Hybrid Inorganic-Microbial Systems: A New Direction For Solar-To-Fuel Conversion

Yiming Wang Literature Seminar October 26, 2017

The energy appetite of our global society is enormous. The annual total global energy consumption is about 15TW, among which 85% comes from fossil fuel[1]. Even though the fossil fuel reserve on earth is abundant, it is not a renewable energy source. Besides, burning fossil fuel generates CO_2 which will cause greenhouse effect[2]. Renewable energy making use of solar energy, wind or water power is emerging as a promising alternative to fossil fuel. However, renewable energy is still not cheap enough to replace the fossil fuel completely. Moreover, most of the renewable energy can not be converted into direct fuel that can be readily used in our daily life. Therefore, it is imperative to develop technology that can make renewable energy into a direct fuel[3].

Among all the renewable energy source, solar energy is the most promising one. The total solar energy that can reach the earth each year (120,000TW) is more than enough to satisfy the global energy demand (15TW). However, we can directly collect only a small part of the total solar energy (0.009TW). Therefore, solar energy still has huge potential that is underdeveloped[4].

Both nature and human has their own way to utilize the solar energy. Natural photosynthetic organism can convert solar energy to biomass making use of water and CO_2. Their solar-to-biomass conversion efficiency is about 1%[5]. However, man-made materials like photovoltaics can convert light to electricity in much higher efficiency (18±2%) than photosynthetic organism. Moreover, photovoltaics is scalable and cost effective[6]. However, restrained by the diurnal condition, photovoltaics can only intermittently generate electricity, which is only a temporary energy source that needs to be stored properly[7]. Current methods for electricity storage include using batteries or generating hydrogen from water splitting[8]. Nevertheless, none of these energy storage technique is cheap and stable enough to compete with direct burning of fossil fuel.

Therefore, researchers have been seeking to combine the strength of nature organism and man-made materials[9]. Recently, researches about using both inorganic materials and bacteria for artificial photosynthesis has been reported. In those hybrid inorganic-microbial systems, semiconductors or photovoltaics were used for solar energy capturing, and non-photosynthetic bacteria (chemoautotroph) were used to generate liquid fuel. The principle of these systems could be considered as separating the light and dark reaction in photosynthesis and let inorganic materials to be responsible for light reaction and let bacteria do dark reaction. Inorganic materials were chosen because of their high light harvesting efficiency[10]; Bacteria were chosen because unlike nature photosynthetic organism, they can produce target liquid fuel as a waste out of their body, therefore avoid extra processing of biomass. Besides, the non-photosynthetic bacteria are also self-replicable and their metabolism pathway are easier to be engineered[11,12].

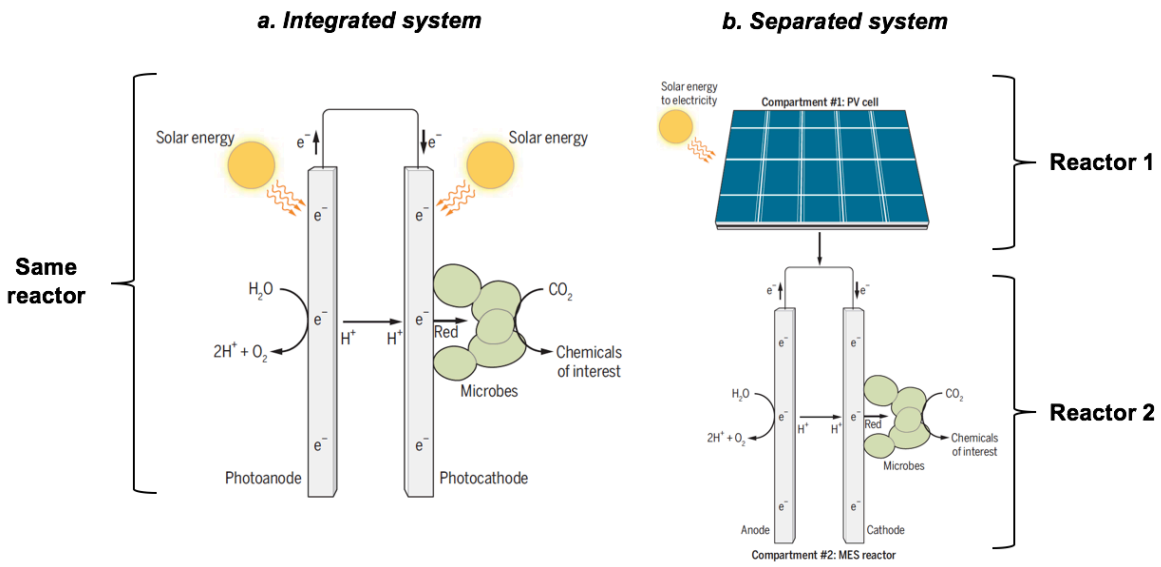

Figure 1. Two kinds of hybrid inorganic-microbial systems[13]

Currently two kinds of hybrid inorganic-microbial systems have been developed. The first is the integrated system in which a photoanode and photocathode are combined in the same reactor to convert solar energy into reducing equivalents that are directly used by the bacteria attached on the cathode to reduce CO_2 into liquid fuel. Whereas the whole setup could also be separated into two reactors, in which photovoltaic cell is used to convert solar energy into electricity, which is then used to power a separate microbial electrosynthesis reactor for CO_2 reduction[13]. The leading group on the integrated inorganic-microbial systems is Professor Peidong Yang's group in UC Berkeley, whereas on separated systems is Professor Daniel Nocera's group from Harvard university. I will introduce both of their work in the following context.

One of the interesting example of integrated inorganic-microbial systems is the semiconductor nanoarray-bacteria hybrids from Professor Peidong Yang's group[14]. In this paper, TiO_2 nanowire and silica nanowire were used as photoelectrodes for light harvesting and water splitting. Photogenerated holes in TiO_2 photoanode will be used for oxygen evolution, whereas photogenerated electrons in Si photocathode will be used for Pt catalyzed H_2 evolution. An anaerobic bacterium, *Sporomusa ovata*, was directly grow on the Si nanowire and reducing CO_2 to acetate using H_2 as the reducing equivalent. Besides light harvesting and water splitting, both TiO_2 and Si have their special benefits in the system. As a large band gap semiconductor, photoanode TiO_2 will absorb higher energy photons in the light spectrum and therefore was placed in front of the Si nanowire-bacteria hybrid to absorb UV light and protect the bacteria from photodamage. Si nanowire photocathode, on the other hand, can create local anaerobic environment because of the limited solubility of O_2 and the depletion effect at the deep groove in nanowire. This can enhance the oxygen tolerance of anaerobic bacteria and make the system compatible with ambient air.

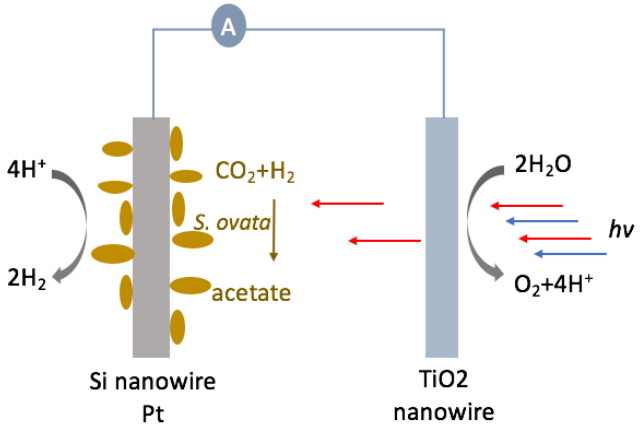

Figure 2. Nanowire-Bacteria Hybrids
Adapted from[14]

After developed some early systems, Professor Peidong Yang's group was seeking to integrate the system even more. In the paper published in Science last year[15], they described a system that integrate light harvesting, equivalent generation and CO_2 reduction on a single bacterium. They grew the acetogenic bacterium *Moorella thermoacetica* in the presence of cadmium and cysteine, which triggered the production of cadmium sulfide (CdS) nanoparticles that directly precipitated on the surface of the bacteria. The CdS nanoparticles served as light harvesters; upon illumination, CdS generated electron-hole pairs and fed electrons into the bacterial cell, where they were used by the bacteria to reduce CO_2 to acetate. Oxidation of cysteine to cystine replenished the electron pool. Most traditional nanoparticle syntheses require organic capping ligands to control the particle shape. These ligands present a barrier to charge transfer between the semiconductor and the catalyst, often requiring electron tunneling[16]. However, the ligand-free approach taken here may help to establish a favorable interface between the bacteria and the semiconductor, resulting in improved efficiencies. One of the interesting observation in this system is that when the bacteria were under simulated sunlight with 12 hours' light-dark cycle, they kept producing acetate even when there was no light. This might be attributed to the accumulation of reducing species like NADP or acetyl-CoA in the bacteria. This is different from the previous system where H_2 was used as the reducing equivalent of the bacteria which can not accumulate because of their limited solubility in water. One of the challenge of this system addressed by the author is its light sensitivity. Without the protection of CdS nanoparticles, the bare bacteria immediately died when exposed to light. Therefore, the growth of the bacteria was largely restrained by the CdS nanoparticles, which can not self-replicate along with the bacteria.

Unlike integrated hybrid inorganic-microbial systems, the designing logic for separated inorganic-microbial system is completely different. Because commercially available photovoltaics already did a good job in converting solar energy to electricity, the goal for separated system is just to incorporate bacteria into electricity driven water splitting system so to transform hydrogen into the target fuel product. One of the leading work from Professor Daniel Nocera's group published in Science last year described a single reactor water splitting system coupled with bacteria[17]. In their systems, aerobic bacteria were suspended in the electricity driven water splitting cell and were in direct contact with both cathode and anode. The H_2 generated on cathode was used as reducing equivalent for CO_2 reduction in bacteria, whereas O_2

generated on anode was also necessary for the survival of the aerobic bacteria. This posed a challenge to catalyst selection. Both catalysts for hydrogen evolution and oxygen evolution need to operate at biological relevant neutral pH and produce minimal toxicants during catalysis. Therefore, for the oxygen evolution catalyst on the anode, they chose to use an earth abundant and self-repairing inorganic catalyst developed by their own group--CoP_i[18]. Because CoP_i was directly precipitated from Co^{2+} and phosphate buffer under constant potential, self-repairing was achieved by a dynamic equilibrium exchange between the Co^{2+} in the solution and Co^{3+} in the solid phase catalyst. Together with ROS resistant hydrogen evolution catalyst CoP alloy on the cathode, all the Co^{2+} dissociated from the catalyst will be recaptured by the CoP_i and thus minimize the toxicity of Co^{2+} to the bacteria while make up for the loss of catalyst. Besides, this paper did a preliminary scalability test by scaling up the reactor volume by ten times, the electricity-to-organic efficiency ("Organic" refers to the targeted product in the bioelectrochemical reactor) is not seriously decreased, which means this system is scalable. Moreover, because this system incorporated aerobic bacteria, it could operate in ambient air.

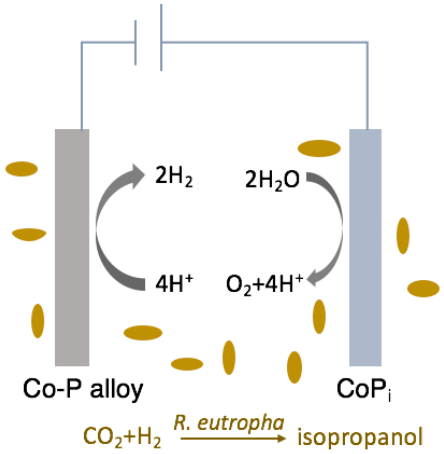

Figure 3. Water Splitting-Bacteria System
Adapted from[17]

As summary, integrated system has higher efficiency and selectivity compared with separated system. This is because the intrinsic efficient metabolism pathway of anaerobic bacteria as well as the integration of light harvesting and CO_2 reduction minimize the intermediates that could lower the efficiency. However, the integrated systems are more light sensitive and air sensitive, the culturing system could be very demanding. Therefore, they can be very hard to scale up. The separated system, on the other hand, are cheaper and more robust in ambient air, thus could be easier to scale up. Even though the efficiency of separated systems could be partially compromised by the O_2 respiration of aerobic bacteria, this can be made up by the cheap and abundant electricity generated from photovoltaics.

In conclusion, developing hybrid inorganic-microbial system is still a relatively new area. All the paper published so far are only prove-of-concept and need to be optimized on both inorganic materials and microbial engineering. For inorganic materials, more efficient and biocompatible catalysts for HER and OER need to be developed. Besides, incorporating commercially available photovoltaics cells with the system remains to be realized. On microbial engineering side, new metabolism CO_2 reduction pathway that can avoid using H_2 as intermediate and generate more value-added chemicals need to be achieved. This area still needs

close collaboration between material chemist and microbial engineers to make it more competitive and practical.

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