Photosynthetic conversion of CO₂ to acetic acid by an inorganic-biological hybrid system

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Since 7000 BCE, humans have fermented sugars into ethanol, and since work by Louis Pasteur in the 1850s, we have known that microorganisms are responsible for this miraculous feat of chemical synthesis [1]. Since then, the ability of biological organisms to cheaply and selectively transform chemicals into useful products has been exploited on a global scale from agriculture to biotechnological synthesis of pharmaceutical compounds. Recently, photosynthetic conversion of CO₂ into organic compounds using solar energy by algae, cyanobacteria and plants has garnered much attention as a possible solution to mitigate climate change resulting from rising levels of greenhouse gases. However, despite the remarkable capabilities of biology to fix CO₂ into compounds that might be used as food, fuel or commodity chemicals, their efficiencies typically remain too low (~0.2%–1.6%) due to their limited light absorption [2].

Recently, efforts have been directed to augmenting bacterial CO₂ fixation with inorganic, semiconductor light harvesters in the form of photoelectrochemical devices [3–5]. Such devices often employ a biocompatible semiconductor electrode and metal co-catalysts that split water into hydrogen and oxygen with a photogenerated electron-hole pair. The hydrogen is then fed to autotrophic bacteria that combine it with CO₂ to produce a number of compounds including organic acids, alcohols and methane. While such photovoltaic and photoelectrochemical devices can achieve significantly higher solar-energy conversion efficiencies (10%–20%), their widespread implementation is still plagued by manufacturing and material costs associated with the microfabrication techniques required to produce such devices.

Again, biological systems offer a potential solution to the high cost associated with semiconductor synthesis. Bacteria, yeast, and viruses have all been shown to produce a variety of metal, and metal chalcogenide semiconductor nanoparticles, affording a low cost route to light absorbing

nanomaterials at mild conditions (i.e., low temperature, neutral pH, non-hazardous precursors) [6]. Recent work by Sakimoto *et al.* [7] has adopted such an approach by inducing the bacterium *Moorella thermoacetica* (*M. thermoacetica*) to precipitate and decorate itself with cadmium sulfide nanoparticles (Fig. 1). This cyborgian bacteria, *M. thermoacetica*-CdS, when illuminated by sunlight, is able to use the photogenerated electrons to reduce CO₂ into acetic acid with exceedingly high quantum efficiencies. While many synthetic CO₂ reducing catalysts can achieve high efficiencies in converting to C₁ products (such as methane, carbon monoxide, formic acid, etc.), this C₂ product holds great promise as a non-volatile, non-toxic intermediate that could serve as a biofeedstock commodity chemical, ready to be upgraded to a variety of biofuels, biopolymers, and pharmaceutical precursors [3,8]. This first generation system opens up a new parameter space to investigate such bio-inorganic hybrid systems: biosynthesizing smaller band gap semiconductors to increase light absorption and energy conversion efficiency, genetic engineering to produce more complicated organic molecules, and more.

Corresponding author Prof. Peidong Yang of the University of California, Berkeley noted that though previous work between bacteria and semiconductor nanoparticles has investigated their photostabilizing properties, the interaction in their hybrid system is seemingly biocompatible, feeding the bacterium rather than killing it. The nature of this interaction is not yet fully understood, but Yang noted that the light absorbing properties of CdS might serve as a useful optical probe to study the behavior of biotic-abiotic interactions, first in this hybrid system, and potentially generalized to other lingering questions in biology. This revolutionary work signals a new emergent partnership between materials chemists and biologists to work together towards designing and characterizing the next generation of advanced nano-bio technologies.

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Figure 1 Schematic photosynthesis behavior of the *M. thermoacetica*-CdS hybrids. (a) The growth of the cells and bioprecipitation (loading) of the CdS nanoparticles (shown in yellow) through photosynthetic conversion of CO₂ (center right) to acetic acid (right). (b) Pathway diagram for the *M. thermoacetica*-CdS system. There are two possible routes to generate reducing equivalents, [H]: generation outside the cell (dashed line) or generation by direct electron transport to the cell (solid line). Reprinted with permission from Ref. [7], Copyright 2016, American Association for the Advancement of Science.

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