

Semiconductor Nanowires for Artificial Photosynthesis

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Abstract

In this perspective, we discuss current challenges in artificial photosynthesis research, with a focus on the benefits of a nanowire morphology. Matching the flux between electrocatalysts and light-absorbers, and between individual semiconducting light-absorbers, are two major issues to design economically viable devices for artificial photosynthesis. With the knowledge that natural photosynthesis is an integrated nanosystem, individual building blocks of biomimetic artificial photosynthesis are discussed. Possible research directions are presented under an integrated device design scheme, with examples of our current progress in these areas. Coupling all of the components together, including electrocatalysts, light-absorbers, and charge transport units, is crucial due to both fundamental and practical considerations. Given the advantages of one-dimensional nanostructures, it is evident that semiconductor nanowires can function as essential building blocks and help to solve many of the issues in artificial photosynthesis.

Keywords: Nanowire, Artificial Photosynthesis, Solar Water Splitting

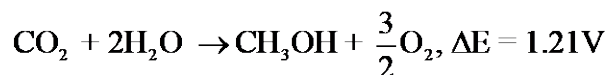
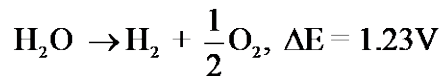
Introduction

The energy challenges facing humanity in the 21st century are of great importance. The human population has surpassed 7 billion, and technology is expected to provide ~20-40 terawatts (TW) of power for a global population of ~10 billion by 2050.^{1,2} Despite this dramatic growth in demand, the majority of primary energy sources utilized globally are derived from non-renewable resources.^{2,3} Furthermore, the use of resources such as fossil fuels leads to pollution at the local and global level,^{3,4} affecting the health and quality of life on the whole planet.

To address these challenges while maintaining an increasing standard of living will require a dramatic shift in the way that energy is harvested, converted, and stored. In particular, the large solar resource ($\sim 10^5$ TW)^{3,5} can provide a means to sustainably meet the energy needs of humanity. However, the intermittent nature of this resource implies that energy storage will be a key component to a future renewable energy infrastructure.⁵ In particular, the conversion of solar energy directly into chemical fuels such as hydrogen or hydrocarbons provides a flexible storage option that can be used to supply the transportation sector, as a backup power supply in the case of blackouts, or for grid-scale load leveling. The overall process would be carbon-neutral, and thus has additional benefits for the environment and public health.

The direct conversion of sunlight into energy stored in chemical bonds, termed as artificial photosynthesis,^{2,3,6-8} mimics the natural photosynthesis process occurring in plants.⁹ The original demonstration of this concept dates back to the 1970s, using TiO₂ as a light absorber to split water into H₂ and O₂.¹⁰ The overall process consists of two parts: light absorption and generation of excited charge carriers, and the utilization of photo-excited carriers to drive catalytic reactions. The former process typically uses semiconductors to absorb photons and generate carriers, which are subsequently separated at either a semiconductor/electrolyte interface^{11,12} or an embedded solid junction.^{13,14} The photo-generated carriers subsequently move to a catalytic center to drive oxidation/reduction reactions in the solution. Therefore, artificial photosynthesis is an integrated system that combines multiple different processes (Figure 1).¹⁵

For the practical application of solar fuels as a renewable energy resource, high solar-to-fuel conversion efficiency is necessary.^{5,16-18} The energy input requirement for such a process is fundamentally limited by the nature of the chemical reactions involved. As show below, the thermodynamic potential needed to drive the reaction of interest is typically greater than 1V.



In addition to the thermodynamic potential, an electrochemical overpotential is needed to overcome the kinetic barriers for a high reaction rate.¹⁹ This voltage restriction limits the choice of materials to wide band gap semiconductors if only one light-absorber is utilized.²⁰ To circumvent this problem, a dual light-absorber approach has been proposed, based on separate semiconductor materials that harness different portions of the solar spectrum. This process, known as “Z-scheme”,^{6,21-24} mimics the natural photosynthetic process of two-photon absorption to drive the overall electrochemical reaction. Within such a process one semiconductor acts as a photocathode for reduction, while the other acts as a photoanode for oxidation. In these electrodes, photo-excited minority carriers move to the solution for a catalytic reaction, while majority carriers recombine at the interface connecting these light absorbers (Figure 1c). The flexibility of material choices, along with the use of visible wavelengths for energy conversion, makes “Z-scheme” one of the most promising directions for solar-to-fuel conversion.^{16,17,20}

Due to the integrated nature of the components in artificial photosynthesis, an efficient solar-to-fuel device should operate in harmony such that there is no significant bottleneck hindering the charge flux. Under the “Z-scheme” approach there are two major issues that should be addressed: i) matching the flux between current-generating light-absorbers and the current-consuming electrocatalysts, *i.e.*, is the electrocatalyst capable of handling the chemical reactions efficiently and selectively under the flux of photo-excited carriers? ii) matching the flux between different light absorbers, *i.e.*, could both the photoanode and photocathode provide the necessary photocurrent flux for practical applications, while maintaining a desirable voltage output? These two questions are currently not fully

answered, due to the inadequacy of catalyst and material development, and the lack of structural design based on a device integration approach. The introduction of nanomaterials and nanostructures, particularly a one-dimensional nanowire morphology,^{25,26} could contribute to tackling these issues in a variety of ways.²⁷⁻³⁰ This perspective describes some of our current progresses in semiconductor nanowires for artificial photosynthesis, and considerations for future research directions in this field.

Nanowires for studying the electrocatalyst/light-absorber interface

To address the issue of flux matching between the electrocatalyst and light-absorbers, nanowire array electrodes can provide a reduced overpotential for solar-to-fuel conversion, and are an ideal platform for a quantitative investigation of the interface between electrocatalysts and light-absorbing semiconductor junctions. It has been proposed that to be economically viable, a solar-to-fuel energy conversion efficiency of between 5~10% is desired.^{5,17,18} This corresponds roughly to a photo-generated carrier flux of $\sim 10 \text{ mA/cm}^2$ under one-sun irradiation, which is equivalent to approximately $620 \text{ el}/(\text{nm}^2 \cdot \text{sec})$ (electrons per square nanometer per second). Typical materials have a surface atom density of $\sim 10^{15} \text{ atom/cm}^2$, or equivalently $\sim 10 \text{ atom/nm}^2$. This sets a $\sim 62 \text{ sec}^{-1}$ lower limit of turn-over frequency (TOF) for the electrocatalyst on a planar electrode, assuming that all surface atoms are electrochemically active. Practically, a higher TOF is needed because not all surface atoms are catalytic centers, and a reduced co-catalyst loading may be desirable to avoid blocking the photon flux and reduce cost. To achieve a higher current density (and therefore a higher TOF), an increased

overpotential is required based on the Butler-Volmer equation,¹⁹ which leads to a reduced energy conversion efficiency.

Upon examining several electrocatalysts studied for the hydrogen evolution (HER),³¹⁻³⁶ oxygen evolution (OER),³⁷⁻⁴³ and CO₂ reduction,⁴⁴⁻⁴⁶ a non-negligible overpotential loss may be present owing to an inadequate TOF (Figure 2). This implies that increased effort is necessary to develop advanced electrocatalysts, especially for the OER and CO₂ reduction. One actively studied approach is to develop biomimetic structures as catalytic centers.^{39,47,48} Alternately, with presently available electrocatalysts, the introduction of large surface area electrode such as nanowire arrays can alleviate this mismatch. As shown in Figure 2, the increase of roughness factor (the ratio between surface area and the projected electrode area) reduces the required overpotential by decreasing the surface flux of charge carriers. 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, while also providing a direct current path for charge collection with high carrier mobility. This sheds light on the fundamental properties of the interface between the electrocatalyst and semiconductor light absorber beyond previous investigations.

With this concept in mind, we quantitatively investigated the required loading of Pt nanoclusters on p-Si nanowire array photocathodes for the HER.⁴⁹ Despite the recent progress of earth-abundant electrocatalysts for HER,^{36,50,51} Pt is still the standard HER electrocatalyst used at the photocathode. Accordingly, 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),⁵² a highly conformal coating of Pt nanoparticles with tunable sizes ranging from 0.5-3 nm was deposited onto p-Si nanowire array photocathodes (Figure 3). The electrochemical and photoelectrochemical (PEC) performance were measured using as little as 1 cycle of ALD Pt, which corresponds to a surface mass loading of $\sim 10 \text{ ng/cm}^2$, 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 solar-to-fuel 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 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. Further investigations to quantify the lower limits of Pt loading with different nanostructures, and to optimize the ALD Pt nanocluster interface with various photocathode materials, are desirable.

It is also important to investigate the interface between electrocatalysts and light-absorbing semiconductors. Much of the research in this area has focused on screening potential electrocatalysts and reporting the most promising performance, while few studies describe control of the charge transfer process between the underlying substrate and electrocatalyst. It is possible that besides an inadequacy of TOF, a sluggish reaction rate may arise from difficulty in charge injection from the semiconductor across the

interface to reach the electrocatalyst, or that the existence of an electrocatalyst at the semiconductor/electrolyte interface could modify the energetics of charge separation,^{53,54} Additionally, it is interesting to study nanostructures such as nanowires, which can contain surface states with distinctive reaction activities.⁵⁵ Precise co-catalyst loading,^{56,57} and a well-controlled interface to link the semiconductor and electrocatalyst are crucial to optimize performance. With their well-defined structure and large surface area, nanowires are an ideal platform for such investigation, providing quantitative information as in the case of the Si photocathode with ALD Pt nanoclusters. Furthermore, it will be intriguing to study these systems microscopically at the single nanowire or nanoparticle level.⁵⁸ In the absence of statistical variations present in large ensembles, an improved understanding of the fundamentals of photoelectrodes and electrocatalysts can be unveiled by measuring individual structures.

Nanowires for semiconductor light-absorbers

The second major issue facing present solar-to-fuel conversion devices is matching the flux between different light absorbers in the “Z-scheme”. This requires a well-designed choice of material combinations with suitable band gaps, and a low-resistance charge transfer pathway between the two light absorbers.⁵⁹ According to theoretical calculations that take into account overpotentials and other losses,^{16,17} the target band gaps for a pair of electrodes are around 1.1eV and 1.7eV for optimized efficiency. However, upon examining several typical semiconductors for PEC applications (Figure 4), the choice of available materials with band gaps ranging between 1.5eV to 2.0eV is limited. In

addition, unlike photovoltaic cells, which aim to maximize power output, the nature of the chemical reactions in artificial photosynthesis requires a minimum voltage output to drive the reaction. Therefore, not only the band gap of the materials but also the band alignment and the resultant photovoltage output of the junction are important.

For the photocathode, Si^{60,61} ($E_g = 1.1\text{eV}$) and InP⁶² ($E_g = 1.3\text{eV}$) have been reported to generate high current densities with photovoltages of greater than 500mV. Therefore, the development of photocathodes can focus on reducing the raw material usage and fabrication costs, for example via solution-phase synthesis of semiconductor nanomaterials.^{63,64} Comparatively, the photoanode deserves more attention.⁶⁵ Presently there is no stable photoanode device capable of providing a photocurrent of greater than 10 mA/cm², while at the same time providing adequate photovoltage to couple with the photocathode. This is typically observed in the use of conventional oxide or nitride materials, which intrinsically have low hole mobilities due to the localized *p*-orbital nature of the valance band.⁶⁶ Novel materials, including compound semiconductors with junction engineering and corrosion protection, should be developed for photoanode research using advanced synthesis techniques.

The introduction of a nanowire morphology could help to improve the performance of existing photoanode materials. The nanowire morphology provides a large surface area for co-catalyst loading and electrochemical reaction sites, while at the same time leading to enhanced charge collection efficiency, especially for indirect band gap semiconductors with short minority carrier diffusion lengths.^{12,26,67} For example, TiO₂ rutile nanowire

photoanodes have been well studied, and the nanowire morphology has proven to be beneficial.⁶⁸⁻⁷⁰ In particular, when care was taken to improve the surface properties of the nanowires by a thin epitaxial coating, significant improvement was observed (Figure 5a).⁶⁹

As an extension of the nanowire morphology, core-shell structures demonstrate unique advantages,^{71,72} Although single-composition nanowire electrodes improve charge separation within the band-bending region, charge transport through the electrode may still be restricted by a large resistivity of the bulk material in the core of nanowire. A core-shell configuration can alleviate this issue, by designing a photoactive shell for charge separation and a conductive core for charge collection. This could further benefit from light scattering and trapping in the shell material due to the nanowire geometry.^{73,74} Additionally, the heterojunction between two materials can provide extra photovoltage (Figure 5b), which is crucial for the successful application of a “Z-scheme” approach.^{71,75} It is likely that with appropriate structures of the nanowire morphology,⁶⁷ oxide or nitride based photoanodes can generate high photocurrent densities with satisfying photovoltage outputs.

The progress in novel material development could also benefit from the nanowire structure. Facile synthesis techniques for nanowire materials, using either gas-phase^{76,77} or liquid-phase⁶³ approaches, could help to produce materials with unique properties. Despite the limited number of materials available with band gap between 1.5eV and 2.0eV (Figure 4), this band gap range overlaps with compound III-V semiconductor

alloys that have tunable band gaps. III-V semiconductor nanowires, including GaAs,⁷⁷ GaP,^{63,64} and $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys,⁷⁸ have been prepared and applied for PEC applications. For example, we have demonstrated liquid-phase synthesis of surfactant-free GaP nanowires in large quantities,⁶³ with careful control of carrier type and concentration by adding dopant precursors during the nanowire synthesis (Figure 5c).⁶⁴ This builds up a unique pathway of low-cost III-V materials for solar-to-fuel application, which can be extended to other compound semiconductors with tunable material properties.

In addition to photocurrent requirements, the stability issue of photoanode materials, in particular the issue of photocorrosion, requires further attention. The oxidative environment at the photoanode suggests the use of a stable protection layer, especially for compound semiconductors in an aqueous electrolyte. The ALD technique,⁵² with its pinhole-free coating capability, is one promising approach for a protection layer, as demonstrated for the case of a Si photoanode⁷⁸ and Cu_2O photocathode.⁸⁰ In combination with the versatile deposition of electrocatalysts via ALD,^{56,57} a multi-layer ALD coating consisting of a protection layer and electrocatalyst sequentially is feasible, as shown in our ALD TiO_2/Pt coatings of Si NW photocathodes.⁴⁹ Additionally, the presence of ALD oxide layer could help to reduce the surface recombination therefore improve the overall performance of the nanostructure photoelectrodes, as demonstrated by the alumina coating on a hematite photoanode.⁸¹

Nanowires for integrated solar-to-fuel conversion systems

In the above discussion, we considered individual components for artificial photosynthesis, with a focus on the constraints of current matching and corresponding improvements needed. An integrated system with interconnected components is the key concept to be addressed.¹⁵ In addition to the efforts to improve individual components, it is critical to assemble all the pieces together and demonstrate overall solar-to-fuel conversion under such an integrated system. This also acts as the final milestone for consideration of a solar-to-fuel application for commercialization. Furthermore, an integrated standalone system is fundamentally intriguing, in order to mimic the microscopic spatial control of natural photosynthesis. In chloroplasts, the components of photosynthesis are carefully arranged:^{3,9,14} 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 microscopic spatial control is a crucial aspect of our pursuit of artificial photosynthesis.

Using Si and TiO₂ nanowires as building blocks, a proof-of-concept solar-to-fuel conversion nanodevice was demonstrated for solar water splitting (Figure 6).²⁴ Equipped with knowledge of the various interfaces involved,^{59,71} 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 TiO₂ 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,⁶⁷. As discussed above, the bottleneck of the constructed system is the TiO₂ photoanode, whose band gap is in the UV region. Despite this limitation, unassisted solar water splitting was observed with 0.12% solar-to-fuel efficiency, comparable with natural photosynthesis.^{3,9}

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.¹⁵ By implementing the advances discussed in earlier sections, 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 CO₂ reduction. Ideally, an overpotential of less than 100mV at 10 mA/cm² 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. Of particular importance is the protection of compound semiconductors via ALD techniques, which opens up a new avenue for photoanode development. 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.

Concluding remarks

Artificial photosynthesis, a renewable energy approach that stores solar energy in chemical bonds, is an interesting research field for both fundamental research and practical applications. While nature has evolved for millions of years to tackle the challenges of photosynthesis, we are just beginning our journey. Within this perspective we discussed current challenges in the research field. In particular, we discussed the benefits of the nanowire structure and possible future research directions, with an emphasis on design principles that are based on an integrated artificial photosynthesis architecture. Nanostructures are powerful tools for the design and realization of integrated microscopic systems, and it is possible that their use will enable practical applications of efficient and affordable solar-to-fuel conversion. Once realized, this will drastically change our use of energy resources, the life that we enjoy, and foremost the planet that we call home.

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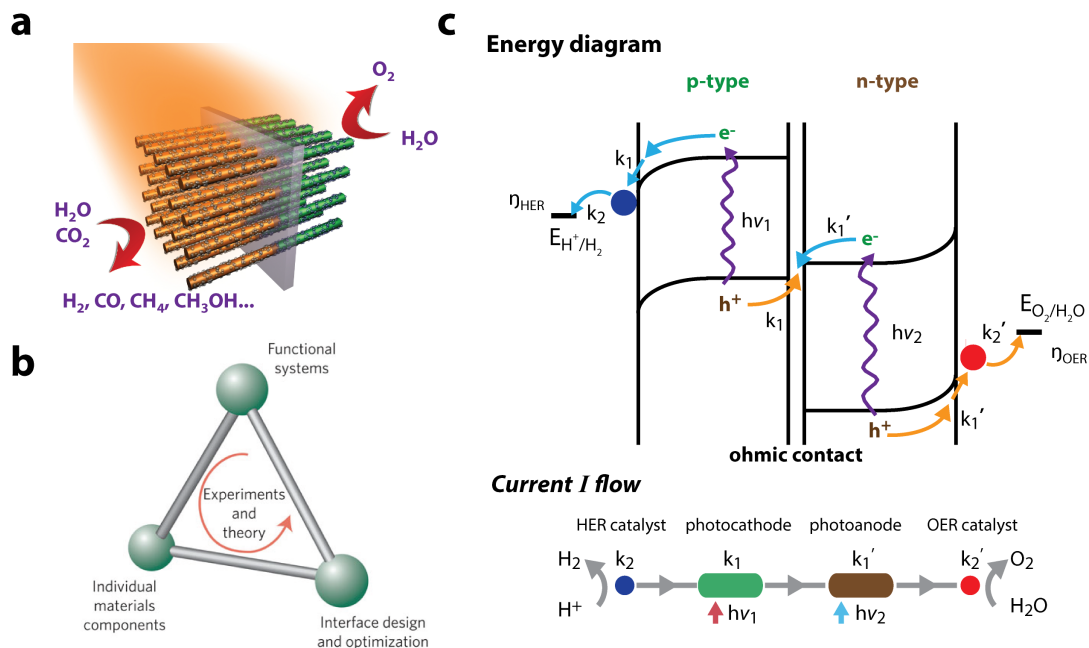


Figure 1 Semiconductor nanowires for artificial photosynthesis. A schematic standalone device based on nanowires is shown in (a), which captures many of the features in natural photosynthesis. Its energy diagram under “Z-scheme” is depicted in (c), using water splitting as an example. In an ideal situation, 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 (b) reproduced with permission from Ref. 15, copyright © 2012 Nature Publishing Group.

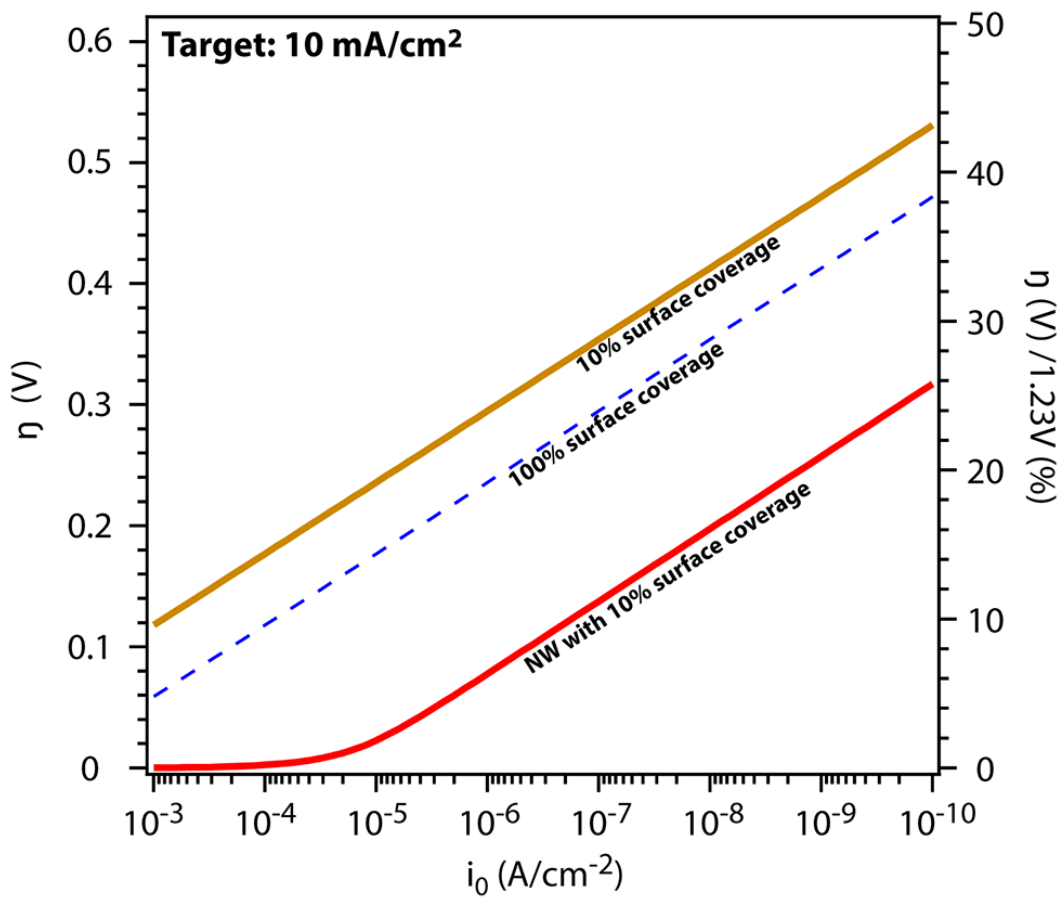


Figure 2 An examination of the flux matching between electrocatalysts and light-absorbers. Here, the required overpotential η (left y-axis) to satisfy a charge flux of 10 mA/cm² is plotted against the exchange current density i_0 (x-axis) of a planar electrode. The dashed blue curve represents a simulation for one electrode with 100% surface coverage of an electrocatalyst, assuming a 59 mV/dec Tafel slope in the Butler-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.

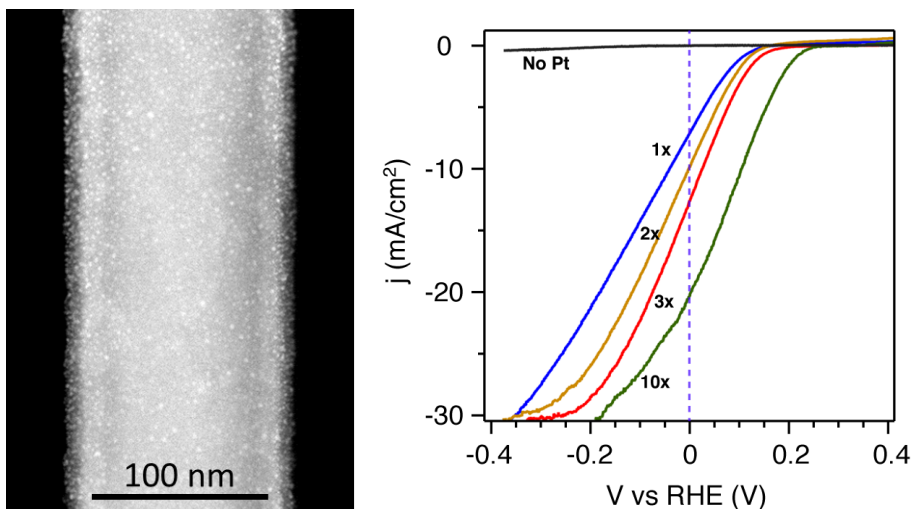


Figure 3 ALD is a versatile deposition technique that can precisely deposit electrocatalysts on high-aspect-ratio surfaces in a controllable manner (left), which helps to explore the lower limits of Pt electrocatalyst loading on p-Si nanowire array photocathodes (right). The electrode is tested under 100 mW/cm² simulated AM1.5G illumination, with 0.5M H₂SO₄ electrolyte. Reproduced with permission from ref. 49, copyright © 2013 American Chemical Society.

Theoretical photocurrent density under one-sun illumination

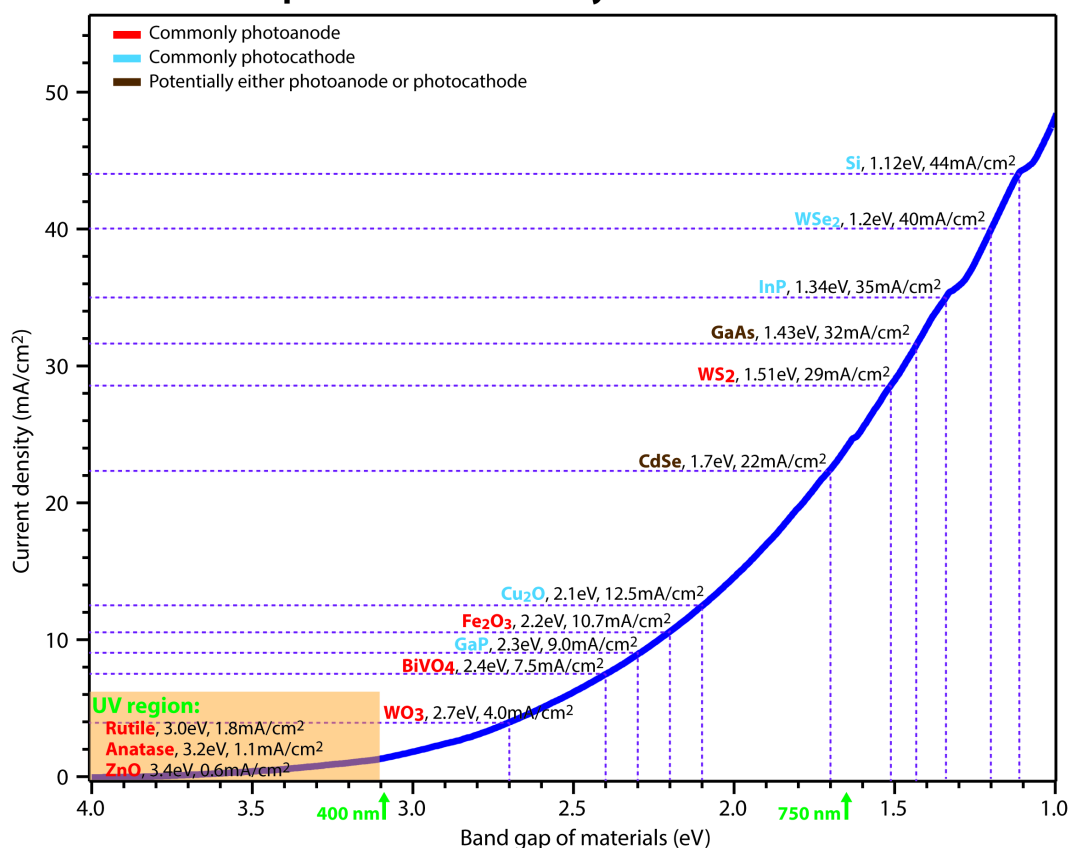


Figure 4 Theoretical photocurrent densities for semiconductors under one-sun illumination. The blue curve is the integrated photon flux at different cut-off energies, based on the AM1.5G solar spectrum (ASTM G173-03 reference). The theoretical photocurrent is calculated assuming that all incident photons above the semiconductor band gap contribute to the photocurrent. Several of the semiconductors used in solar-to-fuel conversion are also listed, along with their reported band gaps in bulk phases.⁸² The arrows at the bottom indicate the regions of ultraviolet (UV) (below 400nm), visible (400nm ~ 750nm), and infrared (IR) spectra.

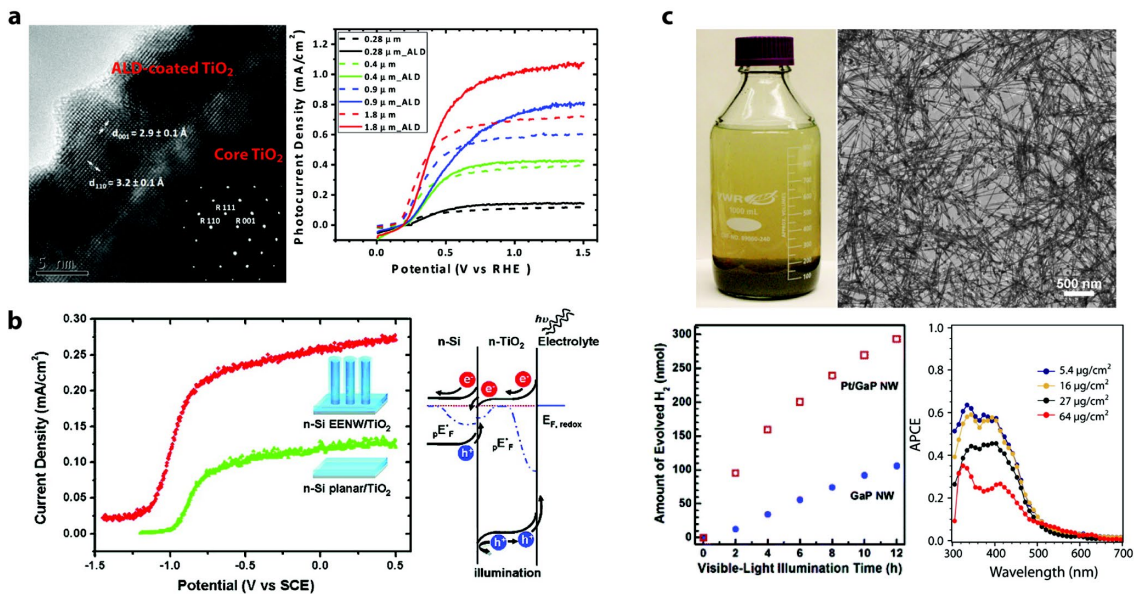


Figure 5 **a**, An epitaxial TiO_2 ALD coating on TiO_2 rutile nanowires results in enhanced photocurrent for OER⁶⁹. **b**, The heterojunction within core-shell Si/ TiO_2 nanowires leads to additional photovoltage output for photoanode applications⁷¹. **c**, GaP nanowires can be synthesized in large quantities via a solution-phase approach, and function as a low-cost photocathode material^{63,64}. Reproduced with permission from refs. 63, 64, 69, and 71, copyright © 2008-2012 American Chemical Society.

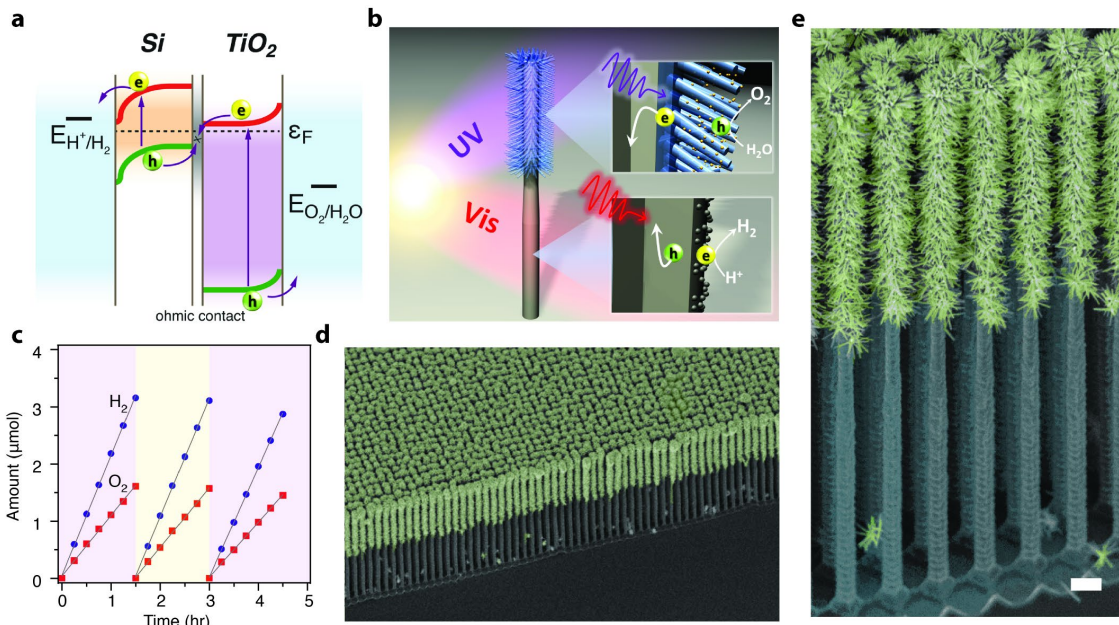


Figure 6 A proof-of-concept fully integrated nanosystem for direct solar water splitting was demonstrated²⁴. (a). The tree-shaped heterostructure is designed based on different material properties of Si and TiO₂ photoelectrodes (b), which leads to unassisted water splitting (c). The overall integrated structure contains spatial separation of the photocathode and photoanode (d,e), analogous with natural photosynthesis. Reproduced with permission from ref. 24, copyright © 2013 American Chemical Society.

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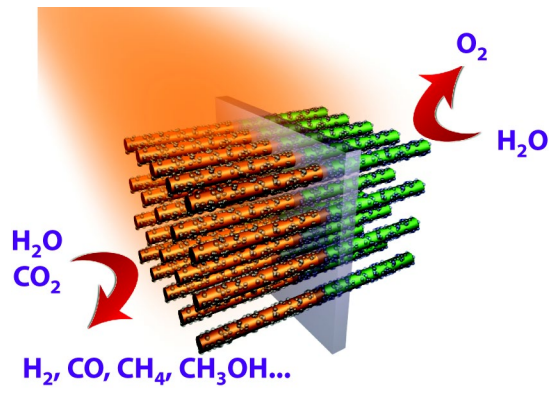
Notes

The authors declare no competing financial interests.

Acknowledgement

N.P.D. acknowledges support from the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE) Postdoctoral Research Awards under the SunShot Solar Energy Technologies Program. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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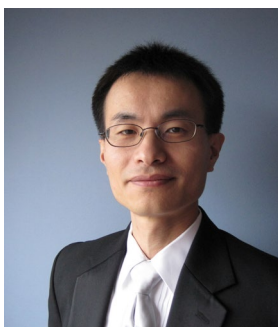
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Young Investigator Award, MRS Young Investigator Award, Julius Springer Prize for Applied Physics, ACS Pure Chemistry Award, and Alan T. Waterman Award. According to ISI (Thomas Reuters), Yang is ranked as No. 1 in materials science and No. 10 in chemistry for the past 10 years based on average citation per paper, and he has an h-index of 105. His main research interest is in the area of one dimensional semiconductor nanostructures and their applications in nanophotonics and energy conversion.