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Fuel for thought

The worlds of nanotechnology and energy meet to unveil a realm of functional materials for fuelling the challenge of low-carbon, sustainable energy.

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Increases in the price of oil, Earth's most visible energy source, create intense responses. Both the finite resources of fossil fuels and the threat of climate change have sensitized society and inspire innovation in the scientific community. In earlier oil crises, chemists reacted sensitively and provided, through catalysis, strategic technologies for non-nuclear alternative energies. This time, however, other scientific disciplines are rising to the energy challenge, creating an interdisciplinary wave of activity.

The properties of nanomaterials can be exploited for energy purposes: their surfaces have active sites, allowing heterogeneous catalysis, whereas the inner interfaces and global size control the charge andelectron-transport properties for electronics(Fig. 1). Nanotechnology is therefore a major contributor to the resolution of the sustainable energy problem. An excellent insight into the state-of-the-art nanosciencebased alternative-energy technologies was provided at a European Science Foundation conference held in the Ötz Valley, Austria, in June 2008. The topics and applications discussed included photovoltaics, hydrogen production, fuel-cell batteries, thermoelectrics, environmental catalysis, and energy-saving applications such as organic light-emitting diodes (Fig. 1).

Despite the efforts spent on the physical aspects and metrology of nanoscience, there remains an enormous need for fundamental research into understanding nanoscale effects and hence realizing the rational design[1] of materials for energy applications. Intensive discussions illustrated this for the desired properties of titania[2] (TiO_2), a solar-energy-harvesting material that has been studied for a number of years. One of the remaining questions is the mechanism of charge generation in TiO_2. The defects that create the electronic charge required for energy applications are usually assumed to originate from bridging oxygen vacancies. Recently, high-resolution scanning tunneling microscopy and photoelectron spectroscopy experiments on TiO_2 surfaces were used to demonstrate that it is more likely to be Ti interstitials that are responsible for the defect state in the bandgap[2]. Nevertheless, it is difficult to predict which real structure creates the optimum material for free charge-carrier diffusion and exciton activation. Richard Schaller[3] (Los Alamos National Laboratory) and Arthur Nozik[4] (National Renewable Energy Laboratory, University of Colorado) described the effects of multiple electron–hole pairs (multiexcitons) on the transport efficiency of dye-sensitized solar cells (DSCs). Generation of multiexcitons has a positive effect on the transport efficiency of solar cells only if the semiconducting structures are of nanoscopic dimensions. Creative designs of nanocomposites are therefore necessary[5] to exploit the effect, as metallic transport efficiency is required as well as a semiconductor structure that generates multiexcitons.

The importance of harvesting solar energy was again highlighted by Michael Grätzel[6] (Ecole Polytechnique Fédérale de Lausanne) and Peng Wang[7] (Changchun Institute of Applied Chemistry). Wang described DSCs that are based on organic optoelectronic materials. Grätzel emphasized the need for sensitizers with high molar-extinction coefficients and detailed a DSC with an inorganic Ru-based sensitizer and a non-volatile liquid electrolyte. The device remained stable for 1,000 hours; an unprecedented demonstration of long-term stability. The efficiency of DSCs can now cross the 10% limit, which means that applications in window panes could become realistic.

The contradictory role of chemical and structural defects in being either beneficial or detrimental for the function of photovoltaic systems is caused by the conflicting requirements for charge separation and carrier transport. The number of conflicting properties to be optimized is increased further when surface reactions are added, such as in water-splitting systems, or for the inverse, the fuel cell[8]. Despite being the initiators of unwanted solid-state dynamics in photovoltaic materials, active surface sites

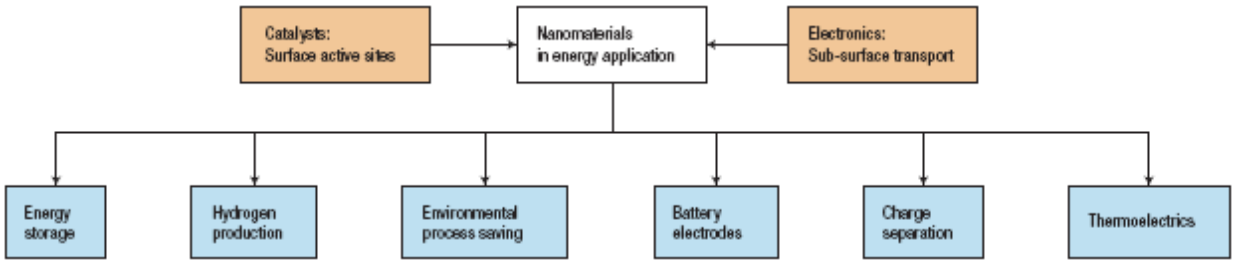

Fig. 1: Nanomaterials have a central role in many approaches addressing the energy challenge. The surface properties influence the catalytic nature of nanomaterials, and the structure beneath the surface determines the electronic transport properties. The independent control of surface and subsurface properties is key to designing and fabricating devices for energy applications.

representing localized defects are crucial for performing catalytic processes involving hydrogen and oxygen.

Water-splitting systems convert photon energy into hydrogen energy and are an elegant example of a combination of charge separation and heterogeneous redox chemistry. Kazunarei Domen (University of Tokyo) presented an overview of the history of the development of heterogeneous photocatalysts as well as concepts for better materials. Here it is thought that the uncontrolled defect structures are the origin of the underperformance of present systems. Nominally, oxy-nitrides based on Zn and Ge act as photocatalysts under visible light, in particular when combined with a hydrogen recombinator. However, they exhibit strong sensitivities in performance and stability because of their defect structure[9]. As an example, Domen explained how calcinations could overcome these problems in a Rh-loaded ZnGe photocatalyst for watersplitting. Calcinating the catalyst decreases the density of defects that act as electron– hole recombination sites and the apparent quantum efficiency increases from 0.2% (non-calcinated) to 2% (calcinated)

Knowledge gained from model studies can be used to design and fabricate greatly improved catalysts from nanomaterials. Ib Chorkendorff (Technical University of Denmark) highlighted the need to identify the active sites in catalysts for hydrogen evolution[10]. Using experimental surfacescience techniques along with theory, Chorkendorff was able to conclude that the edge site of nanoparticulate MoS_2 on Au(111) is catalytically active. However, only one in four of these sites evolves hydrogen at any one time; by tuning the electronic structure of the edge sites so that more are active, it should be possible to substantially increase the efficiency of hydrogen evolution.

The importance of understanding the electronic structure of active sites in heterogeneous catalysts is corroborated by energy-storage systems where the compositional and structural dynamics of nanomaterials are the essence of high-performance catalysts. Studies of nanostructured Cu catalysts for methanol synthesis reveal a correlation between non-equilibrium structures (defects) in Cu and catalytic activity[11]. Again it is surface features creating unique geometric and electronic situations that allow active sites to form.

Nanotechnology and energy needs both carry strong socio-ethical implications; we need to discuss the factual and perceived dangers of nanomaterials, in particular when they are manufactured for energy applications. Though these issues are usually outside the scope of technical meetings, Bengt Kasemo (Chalmers University of Technology, Sweden) addressed the topic of ‘nanoethics’, providing insights into ‘interfacial’ challenges between science and society[12]. The history of innovations created during earlier oil crises is an example of non-sustained efforts motivated by short-lived ventures of the energy market with funding bodies. Such wasteful use of scientific innovation is an inadequate response to the challenge of energy provision for our fast-growing worldwide population.

The creativity of nanoscience has the ability to contribute to the energy challenge. However, it is clear that continual effort is essential to convert some of the concepts discussed at the meeting into real technology. The chemical concepts/models are far ahead of robust synthesis protocols, physical verification and metrology. Although the efforts in creating alternative solutions should continue, it is now time to prioritize consolidation by involving other disciplines such as theory, chemical and process engineering for completing our understanding of the chemical physics of nanoscale materials in energy applications.

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