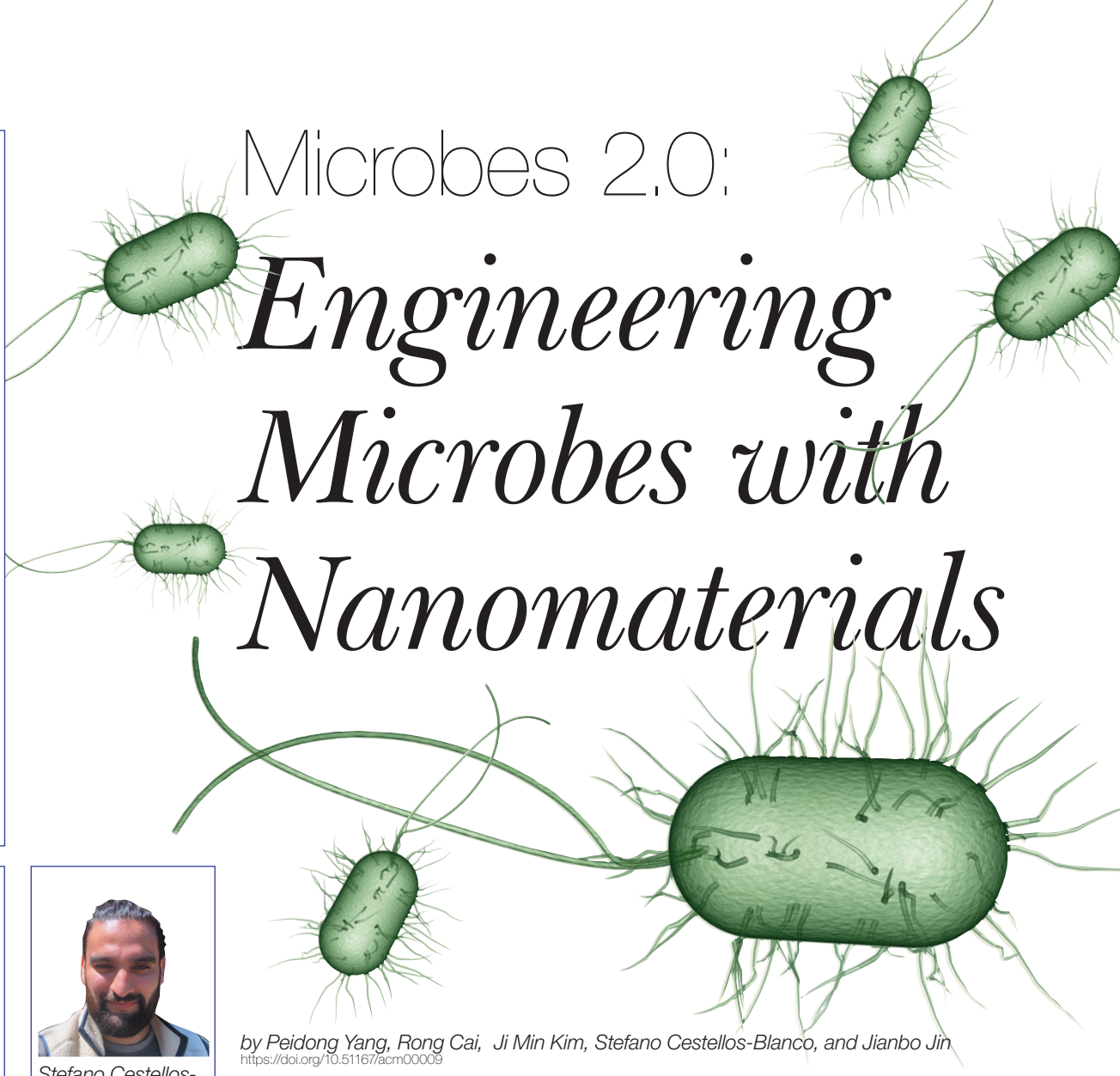
Microbes 2.0:

Engineering Microbes with Nanomaterials



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While you are enjoying bread and wine, have you ever wondered what creates such fascinating foods? Bakers? Brewers? Humans have teamed with microorganisms for thousands of years. Baker's yeast causes bread to rise; brewer's yeast ferments sugar into alcohol to make wine and beers. All those fascinating processes and endless flavors are created by microbes.

Small organisms, giant effect

Microbes are collectively referred to these small living organisms, which are too small to be seen without magnification. Although too small to be seen, they profoundly influence all aspects of the earth and its residents. Proceeding green plants for billions of years, bacteria invented photosynthesis to obtain energy from sunlight. Oxygen, generated from photosynthesis, set off aerobic respiration and ozone formation, both of which pave the way for the explosion in species diversification. Trillions of bacteria inhabit human beings. Instead of threatening us, this diverse community of microbial cells offers vital help. They are capable of breaking down large, complex carbohydrates into small, easily digestible sugar, providing us an efficient approach to extract nutrition from apples, potatoes, and cereal.[1] They also encode hormones and neurotransmitters, which may subtly shape our moods, emotion, and even our personalities.[2,3] An imbalance in the human microbial ecosystem could lead to immune disorder, obesity, or depression.[4] The rapid development of genetic sequencing technologies enables us to view the ubiquity and diversity of microorganisms. Given that microbes inhabit and shape every corner on the earth, scientists are studying the microbiome to understand the world and launch innovations in energy, health, agriculture, and more.[5]

Microbes 1.0

The initial phase of exploitation of microbes for human issues relies on the natural capacities of microorganisms. One of the best proofs is bio-mining. Mining used to be an energy-intensive

process. As the world is moving toward a carbon-neutral society, mining firms start a green business with bacteria. Bacteria *Acidithiobacillusor* and *Leptospirillum* are hired to work in an ore heap with dilute acid. They oxidize iron and sulfur to reactive ferric iron and sulfuric acid, freeing the valuable metal from rocky material. Later, *Desulfovibrio* and *Desulfotomaculum* are employed to clean up the acidic runoff by neutralizing acid and creating sulfides. The generated sulfides can further bond to copper, nickel, and other metals, which pull out a few last precious metals. With the increasing scarcity of high-grade ores, cost-efficient bio-mining has seen unprecedented growth in recent years.[6]

Another way of tapping into the unlimited potential of microorganisms is in bioremediation. Microbes have surprising capacities to detoxify organic chemicals or heavy metals.[7] Agencies and companies have employed microbes to clean up toxic pollutants, ranging from removing oil spills in the ocean to water treatment in sewage for decades.[8] An emerging issue we are facing today is microplastics, which are small plastics less than 5 µm. These less visible and pervasive plastic pieces can be ingested by a wide range of creatures and eventually accumulated in humans through the food chain. An attractive way of tackling microplastics pollution is to employ plastic munching bacteria.[9] More progress can be found in microbial fuel cells[10] and microbial sensors[11]. In these microbial applications, scientists have identified and validated microbes with novel capacities, screened out the most suitable workhorse for industrial use, and gained numerous insights into their characteristics through biological techniques.

Microbes 2.0

With the booming of genetics and nanotechnology, we unlocked a new phase of utilizing microbes. Beyond seeking microbes with new capacities, scientists today can design and create microbes with specific capabilities to perform the desired task.

The classical strategy to engineer microbes is termed as DNA recombination. This technology makes it possible to transfer genetic material from one organism to another. By introducing foreign DNA to host cells, we can function bacteria with new networks, and eventually create improved or novel microorganisms through gene coding. Recombinant bacteria have been used to synthesize indispensable products such as drugs, vitamins, and enzymes.[12] People have already benefited from their medical, industrial, and agricultural uses.

A novel strategy to engineer microbes is built upon nanotechnology, which studies the materials on an ultra-small scale with unique and exciting properties. These novel materials are between 1 and 100 nanometers in size, which are similar to the width of DNA (~2.5 nm) or enzyme molecules (1-10 nm) in microbes (200 nm - 2 µm) (Figure 1).[13] Due to their parallel dimension to biological molecules, nanomaterials have excellent potential for integrating with microorganisms. Superior to biological molecules, nanomaterials often take on unique optical and electrical properties. Exemplarily, inorganic semiconductor materials show an outstanding efficiency in light-harvesting with up to 20% solar-to-electricity conversion rates.[14] In contrast, plants can only use ~ 0.25% of the sunlight's energy that falls on them.[15] These emergent properties have made significant impacts in electronics, energy, and other fields. From the genetic engineering of microbes, we learned biological systems are quite robust and easily tolerate/adapt to the addition of new components. We decided to equip bacteria with nanomaterials, which may allow us to graft nanomaterials' superior properties to microbes.

Photosynthetic biohybrid systems

While we benefit from all the advantages granted in a modern society, we need to spare a moment to reflect the cost of our prosperity. The inevitable depletion of fossil fuels and the release of harmful greenhouse gas put a question mark on our sustainability. Transition to renewable alternatives becomes imperative.[16,17] Leaves harvest energy from the sun to turn carbon dioxide into the carbohydrates. Given the sun's unparalleled energy abundance, scientists have been working to devise a similar process to obtain hydrocarbon fuels and close the carbon cycle. Although inorganic materials excel in solar capture, they do not hold the upper hand over biology regarding CO_2 fixation. Inorganic catalysts for CO_2 reduction have produced mostly C_1 compounds such as carbon monoxide, methane, methanol, and formate.[18] However, we are looking for C_{2+} products with high energy density and can be readily integrated into current infrastructures. Practical solutions can be combining the strengths of biocatalytic machinery with synthetic materials to establish semi-artificial photosynthesis

Encouraged by the potential of microbes engineered by nanomaterials, we decide to construct photosynthetic biohybrid systems (PBSs) by integrating the microbes and synthetic materials. Acetogenic bacteria live from converting CO_2 into acetic acid (C_2 product) via the Wood-Ljungdahl pathway (WLP), one of the oldest biochemical ways for CO_2 fixation.[19] Their efficient CO_2 fixation metabolism with high-specificity qualifies them as great catalytic workhorses. Naturally, acetogens grow by oxidizing organic compounds or inorganic hydrogen to obtain reducing equivalents, which are usually coupled to CO_2 reduction. Recent research found some acetogenic bacteria can get reducing power directly from electrodes.[20] Hence, we think it is possible to integrate acetogenic bacteria with inorganic semiconductor materials to accomplish our overall goal—generating hydrocarbon (C_{2+}) from sunlight and carbon dioxide, and storing solar energy directly into chemical bonds in the form of liquid sunlight.

The first non-photosensitive bacterium to carry artificial photosynthesis. To build an efficient hybrid system, constructing a favorable interface between biotic and abiotic components is imperative. For example, the use of foreign semiconductor materials – which often contain toxic metals – creates an inhospitable environment to microorganisms

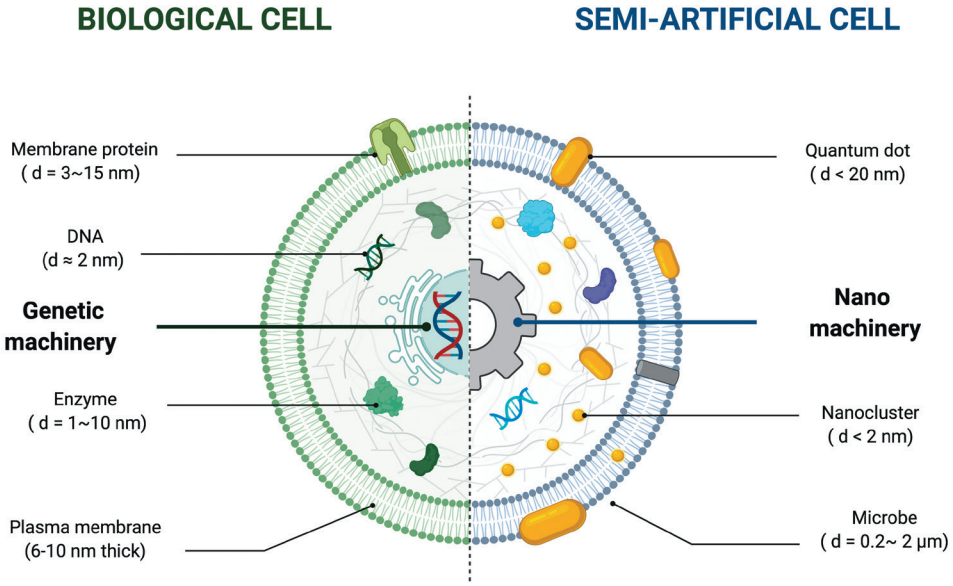


Figure 1: Nanomaterials, with parallel dimension to biological molecules, have become new machinery to engineer microorganisms. Created with BioRender.com

and inhibit the construction of efficient hybrid systems. To address this problem, we found an answer from nature. We took advantage of one character of microorganisms in responding to foreign materials. Some microorganisms can induce nanoparticles' precipitation as a protective response to toxic metal ions under mild conditions.[21] Harnessing this phenomenon, we induced the self-precipitation of inherently biocompatible CdS nanoparticles, which served as a light absorber.

A hybrid system is established by combining acetogenic bacteria, *Moorella thermoacetica*, and its biologically precipitated CdS nanoparticles (Figure 2). The photosynthesis of acetic acid from the hybrid *M. thermoacetica* and CdS was processed in two steps. First, the addition of Cd^{2+} and cysteine triggers the precipitation of CdS. Careful characterization with scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and energy-dispersive x-ray (EDX) spectroscopy mapping confirmed the precipitation of membrane-bound CdS nanoparticles with a few nanometer diameters. Second, sunlight excites these membrane-bound CdS nanoparticle to generate electrons. As these light-generated electrons travel through the bacterium, they interact with multiple enzymes, triggering a cascade of reaction that eventually turns CO_2 into acetate, a feedstock for valuable chemicals. The *M. thermoacetica*-CdS hybrids produced photosynthetic acetate from CO_2 with 2.44±0.62% quantum yield. (Quantum yield reflects the bacterium's ability to make acetate for each photon input.) In the absence of either light or CdS, *M. thermoacetica* did not produce acetate. Considering the lower quantum yields (0.2-1.6%) from plant and algae, *M. thermoacetica*-CdS PBS provides a novel and promising route for solar-fuel conversion.[22]

We naturally encountered a fundamental question "how could the photo-generated electrons transfer from CdS to the bacterium?" The mechanism of charge-transfer from electrodes to bacteria has been investigated on several species of bacteria. Interestingly, membrane-bound proteins can transfer electrons across the cell membrane by directly interfacing with electrodes.[23] However, the semiconductor-to-bacterium photoelectron transfer mechanism had not been primarily studied. Given the translucent and light-activated characteristics of CdS, we applied transient absorption (TA) and time-resolved infrared (TRIR) spectroscopies to lift the veil. Two electron transfer pathways were found between *M. thermoacetica* and CdS: (1) Photo-induced electrons transfer into those energy-transducing enzymes, stimulating acetate generation at a short-time scale (3 h). (2) Electrons also move into membrane-bounded hydrogenase, which generates molecular H_2 as powerful reducing equivalents to drive acetate production at a long-time scale (24 h).[24] We are quite excited about these new findings as they demonstrate, besides genetic mining and proteomics, the conventional spectroscopic methodology could also extract significant insight from complex biotic-abiotic hybrids. They ultimately become the rational frame for us to design the next generation of PBS.

Gold nanoclusters, bacterium took a surprising shine to. To improve the photosynthetic quantum yield, we planned to place light-absorbers inside the microbes. A nanocluster made of 22 gold atoms was selected for its ultra-small size: a single Au_{22} nanocluster (AuNC) is only 1 nm in diameter, allowing each cluster to slip through the bacterial cell wall. AuNCs also possess chromophore-like discrete energy levels with high light absorption capacities and luminescence, which qualify them as great light capturers. We added AuNCs to *M. thermoacetica* in its exponential growth phase to incorporate AuNCs into bacterium cells. Successful incorporation was evidenced by strong photoluminescence emission from AuNCs across the whole bacterium under structure illumination microscopy. By incorporating AuNCs into the cell, we effectively streamlined the solar-to-electricity conversion process with the CO_2 reduction pathway inside the bacteria. The *M. thermoacetica* and AuNCs hybrids produced 33% more acetate production than previous *M. thermoacetica* and CdS hybrids. The higher overall quantum yield of 2.86 ± 0.38% indicates we effectively streamlined the electron transfer process for the CO_2 reduction pathway inside the bacteria. Besides, we also notice that AuNCs are biocompatible light absorbers. They can eliminate reactive oxygen species, which yields high bacterium viability of *M. thermoacetica* and AuNCs hybrids.[25]

Nanowires based photosynthetic biohybrid community. In nature, bacteria tend to adhere to the exposed surface and aggregate to obtain structural and functional benefits. These groups of microorganisms that share a common living space are defined as a microbial community.[26] To target a microbial community, several centimeters in size, we decided to integrate acetogenic *Sporomusa ovata* (*S. ovata*) with silicon nanowire electrodes. The large surface area (~ cm^2) of

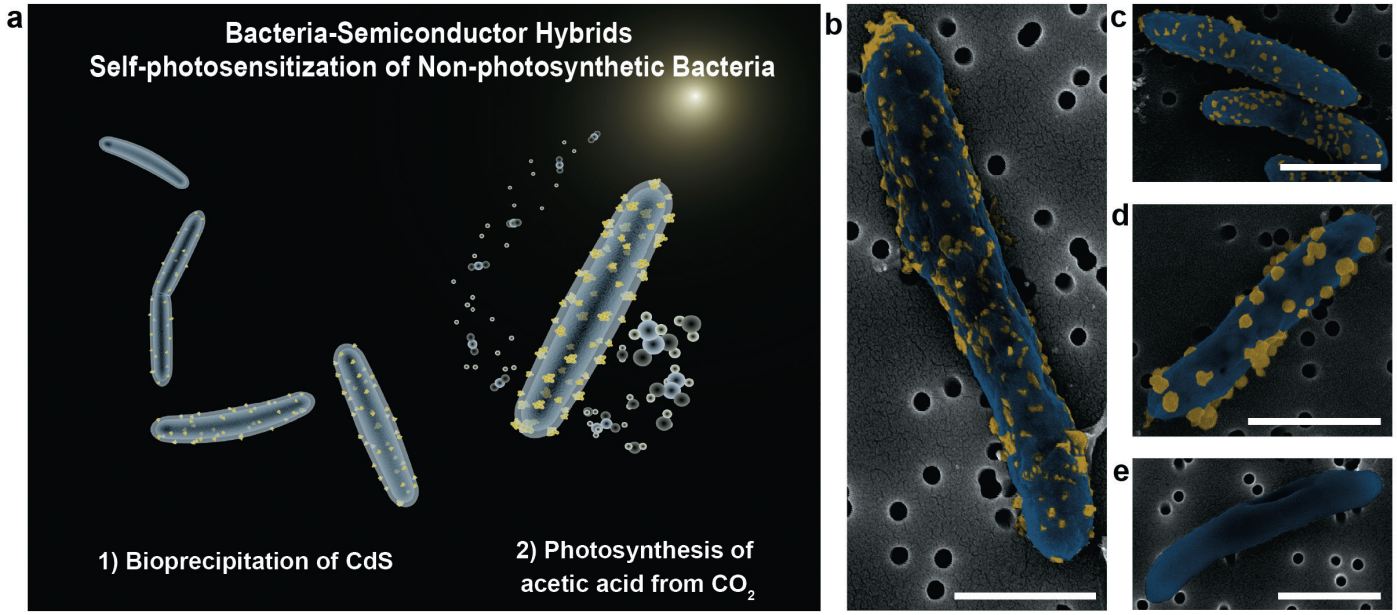


Figure 2: *M. thermoacetica*-CdS hybrids system. (a) showing the photosensitizing of *M. thermoacetica* by bio-precipitation of CdS. (b, c) SEM showing the *M. thermoacetica* with bio-precipitated CdS. (d) showing large CdS particles obtained after additional ripening. (e) CdS free *M. thermoacetica*. Scale bars 1μm. Reprinted with permission from Sakimoto et al. ©2016 AAAS.

the silicon wafer (Figure 3) supports bacteria to aggregate. The nanowires' dimensional geometry, which is close to the rod-shaped cells, provides an efficient structure to assist electrons and nutrition exchange (Figure 4).

S. ovata have been well documented for microbial electrosynthesis. The Lovely group first paired acetogenic *S. ovata* with a graphite cathode, facilitating direct electron transfer to the bacteria and reduced CO_2 into carbon compounds. The Faradaic efficiency of acetate, the main by-product of the WLP from *S. ovata*, was found to be over 85%.[20] (Faradaic efficiency reflects the bacterium's ability to make acetate for each electron input). In 2015, our group integrated this biocatalyst with silicon nanowire electrodes. The high surface area of silicon nanowire electrodes allowed higher biocatalysts loading per unit reactor volume. At the same time, the semiconductor electrodes functioned as light absorbers and converted sunlight directly into electricity. This system could be entirely operated under sunlight without external electricity input and achieve a cathodic current density of ~0.35 mA/cm^2 at approximately 90% Faradaic efficiency.

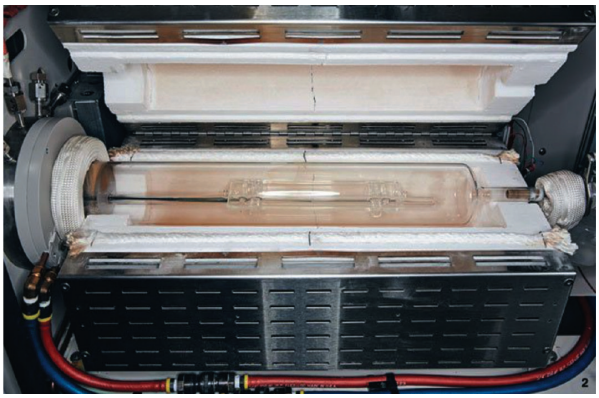
Bacteria are known to survive as a diverse community. Therefore, they can exchange metabolic by-products between species. The formation of synergistic multispecies consorts could minimize the loss in metabolites exchange, representing a highly effective energy exchange pathway in nature. Inspired by nature, we used acetate as a feedstock to be upgraded to value-added carbon products by genetically engineered *E. coli* (Figure 4). As a proof of concept, solar-generated acetate was fed to *E. coli*, which converted acetate into value-added multicarbon products, such as *n*-butanol, polyhydroxybutyrate (PHB), and isoprenoid compounds. Although the metabolic interaction is not reciprocal, this system foreshadows possible opportunities in pairing distinct bacteria together to catalyze complex reactions.[27]

Promoting healthy living by tuning pH. Nanowire arrays created a micro-environment between microbes. By calculating the local pH around the nanowires, we noticed the electrolytes became alkalized during electrolysis (Figure 4). The resulted alkaline environment collapses the electrochemical gradient across the membrane, which could impair the ATP generation. To fix this problem, we decreased the initial bulk electrolyte pH and increased buffering capacity. A clear transition of bacteria from the top aggregation to the close-packed structure was observed under SEM. With such high bacteria loading density, the acetate current could be improved to ~0.65 mA/cm^2 with a Faradaic efficiency of 85~95%. The product's final titer could be around 1.7–2.0 g/L after a week-long stable acetate production with a solar-to-chemical efficiency of ~3.6% efficiency.[28]

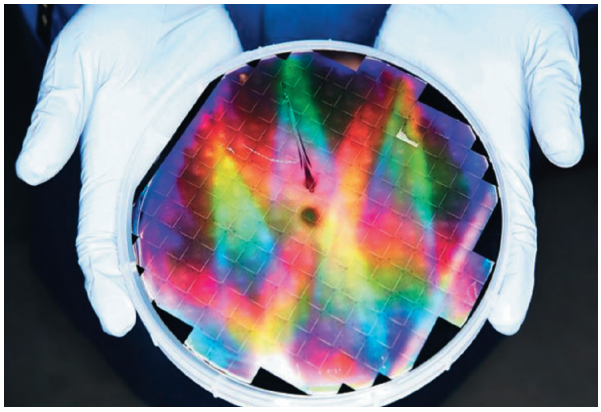
Making a photosynthetic biohybrid system

Constructing photosynthetic semiconductor biohybrids allows us to bring unique inorganic characteristics to organic microbes, which provides a renewable solution to solve the energy problem and mitigate climate change.

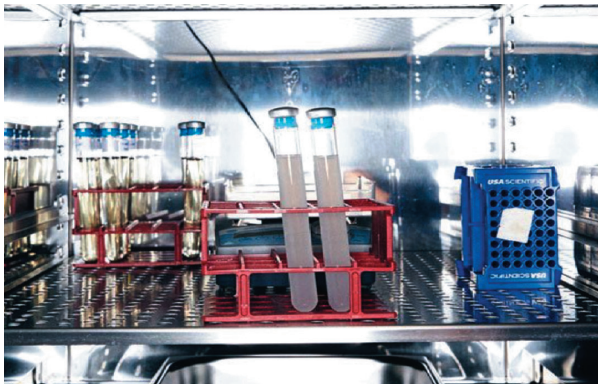
1 Silicon nanowires are grown from gaseous precursors flowing through this reactor.



2 Silicon nanowires can also be etched from larger surfaces such as this 6" silicon wafer. It gets cut into pieces that serve as electrodes inside the device.



3 Bacteria in this icubator will be seeded on an electrode to act as living catalysts.



4 Inside this device, light powers the reaction, which converts carbon dioxides into fuels. The tubing allows CO_2 gas to enter the system continuously for days.

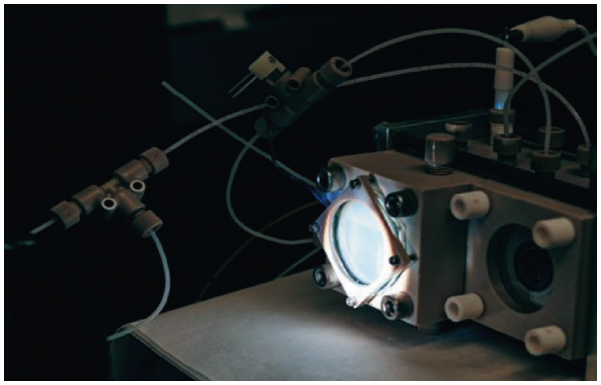
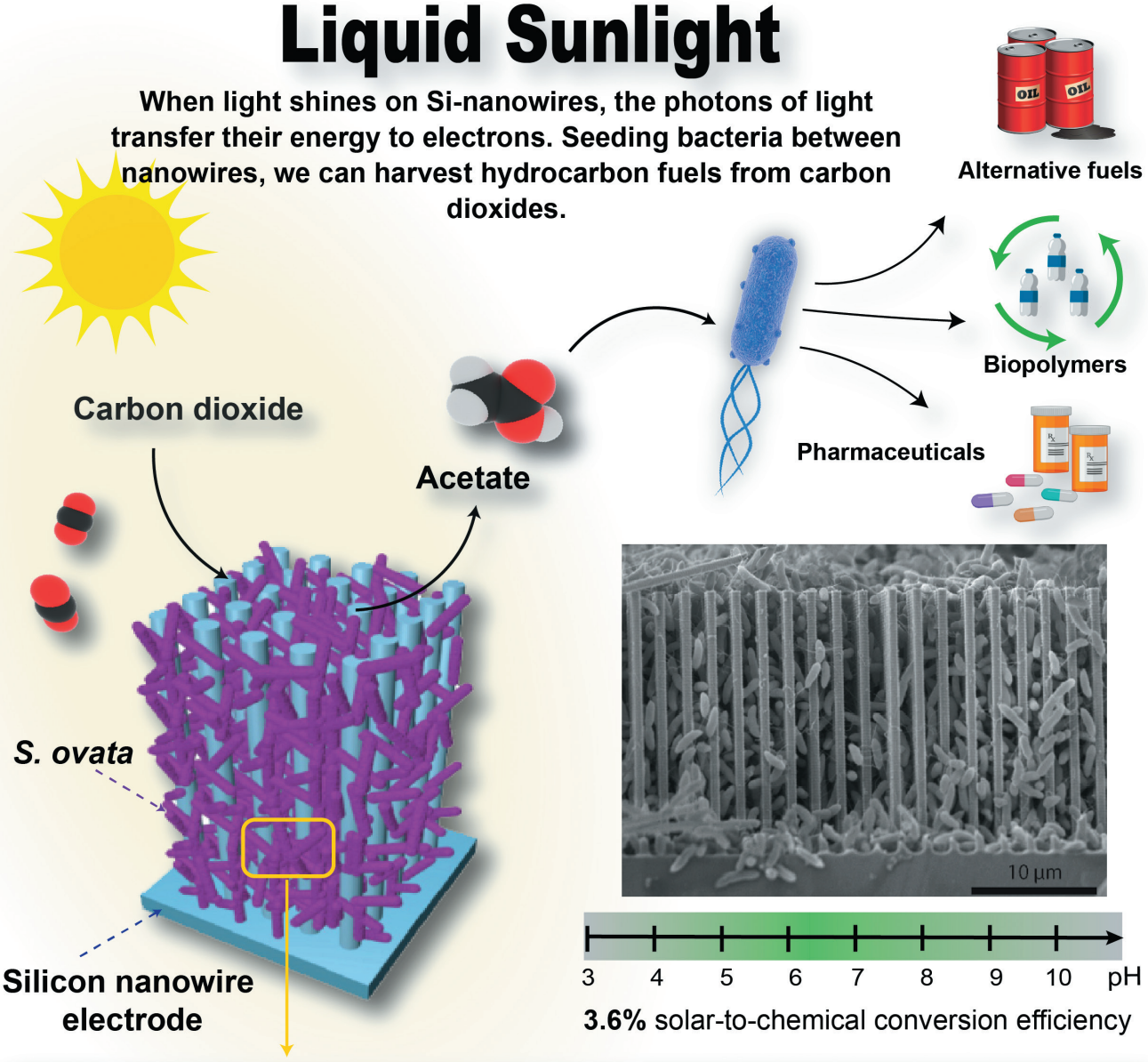


Figure 3. Making a photosynthetic biohybrid system. Reprinted with permission from MIT Tech Review. Image credit: Katherine Bourzac

Liquid Sunlight

When light shines on Si-nanowires, the photons of light transfer their energy to electrons. Seeding bacteria between nanowires, we can harvest hydrocarbon fuels from carbon dioxides.



Acetogenic bacteria, *S. ovata*, live from converting two molecules of CO_2 to acetate via the **Wood-Ljungdahl pathway**, which is one of the oldest biochemical pathways for CO_2 fixation. Naturally, *S. ovata* grow by oxidation orgainc compounds or hydrogen to obtain reducing equivalents. Coupled with Si-nanowires, *S. ovata* obtain reducing equivalents from solar energy.

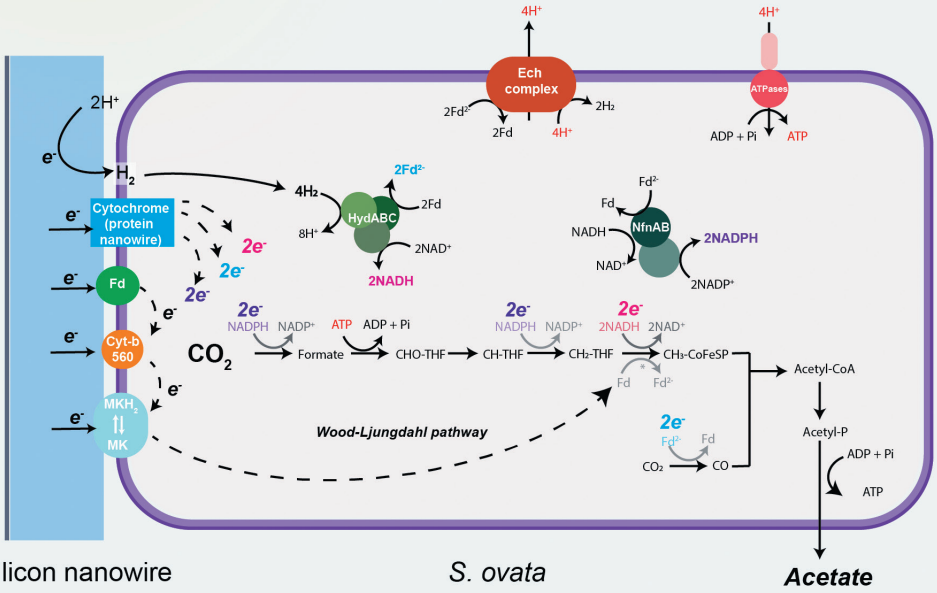


Figure 4: Liquid sunlight. Created with BioRender.com. The Wood-Ljungdahl pathway was adapted from Ref [19].

Electron and energy profile of PBS. In acetogenic bacteria, the WLP pathway for acetate synthesis consists of two separate branches: the methyl-branch and the carbonyl branch (Figure 4). In the carbonyl branch, one molecule of CO_2 is reduced to CO (2e-) via the carbon monoxide dehydrogenase/acetyl-CoA synthase (CODH/ACS). In the methyl-branch, the first reaction is reducing one molecule of CO_2 to formate (2e-). The formyl group is then bound to tetrahydrofolate (THF), yielding formyl-THF with ATP hydrolysis. Water is split off to yield methenyl-THF, which in turn is reduced to methyl-THF via methylene-THF (4e-). The methyl is eventually transferred via a corrinoid iron-sulfur protein (CoFeSP) to the CODH/ACS. This bifunctional enzyme fuses the bounded CO (from carbonyl group), the methyl group (from the methyl branch) with CoA to form acetyl-CoA.[29] At this point, bacteria have activated inert CO_2 and realizing C-C bonds at low energy input (one ATP). Acetate is generated with one ATP from acetyl-CoA, where CoA only has a catalytic function. The overall reaction is summarized as:

$2\ CO_2 + 8\ [H] \rightarrow\ CH_3COOH + 2\ H_2O$

where [H] is reducing equivalent ($1e^- + 1H^+$).

The next question to ask is "where do the electrons come from?". When light illuminates the semiconductor nanowires/nanoparticles, the photo-excited electrons will be generated at the semiconductor/electrolyte interface and are fed to the associated microorganisms across the cell membrane. These free electrons are highly active. They can also react with water to generate H_2 and reduce redox proteins on the cell membrane. Inside the bacteria, 4 molecules of H_2 are oxidized by a soluble hydrogenase (HydABC) to generate 2 molecules of reduced ferredoxin ($2e^-$) and 2 molecules of NADH ($2e^-$). An enzyme named transhydrogenase (NfnAB) further interconverted one molecule of reduced ferredoxin and one molecule of NADH to generate 2 molecules of NADPH ($2e^-$). NADH, NADPH, and ferredoxin (Fd^{2-}) are electron carriers in WLP.[19] In methyl-branch, both reduction of CO_2 to formate and methenyl-THF to methylene-THF depend on NADPH. The NADH contributes to the reduction of methylene-THF to methyl-THF, and the reduced ferredoxin assist in CO_2 reducing to CO. Although it is still unclear how those electrons entered from membrane proteins are involved in CO_2 fixation, they play important roles as reducing equivalents.

Finally, all the creatures on earth comply with two requirements to sustain: biomass production and energy conservation. So far, we have mapped out how acetogenic bacteria fix CO_2 to produce biomass. The last question becomes how they conserve energy. A proposed mechanism is the membrane-bound, potentially ion-translocating enzyme, energy-converting hydrogenase (Ech) catalyzed exergonic electron transfer from reduced ferredoxin to generate a chemiosmotic gradient that is used for ATP generation.[19]

Conclusion

We aimed to combine biocatalytic machinery's strengths with synthetic materials to establish semi-artificial photosynthesis in the past ten years. We have converted a non-photosynthetic bacterium to carry out artificial photosynthesis by integrating light-harvesting materials with acetogenic *M. thermoacetica*. Meanwhile, we employed nanowire electrodes to construct photosynthetic biohybrid communities, which produced high-value chemicals from CO_2. The illustrated biohybrid approaches play to the strengths of each component: the replication, self-healing and specificity of whole organisms and the remarkable solar energy capture of semiconducting nanomaterials. PBSs are exciting examples for the conversion of sunlight into liquid fuels and value-added chemicals (C_{2+}). Fundamentally, the photosynthetic function of this PBS originates from a "photon-in, C-C chemical bond-out" materials/biology interface that spans multiple orders of magnitude both in the length and time scale.

Our achievements demonstrate the synthetic material could be functionally coupled to microbes in a fully integrated fashion, which will result in microbes having desirable functions and characteristics. Inorganic materials bring unique optical and electrical properties to the host microbes, which genetic technology cannot. Leveraging nanotechnology's rapid development, we have observed and characterized PBSs with a series of microscopic and spectroscopic techniques. These techniques bring us a direct and vivid understanding of semi-artificial microbes. There is good reason to believe nanotechnology has excellent potential to create complex, robust, and reliable engineered bacteria. These smallest creatures may one day allow us to resolve the most pressing problems of pollution, energy, and hunger. ◆

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