Towards systems materials engineering

Peidong Yang and Jean-Marie Tarascon

System-level planning of theoretical and experimental efforts is increasingly important for the development of modern materials science.

Materials science has evolved over the past decades so that there is now an increasing need for efforts from the various subfields of materials science and engineering to come together to solve grand challenges. Such issues were discussed at a symposium on energy at the Collège de France[1] that involved both the socio-economical stakes as well as the technological challenges. Indeed, nowhere has this become more obvious than in the area of energy storage and conversion, where it seems clear there is a trend towards an emerging new field of integrated systems materials engineering.

Over the past decade, similar developments have occurred in the biological sciences and have resulted in the emergence and rapid evolution of the field of systems biology, which emphasizes the study of interactions between the individual components of biological systems to understand how they give rise to the functionality and behaviour of the entire system[2]. Hiroaki Kitano, in a perspective written in *Science*[3], describes the philosophy of this new cross-disciplinary field by saying that "To understand biology at the system level, we must examine the structure and dynamics of cellular and organismal function, rather than the characteristics of isolated parts of a cell or organism."

In this day and age, investigating isolated components is no longer sufficient to solve the kinds of technological challenges involved in the development of an environmentally benign energy infrastructure. Very often, we have to pay considerable amounts of attention to studying the interface between individual components within a device or system. Therefore it becomes increasingly clear that as the traditional disciplinary lines continue to fade away, modern science will become significantly more integrated and correspondingly far more effective. In this Commentary we discuss a few examples from the field of energy that serve to illustrate the need for synergistic collaborations.

Artificial photosynthesis

The generation of liquid fuels via the direct conversion of solar energy within a fully integrated system is an attractive goal, but so far there has yet to be a system that can demonstrate the required efficiency and durability, or be manufactured at a reasonable cost. In contrast, nature can do all of these with remarkable ease and provide an exquisite archetype. Natural photosynthesis is not only a source of oxygen, food and fossil fuels, but it can capture roughly 100 of the 178,000 terawatts of solar energy striking the Earth daily with an overall efficiency typically less than 1%. In perspective, this accounts for approximately ten times the amount of energy that is produced and consumed by humans across the globe[4]. Natural photosynthetic systems achieve this by capturing photons from the solar spectrum with chlorophyll molecules[5] and the absorbed photons' energy is used to create spatially separated electron–hole pairs. The holes are stored by the oxygen-evolving complex in photosystem II to oxidize water to oxygen, whereas the electrons are stored in chemical bonds by photosystem I to reduce nicotinamide adenine dinucleotide phosphate (NADP) to be stored as adenosine triphosphate (ATP) and NADPH. In the following 'dark reaction', ATP, NADPH and CO_2 are used in the Calvin–Benson cycle to make food in the form of sugar and starch via the enzyme Rubisco[6].

A great deal can be learnt from the photosynthetic organisms that routinely carry out the conversion of carbon dioxide and water to carbohydrates 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. 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 robust ion-conducting membranes that are impermeable to the product fuel and oxygen must be developed (Fig. 1a).

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Several significant accomplishments have already been demonstrated on the component level, but a final solution is still far from becoming available. Fujishima and Honda's discovery[7] that TiO_2 is capable of splitting water in the presence of sunlight is truly remarkable, yet the intrinsic materials limitations associated with TiO_2 limits photon absorption to the ultraviolet portion of the solar spectrum. Tuner's embedded-junction approach[8] captures most of the solar spectrum, giving rather high solar-conversion efficiency, yet it suffers from high manufacturing costs and materials stability issues. The Miller approach of using silicon triple junctions coupled with catalysts has shown some promise[9], especially with the recent demonstration of incorporating low-cost, earth-abundant catalysts from the Nocera group[10]. However, it remains to be seen whether these essentially photovoltaics–electrolysis approaches can be made economically viable.

Additionally, strategies for the integration of individual components into a complete

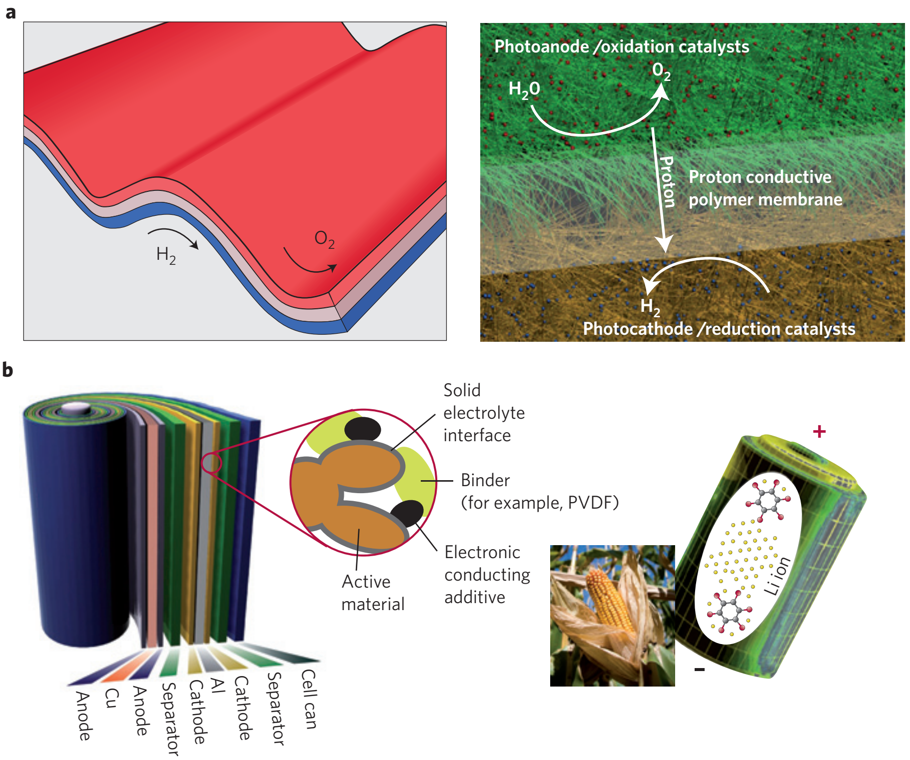

Figure 1 | Individual components within overall systems. **a**,**b**, Systems materials engineering with artificial photosynthesis (**a**) and batteries (**b**) as examples. **a**, Schematic illustration (left) and a zoomed-in view (right) of a bilayer nanowire fabric-based composite membrane for direct solar water-splitting. The top layer is a high-surface-area nanowire mesh decorated with oxidation catalysts. This part serves as a photoanode responsible for water oxidation; the bottom layer is a high-surface-area nanowire mesh decorated with reduction catalysts. This is the photocathode responsible for water reduction. **b**, Left: Schematic of a cylindrical Li-ion battery configuration showing all the layers with a zoomed-in view of the electrode material to convey its composite nature, it is made of (i) an electrochemical active material, (ii) a binder for mechanical cohesion and (iii) a carbon additive to provide electronic percolation through the electrode. Defining the correct ratio between these three components is essential for optimizing the battery performances. Right: Such electrodes can either contain inorganic active materials or organic active materials produced from biomass. Panel **b** reproduced with permisison from: left, ref. 23, © 2001 NPG; right (battery), ref. 24, © 2009 ACS; right (corn), © istockphoto/thinkstock.

and functioning system are needed. In the 1970s, Art Nozik proposed the idea of photochemical diodes[11] for the purpose of direct solar water-splitting. This idea is quite appealing as it is essentially a direct copy of natural photosynthetic systems. The central part of this photochemical diode is the coupled photocathode and photoanode, which mimics photosystems I and II in natural photosynthesis. The greatest benefit of this design is that the combined photovoltages from two small-bandgap electrodes can be used to drive the spontaneous solar water-splitting, so that a larger part of the solar spectrum can be used and higher energy-conversion efficiency can be obtained. However, this design also introduces significant challenges at the component, interface and system level, which partially explains why this concept has yet to be implemented. Examining the various interfaces in such a design (Fig. 1a) quickly reveals many important system-level issues that must be addressed. First, the current density of the photocathode and photoanode needs to be matched and that requires the discovery of small-bandgap, earth-abundant, photochemically stable semiconductors. The catalytic activity of the chemical transformation (that is, turnover frequency) has to be matched with the solar flux and current densities generated at photoelectrodes. This clearly requires the development of better catalysts with high turnover frequency and low overpotential, as well as high-surface-area semiconductor electrodes for catalyst decoration (Fig. 1a).

When it comes to the energy conversion efficiency of the final solar energy conversion device, there are again many important system-level considerations. How can a better junction be designed to maximize charge separation and minimize carrier recombination? How can good contact be made with the light-absorbing semiconductors to maximize the charge extraction? Can a better transparent electrode be developed? Can better surface structures be designed for antireflection or light-trapping purposes? Most of these issues no longer revolve around a single material component, but instead are mostly related to the interface, and therefore the problem must be evaluated holistically to develop solar cells with high energy-conversion efficiency while employing cheap and low-energy processes.

Success in developing an integrated solar fuel generator that can efficiently split water under sunlight or convert carbon dioxide to liquid fuel clearly requires scientific breakthroughs on two main fronts: The first is to discover components for light absorption, charge transport, fuel-forming and oxygen-evolving catalysis, and electrocatalysts that are made of earth-abundant materials and with scalable manufacturing processes, thermodynamically and kinetically compatible, and durable in long exposure in the field. The second is to overcome major obstacles for the efficient coupling and integration of the components into a complete artificial photosynthetic system. More importantly, we will need to expand the fundamental scientific knowledge for taking nanoscale functional units and assembling them into macroscopic functional devices, and ultimately combine them into a system that can be easily manufactured. At the system level, these seemingly disparate disciplines all become integral parts of the solution. Insights not just from traditional materials science, but also from chemistry, physics, electrical and mechanical engineering will all contribute to finding a viable solution.

Electrochemical energy storage

The field of energy storage is enjoying a similar renaissance of interdisciplinary endeavours. This should come as no surprise as the design of high-performance batteries is a problem that requires the positive and negative electrodes (both of which are a composite of a multi-component system consisting of an active material, binder and a conductive additive, Fig. 1b) to be precisely coupled with a fluid electrolyte while simultaneously optimizing the numerous resulting interfaces. Clearly the challenges for electrochemists are enormous. Understanding surface science, coating techniques, grafting methods,

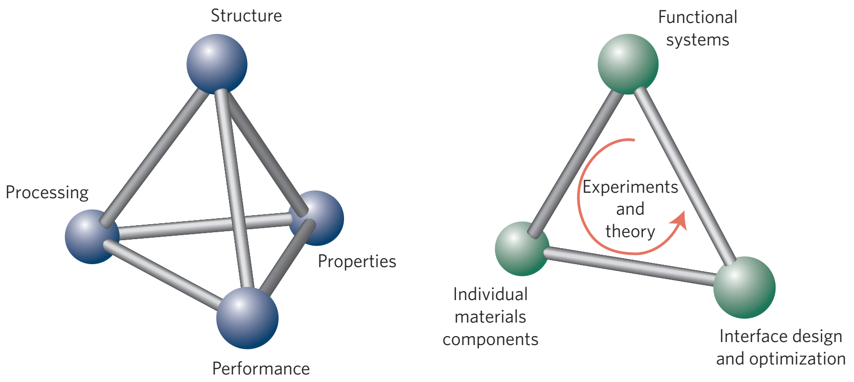

Figure 2 | The traditional materials science tetrahedron (left) versus the emerging systems materials engineering triangle (right). The traditional materials science tetrahedron emphasizes the interdisciplinary research on materials structure, processing, properties and performance. The systems materials engineering triangle illustrates the importance of system-level planning of the research efforts starting from individual components and followed by interface optimization.

or wisely designing additive organic molecules has become essential to control interfaces. Additionally, the development of *in situ* experiments that allow for direct observation of the device provide valuable information about the mechanisms of electrochemical reactions, the evolution of the interfaces, and more importantly about dynamic processes with good time and spatial resolution.

A prime example can be found in the lessons learned through the adoption of nanosizing techniques, which breathed new life into the field by circumventing charge-transport limitations in electrode materials by reducing particle size and exploiting carbon coatings[12,13]. From such an approach, compounds disregarded for several decades because of their insulating nature ($LiFePO_4$) or large volume changes (Si) have now become the most lauded materials for the next generation of batteries to power electric vehicles. This reminds us that the true value in studying materials is intimately tied to their applications, but the properties a compound possesses can never be attributed to a single factor and is instead a harmonious integration of the atomic structure, the elemental composition and the material's microstructure.

By taking advantage of recent materials innovations like nanosizing and confinement, and cross-disciplinary collaborations, there is now renewed hope in systems like Li–S and Li–air[14]. However, the reality frequently turns out to be a nightmare due to intrinsic materials limitations and the broad knowledge-base required to successfully address the issues. Fuel cells are a prime example, where the main limitation for widespread deployment is rooted in the inability to find catalysts that can outperform expensive metals like Pt to facilitate the oxygen reduction reaction. The story is the same in the development of Li–air technology, which is also hindered by sluggish kinetics at the oxygen electrode. The only way to overcome the slow kinetics of such electrodes is by applying considerable overpotentials, which then results in poor device efficiency. The design of low-cost and high-activity catalysts is therefore a critical area for multiple technologies, and mastering these reactions is absolutely necessary to achieve a sustainable energy future. Several approaches are being pursued and include: high-throughput combinatorial chemistry, revisiting the catalytic activities of various oxides such as perovskites[15], and the return to molecular organic chemistry[16].

Systems materials engineering 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.

In the 1980s, Mizushima and co-workers proposed the concept of a purely solid-state inorganic electrolyte for Li batteries[17]. Decades have passed, materials with ionic conductivities matching liquid electrolytes[18] have been found, but few have been successfully integrated into a working device due to the difficulties of controlling the interfaces and ensuring attractive energy density and rate capabilities. This is beginning to change thanks to engineering advances in spark-plasma sintering[19], which allows for a more coherent continuum between the positive, negative and electrolyte components. Yet, there are still significant challenges associated with solid-state cells, which include effectively transporting ions and electrons across these interfaces. Provided that we can minimize mechanical stresses at the interface that result from changes in the volume on cycling, significant work still remains, which will require close interactions between materials engineers and electrochemists.

The development of 'greener' and more sustainable batteries also calls for increased collaboration across disciplines (Fig. 1b). To design and develop electrodes having a minimal environmental footprint made via eco-efficient processes, chemists and biologists have been using more and more biomimetic approaches[20]. For instance, can redox-active organic molecules that are abundant in biomass be turned into attractive electrode materials? What about compounds that play a role in photosynthesis? Compounds involved in proper cellular function? Optimism must prevail as present studies relying on engineered bacteria and viruses have been successfully used[20,21] for the templated synthesis of Li-ion battery electrodes. The question, can electrode materials of the future be biologically produced, lacks a clear answer today. Therefore the design and assembly of battery components that are inspired by nature must continue to be explored, and the expertise of biologists will be indispensible.

Future innovations in the harvest and redistribution of energy will be driven by research that focuses on the integration of seemingly disparate components into the larger device. By working at the intersection of various subdisciplines, several new avenues of groundbreaking research have become available. Several inorganic materials, such as WO_3, TiO_2 or Fe_2O_3, play key roles across the fields of photoelectrolysis, electrochromics, photovoltaics and batteries. The challenge here lies in how to take advantage of these materials, which all possess tunable optical, photoelectrochemical and electrochromic properties, and whose chemistry may be compatible with the manufacture of multifunctional architectures. For instance, remarkable similarities exist between the assembly of plastic Li-ion batteries and organic photovoltaic batteries, and therefore this could be a fertile area for development of low-cost self-sustaining solar cells. Could

TiO_2 be manipulated so that conversion and storage functionalities are incorporated into a single device? Could redox amphoteric polymers be used simultaneously as the positive and negative electrode in a Li-ion cell? To promote this kind of evolution in how scientists approach complex problems, researchers must keep their minds open to new possibilities, free of the indoctrination of their respective communities.

The two examples we have discussed here illustrate the trend. Although the paradigm of the traditional materials science tetrahedron is still highly relevant in many areas of materials research, it is now increasingly important to also think and plan research at the systems level for both experimental and theoretical efforts (Fig. 2). The most recent materials genome initiative[22] is another perfect example of the pressing need for the discovery of system-level materials and their design using combinatorial and genomic approaches. The integration of computational and analytical tools together with high-throughput screening of materials should prove highly relevant for the discipline of systems materials engineering. To paraphrase the definition of systems biology, systems materials engineering 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. ❒

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