

UC Berkeley

UC Berkeley Previously Published Works

Title

Molecular insights and future frontiers in cell photosensitization for solar-driven CO₂ conversion

Permalink

<https://escholarship.org/uc/item/8zp9705k>

Journal

iScience, 24(9)

ISSN

2589-0042

Authors

Cestellos-Blanco, Stefano

Kim, Ji Min

Watanabe, Nicholas George

et al.

Publication Date

2021-09-01

DOI

10.1016/j.isci.2021.102952

Copyright Information

This work is made available under the terms of a Creative Commons Attribution-NonCommercial-NoDerivatives License, available at

<https://creativecommons.org/licenses/by-nc-nd/4.0/>

Peer reviewed

Perspective

Molecular insights and future frontiers
in cell photosensitization
for solar-driven CO₂ conversion

Stefano Cestellos-Blanco,^{1,5} Ji Min Kim,^{1,5} Nicholas George Watanabe,² Rachel Rebecca Chan,²
and Peidong Yang^{1,2,3,4,*}

SUMMARY

The conversion of CO₂ to value-added products powered with solar energy is an ideal solution to establishing a closed carbon cycle. Combining microorganisms with light-harvesting nanomaterials into photosynthetic biohybrid systems (PBSs) presents an approach to reaching this solution. Metabolic pathways precisely evolved for CO₂ fixation selectively and reliably generate products. Nanomaterials harvest solar light and biocompatibly associate with microorganisms owing to similar lengths scales. Although this is a nascent field, a variety of approaches have been implemented encompassing different microorganisms and nanomaterials. To advance the field in an impactful manner, it is paramount to understand the molecular underpinnings of PBSs. In this perspective, we highlight studies inspecting charge uptake pathways and singularities in photosensitized cells. We discuss further analyses to more completely elucidate these constructs, and we focus on criteria to be met for designing photosensitizing nanomaterials. As a result, we advocate for the pairing of microorganisms with naturally occurring and highly biocompatible mineral-based semiconductor nanomaterials.

INTRODUCTION

For the first time in modern history, the atmospheric concentration of CO₂ exceeded 410 ppm in 2017. While this number may seem inconsequentially small, it represents a level of CO₂ that has resulted in disastrous climatic patterns which will only continue to worsen (Sellers et al., 1996). Although several leading countries are investing in renewable energy harvesting, the rate of decarbonization is much too slow to affect meaningful change, especially now that greenhouse gas emissions are driven by industrializing countries (Mitchell et al., 2000; Samset et al., 2020). To avert permanent catastrophes, we must find a strategy to reconstitute CO₂ to economically viable products.

Photosynthesis is the most crucial terrestrial process undertaking the absorption and conversion of CO₂ to carbon-based chemicals (Barber, 2009). Plants and several microorganisms harvest solar light, which they use to transform CO₂ and H₂O to glucose and O₂ through Z-scheme linked catalytic centers. While plant-based photosynthesis provides an avenue for decreasing atmospheric CO₂, it is important to develop other approaches for CO₂ conversion that operate in faster time scales and do not require arable land (Fedoroff and Cohen, 1999; Williams and Laurens, 2010; Zhu et al., 2010). Electrocatalyst-based CO₂ reduction has made outsize strides in the past decades (Ross et al., 2019); however these platforms often require costly metals and complicated catalyst synthesis. In order to overcome these challenges, inspiration can be drawn from natural photosynthesis by reducing CO₂ biocatalytically driven with solar energy.

Society would be ill-advised not to take advantage of the unmatched amount of energy provided by the sun. Earth's biomass is a result of plants and organisms effectively utilizing solar energy (Kim et al., 2015; Bourzac, 2016). A critical amount of research and development has yielded commercially viable photovoltaic cells that routinely reach 20% solar-to-electricity conversion rates (Green et al., 2019). While solar cells are beginning to make a dent in the energy landscape, the link between solar energy harvesting and CO₂ conversion remains elusive.

Materials that can both efficiently harvest solar energy and act as CO₂ reduction catalysts have not been identified. Therefore, the scientific community has largely depended on either powering CO₂ fixation

¹Department of Materials Science and Engineering, University of California, Berkeley, CA, USA

²Department of Chemistry, University of California, Berkeley, CA, USA

³Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

⁴Kavli Energy NanoScience Institute at the University of California, Berkeley, CA, USA

⁵These authors contributed equally

*Correspondence: p_yang@berkeley.edu
<https://doi.org/10.1016/j.isci.2021.102952>



platforms by external photovoltaic cells or integrated CO₂ catalysts into photoelectrochemical systems. For instance, photovoltaic-driven electrolysis has reached 30% solar-to-water splitting efficiency through a variety of engineering adaptations (Jia et al., 2016). While integrated photoelectrochemical platforms typically consisting of metal nanocrystals in a semiconductor platform can reach high CO₂ turnover rates, products are largely C₁ with poor selectivity (Barton et al., 2008; Kong et al., 2016; Sahara et al., 2016; Zhou et al., 2016).

Recently, a new approach for solar-powered CO₂ fixation has been introduced. Semiconductor nanomaterials have been directly interfaced with electroautotrophic bacteria to convert CO₂ to multi-carbon products, thus realizing photosynthetic biohybrid systems (PBSs) (Liu et al., 2015; Tremblay et al., 2015; Sakimoto et al., 2016a; Zhang et al., 2018; Kumar et al., 2019). The cornerstone bacteria in these systems were acetogens encompassing the Wood-Ljungdahl pathway though other strains have now been incorporated to diversify products (Wang et al., 2019a; Cestellos-Blanco et al., 2020; Xu et al., 2021). The interface between solar harvesting nanomaterials and whole-cell bacteria allows for solar energy to drive CO₂ reduction to multi-carbon products through “living” biocatalysts that self-repair, self-generate, and are highly selective. As a diversity of scientists begin to move this field forward, it is essential to reflect on how we can improve our understanding of the fundamental processes that underlie the biohybrid coupling to create more seamless interfaces. In this perspective, we analyze studies that aim to enhance our comprehension and suggest new bioinspired semiconductor materials to realize the potential of PBSs.

As the field of photosynthetic semiconductor biohybrids advances, it is important to deeply investigate the interfaces and processes that it is based upon. Several research groups have taken up this task through a variety of methods, including spectroscopic, transcriptional, and proteomic analyses (Figure 1). Although there remain unanswered questions, these studies build a foundation for further exploration.

CHARGE TRANSFER PATHWAY AND METABOLIC ANALYSES

Whole-cell biocatalysts can be coupled with semiconductor nanoparticles. The cells, typically autotrophic bacteria, take up photoexcited electrons to perform cellular functions, including CO₂ fixation. Translucent and light-activated photosensitized organisms provide the opportunity to study *in situ* charge uptake through spectroscopic methods. Kornienko et al. (Kornienko et al., 2016) employed transmittance-based transient absorption (TA) spectroscopy and time-resolved infrared (TRIR) spectroscopy to discern the path of photoexcited reducing equivalents in *Moorella thermoacetica* – CdS. This was carried out by studying the correlation between CO₂ conversion rates and hydrogenase activity over different timescales. TA spectroscopy probed the *M. thermoacetica* – CdS system to understand charge carrier lifetime. The decay lifetimes for electron transfer kinetics decreased with increased hydrogenase activity, with bare CdS owning the slowest decay. This illustrates that cellular processes are responsible for quickly using the photogenerated charge. However, inhibition of hydrogenase did not lead to significantly different lifetimes, indicating that at least two mechanisms are present for electron uptake. To investigate this observation, TRIR spectroscopy was employed to explain decreased photosynthetic rates at small timescales. The absence of vibrational modes characteristic to the catalytic cycle of hydrogenase confirms other electron transfer mechanisms that predominate at shorter timescales when hydrogenase expression has not yet been elevated. Therefore, charge uptake from photoexcited CdS may occur through a molecular hydrogen intermediate or directly by charge uptaking cellular proteins.

Genetic analysis of photosensitized bacteria may provide more information. A study conducted by Jin et al. (Jin et al., 2021) performed a transcriptome analysis of the pairing between acetogen *Clostridium autoethanogenum* and CdS nanoparticles to differentiate between direct electron transfer and H₂-mediated mechanisms. Hierarchical clustering and principal component analysis of sequencing data were used to compare gene expression in carbon metabolism and energy conservation pathways between CdS light-exposure conditions and H₂-autotrophic growth conditions. Although genes for the Wood-Ljungdahl pathway of CO₂ fixation were highly expressed in both systems, genes associated with energy conservation were more activated in the CdS-driven system. Notably, the *rnfC* gene encoding for the Rnf complex which couples ferredoxin oxidation with NAD⁺ reduction was 1.6X more upregulated in the CdS containing system. The authors suggest that photoexcited electrons from CdS are transported across the cell membrane by metal or flavin molecules. Furthermore, Ni/Fe hydrogenase genes were 3.8X more upregulated than in the H₂-autotrophic cultures. This confirms that both hydrogenases and the Rnf complex are involved in CO₂ to acetate conversion linked autotrophic growth in

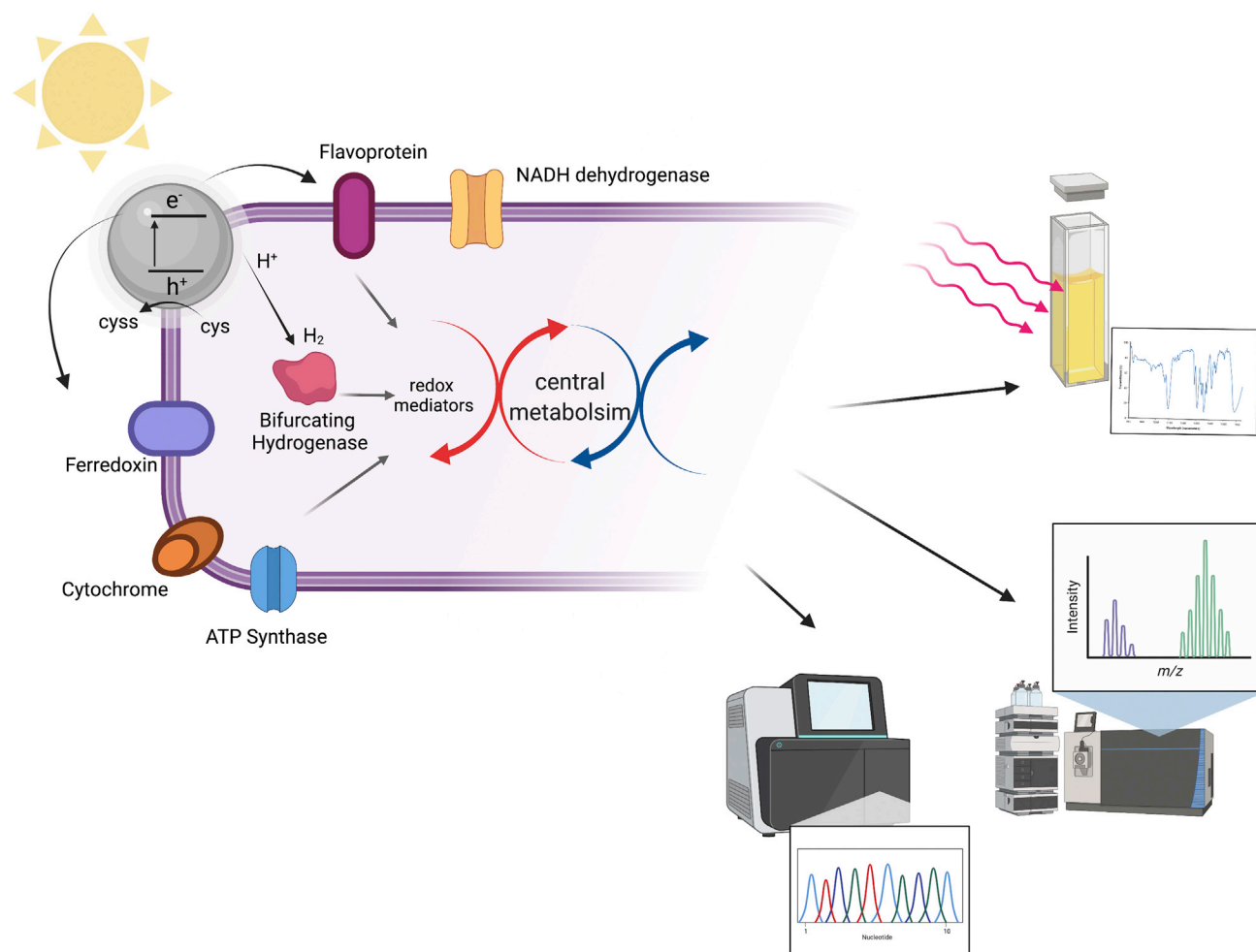


Figure 1. Overview of methods employed to study CdS-bacteria hybrids

These approaches encompass transcriptional, proteomic, and metabolic analysis, as well as transient absorption and time-resolved infrared spectroscopy.

C. autoethanogenum-CdS. It should be noted that it is not clear whether the authors performed transcriptome analysis on light-deficient *C. autoethanogenum*-CdS in order to tease out any effects on gene regulation stemming from the toxicity of Cd.

Proteomic and metabolomic characterization offers further insight into how increased genetic expression of specific genes also activates certain metabolic pathways. Zhang et al. studied these changes in the *M. thermoacetica*-CdS inorganic hybrid system using mass spectrometry and proteomic analysis (Zhang et al., 2019b). The upregulation of electron transfer and energy conservation proteins flavoprotein (moth_1517), ferredoxin (moth_1200), and NADP dehydrogenase (moth_2186) confirms that these proteins are active in charge transfer from photoexcited CdS to *M. thermoacetica*. The authors posit that electrons taken up by these enzymes are further shuttled across the cell membrane by menaquinones. Additionally, enzymes part of the Wood-Ljungdahl pathway including formate dehydrogenase (Mt, moth_2312), CO dehydrogenase (CODH, moth_1972), acetyl-CoA synthase (ACS, moth_1201), and phosphate transferase (moth_0864) are more upregulated in *M. thermoacetica*-CdS compared with bare *M. thermoacetica*. The Wood-Ljungdahl pathway results in the production acetyl-CoA which is partially used to generate citrate with oxaloacetic acid by citrate synthase. The authors found upregulation of citrate synthase and observed a higher concentration of citrate in the *M. thermoacetica*-CdS samples. This suggests that photosensitization with CdS impacts *M. thermoacetica* holistically in particular processes downstream of the Wood-Ljungdahl pathway and that acetate production alone does not capture the full physiological changes in PBSs.

In addition to CO₂ fixation, bio-inorganic hybrids for light-driven denitrification have also been realized between *T. denitrificans* and CdS. In this study, the authors demonstrate that gaseous nitrous oxide (N₂O), a valuable chemical oxidant, can be produced with high purity from nitrate (NO₃[−]) by harnessing bacterial metabolism driven by light (Chen et al., 2019). A set of enzymes in autotrophic denitrifiers reduce nitrate to nitrite (nitrate reductase), nitrite to nitric oxide (nitrite reductase), nitric oxide to nitrous oxide (nitric oxide reductase), and nitrous oxide to N₂ (nitrous oxide reductase). Over the course of *T. denitrificans*-CdS photosensitization, all of the initial nitrate was depleted. Of the nitrogenous products formed, 72% was converted to nitrous oxide, while significantly smaller amounts of ammonia and N₂ were also detected. Each of the enzymes involved in the denitrifying process was upregulated under the light-driven CdS conditions compared with *T. denitrificans* alone, confirming activation of the enzymatic pathway from CdS photosensitization. The authors propose that quinols and cytochromes embedded in the membrane of *T. denitrificans* directly accept electrons from CdS nanoparticles and serve as electron donors for denitrifying proteins.

Altogether these reports present important techniques applied to understanding the charge transfer pathways and cellular changes in photosensitized cells. However, narrowing down to specific pathways and elucidating the mechanistic basis remains largely unexplored due to the complex nature of this semiconductor/whole-cell interface. The field of bioelectrochemistry, where electrotrophic cells are paired with an electrode, has seen the development of various approaches to specifically analyze proteins, redox shuttles, and pathways involved in charge transfer (Bose et al., 2014; Wang et al., 2019b; Saunders et al., 2020; Kretzschmar and Harnisch, 2021). Electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy can be applied to study redox-active molecules/proteins and characteristics of biofilm-laden electrodes (Fricke et al., 2008; Kim et al., 2011). Light microscopy has been used in conjunction with a fluorescent membrane potential indicator to elucidate extracellular electron transfer bioenergetics (Pirbadian et al., 2020). Given that single charge uptake pathways have not been definitively identified in photosensitized cells, it is important to note a model bioelectrochemical study that identified the mode of extracellular charge transfer in gut bacterium *Listeria monocytogenes* (Light et al., 2018). The authors found that a flavin-based pathway transports electrons intracellularly to a charge acceptor. Mutants with reduced charge transfer identified via electrochemical output were then studied to reveal the genetic locus responsible for extracellular electron transfer. The locus encodes for NADH dehydrogenase that links electron transport to a membrane-bound quinone pool. A flavoprotein along with flavins then routinely depletes the quinone pool stock through electron transfer to an extracellular species. It is worth mentioning that orthologues of this locus are present in many other similar intestinal species. An emulative approach could be applied to the study of PBS where a mutant screen is undertaken to ascertain if there is an activated pathway enabled by a specific genetic locus. It will be interesting to determine if the pathway dedicated to extracellular electron transfer is activated, indicating that all or part of the pathway is necessary for charge uptake from light-activated intracellular nanoparticles. This would then also aid in understanding how to best design the nanoparticles to associate with the immediate biological charge uptake mechanism. And finally, it would help to steer efforts toward targeting specific enzymes for the intracellular nanoparticle-enzyme association by having a specialized toolkit to analyze any changes in the charge uptake pathway.

CRITERIA FOR PHOTSENSITIZER NANOMATERIALS

Mechanistic studies have rendered insight into the semiconductor-microorganism interface and how the living systems adapt to light-harvesting nanomaterials. These studies also serve to highlight future challenges for semiconductor-microorganism pairings. Nanomaterial-organism incompatibility, such as nanomaterial cytotoxicity and unoptimized charge flux across abiotic-biotic interfaces, limit the development of more energy-efficient and sustainable PBS (Lewinski et al., 2008; Su et al., 2020). It is important to establish the criteria which could be used to optimize the light-harvesting capability and subsequent charge transfer to redox-active molecules.

One aspect is improving the properties of the semiconducting nanomaterial. Tailoring the bandgap of these materials to absorb visible light is one such criterion. Gaps greater than 3.2 eV correspond to UV or higher energy radiation, which comprises at most 5% of the incident sunlight and can also cause DNA pyrimidine dimerization, damage, and cell death (Schreier et al., 2007). CdS is a prototypical material that has successfully photosensitized microorganisms; however, it is dependent on the UV region and is harmful to humans and the environment. By using materials that do not rely on UV irradiation for

photoexcitation, the detrimental effects of UV light on living organisms can be avoided while allowing for higher intensity light to be harvested. Notably, Guo et al. (Guo et al., 2018) showed that indium phosphide can be used as a photosensitizing material that absorbs in the visible light spectrum. In addition to bandgap customization, matching the potentials of the nanomaterial conduction band to those for reductive water splitting, electron transfer proteins (e.g. cytochromes), and charge carrying coenzymes, such as NAD(P)⁺, improves the material-microbe interface (Chen et al., 2020). Through the coupling of these potentials, electron transfer by hopping from the nanomaterial to the redox couples is facilitated (Nakamura et al., 2013; Zhou et al., 2015; Ding et al., 2019).

Another important facet is fostering favorable interactions between nanomaterials and cell membranes to maximize the biocompatibility of the material. Notable criteria are the dimensions of the material and its surface charge. Because association with the membrane involves adhesion to the bilayer, subsequent deformation, and sometimes endocytotic encapsulation of the particle, using larger particles risks the chance of compromising the cell membrane by creating a pore/hole in the membrane (Verma and Stellacci, 2010; Contini et al., 2018). Spherical nanoparticles have been shown to be the more efficacious relative to other morphologies, in terms of microbe acceptance, given the low surface area-to-volume ratio of a sphere (Verma and Stellacci, 2010). Cell membranes generally are negatively charged, which results in cationic nanoparticles having stronger affinities due to electrostatic attraction. Indium phosphide, for instance, forms cationic nanoparticles and has seen much popularity in making biocompatible quantum dots in addition to direct photosensitization of yeast biohybrids (Devatha et al., 2017; Guo et al., 2018; Jo et al., 2020). However, highly charged cationic nanoparticles may also have antimicrobial properties (Zhang et al., 2020).

Since cells are intrinsically anisotropic and compartmentalized, the location of the nanomaterial on or in the cell could affect the synergy required for photosensitization. Gold nanoclusters can be assimilated within the confines of the cell, where the nanoclusters absorb light and provide electrons necessary in the Wood-Ljungdahl pathway and other cell functions (Zhang et al., 2018). In contrast, cadmium and iron sulfide nanoparticles adhere to the cell membrane (Sakimoto et al., 2016a; Deng et al., 2020). Nanomaterial location, relative to the cell, impacts the electron transfer pathway (Luo et al., 2021). For intracellular nanomaterials, photogenerated electrons may be transferred directly to enzymatic mediators and metabolic charge carriers. Extracellular and membrane-associated light harvesters supply electrons through both mediated and direct transfer pathways. In the mediated pathway, for instance, H₂O is reduced to H₂, which then fuels the reduction of redox molecules like NAD⁺ and Fd_{ox} on bifurcating hydrogenase, whereas in the direct pathway, membrane-bound proteins like ferredoxin, flavoprotein, cytochrome, or RnF directly take up photoexcited charge carriers (Kremp et al., 2020). Either pathway ultimately provides reducing equivalents to metabolic pathways such as the Wood-Ljungdahl pathway.

In the two-branch Wood-Ljungdahl pathway, CO₂ is reduced to CO while additional CO₂ is reduced to formate and subsequently bound as a methyl group. These are combined by acetyl-CoA synthase to form acetyl-CoA (Ragsdale and Pierce, 2008). Acetyl-CoA can be used as a building block in protein biosynthesis or converted to acetate, extracting ATP in the process. Given the demonstrations of nanomaterials binding to specific biostructures (Kornienko et al., 2018), photosensitizing nanoparticles could be designed to target enzymatic complexes in the Wood-Ljungdahl pathway to provide photoexcited electrons directly. Ding et al. (Ding et al., 2019) showcased this concept by synthesizing nanoparticles with a zinc sulfide shell that enhance binding to proteins like hydrogenase. Brown et al. (Brown et al., 2016) also achieved specific coupling between extracted and purified nitrogenase and CdS nanorods. For this purpose, it is important to tailor the conduction band edge potential to that of a specific biological process and leverage surface chemistry. While the basis of the Wood-Ljungdahl pathway is nearly identical among acetogenic bacteria, each species has its own intrinsic hydrogenases and charge transporting conduits (Schuchmann and Müller, 2014). As such, matching the material conduction band potentials to those of the relevant redox couples is paramount to synergistically joining material and microbe.

Our final criterion concerns biogenic nanomaterials, which are manufactured *in situ* by microorganisms. This approach, which utilizes microbial biomineralization, has been successful in forming nanomaterial-decorated membranes with no significant impairment on cell viability (Sakimoto et al., 2016a; Bandala et al., 2020). Choi et al. (Choi and Lee, 2020) have compiled an extensive list of biomanufactured nanomaterials produced both through microbes and bacteriophages. Notably, Yu and Leadbetter (Yu and

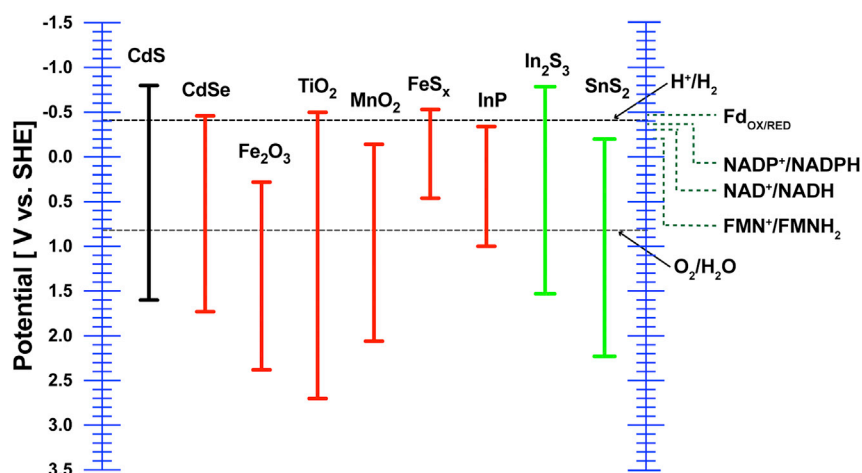


Figure 2. Bandgap positions of a representative photosensitizer CdS (black) and various promising minerals (red, green)

The bandgap energies are shown with respect to standard hydrogen electrode at pH 7, and the redox potentials of H₂O and biological electron carriers. Red bars denote reported biosynthesized nanomaterials. Green bars represent yet-to-be biosynthesized nanomaterials (Vogel et al., 1994; Sakai et al., 2005; Tvrdy et al., 2011; Kracke, Vassilev and Krömer, 2015; Jiang et al., 2017; Shown et al., 2018; Zhang et al., 2019a; Guo et al., 2021). Fd, ferredoxin; NADP, nicotinamide adenine dinucleotide phosphate; NAD, nicotinamide adenine dinucleotide; FMN, flavin mononucleotide.

Leadbetter, 2020) have shown that bacteria can oxidize extracellular manganese to synthesize tetravalent manganese oxide (i.e., birnessite), a reported semiconductor and a major component of desert mineral rock varnish. Microbes can directly play an important role in the formation of naturally formed mineral semiconductors (Bower et al., 2015). Several naturally occurring minerals are redox-active and electrically conductive and, while maintaining close contact with microorganisms, support microbial metabolism (Lu et al., 2019). These intimate interactions with minerals stimulate upregulation of key enzymes for central metabolism and redox enzymes for extracellular electron transfer (EET) (Wang et al., 2018).

EARTH-ABUNDANT SEMICONDUCTOR MINERALS AS BIOGENIC AND COMPATIBLE PHOTOSENSITIZERS

This relation between microorganisms and minerals has motivated the creation of more seamlessly interfaced and biocompatible systems. Recent publications on the redox and electrochemical activity between minerals and microorganisms have noted the remarkable metabolic versatility and diversity of electroactive microbes. Lu et al. (Taylor-George et al., 1983; Lu et al., 2019) have reported that desert rock varnish is bacteria-driven and consists mainly of semiconducting iron and manganese (hydr)oxides that absorb in the visible light spectrum. They claim that the main compounds in the photoactive varnish can supply *Pseudomonas aeruginosa* with extracellular electrons upon exposure to light. Liu et al. (Liu et al., 2020), however, have noted that minerals can also “courier” electrons. From their findings, hematite can mediate the reduction of outer membrane c-type cytochromes under dark conditions by shuttling electrons from a ferrous iron source to the ferric iron bound in the c-type cytochromes. Mineral iron sulfides can also mediate electron flow (Nakamura et al., 2013). Sulfate-reducing bacteria could biomineralize these compounds on their membranes, which acts as an electrical conduit and facilitates transmembrane electron transfer. In another study, Yu et al. (Yu et al., 2020) report improved rates of EET by using iron sulfide nanomaterials. In all of these investigations, microbes were able to either utilize extracellular minerals or decorate and functionalize themselves with these naturally occurring inorganic compounds, further highlighting the ability of microbes to mesh with inorganic compounds and create functional photosynthetic hybrids.

Mineral-based photosensitization looks to be a promising direction of study. Through functionalizing microbes with biocompatible and biomanufactured analogs, the all-too-common problematic cytotoxic properties of nanomaterials can be dodged. The minerals themselves pose to be natural, “organic” counterparts to laboratory synthesized “artificial” nanomaterials. Figure 2 depicts several semiconducting minerals with their respective band edge positions, which have either been successfully integrated into autotrophic microbes as light

harvesters or are promising photosensitizers. The photoactive minerals whose conduction band edges are positioned lower than the redox potential of proton reduction, such as MnO_2 and InP , could provide a platform to investigate direct electron transfer pathways. Along with the efficient electron transfer to microorganisms, employing an apt hole scavenger is crucial to avoid creating a cytotoxic oxidative environment. The oxidation of sulfur substances is a common strategy that can provide reducing reagents necessary for anaerobic respiration, and sulfur compounds such as cysteine have been used as sacrificial hole scavengers in typical biohybrid systems (Luther et al., 2011; Sakimoto et al., 2016a).

It is necessary to promote long-term and economically viable solar-to-chemical production in PBSs. In photosensitized bacteria, typical hole scavengers such as cysteine, ascorbic acid and HEPES limit large-scale application. Sakimoto et al. (Sakimoto et al., 2016b) devised TiO_2 nanoparticles loaded with Mn(II) phthalocyanine for the solar-driven regeneration of cysteine hole scavengers. However, TiO_2 coupled water oxidation creates oxygen and reactive oxygen species (ROS) which are cytotoxic to autotrophic bacteria. A metal organic framework nanosheet coating was conceived in order to protect autotrophic bacteria from oxygen and ROS (Ji et al., 2018). Furthermore, strictly anaerobic *S. ovata* were adapted to resist higher oxygen concentrations (Shi et al., 2021). However, these techniques have not yet been applied to photosensitized bacteria. In addition to hole scavenger regeneration it is important to identify and employ alternative hole scavengers that are more inexpensive relative to the products and lack biological activity (Kamat and Jin, 2018; Göbbels et al., 2021). The cost of the photosensitizer needs to also be taken into account. While gold nanoclusters (Zhang et al., 2018) or indium phosphide nanoparticles (Guo et al., 2018) as photosensitizers are unlikely to render economically viable systems, these have shown that cells can be photosensitized by a wider variety of light-active nanoparticles. With this in mind, we advocate for the exploration of earth-abundant and inexpensively processed minerals as photosensitizers. Another advantage of using semiconducting minerals is that these can be biogenically re-fabricated in case of degradation or loss of the material thus potentially prolonging the stability of PBS. Overall, in order to ensure economic viability and applicability of PBS, the hole scavenger needs to be regenerated and low cost, as well as biocompatible hole scavengers need to be employed. These measures could also increase product titer and scalability.

PBS presents a strategy for the conversion of CO_2 to value-added chemical production using solar photons. While much effort has gone into elucidating how these hybrid systems function, explicit pathways with comprehensive explanations remain elusive. Furthermore, there is room for improvement in semiconductor nanomaterial selection. Bandgap and band edge design and synergistically meshing nanomaterial with cells are areas where progress can be made. Last, naturally occurring semiconducting minerals play an active role in microbial electron transport. This specific marriage looks to be a promising area of research, which could shed light on the origins of photosynthesis.

ACKNOWLEDGMENTS

This work was supported by NASA, Center for the Utilization of Biological Engineering in Space, under award NNX17AJ31G. S.C.-B. acknowledges a personal fellowship from the Philomathia Foundation. J.M.K. is supported by the Kwanjeong Educational Foundation. Figure 1 was generated with BioRender.com.

AUTHOR CONTRIBUTIONS

S.C.-B., J.M.K., N.G.W., R.R.C., and P.Y. co-wrote the perspective.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

- Bandala, E.R., Stanisic, D., and Tasic, L. (2020). Biogenic nanomaterials for photocatalytic degradation and water disinfection: a review. *Environ. Sci. Water Res. Technol.* 3195–3213. <https://doi.org/10.1039/d0ew00705f>.
- Barber, J. (2009). Photosynthetic energy conversion: natural and artificial. *Chem. Soc. Rev.* 38, 185–196. <https://doi.org/10.1039/B802262N>.
- Barton, E.E., Rampulla, D.M., and Bocarsly, A.B. (2008). Selective solar-driven reduction of CO_2 to methanol using a catalyzed p-GaP based photoelectrochemical cell. *J. Am. Chem. Soc.* 130, 6342–6344. <https://doi.org/10.1021/ja0776327>.
- Bose, A., Gardel, E.J., Vidoudez, C., Parra, E.A., and Girguis, P.R. (2014). Electron uptake by iron-oxidizing phototrophic bacteria. *Nat. Commun.* 5, 3391. <https://doi.org/10.1038/ncomms4391>.
- Bourzac, K. (2016). Liquid sunlight: fuels created by artificial photosynthesis are getting much closer to reality. *Proc. Natl. Acad. Sci. U S A*, 4545–4548. <https://doi.org/10.1073/pnas.1604811113>.
- Bower, D.M., Hummer, D.R., Steele, A., and Kyono, A. (2015). The co-evolution of Fe-oxides,

ti-oxides, and other microbially induced mineral precipitates in sandy sediments: understanding the role of cyanobacteria in weathering and early diagenesis. *J. Sediment. Res.* 85, 1213–1227. <https://doi.org/10.2110/jsr.2015.76>.

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., and King, P.W. (2016). Light-driven dinitrogen reduction catalyzed by a CdS:nitrogenase MoFe protein biohybrid. *Science* 352, 448–450. <https://doi.org/10.1126/science.aaf2091>.

Chen, H., Dong, F., and Menteer, S.D. (2020). The progress and outlook of bioelectrocatalysis for the production of chemicals, fuels and materials. *Nat. Catal.* 225–244. <https://doi.org/10.1038/s41929-019-0408-2>.

Cestellos-Blanco, S., Zhang, H., Kim, J.M., Shen, Y., and Yang, P. (2020). Photosynthetic semiconductor biohybrids for solar-driven biocatalysis. *Nat. Catal.* 245–255. <https://doi.org/10.1038/s41929-020-0428-y>.

Chen, M., Zhou, X., Yu, Y., Liu, X., Zeng, R.J., Zhou, S., and He, Z. (2019). Light-driven nitrous oxide production via autotrophic denitrification by self-photosensitized *Thiobacillus denitrificans*. *Environ. Int.* 127, 353–360. <https://doi.org/10.1016/j.envint.2019.03.045>.

Choi, Y., and Lee, S.Y. (2020). Biosynthesis of inorganic nanomaterials using microbial cells and bacteriophages. *Nat. Rev. Chem.* 638–656. <https://doi.org/10.1038/s41570-020-00221-w>.

Contini, C., Schneemilch, M., Gaisford, S., and Quirke, N. (2018). ‘Nanoparticle–membrane interactions’. *J. Exp. Nanosci.* 62–81. <https://doi.org/10.1080/17458080.2017.1413253>.

Deng, X., Dohmae, N., Kaksonen, A.H., and Okamoto, A. (2020). Biogenic iron sulfide nanoparticles to enable extracellular electron uptake in sulfate-reducing bacteria. *Angew. Chem. Int. Edition* 59, 5995–5999. <https://doi.org/10.1002/anie.201915196>.

Devatha, G., Roy, S., Rao, A., Mallick, A., Basu, S., and Pillai, P.P. (2017). ‘Electrostatically driven resonance energy transfer in “cationic” biocompatible indium phosphide quantum dots’. *Chem. Sci.* 8, 3879–3884. <https://doi.org/10.1039/c7sc00592j>.

Ding, Y., Bertram, J.R., Eckert, C., Bommarreddy, R.R., Patel, R., Conradie, A., Bryan, S., and Nagpal, P. (2019). Nanorg microbial factories: light-driven renewable biochemical synthesis using quantum dot-bacteria nanobiohybrids. *J. Am. Chem. Soc.* 141, 10272–10282. <https://doi.org/10.1021/jacs.9b02549>.

Fedoroff, N.V., and Cohen, J.E. (1999). Plants and population: is there time? *Proc. Natl. Acad. Sci. U S A* 96, 5903–5907. <https://doi.org/10.1073/pnas.96.11.5903>.

Fricke, K., Harnisch, F., and Schröder, U. (2008). On the use of cyclic voltammetry for the study of anodic electron transfer in microbial fuel cells. *Energy Environ. Sci.* 1, 144–147. <https://doi.org/10.1039/B802363H>.

Göbbels, L., Poehlein, A., Dumnitich, A., Egelkamp, R., Kröger, C., Haedter, J., Hackl, T., Feld, A., Weller, H., Daniel, R., et al. (2021).

Cysteine: an overlooked energy and carbon source. *Sci. Rep.* 11, 1–15. <https://doi.org/10.1038/s41598-021-81103-z>.

Green, M.A., Hishikawa, Y., Dunlop, E.D., Levi, D.H., Hohl-Ebinger, J., Yoshita, M., and Ho-Baillie, A.W.Y. (2019). Solar cell efficiency tables (Version 53). *Prog. Photovolt. Res. Appl.* 27, 3–12. <https://doi.org/10.1002/pip.3102>.

Guo, J., Suástegui, M., Sakimoto, K.K., Moody, V.M., Xiao, G., Nocera, D.G., and Joshi, N.S. (2018). Light-driven fine chemical production in yeast biohybrids. *Science*. <https://doi.org/10.1126/science.aat9777>.

Guo, Q., Tang, G., Zhu, W., Luo, Y., and Gao, X. (2021). In situ construction of Z-scheme FeS₂/Fe₂O₃ photocatalyst via structural transformation of pyrite for photocatalytic degradation of carbamazepine and the synergistic reduction of Cr(VI). *J. Environ. Sci.* 101, 351–360. <https://doi.org/10.1016/j.jes.2020.08.029>.

Ji, Z., Zhang, H., Hao, L., Yaghi, O.M., and Yang, P. (2018). Cytoprotective metal-organic frameworks for anaerobic bacteria. *Proc. Natl. Acad. Sci. U S A* 115, 201808829. <https://doi.org/10.1073/pnas.1808829115>.

Jia, J., Seitz, L.C., Benck, J.D., Huo, Y., Chen, Y., Ng, J.W.D., Bilir, T., Harris, J.S., and Jaramillo, T.F. (2016). Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. *Nat. Commun.* 7, 13237. <https://doi.org/10.1038/ncomms13237>.

Jiang, C., Moniz, S.J.A., Wang, A., Zhang, T., and Tang, J. (2017). Photoelectrochemical devices for solar water splitting—materials and challenges. *Chem. Soc. Rev.* 4645–4660. <https://doi.org/10.1039/c6cs00306k>.

Jin, S., Jeon, Y., Jeon, M.S., Shin, J., Song, Y., Kang, S., Bae, J., Cho, S., Lee, J., Kim, D.R., and Cho, B. (2021). Acetogenic bacteria utilize light-driven electrons as an energy source for autotrophic growth. *Proc. Natl. Acad. Sci. U S A* 118. <https://doi.org/10.1073/pnas.2020552118>.

Jo, J.H., Jo, D.Y., Lee, S.H., Yoon, S.Y., Lim, H.B., Lee, B.J., Do, Y.R., and Yang, H. (2020). InP-based quantum dots having an InP core, composition-gradient ZnSeS inner shell, and ZnS outer shell with sharp, bright emissivity, and blue absorptivity for display devices. *ACS Appl. Nano Mater.* 3, 1972–1980. <https://doi.org/10.1021/acsnm.0c00008>.

Kamat, P.V., and Jin, S. (2018). Semiconductor photocatalysis: “tell us the complete story!”. *ACS Energy Lett.* 3, 622–623. <https://doi.org/10.1021/ACSENERGYLETT.8B00196>.

Kim, T., Kang, J., Lee, J.H., and Yoon, J. (2011). Influence of attached bacteria and biofilm on double-layer capacitance during biofilm monitoring by electrochemical impedance spectroscopy. *Water Res.* 45, 4615–4622. <https://doi.org/10.1016/j.watres.2011.06.010>.

Kim, D., Sakimoto, K.K., Hong, D., and Yang, P. (2015). Artificial photosynthesis for sustainable fuel and chemical production. *Angew. Chem. Int. Ed.* 54, 3259–3266. <https://doi.org/10.1002/anie.201409116>.

Kong, Q., Kim, D., Liu, C., Yu, Y., Su, Y., Li, Y., and Yang, P. (2016). Directed assembly of

nanoparticle catalysts on nanowire photoelectrodes for photoelectrochemical CO₂ Reduction. *Nano Lett.* 16, 5675–5680. <https://doi.org/10.1021/acs.nanolett.6b02321>.

Kornienko, N., Sakimoto, K.K., Herlihy, D.M., Nguyen, S.C., Alivisatos, P., Harris, C.B., Schwartzberg, A., and Yang, P. (2016). Spectroscopic elucidation of energy transfer in hybrid inorganic-biological organisms for solar-to-chemical production. *Proc. Natl. Acad. Sci. U S A* 113, 11750–11755. <https://doi.org/10.1073/pnas.1610554113>.

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

Kracke, F., Vassilev, I., and Krömer, J.O. (2015). Microbial electron transport and energy conservation - The foundation for optimizing bioelectrochemical systems. *Front. Microbiol.* 6, 575. <https://doi.org/10.3389/fmicb.2015.00575>.

Kremp, F., Roth, J., and Müller, V. (2020). The Sporomusa type Nfn is a novel type of electron-bifurcating transhydrogenase that links the redox pools in acetogenic bacteria. *Sci. Rep.* 10, 14872. <https://doi.org/10.1038/s41598-020-71038-2>.

Kretzschmar, J., and Harnisch, F. (2021). Electrochemical impedance spectroscopy on biofilm electrodes—conclusive or euphonious? *Curr. Opin. Electrochem.* 29, 100757. <https://doi.org/10.1016/j.coelec.2021.100757>.

Kumar, M., Sahoo, P.C., Srikanth, S., Bagai, R., Puri, S.K., and Ramakumar, S.S.V. (2019). Photosensitization of electro-active microbes for solar assisted carbon dioxide transformation. *Bioresour. Technol.* 272, 300–307. <https://doi.org/10.1016/j.biortech.2018.10.031>.

Lewinski, N., Colvin, V., and Drezek, R. (2008). Cytotoxicity of nanoparticles. *Small*, 26–49. <https://doi.org/10.1002/sml.200700595>.

Light, S.H., Su, L., Rivera-Lugo, R., Cornejo, J.A., Louie, A., Lavarone, A.T., Ajo-Franklin, C.M., and Portnoy, D.A. (2018). A flavin-based extracellular electron transfer mechanism in diverse Gram-positive bacteria. *Nature* 562, 140–144. <https://doi.org/10.1038/s41586-018-0498-z>.

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

Liu, T., Wang, Y., Liu, C., Li, X., Cheng, K., Wu, Y., Fang, L., Li, F., and Liu, Ch. (2020). Conduction band of hematite can mediate cytochrome reduction by Fe(II) under dark and anoxic conditions. *Environ. Sci. Technol.* 54, 4810–4819. <https://doi.org/10.1021/acs.est.9b06141>.

Lu, A., Ding, H., Xu, X., Li, Y., Ren, G., Liang, J., Liu, Y., Hong, H., Chen, N., and Chu, S. (2019). Photoelectric conversion on Earth’s surface via widespread Fe- and Mn-mineral coatings. *Proc. Natl. Acad. Sci. U S A* 116, 9741–9746. <https://doi.org/10.1073/pnas.1902473116>.

- Luo, B., Wang, Y.Z., Li, D., Shen, H., Xu, L.X., Fang, Z., Xia, Z., Ren, J., Shi, W., and Yong, Y.C. (2021). A periplasmic photosensitized biohybrid system for solar hydrogen production. *Adv. Energy Mater.* 11, 2100256. <https://doi.org/10.1002/aenm.202100256>.
- Luther, G.W., Findlay, A.J., Macdonald, D.J., Owings, S.M., Hanson, T.E., Beinart, R.A., and Girguis, P.R. (2011). Thermodynamics and kinetics of sulfide oxidation by oxygen: a look at inorganically controlled reactions and biologically mediated processes in the environment. *Front. Microbiol.* 2, 62. <https://doi.org/10.3389/fmicb.2011.00062>.
- Mitchell, J.F.B., Johns, T.C., Ingram, W.J., and Lowe, J.A. (2000). The effect of stabilising atmospheric carbon dioxide concentrations on global and regional climate change. *Geophys. Res. Lett.* 27, 2977–2980. <https://doi.org/10.1029/1999GL01213>.
- Nakamura, R., Kai, F., Okamoto, A., and Hashimoto, K. (2013). Mechanisms of long-distance extracellular electron transfer of metal-reducing bacteria mediated by nanocolloidal semiconductive iron oxides. *J. Mater. Chem. A* 1, 5148–5157. <https://doi.org/10.1039/c3ta01672b>.
- Pirbadian, S., Chavez, M.S., and El-Naggar, M.Y. (2020). Spatiotemporal mapping of bacterial membrane potential responses to extracellular electron transfer. *Proc. Natl. Acad. Sci. U S A* 117, 20171–20179. <https://doi.org/10.1073/PNAS.2008021117>.
- Ragsdale, S.W., and Pierce, E. (2008). Acetogenesis and the Wood-Ljungdahl pathway of CO₂ fixation. *Biochim. Biophys. Acta* 1784, 1873–1898. <https://doi.org/10.1016/j.bbapap.2008.08.012>.
- Ross, M.B., Luna, P.D., Li, Y., Dinh, C.T., Kim, D., Yang, P., and Sargent, E.H. (2019). Designing materials for electrochemical carbon dioxide recycling. *Nat. Catal.* 2, 648–658. <https://doi.org/10.1038/s41929-019-0306-7>.
- Sahara, G., Kumagai, H., Maeda, K., Kaeffer, N., Artero, V., Higashi, M., Abe, R., and Ishitani, O. (2016). Photoelectrochemical reduction of CO₂ coupled to water oxidation using a photocathode with a Ru(II)-Re(I) complex photocatalyst and a CoOx/TaON photoanode. *J. Am. Chem. Soc.* 138, 14152–14158. <https://doi.org/10.1021/jacs.6b09212>.
- Sakai, N., Ebina, Y., Takada, K., and Sasaki, T. (2005). Photocurrent generation from semiconducting manganese oxide nanosheets in response to visible light. *J. Phys. Chem. B* 109, 9651–9655. <https://doi.org/10.1021/jp0500485>.
- Sakimoto, K.K., Wong, A.B., and Yang, P. (2016a). Self-photosensitization of nonphotosynthetic bacteria for solar-to-chemical production. *Science* 351, 74–77. <https://doi.org/10.1126/science.123317>.
- Sakimoto, K.K., Zhang, S.J., and Yang, P. (2016b). Cysteine–cystine photoregeneration for oxygenic photosynthesis of acetic acid from CO₂ by a tandem inorganic–biological hybrid system. *Nano Lett.* <https://doi.org/10.1021/acs.nanolett.6b02740>.
- Samset, B.H., Fuglestad, J.S., and Lund, M.T. (2020). Delayed emergence of a global temperature response after emission mitigation. *Nat. Commun.* 11. <https://doi.org/10.1038/s41467-020-17001-1>.
- Saunders, S.H., Tse, E.C.M., Yates, M.D., Otero, F.J., Trammell, S.A., Stemp, E.D.A., Barton, J.K., Tender, L.M., and Newman, D.K. (2020). Extracellular DNA promotes efficient extracellular electron transfer by pyocyanin in *Pseudomonas aeruginosa* biofilms. *Cell* 182, 919–932.e19. <https://doi.org/10.1016/j.cell.2020.07.006>.
- Schreier, W.J., Schrader, T.E., Koller, F.O., Gilch, P., Crespo-Hernández, C.E., Swaminathan, V.N., Carell, T., Zinth, W., and Kohler, B. (2007). Thymine dimerization in DNA is an ultrafast photoreaction. *Science* 315, 625–629. <https://doi.org/10.1126/science.1135428>.
- Schuchmann, K., and Müller, V. (2014). Autotrophy at the thermodynamic limit of life: a model for energy conservation in acetogenic bacteria. *Nat. Rev. Microbiol.* 12, 809–821. <https://doi.org/10.1038/nrmicro3365>.
- Sellers, P.J., Bounoua, L., Collatz, G.J., Randall, D.A., Dazlich, D.A., Los, S.O., Berry, J.A., Fung, I., Tucker, J., Field, C.B., and Jensen, T.G. (1996). Comparison of radiative and physiological effects of doubled atmospheric CO₂ on climate. *Science* 271, 1402–1406. <https://doi.org/10.1126/science.271.5254.1402>.
- Shi, X.C., Tremblay, P.L., Wan, L., and Zhang, T. (2021). Improved robustness of microbial electrosynthesis by adaptation of a strict anaerobic microbial catalyst to molecular oxygen. *Sci. Total Environ.* 754, 142440. <https://doi.org/10.1016/J.SCITOTENV.2020.142440>.
- Shown, I., Samireddi, S., Chang, Y.C., Purikam, R., Chang, P.H., Sabbah, A., Fu, F.Y., Chen, W.F., Wu, C.I., and Yu, T.Y. (2018). Carbon-doped SnS₂ nanostructure as a high-efficiency solar fuel catalyst under visible light. *Nat. Commun.* 9, 1–10. <https://doi.org/10.1038/s41467-017-02547-4>.
- Su, Y., Cestellos-Blanco, S., Kim, J.M., Shen, Y., Kong, Q., Lu, D., Liu, C., Zhang, H., Cao, Y., and Yang, P. (2020). Close-packed nanowire-bacteria hybrids for efficient solar-driven CO₂ fixation. *Joule* 4, 800–811. <https://doi.org/10.1016/j.joule.2020.03.001>.
- Taylor-George, S., Palmer, F., Staley, J.T., Borns, D.J., Curtiss, B., and Adams, J.B. (1983). Fungi and bacteria involved in desert varnish formation. *Microb. Ecol.* 9, 227–245. <https://doi.org/10.1007/BF02097739>.
- Tremblay, P.L., Höglund, D., Koza, A., Bonde, I., and Zhang, T. (2015). Adaptation of the autotrophic acetogen *Sporomusa ovata* to methanol accelerates the conversion of CO₂ to organic products. *Sci. Rep.* 5, 16168. <https://doi.org/10.1038/srep16168>.
- Tvrđ, K., Frantsuzov, P.A., and Kamat, P.V. (2011). Photoinduced electron transfer from semiconductor quantum dots to metal oxide nanoparticles. *Proc. Natl. Acad. Sci. U S A* 108, 29–34. <https://doi.org/10.1073/pnas.1011972107>.
- Verma, A., and Stellacci, F. (2010). Effect of surface properties on nanoparticle-cell interactions. *Small*, 12–21. <https://doi.org/10.1002/sml.200901158>.
- Vogel, R., Hoyer, P., and Weller, H. (1994). Quantum-sized PbS, CdS, Ag₂S, Sb₂S₃, and Bi₂S₃ particles as sensitizers for various nanoporous wide-bandgap semiconductors. *J. Phys. Chem.* <https://doi.org/10.1021/j100063a022>.
- Wang, B., Jiang, Z., Yu, J.C., Wang, J., and Wong, P.K. (2019a). Enhanced CO₂ reduction and valuable C₂₊ chemical production by a CdS-photosynthetic hybrid system. *Nanoscale* 11, 9296–9301. <https://doi.org/10.1039/c9nr02896j>.
- Wang, F., Gu, Y., O'Brien, J.P., Yi, S.M., Yalcin, S.E., Srikanth, V., Shen, C., Vu, D., Ing, N.L., Hochbaum, A.I., et al. (2019b). Structure of microbial nanowires reveals stacked Hemes that transport electrons over micrometers. *Cell* 177, 361–369.e10. <https://doi.org/10.1016/j.cell.2019.03.029>.
- Wang, T., Zhang, D., Dai, L., Dong, B., and Dai, X. (2018). Magnetite triggering enhanced direct interspecies electron transfer: a scavenger for the blockage of electron transfer in anaerobic digestion of high-solids sewage sludge. *Environ. Sci. Technol.* 52, 7160–7169. <https://doi.org/10.1021/acs.est.8b00891>.
- Williams, P.J.L.B., and Laurens, L.M.L. (2010). Microalgae as biodiesel & biomass feedstocks: review & analysis of the biochemistry, energetics & economics. *Energ. Environ. Sci.* 3, 554–590. <https://doi.org/10.1039/b924978h>.
- Yu, H., and Leadbetter, J.R. (2020). Bacterial chemolithoautotrophy via manganese oxidation. *Nature* 583, 453–458. <https://doi.org/10.1038/s41586-020-2468-5>.
- Xu, M., Tremblay, P.L., Ding, R., Xiao, J., Wang, J., Kang, Y., and Zhang, T. (2021). Photo-augmented PHB production from CO₂ or fructose by *Cupriavidus necator* and shape-optimized CdS nanorods. *Sci. Total Environ.* 753, 142050. <https://doi.org/10.1016/J.SCITOTENV.2020.142050>.
- Yu, Y.Y., Wang, Y.Z., Fang, Z., Shi, Y.T., Cheng, Q.W., Chen, Y.X., Shi, W., and Yong, Y.C. (2020). Single cell electron collectors for highly efficient wiring-up electronic abiotic/biotic interfaces. *Nat. Commun.* 11, 1–10. <https://doi.org/10.1038/s41467-020-17897-9>.
- Zhang, J., Wang, H., Yuan, X., Zeng, G., Tu, W., and Wang, S. (2019a). Tailored indium sulfide-based materials for solar-energy conversion and utilization. *J. Photochem. Photobiol. C*, 1–26. <https://doi.org/10.1016/j.jphotochemrev.2018.11.001>.
- Zhang, R., He, Y., Yi, J., Zhang, L., Shen, C., Liu, S., Liu, L., Liu, B., and Qiao, L. (2019b). Proteomic and metabolic elucidation of solar-powered biomanufacturing by bio-abiotic hybrid system. *Chem.* <https://doi.org/10.1016/j.chempr.2019.11.002>.
- Zhou, X., Liu, R., Sun, K., Chen, Y., Verlage, E., Francis, S.A., Lewis, N.S., and Xiang, C. (2016). Solar-driven reduction of 1 atm of CO₂ to formate at 10% energy-conversion efficiency by use of a TiO₂-protected III–V tandem photoanode in conjunction with a bipolar membrane and a Pd/C cathode. *ACS Energ. Lett.* 1, 764–770. <https://doi.org/10.1021/acsenenergylett.6b00317>.
- Zhou, S., Tang, J., and Yuan, Y. (2015). Conduction-band edge dependence of

carbon-coated hematite stimulated extracellular electron transfer of *Shewanella oneidensis* in bioelectrochemical systems. *Bioelectrochemistry* 102, 29–34. <https://doi.org/10.1016/j.bioelechem.2014.11.005>.

Zhang, Y., Hudson-Smith, N.V., Frand, S.D., Cahill, M.S., Davis, L.S., Feng, Z.V., Haynes, C.L., and Hamers, R.J. (2020). Influence of the spatial

distribution of cationic functional groups at nanoparticle surfaces on bacterial viability and membrane interactions. *J. Am. Chem. Soc.* 142, 10814–10823. <https://doi.org/10.1021/jacs.0c02737>.

Zhang, H., Liu, H., Tian, Z., Lu, D., Yu, Y., Cestellos-Blanco, S., Sakimoto, K.K., and Yang, P. (2018). Bacteria photosensitized by

intracellular gold nanoclusters for solar fuel production. *Nat. Nanotechnol.* 13, 900–905. <https://doi.org/10.1038/s41565-018-0267-z>.

Zhu, X.-G., Long, S.P., and Ort, D.R. (2010). Improving photosynthetic efficiency for greater yield. *Annu. Rev. Plant Biol.* 61, 235–261. <https://doi.org/10.1146/annurev-arplant-042809-112206>.