrophic methanogens to convert CO₂ directly to CH₄, with a production efficiency of 0.19 μmol/h and a QE of 0.34% (Figure 3A) [49]. Xiao et al. presented a visible light-responding photochemical system for microorganisms that could reduce CO₂ to CH₄ [45]. The biological production of H₂ possesses the advantages of raw material availability, self-sustainable, and system reproducibility [24,66]. Tang’s team initiated the in situ deposition of silica on the surface of Chlorella cells to form the core-shell structure of green algal aggregates. Although cell proliferation leads to the destruction of the aggregate structure, this structure has laid the experimental foundation for developing the field of biohydrogen production [67]. Wang et al. constructed a microaggregate with a positively charged polymer and negatively charged Chlorella pyrenoidosa (CP). The hydrogen production was continuous for 42 h, with an average hydrogen production rate of 0.26 μmol/mg chlorophyll per hour [68]. Wang’s group formed a hybrid system of Escherichia coli and CdS nanoparticles to produce H₂ under anaerobic conditions (Figure 3B) [29]. Using this foundation, Wei et al. presented that H₂ can be produced continuously for 96 h under natural aerobic conditions, by introducing a biomimetic silica encapsulation strategy in E. coli engineered bacteria [30]. Xiao et al. bound E. coli to negatively charged iodine-doped hydrothermal carbon (I-HTCC). A hybrid system was formed via electrostatic interaction, and the hydrogen production efficiency of 2000 W m⁻² was 57.04% higher than that of pure E. coli (Figure 3C) [31]. Wang’s group used Desulfovibrio desulfuricans and CdS nanoparticles to construct a hybrid system with an H₂ yield of 36 μmol/gDCW/h, which achieved continuous H₂ generation for over 10 days (Figure 3D) [53]. Cui et al. self-assembled CdSex S 1-x semiconductor nanoparticles in E. coli to construct a hybrid system, in which the hydrogen yield was 2.6-fold greater than using extracellular nanoparticles (Figure 3E) [69]. Jiang et al and Wang et al. used AgInSx/In₅S₃ and CdSeS@ZnS quantum dots to combine with the surface of E. coli to produce H₂ [33,70]. Chen et al. constructed a self-healing, sustainable, and low-cost photocatalytic material-microbe hybrid system with CdS nanoparticles and Thiobacillusdenitrificans. The proportion of N₂O in the product exceeded 96.4%, and the N₂O yield reached 8.7 mg/L after 68 h of illumination [51].
3.2. Synthesis of High Value-Added Products

The photocatalytic material-microbial hybrid system demonstrates the virtues of high catalytic selectivity, mild reaction conditions, low energy consumption, and environmental friendliness in synthesizing high value-added products. The hybrid system has been developed as a novel and efficient platform for biomanufacturing, and it has been used to produce acetic acid, shikimic acid, and bioplastics [25,28,37,48,71–73].

A series of serious environmental problems are caused by massive CO₂ emissions [74]. The hybrid systems can fix CO₂ to produce high value-added products, which is a sustainable production strategy [75]. Askimoto et al. constructed a hybrid system with *M. thermoacetica* and CdS, and 90% of CO₂ was converted to the target product, acetic acid; a maximum acetic acid production over 12 h could reach 1400 μmol/L, and the quantum yield reached 85% [48]. To further improve the yield of acetic acid, Yang’s group introduced biocompatible intracellular photocatalyst AuNCs in the system to replace CdS [26]. After adding TiO₂, the acetic acid yield was increased by approximately 85%. Following four days of system operation, the biocompatible AuNCs improved the cumulative acetic acid yield by 14%. In addition to inorganic semiconductor materials, organic semiconductor materials are widely used in biosensing, gene/drug delivery, and other fields, due to their excellent biocompatibilities [76,77]. Li et al. combined *C. zofingiensis* with highly efficient light-trapping Au NPs to construct a hybrid system in which smaller Au NPs could enter the interior of *C. zofingiensis*. It promoted a carotenoid production of 10.7 ± 1.2 mg/L, which was 42.7% higher than that of natural microalgae (Figure 4A) [27]. Gai et al. constructed a hybrid system with an *M. thermoacetica* and PDI/PFP p-n heterojunction. The organic semiconductor PDI/PFP had excellent biocompatibility, and the number of surviving cells increased to approximately 300% under light conditions (Figure 4B) [37]. Wang et al. prepared nitrogen-containing compounds by coating CdS NP on R. palustris surface-immobilized with Ns. The accumulated solid biomass (3.44 g/L) reached 2.53 times that of natural cells under visible light radiation [78]. Wang et al. constructed a CdS@C. beijerinckii hybrid system and increased the lignocellulosic butanol yield by 23.6% [79]. Ding et al. designed different photocatalytic materials combined with specific functional microorganisms to produce hydrogen and various chemicals, such as IPA, BDO, MKs, H₂, FA, NH₃, C₂H₅, and PHB [80]. Guo et al. combined InP onto the surface of a genetically engineered yeast strain Δzwf1 (*S. cerevisiae* Δzwf1). They used photogenerated electrons to generate NADPH’s reducing force to promote shikimic acid synthesis.
inside the cell. The final titer of shikimic acid production reached 48.5 ± 2.1 mg/L [28]. Similarly, Xu et al. hybridized g-C3N4 with Ralstoniaeutropha H16, which increased the yield of PHB production of this strain by up to 1.2-fold compared to non-hybridization [71].

**Figure 4.** (A) C. zofingiensis–AuNPs hybrid system, where AuNPs significantly increase the relative electron transport rate in photosystem II, and the ROS level in microalgae (Copyright © 2022, American Chemical Society). (B) (a) PDI/FFP/M. thermoacetica photosynthesis hybrid system. (b) Transport pathway of photogenerated electrons generated by PDI/FFP in light (© 2022 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

### 3.3. Treatment of Environmental Pollution

With the rapid growth of industry and agriculture, refractory organic pollutants are released into the environment. By combining the advantages of photocatalysis and bacterial degradation, pollution can be better degraded [81]. Compared with conventional technologies, the photocatalytic material-microorganism hybrid system reduces the energy consumption generated by a high aeration rate and it significantly improves the degradation efficiency. It has developed a new technology with a sufficient reduction power for oxidative pollutants that need to be degraded [82,83]. Xiao et al. constructed a hybrid system under anaerobic conditions. They believed that the holes on the Ag3PO4 photocatalytic material were removed by the electrons released from *S. oneidensis* MR-1. The electrons generated on Ag3PO4 were efficiently transferred to rhodamine B, to achieve photo-reduction degradation [84]. In their group’s work, a hybrid system was constructed using the photocatalytic material CdS and the microorganism *S. oneidensis* MR-1. Under anaerobic photoexcitation, the electrons generated from the anaerobic respiration of *S. oneidensis* MR-1 act as hole scavengers, and the photocatalytic material CdS continuously generated electrons, thus cleaving the azo bond in the azo dye trypan blue (Figure 5A) [85]. Huang’s team precipitated CdS nanoparticles on the surface of an electrochemically active microorganism (*Geobacter sulfurreducens*) that has two simultaneous degradation pathways. Light-driven CdS nanoparticles generated photogenerated electrons. A part of them was used to reduce the azo dye methyl orange (MO), and microorganisms used the other part for the bioreduction of MO, with 40 mg/L MO able to be wholly degraded within three hours (Figure 5B) [32]. Wang’s group used biofilm-anchored gold nanoclusters alone on the amyloid monomers of genetically modified *E. coli* nanofiber systems to reduce nitrobenzene phenol. Simultaneous anchoring of Cd0.9Zn0.1S QDs and Au nanoparticles were able to degrade the organic dye Congo Red. The photodegradation rate increased with the increase of Au-QDs volume ratio (Figure 5C) [70]. Priyanka’s group added ZnS nanoparticles to *Aspergillus niger* cells to construct a hybrid system for degrading MO (Figure 5D) [86]. Hybrid systems have a massive potential for treating wastewater that is contaminated with heavy metals. As contaminated sites are generally contaminated with multiple heavy metals, many microorganisms have evolved the ability to tolerate and to detoxify multiple heavy metals simultaneously [81]. Yin et al. proposed a possible reaction where TY3-4 could simultaneously remove Cr⁶⁺ and Mn²⁺ [82]. If mineral particles with photocatalytic potential are formed to simultaneously mineralize extracellular metal ions,
as well as to reduce other metal ions, then degradation can be accomplished without any genetic engineering.

**Figure 5.** (A) Schematic illustration of the degradation pathway of MO using the CdS–*G. sulfurreducens* hybrid system (Copyright © 2022, American Chemical Society). (B) *S. oneidensis* MR-1-CdS combines to establish a heterogeneous microbial system for the photocatalytic degradation of trypan blue (© 2022 Published by Elsevier B.V.). (C) Diverse catalytic applications of tunable functional *E. coli* biofilms with anchored nano-objects. (a) The biofilm-anchored Au NPs enable the recyclable catalytic reduction of the toxic *p*-nitrophenol (PNP) into the harmless *p*-aminophenol (PAP). (b) The biofilm-anchored heterogeneous nanostructures (Au NPs/Cd0.9Zn0.1S QDs) photocatalyze the degradation of organic dyes to low-toxic products based on facile light-induced charge separation. (c) The biofilm-anchored quantum dots coupled with the engineered strain enable photoinduced hydrogen production. Electrons are transferred from QDs to hydrogenase using methyl viologen (MV) as a mediator (Copyright © 2022, Oxford University Press). (D) Schematic diagram of the photocatalytic mechanism of light-driven *Aspergillus niger* cell-ZnS nano-biohybrids for enhanced removal of the dye methyl orange (Copyright © 2022, Elsevier).

**4. The Direction of Improvement of the Hybrid System**

After construction of the photocatalytic material-microbe hybrid system, the properties of the material and the microorganism itself are affected. This interaction directly affects the electron transfer efficiency. Therefore, improving the charge transfer efficiency is essential for increasing the efficiency of solar energy to chemical energy conversion [75,87,88]. The interaction between materials and microorganisms can be improved in three ways: the nature of the photocatalytic materials, the microorganisms’ properties, and how to composite the two. Through continued interdisciplinary research in biology, chemistry, and physics, achieving net-zero carbon emissions or even harmful carbon emissions in the future becomes possible.

**4.1. Enhancing the Performances of Photocatalytic Materials**

The photocatalytic material can restrict the properties of the photocatalytic material-microbe hybrid system. Under illumination, it is extremely easy for electrons and holes generated on the material surface to compound, which reduces the transformation efficiency of solar energy to chemical energy. It is possible to attenuate the complexation between electrons and holes by using photocatalytic heterojunction materials or by adding sacrificial electron donors [89]. Jiang et al. designed AgInS2/In2S3 heterojunctions to inhibit
the complexation of photogenerated electron-hole pairs, improving the utilization of photogenerated electrons in microbial H2 production [33]. Gai et al. increased the acetic acid yield of *M. thermoacetica* by designing PDI/PFP p-n heterojunctions to enhance photocatalyst electron-hole pair separation [37].

4.2. Improving the Properties of Microorganisms

Along with the evolution of synthetic biology, it is possible to produce the desired chemicals by designing new metabolic pathways or altering existing microbial cellular metabolic pathways. Although extensive genetic manipulation may burden microbial cell metabolism, mild genetic manipulation combined with photocatalytic materials is desirable [90,91]. It can also enhance the yield of microorganisms by promoting electron shuttle secretion and facilitating biofilm formation. Chen’s group engineered the heterotrophic microorganism *Saccharomyces cerevisiae* at multiple levels, increasing the carbon flux into the aromatic amino acid biosynthesis pathway. Guo et al. genetically engineered *Saccharomyces cerevisiae* by knocking out the ZWF1 gene, which encoded glucose-6-phosphate dehydrogenase in the strain, and decoupled the pathway of NADPH production from the central carbon metabolic pathway to maximize carbon flux [28]. Choi et al. genetically modified *Shewanella* strains so that they could use glucose as a carbon and energy source [92].

4.3. Improving the Combination of Microbes and Materials

Photocatalytic materials can be complexed with microorganisms to generate energy conversion and catalytic cycling [56]. Different combination methods will produce different interface effects and affect microbial metabolic pathways. In semiconductor material-microbial hybrid systems, the properties of the nanoparticles and microorganisms largely change. Wang et al. genetically engineered *E. coli* so that it could express, secrete, and be sufficient for self-assembly and the anchorage of nanocatalysts outside the cell [70]. Guo et al. used natural polyphenols to modify InP nanoparticles to form modular units that are similar to building blocks, for orderly and tight coupling with cells, thus avoiding the harmful effects of photocatalytic materials on cells [28]. Wei et al. genetically engineered *E. coli* to biologically synthesize biocompatible CdS NPs in situ on the cell surface [30]. In the electrode-microbe hybrid system, meeting the requirements for the size of the photoelectrode reactor, the efficiency of electron transfer across the biomixing interface, and continuous microbial growth are the critical questions that drive the development of the system.

5. Summary and Outlook

Currently, the technology for photocatalytic material-microorganism hybrid systems is still in its initial stage. There are still many problems regarding the light energy conversion efficiency, the stability and sustainability of the catalytic system, and the scale of production. In-depth research for improving the system’s temporal stability, biocompatibility, charge transfer efficiency, and energy consumption efficiency is essential to solving the above problems. With the continuous development of materials chemistry and synthetic biology, new photocatalytic materials and microbes that can be applied in the hybrid system will continuously emerge. The selection of suitable photocatalytic materials according to the characteristics of microorganisms, target metabolic pathways, and the surface, composition, structure, and reaction conditions of materials are continuously being optimized. The combination of photocatalytic materials with microbes must affect these microbes. Recently, researchers have found that the number of intracellular proteins and the metabolites of microorganisms changed after binding to photocatalytic materials. The number of substances that are associated with energy metabolism is significantly higher, which is consistent with the logic that photocatalytic materials absorb light energy
to supply energy to the cell. However, the intracellular electron transfer pathways are still unknown. The specific electron transfer chain in microorganisms remains to be studied.

In the future, we should further analyze the energy and charge transfer pathways, the intracellular electron transfer chains, and the priority order of energy utilization in heterogeneous systems. This can improve the energy utilization efficiency and then achieve the purpose of efficiently synthesizing the target product. As well as concern for production efficiency, we need to conduct more in-depth studies on cost, stability, and equipment safety, in order to assess the possibility of achieving mass production in the future. The realization of mass production will be a progressive step in the utilization of light energy.

Author Contributions: J.S., H.L., and G.Z. wrote the related research progress. X.H. revised the review article. All of the authors participated in the discussion, writing, and revision of this review. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Shandong Provincial Key Research and Development Project (2020XGC011304); National Natural Science Foundation of China (Grant No.32001020; No.82130067); Shandong Provincial Natural Science Foundation (ZR2020QB131); Qilu University of Technology Foundation/Shandong Academy of Sciences Foundation (202004).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Data sharing not applicable. No new data were created or analyzed in this study.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Armaroli, N.; Balzani, V. Die Zukunft der Energieversorgung-herausforderungen und chancen. Angew. Chem. 2007, 119, 52–67. https://doi.org/10.1002/ange.200622373.
2. Tennison, I.; Roschnik, S.; Ashby, B.; Boyd, R.; Hamilton, I.; Oreszczyn, T.; Owen, A.; Romanelli, M.; Ruyssevelt, P.; Sherman, J.D.; et al. Health care’s response to climate change: A carbon footprint assessment of the NHS in England. Lancet Planet. Health 2021, 5, e84–e92. https://doi.org/10.1016/s2542-5196(20)30271-0.
3. Li, X.B.; Tung, C.H.; Wu, L.Z. Semiconducting quantum dots for artificial photosynthesis. Nat. Rev. Chem. 2018, 2, 160–173. https://doi.org/10.1038/s41570-018-0024-8.
4. Lewis, N.S. Research opportunities to advance solar energy utilization. Science 2016, 351, aad1920. https://doi.org/10.1126/science.aad1920.
5. Barber, J. Photosynthetic energy conversion: Natural and artificial. Chem. Soc. Rev. 2009, 38, 185–196. https://doi.org/10.1039/b802262n.
6. Fang, X.; Kalathil, S.; Reisner, E. Semi-biological approaches to solar-to-chemical conversion. Chem. Soc. Rev. 2020, 49, 4926–4952. https://doi.org/10.1039/c9cs00496c.
7. Nybo, S.E.; Khan, N.E.; Woolston, B.M.; Curtis, W.R. Metabolic engineering in chemolithoautotrophic hosts for the production of fuels and chemicals. Metab. Eng. 2015, 30, 105–120. https://doi.org/10.1016/j.menb.2015.04.008.
8. Mallick, N.; Bagchi, S.K.; Koley, S.; Singh, A.K. Progress and challenges in microalgal biodiesel production. Front. Microbiol. 2016, 7, 1–11. https://doi.org/10.3389/fmicb.2016.01019.
9. Oliver, N.J.; Rabinovitch-Deere, C.A.; Carroll, A.L.; Nozzi, N.E.; Case, A.E.; Atsumi, S. Cyanobacterial metabolic engineering for biofuel and chemical production. Curr. Opin. Chem. Biol. 2016, 35, 43–50. https://doi.org/10.1016/j.cbpa.2016.08.023.
10. Proppe, A.H.; Li, Y.C.; Aspuru-Guzik, A.; Berlinguette, C.P.; Chang, C.J.; Cogdell, R.; Doyle, A.G.; Flick, J.; Gabor, N.M.; van Grondelle, R.; et al. Bioinspiration in light harvesting and catalysis. Nat. Rev. Mater. 2020, 5, 828–846. https://doi.org/10.1038/s41578-020-0222-0.
11. Fleming, G.R.; Schlau-Cohen, G.S.; Amarnath, K.; Zaks, J. Design principles of photosynthetic light-harvesting. Faraday Discuss. 2012, 155, 27–41. https://doi.org/10.1039/c1fd00078k.
12. Sharkey, T.D.; Bernacchi, C.J.; Farquhar, G.D.; Singsaas, E.L. Fitting photosynthetic carbon dioxide response curves for C4 leaves. Plant Cell Environ. 2007, 30, 1035–1040. https://doi.org/10.1111/j.1365-3040.2007.01710.x.
13. Zhu, X.G.; Long, S.P.; Ort, D.R. What is the maximum efficiency with which photosynthesis can convert solar energy into biomass? Curr. Opin. Biotechnol. 2008, 19, 153–159. https://doi.org/10.1016/j.copbio.2008.02.004.
14. Zhu, X.G.; Long, S.P.; Ort, D.R. Improving photosynthetic efficiency for greater yield. Annu. Rev. Plant Biol. 2010, 61, 235–261. https://doi.org/10.1146/annurev-arplant-042809-112206.
15. Dogan, D.K.; Nocera, D.G. Artificial photosynthesis at efficiencies greatly exceeding that of natural photosynthesis. Acc. Chem. Res. 2019, 52, 3143–3148. https://doi.org/10.1021/acs.accounts.9b00380.
16. Liu, G.; Gao, F.; Gao, C.; Xiong, Y. Bioinspiration toward efficient photosynthetic systems: From biohybrids to biomimetics. *Chem Catal.* 2021, 1, 1367–1377. https://doi.org/10.1016/j.chemcat.2021.09.010.

17. Yang, P. Liquid Sunlight: The Evolution of photosynthetic biohybrids. *Nano Lett.* 2021, 21, 5453–5456. https://doi.org/10.1021/acs.nanolett.1c01217.

18. Zhang, L.; Zhang, Q.; Xie, H.; Guo, J.; Lyu, H.; Li, Y.; Sun, Z.; Wang, H.; Guo, Z. Electropun titania nanofibers segregated by graphene oxide for improved visible light photocatalysis. *Appl. Catal. B Environ.* 2017, 201, 470–478. https://doi.org/10.1016/j.apcata.2016.08.056.

19. Brown, K.A.; Harris, D.F.; Wilker, M.B.; Rasmussen, A.; Khadka, N.; Hamby, H.; Keable, S.; Dukovic, G.; Peters, J.W.; Seefeldt, L.C.; et al. Light-driven dinitrogen reduction catalyzed by a CdS:nitrogenase MoFe protein biohybrid. *Science* 2016, 352, 448–450. https://doi.org/10.1126/science.aaf2091.

20. Caputo, C.A.; Wang, L.; Beranek, R.; Reisner, E. Carbon nitride-TiO$_2$ hybrid modified with hydrogenase for visible light driven *Hydrog. Prog.* 2015, 6, 5690–5694.

21. Kornienko, N.; Zhang, J.Z.; Sakimoto, K.K.; Yang, P.; Reisner, E. Interfacing nature’s catalytic machinery with synthetic materials for semi-artificial photosynthesis. *Nat. Nanotechnol.* 2018, 13, 890–899. https://doi.org/10.1038/s41565-018-0251-7.

22. Cestellos-Blanco, S.; Zhang, H.; Kim, J.M.; Shen, Y.X.; Yang, P. Photosynthetic semiconductor biohybrids for solar-driven biocatalysis. *Nat. Catal.* 2020, 3, 245–255. https://doi.org/10.1038/s41929-020-0248-y.

23. Agapakis, C.M.; Boyle, P.M.; Silver, P.A. Natural strategies for the spatial optimization of metabolism in synthetic biology. *Nat. Chem.* 2012, 8, 527–535. https://doi.org/10.1038/nchembio.975.

24. Li, L.; Xu, Z.; Huang, X. Whole-cell-based photosynthetic biohybrid systems for energy and environmental applications. *Chempluschem* 2021, 86, 1021–1036. https://doi.org/10.1002/cplu.202010017.

25. Sakimoto, K.K.; Wong, A.B.; Yang, P. Self-photosensitization of nonphotosynthetic bacteria for solar-to-chemical production. *Science* 2016, 351, 74–77. https://doi.org/10.1126/SCIENCE.AAD3317.

26. Zhang, H.; Liu, H.; Tian, Z.; Lu, D.; Yu, Y.; Cestellos-Blanco, S.; Sakimoto, K.K.; Yang, P. Bacteria photosensitized by intracellular gold nanoclusters for solar fuel production. *Nat. Nanotechnol.* 2018, 13, 900–905. https://doi.org/10.1038/s41565-018-0267-z.

27. Li, X.; Sun, H.; Mao, X.; Lao, Y.; Chen, F. Enhanced photosynthesis of carotenoids in microalgae driven by light-harvesting gold nanoparticles. *ACS Sust. Chem. Eng.* 2020, 8, 7600–7608. https://doi.org/10.1021/acssuschemeng.0c03151.

28. Guo, J.; Suastege, M.; Sakimoto, K.K.; Moody, V.M.; Xiao, G.; Noceira, D.G.; Joshi, N.S. Light-driven fine chemical production in yeast biohybrids. *Science* 2018, 362, 813–816. https://doi.org/10.1126/science.aat9777.

29. Wang, B.; Zeng, C.; Chu, K.H.; Wu, D.; Yip, H.Y.; Ye, L.; Wong, P.K. Enhanced biological hydrogen production from escherichia coli with surface precipitated cadmium sulfide nanoparticles. *Adv. Energy Mater.* 2017, 7, 1–10. https://doi.org/10.1002/aenm.201700611.

30. Wei, W.; Sun, P.; Li, Z.; Song, K.; Su, W.; Wang, B.; Liu, Y.; Zhao, J. A surface-display biohybrid approach to light-driven hydrogen production in air. *Sci. Adv.* 2018, 4, eaap9253. https://doi.org/10.1126/sciadv.aap9253.

31. Xiao, K.; Tsang, T.H.; Sun, D.; Liang, J.; Zhao, H.; Jiang, Z.; Wang, B.; Yu, J.C.; Wong, P.K. Interfacing iodine-doped hydrothermally carbonized carbon with escherichia coli through an “Add-on” mode for enhanced light-driven hydrogen production. *Adv. Energy Mater.* 2021, 11, 1–13. https://doi.org/10.1002/aenm.2020100291.

32. Huang, S.; Tang, J.; Liu, X.; Dong, G.; Zhou, S. Fast Light-Driven Biocolorization by a Geobacter sulfurreducens-CdS Hybrid. *ACS Sust. Chem. Eng.* 2019, 7, 15427–15433. https://doi.org/10.1021/acssuschemeng.9b02870.

33. Jiang, Z.; Wang, B.; Yu, J.C.; Wang, J.; An, T.; Zhao, H.; Li, H.; Yuan, S.; Wong, P.K. Aghl52/in253 heterostructure sensitization of Escherichia coli for sustainable hydrogen production. *Nano Energy* 2018, 46, 234–240. https://doi.org/10.1016/j.nanoen.2018.02.001.

34. Shen, H.; Wang, Y.Z.; Liu, G.; Li, L.; Xia, R.; Luo, B.; Wang, J.; Suo, D.; Shi, W.; Yong, Y.C. A Whole-cell inorganic-biohybrid system integrated by reduced graphene oxide for boosting solar hydrogen production. *ACS Catal.* 2020, 10, 13290–13295. https://doi.org/10.1021/acscatal.0c03594.

35. Zhou, X.; Zeng, Y.; Tang, Y.; Huang, Y.; Lv, F.; Liu, L.; Wang, S. Artificial regulation of state transition for augmenting plant photosynthesis using synthetic light-harvesting polymer materials. *Sci. Adv.* 2020, 6, eabc5237. https://doi.org/10.1126/sciadv.abc5237.

36. Zeng, Y.; Zhou, X.; Qi, R.; Dai, N.; Fu, X.; Zhao, H.; Peng, K.; Yuan, H.; Huang, Y.; Lv, F.; et al. Photoactive conjugated polymer-based hybrid biosystems for enhancing cyanobacterial photosynthesis and regulating redox state of protein. *Adv. Funct. Mater.* 2021, 31, 1–9. https://doi.org/10.1002/adfm.202007814.

37. Gai, P.; Yu, W.; Zhao, H.; Qi, R.; Li, F.; Liu, L.; Lv, F.; Wang, S. Solar-powered organic semiconductor-bacteria biohybrids for CO$_2$ reduction into acetic acid. *Angew. Chem. Int. Ed.* 2020, 59, 7224–7229. https://doi.org/10.1002/anie.202001047.

38. Qi, R.; Zhao, H.; Zhou, X.; Liu, J.; Dai, N.; Zeng, Y.; Zhang, E.; Lv, F.; Huang, Y.; Liu, L.; et al. In situ synthesis of photoactive polymers on a living cell surface via Bio-palladium catalysis for modulating biological functions. *Angew. Chem.* 2021, 133, 5823–5829. https://doi.org/10.1002/ange.202015247.

39. Liu, C.; Gallagher, J.J.; Sakimoto, K.K.; Nichols, E.M.; Chang, C.J.; Chang, M.C.Y.; Yang, P. Nanowire-bacteria hybrids for unassisted solar carbon dioxide fixation to value-added chemicals. *Nano Lett.* 2015, 15, 3634–3639. https://doi.org/10.1021/acs.nanolett.5b01254.

40. Su, Y.; Cestellos-Blanco, S.; Kim, J.M.; Shen, Y.X.; Kong, Q.; Lu, D.; Liu, C.; Zhang, H.; Cao, Y.; Yang, P. Close-Packed Nanowire-Bacteria Hybrids for Efficient Solar-Driven CO$_2$ Fixation. *Joule* 2020, 4, 800–811. https://doi.org/10.1016/j.joule.2020.03.001.
41. Liu, C.; Sakimoto, K.K.; Colón, B.C.; Silver, P.A.; Nocera, D.G. Ambient nitrogen reduction cycle using a hybrid inorganic-biological system. Proc. Natl. Acad. Sci. USA 2017, 114, 6450–6455. https://doi.org/10.1073/pnas.1706371114.

42. Torella, J.P.; Gagliardi, C.J.; Chen, J.S.; Bediako, D.K.; Colón, B.; Way, J.C.; Silver, P.A.; Nocera, D.G. Efficient solar-to-fuels production from a hybrid microbial-water-splitting catalyst system. Proc. Natl. Acad. Sci. USA 2015, 112, 2337–2342. https://doi.org/10.1073/pnas.1424872112.

43. Liu, C.; Colón, B.C.; Ziesack, M.; Silver, P.A.; Nocera, D.G. Water splitting-biosynthetic system with CO2 reduction efficiencies exceeding photosynthesis. Science 2016, 352, 1210–1213. https://doi.org/10.1126/SCIENCE.AAF5039/SUPPL_FILE/LIU.SM.PDF.

44. Rodrigues, R.M.; Guan, X.; Iriúgez, J.A.; Estabrook, D.A.; Chapman, J.O.; Huang, S.; Sletten, E.M.; Liu, C. Perfluorocarbon nanoemulsion promotes the delivery of reducing equivalents for electricity-driven microbial CO2 reduction. Nat. Catal. 2019, 2, 407–414. https://doi.org/10.1038/s41929-019-0264-0.

45. Xiao, S.; Li, Z.; Fu, Q.; Li, Y.; Li, J.; Zhang, L.; Liao, Q.; Zhu, X. Hybrid microbial photoelectrochemical system reduces CO2 to CH4 with 1.28% solar energy conversion efficiency. Chem. Eng. J. 2020, 390, 124530. https://doi.org/10.1016/j.cej.2020.124530.

46. Honda, Y.; Watanebe, M.; Hagiwara, H.; Ida, S.; Ishihara, T. Inorganic/whole-cell biobrhmocatalyst for highly efficient hydrogen production from water. Appl. Catal. B Environ. 2017, 210, 400–406. https://doi.org/10.1016/j.apcatb.2017.04.015.

47. Rowe, S.F.; Le Gall, G.; Ainsworth, E.V.; Davies, J.A.; Lockwood, C.W.J.; Shi, L.; Elliston, A.; Roberts, L.N.; Waldron, K.W.; Richardson, D.J.; et al. Light-Driven H: Evolution and C=C or C=O Bond Hydrogenation by Shewanella oneidensis: A Versatile Strategy for Photocatalysis by Nonphotosynthetic Microorganisms. ACS Catal. 2017, 7, 7558–7566. https://doi.org/10.1021/acscatal.7b02736.

48. Sakimoto, K.K.; Zhang, S.Y.; Yang, P. Cysteine-Cystine Photoregeneration for Oxigenic Photosynthesis of Acetic Acid from CO2 by a Tandem Inorganic-Biological Hybrid System. Nano Lett. 2016, 16, 5883–5887. https://doi.org/10.1021/acs.nanolett.6b02740.

49. Ye, J.; Yu, J.; Zhang, Y.; Chen, M.; Liu, X.; Zhou, S.; He, Z. Light-driven carbon dioxide reduction to methane by Methanosarcina barkeri-Cds hybrid. Appl. Catal. B Environ. 2019, 257, 117916. https://doi.org/10.1016/j.apcatb.2019.117916.

50. Wang, B.; Jiang, Z.; Yu, J.C.; Wang, J.; Wong, P.K. Enhanced CO2 reduction and valuable C2 chemical production by a CdS-photosynthetic hybrid system. Nanoscale 2019, 11, 9296–9301. https://doi.org/10.1039/c9nr02896j.

51. Chen, M.; Zhou, X.; Yu, Y.; Liu, X.; Zeng, R.J. Light-driven nitrous oxide production via autotrophic denitrification by self-photosensitized Thiobacillus denitrificans. Environ. Int. 2019, 127, 353–360. https://doi.org/10.1016/j.envint.2019.03.045.

52. Liu, G.; Gao, F.; Zhang, H.; Wang, L.; Gao, C.; Xiong, Y. Biosynthetic CdS-Thiobacillus thioparus hybrid for solar-driven carbon dioxide fixation. Nano Res. 2021, https://doi.org/10.1007/s12274-021-3883-0.

53. Martins, M.; Toste, C.; Pereira, I.A.C. Enhanced Light-Driven Hydrogen Production by Self-Photosensitized Biobrhmocatalysis. Angew. Chem. Int. Ed. 2021, 60, 9055–9062. https://doi.org/10.1002/anie.202016960.

54. Park, J.H.; Lee, S.H.; Cha, G.S.; Choi, D.H.; Nam, D.H.; Lee, J.H.; Lee, J.K.; Yun, C.H.; Jeong, K.J.; Park, C.B. Cofactor-Free Light-Driven Whole-Cell Cytochrome P450 Catalysis. Angew. Chem. 2014, 127, 983–987.

55. Rabaey, K.; Rozendal, R.A. Microbial electrocatalysis—Revisiting the electrical route for microbial production. Nat. Rev. Microbiol. 2010, 8, 706–716. https://doi.org/10.1038/nrmicro2422.

56. Xu, L.; Zhao, Y.; Owsusu, K.A.; Zhuang, Z.; Liu, Q.; Wang, Z.; Li, Z.; Mai, L. Recent Advances in Nanowire-Biosystem Interfaces: From Chemical Conversion, Energy Production to Electrophotolysis. Chem. 2018, 4, 1538–1559. https://doi.org/10.1016/j.chempr.2018.04.004.

57. Chen, X.; Lawrence, J.M.; Wey, L.T.; Schertel, L.; Jing, Q.; Vignolini, S.; Howe, C.J.; Kar-Narayan, S.; Zhang, J.Z. 3D-printed hierarchical pillar array electrodes for high-performance semi-artificial photosynthesis. Nat. Mater. 2022. https://doi.org/10.1038/s41563-022-01205-5.

58. Nichols, E.M.; Gallagher, J.J.; Liu, C.; Su, Y.; Resasco, J.; Yu, Y.; Sun, Y.; Yang, P.; Chang, M.C.Y.; Chang, C.J. Hybrid bioinorganic approach to solar-chemical conversion. Proc. Natl. Acad. Sci. USA 2015, 112, 11461–11466. https://doi.org/10.1073/pnas.1508075112.

59. Claassen, N.J.; Sousa, D.Z.; Dos Santos, V.A.P.M.; De Vos, W.M.; Van Der Oost, J. Harnessing the power of microbial autotrophy. Nat. Rev. Microbiol. 2016, 14, 692–706. https://doi.org/10.1038/nrmicro2422.

60. Handoko, A.D.; Wei, F.; Jenndy; Yeo, B.S.; Seh, Z.W. Understanding heterogeneous electrocatalytic carbon dioxide reduction through operando techniques. Nat. Catal. 2018, 1, 922–934. https://doi.org/10.1038/s41929-018-0182-6.

61. Léonard, A.; Dandoy, P.; Danloy, E.; Leroux, G.; Meunier, C.F.; Rooke, J.C.; Su, B.L. Whole-cell based hybrid materials for green energy production, environmental remediation and smart cell-therapy. Chem. Soc. Rev. 2011, 40, 860–885. https://doi.org/10.1039/c1cs00124h.

62. Xiao, S.; Fu, Q.; Li, Z.; Li, J.; Zhang, L.; Zhu, X.; Liao, Q. Solar-driven biological inorganic hybrid systems for the production of solar fuels and chemicals from carbon dioxide. Renew. Sustain. Energy Rev. 2021, 150, 111375. https://doi.org/10.1016/j.rser.2021.111375.

63. Fang, Z.; Zhou, J.; Zhou, X.; Koffas, M.A.G. Abiotic-biotic hybrid for CO2 bioconversion: From electrochemical to photochemical process. Sci. Total Environ. 2021, 791, 148288. https://doi.org/10.1016/j.scitotenv.2021.148288.

64. Welivatte, N.S.; Minteer, S.D. Photo-bioelectrocatalytic CO2 reduction for a circular energy landscape. Joule 2021, 5, 2564–2592. https://doi.org/10.1016/j.joule.2021.08.003.

65. Sakimoto, K.K.; Kornienko, N.; Yang, P. Cyborgian material design for solar fuel production: The emerging photosynthetic biohybrid systems. Acc. Chem. Res. 2017, 50, 476–481. https://doi.org/10.1021/acs.accounts.6b00483.
66. Yang, E.; Omar Mohamed, H.; Park, S.G.; Obaid, M.; Al-Qaradawi, S.Y.; Castaño, P.; Chon, K.; Chae, K.J. A review on self-sustainable microbial electrolysis cells for electro-biohydrogen production via coupling with carbon-neutral renewable energy technologies. Bioreourc. Technol. 2021, 320, 124363. https://doi.org/10.1016/j.biortech.2020.124363.

67. Xiong, W.; Zhao, X.; Zhu, G.; Shao, C.; Li, Y.; Ma, W.; Xu, X.; Tang, R. Silification-Induced Cell Aggregation for the Sustainable Production of H2 under Aerobic Conditions. Angew. Chem. 2015, 127, 12129–12133. https://doi.org/10.1002/ange.201504634.

68. Wang, S.L.; Xu, Z.J.; Lin, S.; Liu, X.M.; Wang, L.; Huang, X. Polymer-chlorelo cells conjugating with aggregation-induced functionality switch towards hydrogen evolution. Sci. China Technol. Sci. 2020, 63, 1416–1425. https://doi.org/10.1007/s11431-020-1628-9.

69. Cui, S.; Tian, L.J.; Li, J.; Wang, X.M.; Liu, H.Q.; Fu, X.Z.; He, R.L.; Lam, P.K.S.; Huang, T.Y.; Li, W.W. Light-assisted fermentative hydrogen production in an intimately-coupled inorganic-bio hybrid with self-assembled nanoparticles. Chem. Eng. J. 2022, 428, 131254. https://doi.org/10.1016/j.cej.2021.131254.

70. Wang, X.; Pu, J.; Liu, Y.; Ba, F.; Cui, M.; Li, K.; Xie, Y.;Nie, Y. Immobilization of functional nano-objects in living engineered bacterial biofilms for catalytic applications. Natl. Sci. Rev. 2018, 6, 929–943.

71. Xu, M.; Tremblay, P.L.; Jiang, L.; Zhang, T. Stimulating bioplastic production with light energy by coupling: Ralstonia eutropha with the photocatalyst graphitic carbon nitride. Green Chem. 2019, 21, 2392–2400. https://doi.org/10.1039/c8gc03695k.

72. Cotton, C.A.; Edlich-Muth, C; Bar-Even, A. Reinforcing carbon fixation: CO2 reduction replacing and supporting carboxylation. Curr. Opin. Biotechnol. 2018, 49, 49–56. https://doi.org/10.1016/j.copbio.2017.07.014.

73. Fuchs, G. Alternative pathways of carbon dioxide fixation: Insights into the early evolution of life? Annu. Rev. Microbiol. 2011, 65, 631–658. ISBN 0901101028.

74. Sellers, P.J.; Bounoua, L.; Collatz, G.J.; Randall, D.A.; Dazlich, D.A.; Los, S.O.; Berry, J.A.; Fung, I.; Tucker, C.J.; Field, C.B.; et al. Comparison of radiative and physiological effects of doubled atmospheric CO2 on climate. Science 1996, 271, 1402–1406. https://doi.org/10.1126/science.271.5254.1402.

75. Pan, Q.; Tian, X.; Li, J.; Wu, X.; Zhao, F. Interfacial electron transfer for carbon dioxide valorization in hybrid inorganic-microbial systems. Appl. Energy 2021, 292, 116885. https://doi.org/10.1016/j.apenergy.2021.116885.

76. Wang, Y.; Feng, L.; Wang, S. Conjugated polymer nanoparticles for imaging, cell activity regulation, and therapy. Adv. Funct. Mater. 2019, 29, 1–20. https://doi.org/10.1002/adfm.201806818.

77. Wang, B.; Queenan, B.N.; Wang, S.; Nilsson, K.P.R.; Bazan, G.C. Precisely defined conjugated oligolectrolytes for biosensing and therapeutics. Adv. Mater. 2019, 31, 1–21. https://doi.org/10.1002/adma.201807671.

78. Wang, B.; Xiao, K.; Jiang, Z.; Wang, J.; Jimmy, C.Y.;Wong, P.K. Biohybrid photoheterotrophic metabolism for significant enhancement of biological nitrogen fixation in pure microbial cultures. Energy Environ. Sci. 2019, 12, 2185–2191. https://doi.org/10.1039/c9ee00252x.

79. Wang, X.; Li, J.; Zhang, C.; Zhang, Y.; Meng, J. Self-assembly of CdS@C. beijerinckii hybrid system for efficient lignocellulosic butanol production. Chem. Eng. J. 2021, 424, 130458. https://doi.org/10.1016/j.cej.2021.130458.

80. Ding, Y.; Bertram, J.R.; Eckert, C.; Bommaretty, R.R.; Patel, R.; Conradie, A.; Bryan, S.; Nagpal, P. Nanorg microbial factories: Light-driven renewable biochemical synthesis using quantum dot-bacteria nanobiobiohybrids. J. Am. Chem. Soc. 2019, 141, 10272–10282. https://doi.org/10.1021/jacs.9b02549.

81. Zuo, W.; Zhang, L.; Zhang, Z.; Tang, S.; Sun, Y.; Huang, H.; Yu, Y. Degradation of organic pollutants by intimately coupling photocatalytic materials with microbes: A review. Crit. Rev. Biotechnol. 2021, 41, 273–299. https://doi.org/10.1080/07388551.2020.1869689.

82. Liu, P.C.; Ma, X.L.; Li, T.T.; Yan, F.; Wu, L.J.; Xiao, X. Elucidation of photodegradation of p-chlorophenol in a biophotoelectric reductive degradation system by density functional theory calculations. Int. Biodeterior. Biodegrad. 2020, 151, 104969. https://doi.org/10.1016/j.ibiod.2020.104969.

83. Xu, Z.; Chen, S.; Guo, S.; Wan, D.; Xu, H.; Yan, W.; Jin, X.; Feng, J. New insights in light-assisted microbial fuel cells for wastewater treatment and power generation: A win-win cooperation. J. Power Sources 2021, 501, 230000. https://doi.org/10.1016/j.jpowsour.2021.230000.

84. Xiao, X.; Ma, X.L.; Liu, Z.Y.; Li, W.W.; Yuan, H.; Ma, X.B.; Li, L.X.; Yu, H.Q. Degradation of rhodamine B in a novel bioelectrochemical reductive system composed of Shewanella oneidensis MR-1 and Ag2PO4. Environ. Int. 2019, 126, 560–567. https://doi.org/10.1016/j.envint.2019.03.010.

85. Xiao, X.; Han, X.; Wang, L.G.; Long, F.; Ma, X.L.; Xu, C.C.; Ma, X.B.; Wang, C.X.; Liu, Z.Y. Anaerobically photoreductive degradation by CdS nanocrystal: Biofabrication process and bioelectron-driven reaction coupled with Shewanella oneidensis MR-1. Biochem. Eng. J. 2020, 154, 107466. https://doi.org/10.1016/j.bej.2019.107466.

86. Priyanka, U.; Lens, P.N.L. Light driven Aspergillus niger-ZnS nanobiobiohybrids for degradation of methyl orange. Chemosphere 2022, 298, 134162. https://doi.org/10.1016/j.chemosphere.2022.134162.

87. Deng, X.; Luo, D.; Okamoto, A. Defined and unknown roles of conductive nanoparticles for the enhancement of microbial current generation: A review. Bioresour. Technol. 2022, 330, 126844. https://doi.org/10.1016/j.biortech.2022.126844.

88. Sakimoto, K.K.; Kornienko, N.; Castellos-Blanco, S.; Lim, J.; Liu, C.; Yang, P. Physical Biology of the materials-microorganism interface. J. Am. Chem. Soc. 2018, 140, 1978–1985. https://doi.org/10.1021/jacs.7b11353.

89. McCuskey, S.R.; Chatsirisupachai, J.; Zeglio, E.; Parlak, O.; Panoy, P.; Herland, A.; Bazan, G.C.; Nguyen, T.Q. Current Progress of interfacing organic semiconducting materials with bacteria. Chem. Rev. 2022, 122, 4791–4825. https://doi.org/10.1021/acs.chemrev.1c00487.
90. Lee, S.J.; Lee, S.-J.; Lee, D.-W. Design and development of synthetic microbial platform cells for bioenergy. *Front. Microbiol.* 2013, 4, 1–13. https://doi.org/10.3389/fmicb.2013.00092.

91. Smanski, M.J.; Zhou, H.; Claesen, J.; Shen, B.; Fischbach, M.A.; Voigt, C.A. Synthetic biology to access and expand nature’s chemical diversity. *Nat. Rev. Microbiol.* 2016, 14, 135–149. https://doi.org/10.1038/nrmicro.2015.24.

92. Choi, D.; Lee, S.B.; Kim, S.; Min, B.; Choi, I.G.; Chang, I.S. Metabolically engineered glucose-utilizing *Shewanella strains* under anaerobic conditions. *Bioresour. Technol.* 2014, 154, 59–66. https://doi.org/10.1016/j.biortech.2013.12.025.