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Systems Materials Engineering Approach for Solar-to-chemical Conversion

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Solar-to-chemical (STC) production using a fully integrated system is an attractive goal, but to-date there has yet to be a system that can demonstrate the required efficiency, durability, or be manufactured at a reasonable cost. One can learn a great deal from the natural photosynthesis where the conversion of carbon dioxide and water to carbohydrates is routinely carried out at a highly coordinated system level. There are several key features worth mentioning in these systems: spatial and directional arrangement of the light-harvesting components, charge separation and transport, as well as the desired chemical conversion at catalytic sites in compartmentalized spaces. In order to design an efficient artificial photosynthetic materials system, at the level of the individual components: better catalysts need to be developed, new light-absorbing semiconductor materials will need to be discovered, architectures will need to be designed for effective capture and conversion of sunlight, and more importantly, processes need to be developed for the efficient coupling and integration of the components into a complete artificial photosynthetic system.

System-level planning is increasingly important for the development of modern materials science[1]. Materials science has evolved over the past decades so that there is now an increasing need for efforts from the various subfields of materials chemistry and physics to come together to solve grand challenges in energy conversion and storage. Today, materials and system design for novel energy conversion and storage applications requires significant attention towards interfaces between different materials components[1], as very often these interfaces are rate-limiting for energy transfer, and consequently limiting the overall energy conversion efficiency.
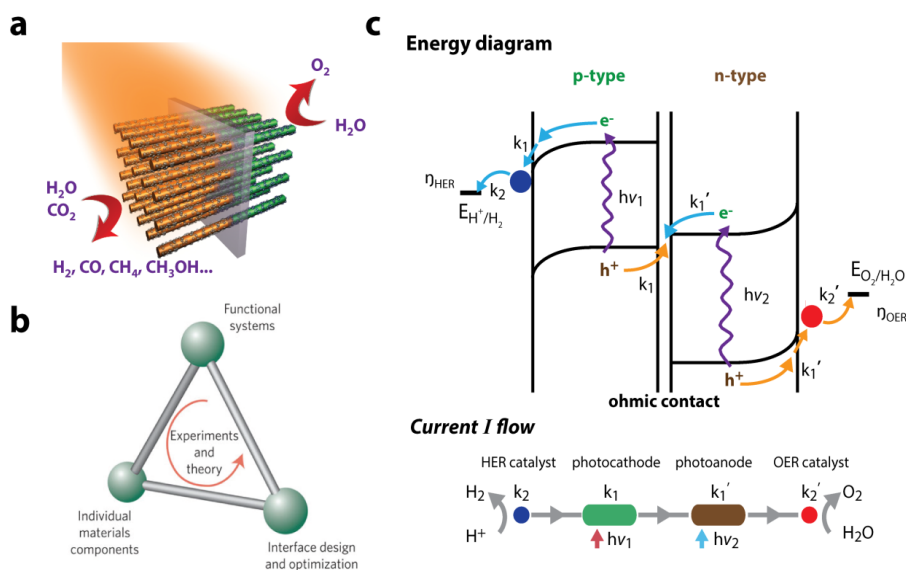

Figure 1 Semiconductor nanowires for artificial photosynthesis of value added chemicals. A schematic standalone device based on nanowires is shown in (**a**), which captures many of the features in natural photosynthesis. Its energy diagram under "Z-scheme" is depicted in (**c**), using water splitting as an example. In an ideal situation, the flux of charge carriers at different components, including the photocurrent from light absorbers (k_1, k_1') and the TOF from electrocatalysts (k_2, k_2'), should be comparable to ensure maximum efficiency. Because of the interrelated nature of the components in artificial photosynthesis, a system-level consideration is needed to consider the balances among the various components, and further device optimization should be based on such consideration (**b**). Panel (**a**) and (**c**) reproduced with permission from Ref. 2, copyright © 2014 American Chemical Society; Panel (**b**) reproduced with permission from Ref. 1, copyright © 2012 Nature Publishing Group.

Let's start the discussion with the following design of a solar-to-chemical (STC) generation system (Figure 1). [1,2] For a typical STC generation process, there are a couple of fundamental reactions that one can think of. The simplest one is solar water splitting while CO_2 reduction can produce different final products depending on number of electrons involved. To make these reactions happen efficiently, we will need to consider several processes synergistically.[2] One will need to worry about light-absorbing semiconductors and designs of suitable heterojunctions for charge separation. It is important that the semiconductor electrodes have high minority carrier mobilities so that photo-excited charges can migrate efficiently towards catalyst/electrolyte interfaces where oxidation or reduction would happen. The length scale of the materials design spans from atomic/molecular level, to nanometer, micrometer, and all the way up to macroscopic device level. The time scales for many of the processes involved also covers many order of magnitudes, from femtosecond for light harvesting/charge generation, to millisecond or second for chemical reactions on the surface (Figure 1). Such complexity in the materials design for this solar-to-chemical conversion process is indeed challenging!

First of all, there is something we can learn from nature. Nature can do all of these with remarkable ease and provides an exquisite archetype. Natural photosynthesis is not only a source of oxygen, food and fossil fuels, but can capture roughly 100 out of the 178,000 terawatts solar energy striking on the earth daily with an overall efficiency typically less than 1%.[3,4] This accounts for approximately ten times the amount of energy that is produced and consumed by humans all over the globe. In plants, photosystem I and II are responsible for the two light-capturing events and cover essentially the entire visible part of solar spectrum. These two light absorption systems generate enough photovoltage or driving force to move the two reactions forward, one is water oxidation, and the other is CO_2 reduction. Even though the efficiency of the natural photosynthesis is not that high for its own good reason, the physics of coupling light absorbers with functional catalysts is quite useful when one tries to develop artificial materials and systems for solar water splitting or CO2 reduction.

One basic concept, photochemical diode, was proposed back in late 70s.[5] This so-called photochemical diodes basically captures the essence of what is happening in natural photosythetic systems. Within this original design, two small bandgap semiconductors were used, one is a *p*-type semiconductor serving as photocathode, the other side is a *n*-type semiconductor serving as photoanodes. Additionally an ohmic contact exists in between these two semiconductors (Figure 1). When a system of such two light-absorbers is in contact with electrolyte, effectively two liquid junction photoelectrochemical cells are established.[6] Each of these two semiconductor/electrolyte junctions will generate their own photovoltage, and the combined photovoltage will provide sufficient driving force to carry out the proton/CO_2 reduction and water oxidation.

Theoretically, one would expect high energy conversion efficiency from such dual light-absorber approach.[7,8] By using two small band gap semiconductors, photons from the whole solar spectrum can be captured and convereted into photocurrent. The resulstant theoretical photocurrent output can be readily approaching and above 20 mA/cm^2. Assuming all of this photocurrent are used for chemcial reaction, theoretically solar energy conversion efficiency ~24% can be expected. This is one of the major advantages of using two semiconductor photoelectrodes within this photochemical diode concept. In reality, when we examine this fundamental design carefully, it turns out to be quite challenging to construct such device with reasonable efficiency. In one aspect, light capture and charge separation in solid-state semiconductors typically happen in the femtosecond time scale; while the chemical reaction typically turns over in the order of magnitude of milisecond or even second. Such an inconsistence of time scales implies that the expected photocurrent (in the form of minority carrier) from sunlight may not be efficiently converted into the flux of chemical reaction. Subsequently, the matching between the solar flux and catalytic activity is a big challenge.[2]

Now, let's first take a look at the issue of matching solar flux to the catalytic activity. A commercially viable STC device should reasonably provide 10 mA/cm^2 photocurrent,[8] which corresponds to delivering about 600 electrons onto a 1-nm^2 flat surface every second. This leads to an important interface issue, since these photo-generated charges have to be passed

onto the catalysts on the surface so that energy can be stored into chemical bonds. In the other word, the turnover frequency (TOF) of the catalysts has to match with the output photocurrent from the photoelectrodes. With an expected current output of 10 mA/cm^2 from the semiconductor, the catalysts located in the area of 1 nm^2 surface will need to be able to process 600 electrons every second accordingly, otherwise the overall efficiency of the STC device will suffer.

Such consideration leads us to revise the original photochemical diodes concept[5] and attempts to remove this obstacle.[9] In the revised design, we have replaced the planar electrode with a high surface-area nanowire array (Figure 1a), which effectively reduces the required flux of chemical reaction on the electrode surface. More importantly, using semiconductor nanowire array electrodes is beneficial due to their high carrier mobility and short distance that minor carriers have to travel in order to reach the electrolyte interface.[9] In this way the issue of matching solar flux with TOF can be removed or at least significatnly alleviated. Assuming the nanowire array has 100 times more surface area to load the catalysts, effectively the 10 mA/cm^2 photocurrent can now spread over a surface of 100 times larger, resulting lower effective operating current and subsequently lower electrochemical overpotentials. Because of the unique capability of stacking the catalysts in third dimension, the requirement of catalyst TOF for solar flux matching can be decreased by orders of magnitude, which will greatly facilitate the construction of a fully integrated photochemical diodes loaded with functional catalyst. As shown more quantitatively in Figure 2, the increase of roughness factor (the ratio between surface area and the projected electrode area) leads to a reduced requirement of overpotentials, which is certainly a significant improvement upon the planar design. While an increased surface area could be accomplished in many forms, the single-crystalline nanowire morphology provides a well-controlled platform for quantitative investigation of the catalyst requirements, at the same time providing a direct current path for charge collection with high carrier mobility. This sheds new light on the fundamental properties of the interface between the electrocatalysts and semiconductor light absorbers.
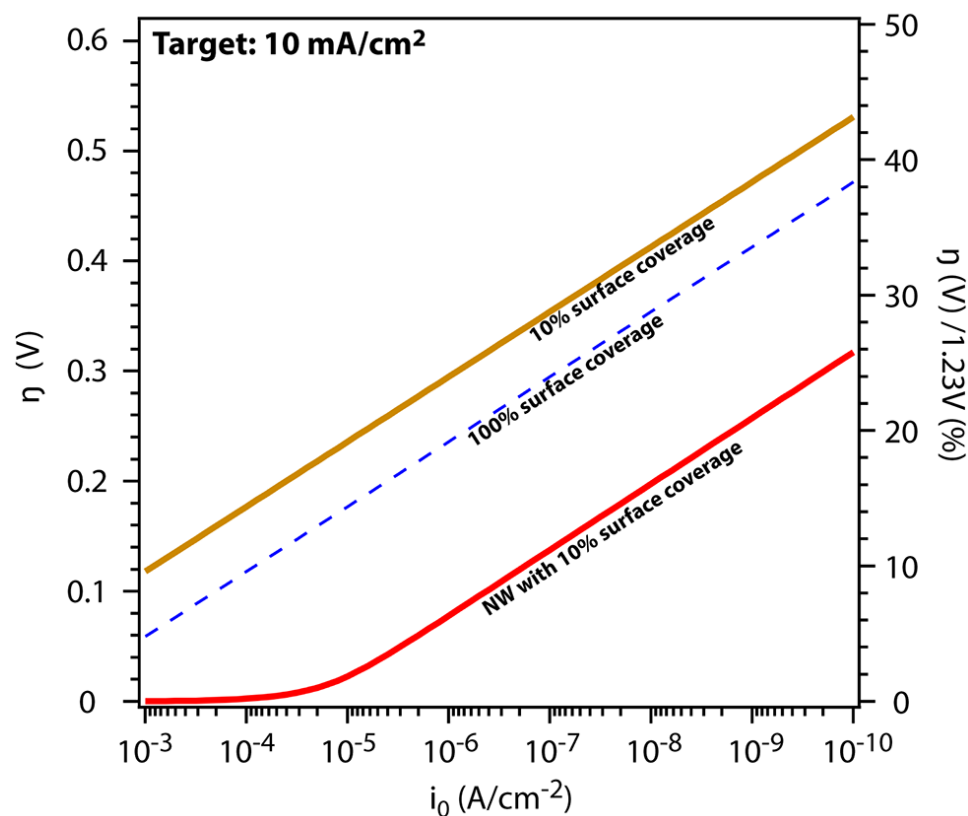
Figure 2 An examination of the flux matching between electrocatalysts and light-absorbers. Here, the required overpotential η (left y-axis) to satisfy a charge flux of 10 mA/cm² is plotted against the exchange current density i$_0$ (x-axis) of a planar electrode. The dashed blue curve represents a simulation for one electrode with 100% surface coverage of an electrocatalyst, assuming a 59 mV/dec Tafel slope in the Bulter-Volmer equation. The solid yellow curve represents the same electrode but with only 10% surface coverage. The benefit of nanowires is shown by the solid red curve, which is the simulation for one electrode with 10% electrocatalyst coverage, but with a roughness factor of 1000. The required η is significantly reduced, which is also illustrated by calculating the ratio between the overpotential η and 1.23V, the thermodynamic energy required to split water (right y-axis). Assuming negligible catalytic activity from the semiconductor surface and negligible catalyst-support interaction, the loss of overpotential is not dependent on the semiconductor used. Reproduced with permission from Ref. 2, copyright © 2014 American Chemical Society

With this concept in mind, we quantitatively investigated the required loading of Pt nanoclusters on Si nanowire array photocathode for the hydrogen evolution reaction (HER).[10] As a typical model system, Pt is still the standard HER electrocatalyst used at the photocathode. And it is worthwhile to investigate the lower limits of Pt loading on Si photocathodes under the desirable charge flux for practical applications. Taking advantage of the precise mass-loading control of atomic layer deposition (ALD), a highly conformal coating of Pt nanoparticles with tunable sizes ranging from 0.5-3 nm was deposited onto Si nanowire array photocathodes (Figure 3). The electrochemical and photoelectrochemical performance were measured using as little as 1 cycle of ALD Pt, which corresponds to a surface mass loading of ~10 ng/cm², or equivalently surface coverage of about 2.7% of a monolayer. Despite these low Pt loading quantities, Si nanowire photocathodes could still provide the necessary charge flux for STC conversion. Furthermore, the slope of the *J-V* curve could be directly controlled by varying the Pt mass loading in sub-monolayer quantities. By quantitatively exploring the lower limits of Pt
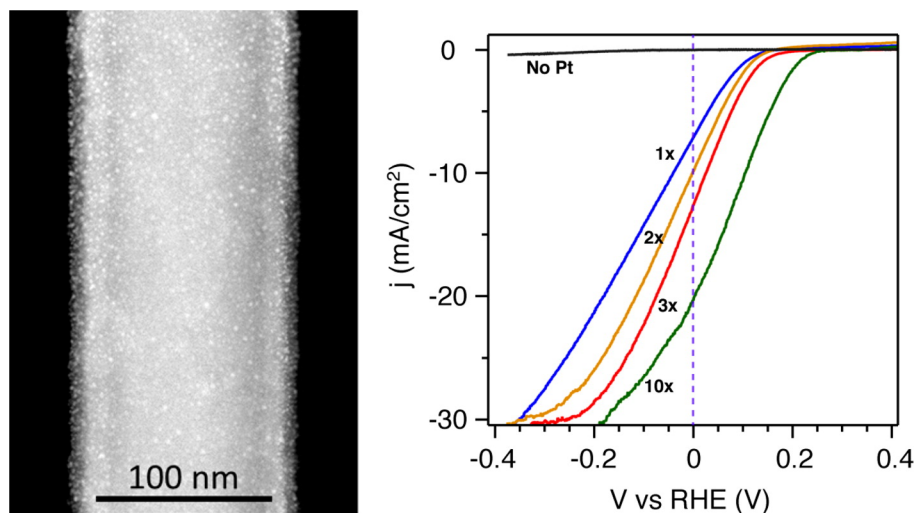
Figure 3 ALD is a versatile deposition technique that can precisely deposit electrocatalysts on high-aspect-ratio surfaces in a controllable manner (left), which helps to explore the lower limits of Pt electrocatalyst loading on p-Si nanowire array photocathodes (right). The electrode is tested under 100 mW/cm^2 simulated AM1.5G illumination, with 0.5 M H$_2$SO$_4$ electrolyte. Reprinted from ref 10. Copyright 2013 American Chemical Society.

co-catalyst loading on high surface area nanowire photoelectrodes, we can establish a general approach for minimizing the cost of precious metal co-catalysts for affordable, efficient solar-to-fuel applications.

With this revised overall design in mind, a system level of planning for materials synthesis and assembly is required.[1] First photocurrents from the photoanode and photocathode have to match, based on the effetive circuit diagram (Figure 1c). Second their combined output photovoltage has to be sufficient to drive the two half reactions. Last but not least, catalysts loaded onto these high surface area arrays has to have suitable TOF to match with the current generated by the nanowire photoelectrodes.

For the photocathode, Si [11] (E$_g$ = 1.1eV) and InP [12] (E$_g$ = 1.3eV) have been reported to generate high current densities with photovoltages of greater than 500mV. Therefore, the development of photocathodes should focus on reducing the raw material usage and fabrication costs, for example via solution-phase synthesis of semiconductor nanomaterials.[13] Comparatively, the photoanode deserves more attention.[14] Although compound semiconductors with junction engineering and corrosion protection have shown promising progress,[15] a more cost-effective candidate of photoanode, such as oxide or nitride based materials, should be considered. At present there is no oxide- or nitride-based photoanode device capable of providing a photocurrent of greater than 10 mA/cm^2, while at the same time providing adequate photovoltage to couple with the photocathode. Advanced material engineering, including improving the material quality as well as designing an appropriate nanostructure, is expected to contribute to this exciting field.

In the above discussion, we considered individual components for artificial photosynthesis, with a focus on the constraints of current matching and corresponding improvements needed. But in the end, an integrated system with interconnected components is the key concept to be

addressed.[16] It is critical to assemble all the pieces together and demonstrate overall STC conversion under such an integrated system. It also acts as the final milestone for consideration of a STC application for commercialization. Furthermore, an integrated standalone system is fundamentally intriguing, in order to mimic the micro- and nanoscopic spatial control of natural photosynthesis. In chloroplasts, the components of photosynthesis are carefully arranged:[3] photosystems I and II are arranged side-by-side on the thylakoid membrane with the electron transport chain between them for efficient charge transfer, while the reduction and oxidation catalytic centers are spatially separated to minimize the undesirable back-reaction of the photosynthetic products. Achieving such nanoscopic spatial control is a crucial aspect of our pursuit of artificial photosynthesis.

Using Si and TiO_2 nanowires as building blocks, a proof-of-concept STC conversion nanodevice was demonstrated for solar water splitting (Figure 4).[16] Equipped with knowledge of the various
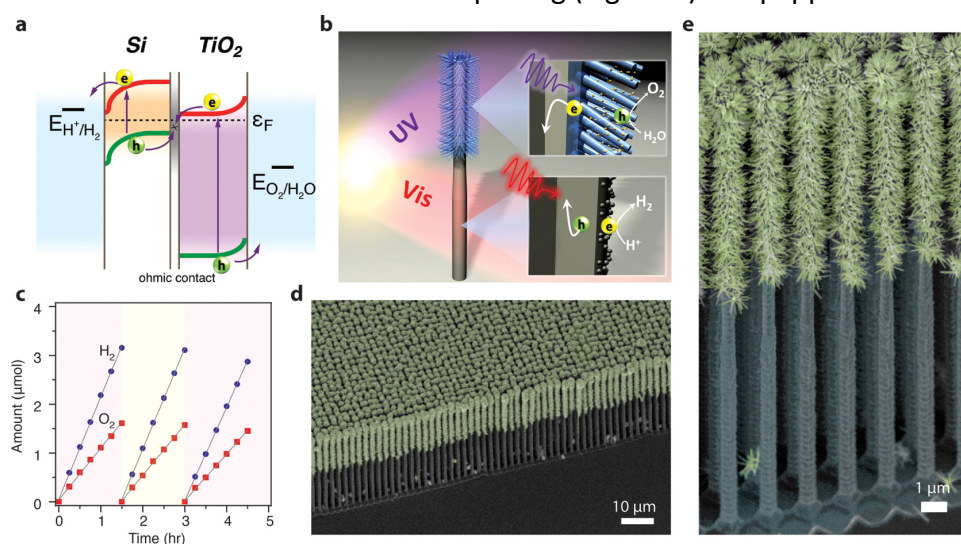

Figure 6 A proof-of-concept fully integrated nanosystem for direct solar water splitting was demonstrated. (**a**). The tree-shaped heterostructure is designed based on different material properties of Si and TiO_2 photoelectrodes (**b**), which leads to unassisted water splitting (**c**). The overall integrated structure contains spatial separation of the photocathode and photoanode (**d**,**e**), analogous with natural photosynthesis. Reproduced with permission from ref. 16, copyright © 2013 American Chemical Society.

interfaces involved,[17,18] a tree-shaped nanowire-based heterojunction device was constructed and loaded selectively with HER and OER electrocatalysts. Compared with the Si nanowire photocathode, the smaller feature size of the TiO_2 nanowire photoanode is motivated by the smaller minority carrier diffusion length in the photoanode and the slower reaction kinetics of OER, in accordance with the design principles of nanowire photoelectrodes.[19] As discussed above, the bottleneck of the constructed system is the TiO_2 photoanode, whose band gap is in the UV region (3.0 eV for anatase). Despite this limitation, unassisted solar water splitting was observed with 0.12% solar-to-fuel efficiency, comparable with natural photosynthesis.[3]

This proof-of-concept device leaves much room for improvement and welcomes performance enhancements by updating individual components with the latest improvements, allowing for a modular design approach.[1] By implementing the advances discussed earlier, continued efficiency improvement is expected. Specifically, the balance between electron flux from the light-absorber and the TOF of the electrocatalyst requires development of electrocatalyst

materials, especially for the OER and CO_2 reduction. Ideally, an overptential of less than 100mV at 10 mA/cm^2 is desired. Nanowire electrodes can help accomplish this by providing a large surface area for catalyst loading. They can also provide a well-controlled system for fundamental studies such as tuning the interface between electrocatalyst and underlying semiconductor light-absorber. The requirements for high photocurrent and photovoltage output rely heavily on photoanode research, which can be further supplemented by improvement of photovoltage output in the photocathode. Nanowire structures provide opportunities for new material discovery, as well as improving the performance of existing materials. Based on these expectations, it is evident that semiconductor nanowires can function as essential building blocks and help to solve many of the issues in artificial photosynthesis.[9]

To wrap up on this discussion, we think in next 5-10 years, there are two levels of ressearch that we have to focus on. The first is to explore advanced components, including both light-absorbers and electrocatalysts, which are stable, scalable, and earth-abundant. The second is to achieve an efficient coupling and integration of these advanced components into a complete artificial photosynthetic system. Moreover, it is important to bear in mind that these two levels of researches are mutually related: the development of indiviudal components requires a blueprint of the integrated system; and the assembled device not only relies on the performance of individual building blocks but also provides feedback for further optimization. When conducting this line of research, one will find that these seemingly disparate disciplines all become integral parts of the solution. And there is no doubt that the ultimate solution of artificial photosynthesis or STC totally relies on insights not just from traditional materials science, but also from chemistry, physics, electrical engineering, mechanical engineering, and other research fields that may be beyond my imagination.

Now here is the take-home message from this solar-to-chemical conversion research. While the paradigm of traditional materials science tetrahedron is still highly relevant in many areas of materials research, it is now increasingly important to think and plan research at the systems level for both experimental and theoretical efforts (Figure 1b). It is no surprise that we are on a similar path as how biology has evolved: with continued advance on the understanding of individual components in biology, the interaction and feedback between these compoents turn to be critical and the disciplie of system biology is born. Similarly, systems materials engineering,[1] which emphasizes the study of the interactions between individual components of a system, and how these interactions give rise to the function and performance of the final system, is now emerging and will provide significant guidance in the advancement of energy storage and conversion research.

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