Title
Solar-driven carbon dioxide fixation using photosynthetic semiconductor bio-hybrids

Journal
Faraday Discussions, 215(0)

ISSN
1359-6640

Authors
Cestellos-Blanco, Stefano
Zhang, Hao
Yang, Peidong

Publication Date
2019-07-04

DOI
10.1039/c8fd00187a

Peer reviewed

Faraday Discussions

Cite this: *Faraday Discuss.*, 2019, **215**, 54

PAPER

Solar-driven carbon dioxide fixation using photosynthetic semiconductor bio-hybrids

Stefano Cestellos-Blanco,[a] Hao Zhang[b] and Peidong Yang *[abc]

Received 19th November 2018, Accepted 28th January 2019
DOI: 10.1039/c8fd00187a

Solar-driven conversion of carbon dioxide to value-added carbon products is an ambitious objective of ongoing research efforts. However, high overpotential, low selectivity and poor CO_2 mass transfer plague purely inorganic electrocatalysts. In this instance, we can consider a class of biological organisms that have evolved to achieve CO_2 fixation. We can harness and combine the streamlined CO_2 fixation pathways of these whole organisms with the exceptional ability of semiconducting nanomaterials to harvest solar energy. A novel nanomaterial–biological interface has been pioneered in which light-capturing cadmium sulfide nanoparticles reside within individual organisms essentially powering biological CO_2 fixation by solar energy. In order to further develop the photosensitized organism platform, more biocompatible photosensitizers and cytoprotective strategies are required as well as elucidation of charge transfer mechanisms. Here, we discuss the ability of gold nanoclusters to photosensitize a model acetogen effectively and biocompatibly. Additionally, we present innovative materials including two-dimensional metal organic framework sheets and alginate hydrogels to shield photosensitized cells. Finally, we delve into original work using transient absorption spectroscopy to inform on charge transfer mechanisms.

Fossil fuel-derived energy has powered industrial development over the past two centuries. However, the exploitation of these energy reserves presents an indisputable complication, as these reserves are finite. Semiconductor-based devices have advanced to aptly capture inexhaustible solar energy in the form of electricity.[1] Although solar cells have been tested industrially at scale, they suffer from a persistent lack of adequate energy storage solutions.[2] Nature evolved to solve this issue in photosynthesis as organisms adapted metabolic pathways to reduce CO_2 and store solar energy in ensuing chemical bonds.[3] The longevity and specificity of carbon fixation in biology is unrivalled by inorganic catalysts.[4] Reaction specificity is established by enzymatic conformations that stabilize CO_2 reduction intermediates while steric hindrances assist in specific product

[a]*Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA. E-mail: p_yang@berkeley.edu*
[b]*Department of Chemistry, University of California, Berkeley, CA 94720, USA*
[c]*Kavli Energy NanoSciences Institute at the University of California, Berkeley, CA 94720, USA*

formation.[5] Furthermore, the genetic code ensures that this metabolism is exactly replicated. At the same time, however, engineered semiconducting materials outpace the light-harvesting ability of natural photosynthesis.[6] For these reasons, combining light-absorbing materials with CO_2-reducing organisms offers an appealing solution for solar-based CO_2 fixation.[4–6]

Progress has been made in coupling light harvesting devices with whole cell organisms to fix CO_2 into value-added chemicals.[7,8] This work relies on the ability of electrotrophic bacteria to take up reducing equivalents from inorganic sources, including nanostructured electrodes.[9] These organisms are commonly paired with a cathode in photoelectrochemical systems where they consume electrons to power the conversion of CO_2 into upgradeable carbon products. Exemplarily, acetogens receive reducing equivalents from solar harvesting electrodes and secrete acetate as a by-product of CO_2 fixation.[7] While these efforts confirm the applicability of an integrated cell-semiconductor system, further improvement may be limited by the extracellular nature of the interface between the cell membrane and the electrode. For instance, it is important to increase the CO_2-reducing current while at the same time maintaining a stable interface between the cells and the cathode. However, increasing the CO_2-reducing current is hampered by the fact that high currents create a local basic environment around the proton-consuming cathode.[7] The local basic environment irreparably damages the cell-semiconductor interface. Furthermore, extracellular electron uptake is not fully understood and therefore difficult to optimize. Although membrane-bound proteins take up electrons, a substantial part of these electrons may be lost due to the sluggish kinetics of charge transfer across the membrane.[10] Collectively these limitations indicate that a paradigm shift is needed to redesign the interface between light-absorbing semiconductors and microorganisms.

In a landmark study, Sakimoto *et al.* confirm the ability to enhance acetogen *Moorella thermoacetica* (*M. thermoacetica*) with cadmium sulfide (CdS) nanoparticles.[11] The nanoparticles, which lie on the surface of the cell membrane, capture solar energy and supply reducing equivalents directly into the bacterium. The consumed reducing equivalents jump-start the cell metabolism, which is reliant on a source of electrons, and enable CO_2-to-acetate conversion *via* the Wood–Ljungdahl pathway (WLP).[3] As this study marked the first report on a photosensitized microorganism for CO_2 reduction, further thorough elaboration and improvement is essential. Here, we discuss our studies that build on the first proof of concept. Briefly, we employ gold nanoclusters instead of cadmium sulfide as less cytotoxic and truly intracellular light harvesters. Secondly, we explore cytoprotective materials to shield bacteria from photooxidation due to harsh light and reactive oxygen species (ROS). Finally, we make inroads in elucidating the charge transfer mechanism at the biologic–inorganic interface using transient absorption spectroscopy.

Sakimoto and coworkers report on the first successful study to incorporate light-absorbing nanoparticles within acetogenic bacteria to enable CO_2-to-acetate conversion.[11] *M. thermoacetica* induces the precipitation of CdS nanoparticles with the addition of Cd^{2+} and a source of sulfur such as cysteine. Through an enzymatic process, the sulfur is reduced to sulfide and readily reacts with Cd^{2+} to form high quality CdS nanoparticles [Fig. 1(a)]. These nanoparticles are primarily anchored on the membrane of *M. thermoacetica* [Fig. 1(b)]. Upon illumination, the CdS nanoparticles deliver photogenerated electrons to metabolic pathways that

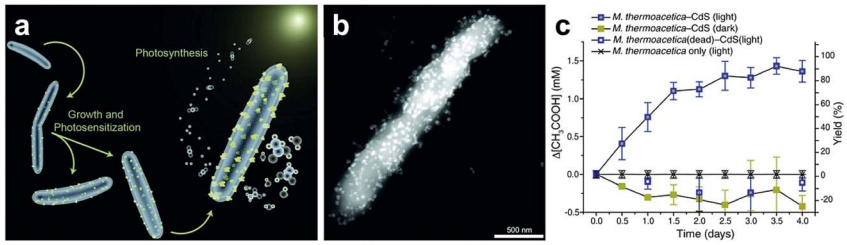

Fig. 1 (a) Model *M. thermoacetica*–CdS construct illustrating early growth stage, CdS nanoparticle ripening (yellow) and CO_2 reduction into acetate. (b) STEM image of *M. thermoacetica*–CdS hybrid. (c) Acetate obtained from *M. thermoacetica*–CdS during photosynthesis with deletional controls. Reproduced with permission.[11] Copyright 2016 The American Association for the Advancement of Science.

realize CO_2 reduction and secrete exogenous acetate [Fig. 1(c)]. Further cysteine is added to serve as a hole scavenger to improve charge separation at the nanoparticle interface. The discovery of photosensitized microorganisms for CO_2 fixation effectively sets up a novel line of investigation. It conceptualizes a new interface between whole microorganisms and semiconductors while confirming light-induced intracellular charge transfer in non-photosynthetic microorganisms. While photosensitized microorganisms enable the photoreduction of CO_2, they also present opportunities for investigating the interface between nanomaterials and whole-cell organisms. Electron transfer without added or produced molecular mediators, such as H_2, viologens or membrane-bound proteins, spurs questions on whether we can inject electrons at various points in biologic charge transport chains. For example, if light-activated nanomaterials jump-start CO_2 reducing pathways, could we potentially target more specific parts of the cell metabolism by material design? Additionally, could we use the light-controlled nanomaterials to set up studies to explore how organisms take up electrons? Applications beyond CO_2 fixation of photosensitized whole-cells merit more in depth discussion.

Furthermore, CdS nanoparticles, while effective light absorbers, pose a known environmental hazard and are acutely cytotoxic to bacteria as they induce oxidative stress.[12] Moreover, a more effective system could be realized with intracellular particles that permeate the whole cell instead of mostly just the membrane.

Gold nanoclusters (AuNCs) are sub-nanometric particles that consist of several gold atoms bound together into a network by ligands such as glutathione. At this level of confined atomicity, AuNCs harbor chromophore-like discrete energy states.[13] Therefore, the clusters act as viable light harvesting centers. Additionally, through synthetic manipulation, their core size may be tuned to optimize for passage through the cell membrane thus enabling intracellular localization of the clusters.[14] Interchangeable surface ligands also enable exquisite control over the biochemical properties of the cluster. $Au_{22}(SG)_{18}$ (SG is glutathione), a type of AuNC, offers water solubility and high fluorescence,[15] a marker for light harvesting, establishing it a prime candidate for microorganism photosensitization[16] [Fig. 2(a)].

Studies have previously confirmed that cells take up AuNCs with high efficiency and low cytotoxicity, as gold and glutathione are individually

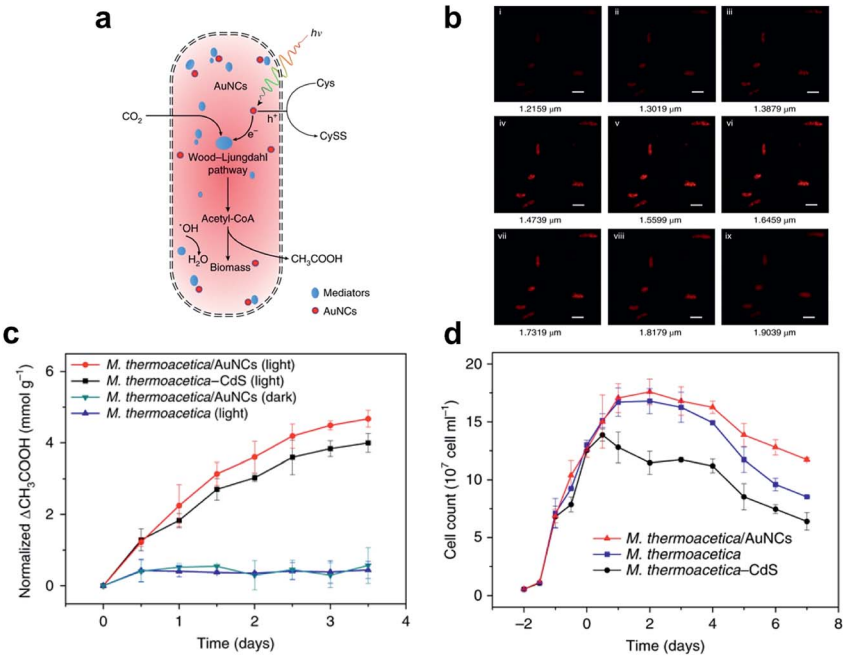

Fig. 2 (a) Schematic of *M. thermoacetica*–$Au_{22}(SG)_{18}$ highlighting pathways to obtain acetate from solar energy. (b) Structure illumination microscopy (SIM) images at different focal planes with emission at 540 nm from $Au_{22}(SG)_{18}$ in *M. thermoacetica*. (c) Normalized acetate production from *M. thermoacetica*–nanoparticle constructs in continuous photosynthesis. (d) Cell counts from *M. thermoacetica*–nanoparticle cultures. Reproduced with permission.[16] Copyright 2018 Nature Publishing Group.

biocompatible.[17] $Au_{22}(SG)_{18}$ specifically, when added to a pre-exponential culture of *M. thermoacetica*, is taken up with over 90% efficiency and remains stable over a period of at least seven days.[16] We have found $\sim 4 \times 10^{-7}$ mg of $Au_{22}(SG)_{18}$ per cell to be an optimal concentration for our experiments. Furthermore, $Au_{22}(SG)_{18}$ does not inhibit growth or other primary cell functions of *M. thermoacetica* at optimal concentrations. In fact, cell numbers and colony-forming units are higher in cultures of *M. thermoacetica*–$Au_{22}(SG)_{18}$ than in *M. thermoacetica*–CdS [Fig. 2(d)]. Advantageously, it has been determined that certain conformations of AuNCs quench radicals, including ROS.[18] In photosensitized bacteria, ROS is created as a toxic by-product upon photo-activation of the nanoparticles.[19] This effect is particularly destructive with CdS. Results show that during photosynthesis the level of intracellular ROS is much lower in *M. thermoacetica*–$Au_{22}(SG)_{18}$ as compared with *M. thermoacetica*–CdS. Altogether, these metrics of improved cell culture viability indicate that CO_2-to-acetate yield may be higher in *M. thermoacetica*–$Au_{22}(SG)_{18}$ constructs.

As hypothesized, $Au_{22}(SG)_{18}$ nanoclusters permeate the entire cellular structure and are found localized beyond the cell membrane.[16] Structure illumination microscopy is employed to resolve the placement of AuNCs in the cells by detecting fluorescence from the AuNCs under excitation at 540 nm. Fig. 2(b) shows fluorescence emission emanating quasi-uniformly in the cells. Images of

AuNCs in *M. thermoacetica* at a series of focal planes demonstrate that AuNCs can indubitably be found throughout the cells. Critically, the improved cell viability and intracellular penetration through the application of $Au_{22}(SG)_{18}$ as a photosensitizer lead to higher rate of acetic acid production [Fig. 2(c)]. After a period of four days of constant photosynthesis, the yield of acetic acid in the *M. thermoacetica*–$Au_{22}(SG)_{18}$ culture is appreciably higher than in the *M. thermoacetica*–CdS construct.[16] Ultimately, AuNCs function as a powerful second-generation photosensitizer. Additional consideration is needed to elucidate the transport mechanism of $Au_{22}(SG)_{18}$ into the cytoplasm, as well as the role of individual charge uptake pathways within the cell.

AuNCs are effective photosensitizers in bacteria for solar-driven CO_2 fixation. While the rate of photooxidation is diminished with the use of AuNCs, it still persists in the system as a whole. Non-photosynthetic bacteria such as *M. thermoacetica* are not evolved to handle the high photon flux required for successful photosynthesis. Furthermore, cysteine, which acts as the hole scavenger in both CdS and AuNC systems, becomes depleted and currently limits the total output of acetic acid.[11,16] A strategy has been developed in which cystine is reduced back to cysteine by photoactive TiO_2 nanocatalysts.[20] Although the photoreduction of cystine increases the availability of cysteine, which allows for a higher acetate yield, it comes at the expense of much higher photooxidation in the system. The TiO_2 nanocatalysts are responsible for photoanodic water oxidation that produces O_2 and toxic amounts of ROS.[19,21] For these reasons, it is necessary to identify cytoprotective materials that will shield the photosensitized bacteria from photooxidative damage.

Advantageously, the cysteine/cystine redox shuttle allows for physical segregation of the photosensitized bacteria and the TiO_2 nanocatalysts. A selective membrane that quenches ROS and restricts O_2 passage while maintaining the diffusion of CO_2 and the redox shuttle would be beneficial. Photosynthetic microorganisms such as cyanobacteria emit extracellular polymers that contain UV-blocking molecules.[22,23] Additionally, a plethora of robust microbes resist changes in temperature, pH, and salinity by forming spores.[24] Diatoms, for instance, synthesize siliceous exoskeletons to protect themselves from environmental stressors. Taking a cue from nature, encapsulation of the photosensitized bacteria would improve their ability to withstand harsh circumstances.[25]

Hydrogels, including alginate, are commonly employed to encapsulate a unit of cells as they allow for unencumbered proliferation. Bacteria grow without restriction as they form microvoids in the soft alginate hydrogel.[26] This offers the advantage that bacteria would not lose their protection as they replicate, and dormant states are not induced by otherwise tight armor.[27] Fig. 3(a) demonstrates the growth of *M. thermoacetica* inside of alginate microspheres produced by a microfluidic injection process (see Experimental section below). *M. thermoacetica* creates microvoids inside of the alginate microspheres as determined by environmental scanning electron microscopy. Moreover, as alginate primarily consists of water, its CO_2 diffusive properties are the same as those of the aqueous culture media. The viability of *M. thermoacetica* decreases over the duration of whole photosynthesis with CO_2 reduction coupled with O_2 evolution. This is due to the strict anaerobic nature of *M. thermoacetica*, as it does not have a protective mechanism against O_2 or ROS. The alginate scavenges and attenuates the concentration of superoxides, hypochlorites and peroxides. This leads to an

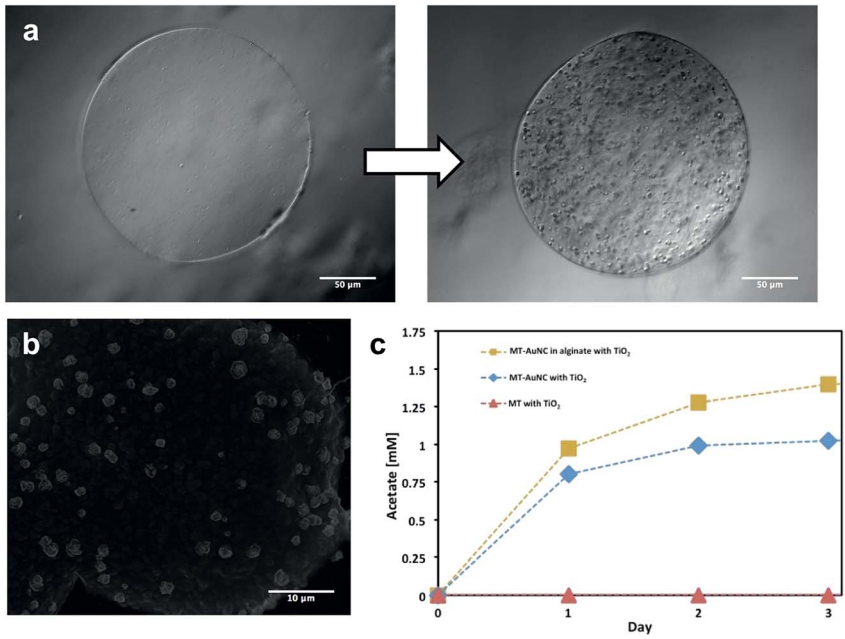

Fig. 3 (a) Differential interference contrast microscopy illustrates *M. thermoacetica* growth from day 0 to day 4 encapsulated in alginate microspheres. (b) Environmental scanning electron microscopy image shows detailed microvoids of an alginate sphere populated with *M. thermoacetica*. (c) CO_2-to-acetate production by encapsulated photosensitized *M. thermoacetica* with light-activated TiO_2 nanoparticles to reduce cystine to cysteine molecular redox shuttle.

increase in acetate during photosynthesis by *M. thermoacetica* [Fig. 3(c)]. A further protective layer may be synthesized on the surface of the bacteria-filled hydrogel.[28] For example, polydopamine and silica have been patterned directly on the surface of alginate to shield cells from stresses.[29]

Metal organic framework (MOF) materials have received consideration as cytoprotective materials that are directly crystallized on or wrap around biological structures.[30,31] Our group has developed a strategy to uniformly wrap photosensitized *M. thermoacetica* with a nanometric thick MOF monolayer for cytoprotection.[32] The MOF monolayer maintains a dynamic wrapping during cell elongation, separation and even of newly grown cell surfaces [Fig. 4(a)]. Importantly, *M. thermoacetica* covered with the MOF monolayer sustains a smaller drop in viability under increasing concentrations of a model ROS, H_2O_2, as compared to the bare *M. thermoacetica* [Fig. 4(c)–(e)]. The viability is enhanced due to the catalytic activity of the MOF enclosure toward decomposition of the ROS. The MOF monolayer contains a zirconium cluster, which like zirconia particles rapidly decomposes H_2O_2 [Fig. 4(b)]. The MOF-wrapped *M. thermoacetica*–$Au_{22}(SG)_{18}$ can continuously produce acetate from CO_2 reduction under oxidative stress. MOF-wrapped photosensitized *M. thermoacetica* was shown to produce up to 200% more acetate than its bare counterpart under whole photosynthesis conditions. Therefore, the MOF cytoprotective method addresses the inherent vulnerability of anaerobes to oxidative stress, and provides a suitable platform for implementing

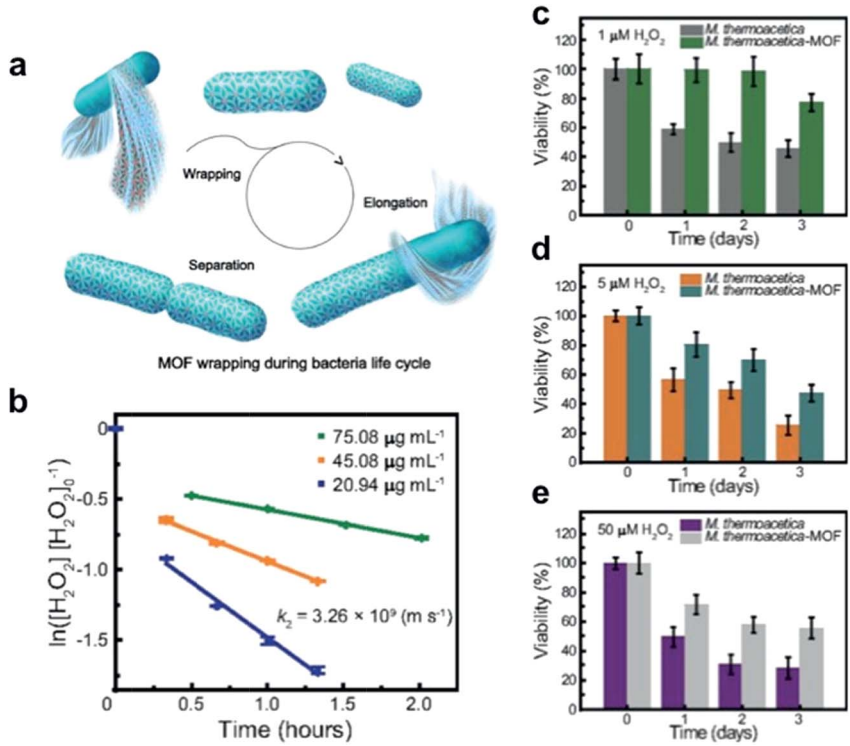

Fig. 4 (a) Depiction of spontaneous zirconium-based MOF-wrapping of *M. thermoacetica* by bonding to membrane-linked phosphate units. (b) Hydrogen peroxide decomposition by zirconium-based MOF. (c)–(e) Enhancement of viability of MOF-wrapped *M. thermoacetica* compared to bare *M. thermoacetica* at various hydrogen peroxide concentrations. This figure reproduced with permission.[32] Copyright 2018 the National Academy of Sciences of the United States of America.

a whole artificial photosynthesis with both carbon dioxide reduction and oxygen evolution reaction.

A final aspect of the photosensitized microorganism system that is worth exploring is the mechanism of electron transfer between the inorganic light harvesting nanoparticles and the cell. While electron transfer processes between a poised electrode and electrotrophic bacteria have been investigated, those studies are limited by the inability to replicate and observe the processes *in situ* by spectroscopic means.[33] Photosensitized bacteria lend themselves as a platform to undertake transmittance-based transient absorption (TA) spectroscopy to study charge carrier lifetimes, as these colloidal suspensions are translucent and modular.[34] By applying controls the molecular basis of charge uptake can be inferred. The biochemical activity of proteins confirmed to take up reducing equivalents can be correlated with the results obtained with TA. In the event of hydrogenase involvement, the photoexcited electrons would help generate H_2, which is then used in the WLP to convert CO_2 into acetate whereas the direct uptake of those electrons by membrane-bound proteins including cytochromes, ferredoxins and flavoproteins would facilitate ATP synthesis[35] [Fig. 5(a)]. In the first of its kind study, Kornienko and colleagues subjected *M. thermoacetica*–CdS

constructs to hydrogen incubation pre-photosynthesis at varying lengths of time in order to ramp up hydrogenase activity.[34] The rate of acetate production is highest in the first three hours for those samples with no hydrogen incubation but the average rate of acetate activity over 48 hours is highest in the samples with the longest hydrogen incubation. While seemingly paradoxical, the results suggest that two electron uptake processes take place. In samples with limited hydrogenase activity, the electrons feed directly into membrane bound proteins accelerating acetate production but ultimately cannot sustain metabolic activity due to a lack of high energy reducing equivalents [H_2, NAD(P)H, Fd]. Whereas samples with sufficient hydrogenase activity, a CdS-to-hydrogenase electron transfer pathway is established to produce high energy reducing equivalents. Accordingly, TA kinetic results demonstrate faster decay kinetics in *M. thermoacetica*–CdS hybrids after hydrogen incubation than in *M. thermoacetica*–CdS grown with glucose and bare CdS [Fig. 5(b)]. These observations support the notion of electron transfer to an acceptor site on hydrogenase.

Moreover, due to the direct intracellular interface formed in *M. thermoacetica*–$Au_{22}(SG)_{18}$, this hybrid system could provide more insight into electron transfer processes. Strong quantum confinement effects and single electron transitions in AuNCs are manifested in their physicochemical properties such as discrete energy levels, multiple absorption bands and enhanced photoluminescence.[36] However, insufficient progress has been made in uncovering photoelectron transfer mechanisms. More efforts are needed to fully understand AuNCs excited state interactions, especially for energy conversions. We have established a model system as our starting point to elucidate the electron-donating ability of $Au_{22}(SG)_{18}$ to methyl viologen (MV^{2+}). The stability of its radical cation ($MV^{+\bullet}$) and the ease of its spectroscopic detection makes MV^{2+} favorable for fundamental studies.[37] TA allows for the spectroscopic determination of electron-transfer yield and associated kinetics of charge transfer in reduced methyl viologen with a characteristic absorption at 600 nm and 390 nm. More controlled experiments could provide new insights in understanding the intracellular photoexcited electron transfer process.

Altogether, photosensitized microorganisms offer a pioneering approach to convert CO_2 to upgradeable hydrocarbons using solar energy. This biohybrid

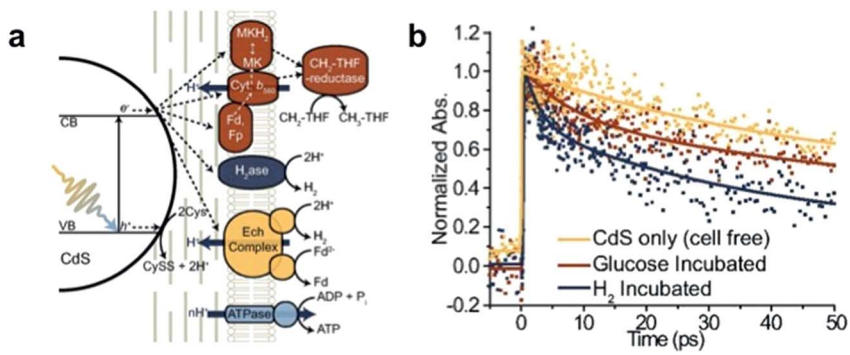

Fig. 5 (a) Schematic featuring possible active photoelectron uptake mechanisms. (b) Transient absorption plot of bare CdS, glucose and H_2 incubated *M. thermoacetica*–CdS. Fig. 5(a) and (b) reproduced with permission.[34] Copyright 2016 the National Academy of Sciences of the United States of America.

approach exploits the replication, self-healing and specificity of CO_2-fixing whole bacteria and the extraordinary solar capture of semiconducting nanoparticles. The intracellular interface, particularly in the AuNC constructs, circumvents the sluggish kinetics associated with extracellular charge uptake. Progress in cyto-protective materials will enable the application of this technology. Additionally, understanding gained through spectroscopic studies will shape future iterations of photosensitizers as well as optimize the pairing process. Finally, we hope engaged readership and research will be drawn to our highlighted areas of active investigation.

Experimental

AuNCs synthesis, *Moorella thermoacetica* growth and photosensitization

Red-emitting $Au_{22}(SG)_{18}$ synthesis is outlined by Zhang and coworkers.[16] Solutions of $HAuCl_4$ (12.5 mL, 20 mM) and glutathione (7.5 mL, 50 mM) were combined into 180 mL of ultrapure water and stirred vigorously. After 120 seconds, the pH of the reaction solution was adjusted to 12.0 with 1 M NaOH and subsequently 0.24 mg $NaBH_4$ was added. The pH of the solution was lowered to 2.5 with 0.3 M HCl after 30 minutes and allowed to react while stirring for 6 hours. Isopropyl alcohol was added at 1 : 1 (v/v) in order to precipitate the AuNCs. The solution was centrifuged at 14 000 rpm in order to collect the AuNCs. Finally, the AuNCs were further washed with methanol.

Extensive *M. thermoacetica* culturing protocols are described in detail in Sakimoto *et al.*[11] Briefly, an initial inoculum of *M. thermoacetica* (ATCC 39073) was cultured in 10 mL anaerobic heterotrophic media at 52 °C after slow thawing from −80 °C. The headspace of the 15 mL volume tube was filled with 80 : 20 mixture of N_2 : CO_2 at 150 kPa. After two subsequent rounds of culturing 0.5 mL of 4 mg mL^{-1} $Au_{22}(SG)_{18}$ was added to each culture tube when $OD_{600} = 0.28$. After 24 hours, each culture was washed at 2500 rpm for 10 min, and the cell pellet was resuspended in 3.5 mL of autotrophic medium supplemented with 0.1 wt% cysteine and 1% (w/v) sodium alginate.

Encapsulation of photosensitized *Moorella thermoacetica*

As previously described, 1% (w/v) sodium alginate was directly added to the autotrophic media which is used to resuspend the AuNCs-containing bacteria. The microbeads were formed by injecting the alginate solution (5 mL per hour) through a 25G needle parallel to a flowing stream of N_2 gas into 6.5 mL of stirred autotrophic media supplemented with 2% $CaCl_2$. We then distributed each 10 mL total solution (alginate spheres and liquid autotrophic media) into 25 mL anaerobic tubes, each with 5 mg of TiO_2 anatase nanopowder. In order to promote enzymatic activity, each tube was pressurized with 150 kPa of 80 : 20 H_2 : CO_2 and incubated for 12 hours at 52 °C.

Photosynthesis, measurements and sample characterization

Before the light experiments, the headspace of each sample tube was exchanged with 80 : 20 N_2 : CO_2 and pressurized to 150 kPa. The light intensity of a 75 W xenon lamp (Newport) with an AM 1.5 G filter was calibrated to 0.2% sun. Acetate concentrations were measured by quantitative ^{1}H-NMR with a sodium 3-

(trimethylsilyl)-2,2′,3,3′-tetradeuteropropionate internal standard. All spectra were processed with MestreNova software. Furthermore, alginate microbeads were imaged with differential interference contrast microscopy using a Zeiss Axioimager upright microscope. Sample preparation for environmental SEM consisted of microtoming individual alginate microspheres with a cryostat (Leica CM3050S). E-SEM was undertaken with an FEI Quanta microscope (Thermo Scientific).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by NASA, Center for the Utilization of Biological Engineering in Space, under Award NNX17AJ31G. H. Z. acknowledges the Suzhou Industry Park Fellowship.

References

1 D. Kim, K. K. Sakimoto, D. Hong and P. Yang, Artificial Photosynthesis for Sustainable Fuel and Chemical Production, *Angew. Chem., Int. Ed.*, 2015, **54**, 3259–3266.

2 T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets and D. G. Nocera, Solar energy supply and storage for the legacy and nonlegacy worlds, *Chem. Rev.*, 2010, **110**, 6474–6502.

3 A. Das and L. G. Ljungdahl, Electron-Transport System in Acetogens, in *Biochemistry and Physiology of Anaerobic Bacteria*, Springer-Verlag, New York, 2003, pp. 191–204.

4 B. Tian, S. Xu, J. A. Rogers, S. Cestellos-Blanco, P. Yang, J. L. Carvalho-De-Souza, F. Bezanilla, J. Liu, Z. Bao, M. Hjort, Y. Cao, N. Melosh, G. Lanzani, F. Benfenati, G. Galli, F. Gygi, R. Kautz, A. A. Gorodetsky, S. S. Kim, T. K. Lu, P. Anikeeva, M. Cifra, O. Krivosudský, D. Havelka and Y. Jiang, Roadmap on semiconductor-cell biointerfaces, *Phys. Biol.*, 2018, **15**, 031002.

5 K. K. Sakimoto, N. Kornienko and P. Yang, Cyborgian Material Design for Solar Fuel Production: The Emerging Photosynthetic Biohybrid Systems, *Acc. Chem. Res.*, 2017, **50**, 476–481.

6 K. K. Sakimoto, N. Kornienko, S. Cestellos-Blanco, J. Lim, C. Liu and P. Yang, Physical Biology of the Materials-Microorganism Interface, *J. Am. Chem. Soc.*, 2018, **140**, 1978–1985.

7 C. Liu, J. J. Gallagher, K. K. Sakimoto, E. M. Nichols, C. J. Chang, M. C. Y. Chang and P. Yang, Nanowire-bacteria hybrids for unassisted solar carbon dioxide fixation to value-added chemicals, *Nano Lett.*, 2015, **15**, 3634–3639.

8 C. Liu, B. C. Colón, M. Ziesack, P. A. Silver and D. G. Nocera, "Water splitting–biosynthetic system with CO_2 reduction efficiencies exceeding photosynthesis, *Science*, 2016, **352**, 1210–1213.

9 D. R. Lovley, Powering microbes with electricity: Direct electron transfer from electrodes to microbes, *Environ. Microbiol. Rep.*, 2011, **3**, 27–35.

10 T. J. Silhavy, D. Kahne and S. Walker, The bacterial cell envelope, *Cold Spring Harbor Perspect. Biol.*, 2010, **2**, a000414.
11 K. K. Sakimoto, A. B. Wong and P. Yang, Self-photosensitization of nonphotosynthetic bacteria for solar-to-chemical production, *Science*, 2016, **351**, 74–77.
12 Z. X. Lu, L. Zhou, Z. L. Zhang, W. L. Shi, Z. X. Xie, H. Y. Xie, D. W. Pang and P. Shen, Cell Damage Induced by Photocatalysis of TiO_2 Thin Films, *Langmuir*, 2003, **19**, 8765–8768.
13 M. A. Abbas, P. V. Kamat and J. H. Bang, Thiolated Gold Nanoclusters for Light Energy Conversion, *ACS Energy Lett.*, 2018, **3**, 840–854.
14 X. D. Zhang, Z. Luo, J. Chen, S. Song, X. Yuan, X. Shen, H. Wang, Y. Sun, K. Gao, L. Zhang, S. Fan, D. T. Leong, M. Guo and J. Xie, Ultrasmall glutathione-protected gold nanoclusters as next generation radiotherapy sensitizers with high tumor uptake and high renal clearance, *Sci. Rep.*, 2015, **5**, 8669.
15 Y. Yu, Z. Luo, D. M. Chevrier, D. T. Leong, P. Zhang, D. E. Jiang and J. Xie, Identification of a highly luminescent $Au_{22}(SG)_{18}$ nanocluster, *J. Am. Chem. Soc.*, 2014, **136**, 1246–1249.
16 H. Zhang, H. Liu, Z. Tian, D. Lu, Y. Yu, S. Cestellos-Blanco, K. K. Sakimoto and P. Yang, Bacteria photosensitized by intracellular gold nanoclusters for solar fuel production, *Nat. Nanotechnol.*, 2018, **13**, 900–905.
17 J. Wang, G. Zhang, Q. Li, H. Jiang, C. Liu, C. Amatore and X. Wang, *In vivo* self-bio-imaging of tumors through *in situ* biosynthesized fluorescent gold nanoclusters, *Sci. Rep.*, 2013, **3**, 1157.
18 B. Santiago-Gonzalez, A. Monguzzi, J. M. Azpiroz, M. Prato, S. Erratico, M. Campione, R. Lorenzi, J. Pedrini, C. Santambrogio, Y. Torrente, F. De Angelis, F. Meinardi and S. Brovelli, Permanent excimer superstructures by supramolecular networking of metal quantum clusters, *Science*, 2016, **353**, 571–575.
19 D. Meissner, R. Memming, B. Kastening and D. Bahnemann, Fundamental problems of water splitting at cadmium sulfide, *Chem. Phys. Lett.*, 1986, **127**, 419–423.
20 K. K. Sakimoto, S. J. Zhang and P. Yang, Cysteine–Cystine Photoregeneration for Oxygenic Photosynthesis of Acetic Acid from CO_2 by a Tandem Inorganic–Biological Hybrid System, *Nano Lett.*, 2016, **16**, 5883–5887.
21 Z. X. Lu, L. Zhou, Z. L. Zhang, W. L. Shi, Z. X. Xie, H. Y. Xie, D. W. Pang and P. Shen, Cell Damage Induced by Photocatalysis of TiO_2 Thin Films, *Langmuir*, 2003, **19**, 8765–8768.
22 M. Ehling-Schulz and S. Scherer, UV protection in cyanobacteria, *Eur. J. Phycol.*, 1999, **34**, 329–338.
23 S. P. Adhikary and J. K. Sahu, UV protecting pigment of the terrestrial cyanobacterium Tolypothrix byssoidea, *J. Plant Physiol.*, 1998, **153**, 770–773.
24 S. H. Yang, D. Hong, J. Lee, E. H. Ko and I. S. Choi, Artificial spores: Cytocompatible encapsulation of individual living cells within thin, tough Artificial shells, *Small*, 2013, **9**, 178–186.
25 J. C. Rooke, A. Léonard, C. F. Meunier and B. L. Su, Designing photobioreactors based on living cells immobilized in silica gel for carbon dioxide mitigation, *ChemSusChem*, 2011, **4**, 1249–1257.

26 P. Allan-Wojtas, L. Truelstrup Hansen and A. T. Paulson, Microstructural studies of probiotic bacteria-loaded alginate microcapsules using standard electron microscopy techniques and anhydrous fixation, *LWT–Food Sci. Technol.*, 2008, **41**, 101–108.

27 J. H. Park, S. H. Yang, J. Lee, E. H. Ko, D. Hong and I. S. Choi, Nanocoating of single cells: From maintenance of cell viability to manipulation of cellular activities, *Adv. Mater.*, 2014, **26**, 2001–2010.

28 J. Niu, D. J. Lunn, A. Pusuluri, J. I. Yoo, M. A. O'Malley, S. Mitragotri, H. T. Soh and C. J. Hawker, Engineering live cell surfaces with functional polymers *via* cytocompatible controlled radical polymerization, *Nat. Chem.*, 2017, **9**, 537–545.

29 B. J. Kim, T. Park, S. Y. Park, S. W. Han, H. S. Lee, Y. G. Kim and I. S. Choi, Control of Microbial Growth in Alginate/Polydopamine Core/Shell Microbeads, *Chem.–Asian J.*, 2015, **10**, 2130–2133.

30 X. Lian, Y. Fang, E. Joseph, Q. Wang, J. Li, S. Banerjee, C. Lollar, X. Wang and H. C. Zhou, Enzyme-MOF (metal–organic framework) composites, *Chem. Soc. Rev.*, 2017, **46**, 3386–3401.

31 M. B. Majewski, A. J. Howarth, P. Li, M. R. Wasielewski, J. T. Hupp and O. K. Farha, Enzyme encapsulation in metal–organic frameworks for applications in catalysis, *CrystEngComm*, 2017, **19**, 4082–4091.

32 Z. Ji, H. Zhang, H. Liu, O. M. Yaghi and P. Yang, Cytoprotective metal–organic frameworks for anaerobic bacteria, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 10582–10587.

33 F. Kracke, I. Vassilev and J. O. Krömer, Microbial electron transport and energy conservation – The foundation for optimizing bioelectrochemical systems, *Front. Microbiol.*, 2015, **6**, 575.

34 N. Kornienko, K. K. Sakimoto, D. M. Herlihy, S. C. Nguyen, A. P. Alivisatos, C. B. Harris, A. Schwartzberg and P. Yang, Spectroscopic elucidation of energy transfer in hybrid inorganic–biological organisms for solar-to-chemical production, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 11750–11755.

35 J. S. Deutzmann, M. Sahin and A. M. Spormann, Extracellular enzymes facilitate electron uptake in biocorrosion and bioelectrosynthesis, *mBio*, 2015, **6**, 1–8.

36 Z. Luo, K. Zheng and J. Xie, Engineering ultrasmall water-soluble gold and silver nanoclusters for biomedical applications, *Chem. Commun.*, 2014, **50**, 5143–5155.

37 M. Zhou, Z. Lei, Q. Guo, Q. M. Wang and A. Xia, Solvent Dependent Excited State Behaviors of Luminescent Gold(I)–Silver(I) Cluster with Hypercoordinated Carbon, *J. Phys. Chem. C*, 2015, **119**, 14980–14988.