

Preparation and Characterization of Nanomaterials for Sustainable Energy Production

Chang-jun Liu,^{†,*} Uwe Burghaus,[‡] Flemming Besenbacher,[§] and Zhong Lin Wang[⊥]

[†]School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China, [‡]Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota 58105-5516, United States, [§]Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark, and [⊥]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, United States

Nanotechnology has played an extremely important role in the design, synthesis, and characterization of various new and novel energy materials and catalysts for processing fuels from fossil fuel resources such as coal, petroleum, and natural gas. Today, fossil fuels still account for 90% of the world's energy consumption, and their use is expected to peak around the year 2050. The widespread use of fossil fuels is plagued with problems such as the generation of increasingly serious environmental problems, the related climate changes we are witnessing, and the fact that the long-term availability of crude oil is limited. Therefore, it is necessary to develop a suite of sustainable energy sources and energy-storage materials. Nanoscience and nanotechnology will play even more important roles in the future.^{1,2} The synthesis and characterization of new and novel functional nanomaterials with well-controlled sizes, shapes, porosities, crystalline phases, and structures are of the utmost importance for breakthroughs in several sustainable energy technologies. However, in the next two to four decades, fossil fuels will most likely remain the primary source of energy in the world. In this respect, new catalysts are required to deal with changes in the fossil fuel supply and to solve the related environmental problems. These changes include utilizing heavy and low-quality crude oil, coal, natural gas, and potentially biogas and methane hydrate. Hydrogen production, desulfurization, isomerization, alkylation, gas-to-liquid conversions, adsorption, carbon dioxide conversion, water-gas shift, and methanation are strategic research topics worldwide. In addition, improving the efficiency of energy use is also important. Fuel cells have been

ABSTRACT The use of nanotechnology to develop a suite of sustainable energy production schemes is one of the most important scientific challenges of the 21st century. The challenge is to design, to synthesize, and to characterize new functional nanomaterials with controllable sizes, shapes, and/or structures. To summarize the progress of the research and development made in this important field, the Fuel Chemistry Division of the American Chemical Society (ACS) organized a symposium on "Nanotechnology for Sustainable Energy and Fuels" during the 240th ACS National Meeting in Boston, MA on August 22–26, 2010, with the ACS Catalysis Division as the cosponsor. This symposium was a global gathering of leading scientists at the intersection of energy and nanotechnology. The topics discussed at the symposium included nanotechnology, not only for traditional fossil fuel production but also for novel processes for renewable energy applications. This article aims to highlight some of the most exciting advances presented at the symposium, including the preparation and characterization of nanomaterials for clean fuel production, CO₂ capture, solar cells and solar fuels, energy conversion and storage materials, hydrogen storage materials, and fuel cells. Finally, possible future developments in this important and timely area are discussed.

developed as a good energy-conversion method with high efficiency. However, the high cost limits fuel-cell applications at present. In addition, the long-term stability of fuel cell catalysts is still highly problematic (catalyst poisoning, carbon corrosion, etc.). Further intense studies on novel fuel-cell structures, new membrane materials, and alternatives to Pt catalysts are needed. For the long-term, renewable energy, such as solar energy or solar fuels, will most likely take the leading position in the energy economy. The development of various nanomaterials for the generation of more efficient and low-cost solar cells is the key in this respect. In addition, hydrogen-based energy is very attractive for certain applications. However, hydrogen production remains a major challenge. Hydrogen storage materials will also be needed for the future development of efficient hydrogen production. These and many other areas were discussed at the Symposium on Nanotechnology for Sustainable Energy and

*Address correspondence to ughg_cjl@yahoo.com.

Published online October 26, 2010.
10.1021/nn102420c

© 2010 American Chemical Society

Fuels, held at the 240th ACS National Meeting in Boston, MA, on August 22–26, 2010.

The synthesis and characterization of new and novel functional nanomaterials with well-controlled sizes, shapes, porosities, crystalline phases, and structures are of the utmost importance for breakthroughs in several sustainable energy technologies

Size Matters on the Nanoscale. It is well-known that the properties of matter change significantly when the size changes from the macroscale to the microscale and from the microscale to the nanoscale. Nanotechnology is often defined as the science and engineering occurring at dimensions of 100 nm and below. Nanomaterials exhibit distinct size-dependent properties in the 1–100 nm range where quantum phenomena are involved. This is one of the major reasons why nanotechnology has a significant impact on energy conversion and storage. There were several presentations on the topic of size-dependent properties at the symposium. Dr. Evgueni Kadossov, a postdoctoral researcher in Dr. Uwe Burghaus's group at North Dakota State University, reported size-dependent bond activation in thiophene and catalyst poisoning.³ They studied the adsorption, decomposition kinetics, and dynamics of thiophene on silica-supported Mo-clusters by Auger electron spectroscopy (AES), multimass thermal desorption spectroscopy, and by collecting adsorption transients (molecular beam

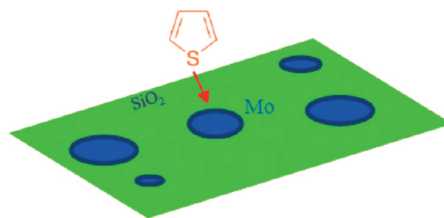


Figure 1. A schematic representation of adsorption of thiophene on a Mo cluster. The size of the clusters shows significant influence.

scattering). Their study indicated the formation of two-dimensional (2D) or three-dimensional (3D) clusters at small and large Mo coverage, respectively. A simple scheme of the model catalyst is depicted in Figure 1. Thiophene adsorbs molecularly below 190 K and begins to decompose above ~ 200 K, which results in catalyst poisoning from the formation of carbon and sulfur residuals. Cluster size effects were clearly observed: small clusters bind molecular thiophene more strongly than large clusters. However, larger clusters decompose C_4H_4S more easily. Increasing the Mo coverage from 0.4 to 2 mL decreased the binding energy from 90 to 76 kJ/mol and decreased the bond activation energy from 79 to 52 kJ/mol. This implies that it is not always the case that smaller is better. Size-dependent properties are truly different for each material, each reaction, and each property. Besenbacher and his co-workers have also observed how the size of MoS_2 significantly influences the hydrodesulfurization properties of a MoS_2 model catalyst under ultrahigh vacuum conditions.⁴

However, it is important to remember that the effects of morphology, structure, and composition of nanomaterials are equally important. It is also important to consider the synergy of size, morphology, structure, and composition for the design and controlled preparation of nano or nanostructured materials. Prof. Suljo Linic from the University of Michigan provided a good example of this. He presented an approach to the design of efficient photocatalysts utilizing composite materials composed of optically active silver nanostructures and semiconductor photocatalysts.⁵ The composite materials show an efficient energy transfer in the form of intense photon flux from

the metal nanoparticles to neighboring semiconductor particles. Compared to pure semiconductor systems, the improved energy transfer leads to a higher concentration of electron/hole pairs on the semiconductor surface with enhanced photocatalytic rates. Prof. Linic suggested that the optical properties of the metallic nanoparticles could be tuned on the basis of their size, shape, and composition. This means that a controllable interaction takes place between the metal and semiconductor materials. The rational manipulation of the photoactivity of the composite materials becomes possible in the visible and UV region of the solar spectrum.

Another example of a size effect is the nickel catalyst used for hydrogen or syngas production *via* reforming or partial oxidation of methane. Catalytic hydrogen production is an important process for both fossil fuel conversion and for biomass utilization. If cheap hydrogen could be easily produced, many problems in energy production and the environment could be solved. Nickel-based catalysts have been extensively employed and investigated because of the high activity, low cost, and plentiful availability of nickel. However, nickel-based catalysts suffer from a rapid deactivation by coke formation and/or particle aggregation at high temperatures. A high steam/carbon ratio has been applied for the industrial production of hydrogen or syngas over Ni-based catalysts, in order to inhibit coke formation and sustain the catalytic processes. This is not energy efficient because a huge amount of energy is wasted to generate steam. Therefore, it is desirable to develop coke-resistant Ni catalysts to reduce the amount of steam used. This becomes even more important because Ni catalysts could also potentially be

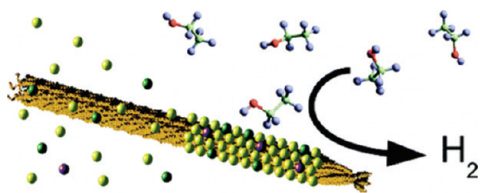


Figure 2. A schematic representation of a Rh–Ni@CeO₂ catalyst prepared *via* the M13 bacteriophage (orange) template. During the preparation, the virus nucleates ceria (yellow), nickel (green), and rhodium (purple) and produces the nanocrystalline catalyst that shows better activity and stability for reforming of ethanol into hydrogen. M13 bacteriophage is a filamentous virus that is composed of 2700 copies of a major coat protein (pVIII) that is both genetically and chemically pliable. Using techniques such as phage display and chemical modification, a resilient template can be prepared that can then be used for material synthesis under a broad range of conditions. Reproduced from ref 8. Copyright 2010 American Chemical Society.

employed in large-scale CO₂-reforming applications.

The Ni particle size has a significant effect on coke formation. Good coke resistance is achieved if the size of the Ni particles is limited to less than several nanometers.^{6,7} Various catalyst preparation methods, promoters, and supports have been considered in order to reach the goal of preparing small and stable Ni particles. During the symposium, Prof. Laszlo Guzzi of the Institute of Isotopes, Hungary, reported on the recent progress made in the preparation of Ni catalysts with controlled size. This was a joint study with Prof. Alain Kiennemann's group in LMSPC, France. They confirmed that a sol–gel preparation produced stable Ni nanoparticles with smaller sizes for CO₂ reforming, compared to the catalyst prepared by an impregnation method. However, the challenge of developing coke-resistant Ni catalysts remains. Further studies are required not only for reforming reactions but also for other reactions such as partial oxidation and methanation.

To make and improve nanocatalysts, new and novel catalyst preparation methods are important. For example, a Rh–Ni@CeO₂ catalyst prepared *via* a virus template (shown in Figure 2) for the oxidative steam reforming of ethanol was presented by Prof. Angela M. Belcher and her co-workers from the Massachusetts Institute of Technology.⁸ Complete (100%) conversion of ethanol was achieved at only 300 °C with 60% H₂ and less than 0.5% CO in the product stream. The catalyst stability was also significantly improved. Furthermore, Dr. Mark A. Allen in Prof. Belcher's group demon-

strated that this novel catalyst preparation method can also be employed to increase the energy or capacity of a Li-ion battery.

Nanotechnology for Solar Cells and Solar Fuels. A significant challenge in the research and development of solar cells and solar fuels is the synthesis and characterization of various novel materials that must both be inexpensive and have high energy-conversion efficiency. Titanium dioxide (TiO₂) is still by far the most investigated material for solar cell and solar fuel applications. It possesses a band gap of 3 eV and therefore can only absorb ultraviolet (UV) light (400 nm or shorter). However, current TiO₂-based cells are very inefficient with incident photon-to-current efficiencies of 10% or less (at the band gap energy) and peak energy conversion efficiencies of 0.6% or less over the whole solar spectrum.⁹ A primary factor limiting the efficiency of these cells is competition between the optical path length required for light absorption and charge diffusion length. It is thus important to engineer systems with both high optical density and high surface area-to-volume ratio.^{9,10} In this regard, Dr. Mingzhao Liu in Prof. Hongkun Park's group at Harvard University reported that visible light photocurrent can be enhanced by coating TiO₂ nanowires with gold or silver nanoparticles. The enhancement has been achieved due to optical scattering from the plasmonic nanoparticles, which increased the effective optical path of the thin film. They prepared the TiO₂ nanowires with mixed anatase and rutile phases by a solution-phase method.¹¹ The nanowires were deposited to form a uniform

network-like thin film and further cross-linked with titanium isopropoxide. Under simulated AM 1.5 G illumination, water photoelectrolysis was catalyzed with high efficiency. A solar energy conversion efficiency of 1.05% set a new record for undoped TiO₂ photoanodes, as reported by Dr. Liu.

A significant challenge in the research and development of solar cells and solar fuels is the synthesis and characterization of various novel materials that must both be inexpensive and have high energy-conversion efficiency

TiO₂ nanotubes (TNTs) also have the potential to play crucial roles in solar cells and solar fuels as well as other areas due to their distinctive structural and chemical properties,¹² as reported in the symposium by Dr. Kenneth J. Balkus from the University of Texas at Dallas. As a semiconductor material, TiO₂ helps to achieve superior photovoltaic performance in dye-sensitized solar cells (DSSCs). Introducing an organic dye or combining TNTs with a semiconductor that has a narrow band gap and energetically high-lying conduction band are two successful techniques in harvesting light. The application of TNTs to dye-sensitized solar cells would benefit a thin-film configuration having smaller diameter nanotubes. The highest solar cell efficiencies today for pure TNT systems are approximately 4%, whereas for some mixed systems around 7% has been reported.¹³ For both types of system there is significant room for improvement.

Moreover, TiO₂ nanocrystal thin films with large surface areas covered by monolayers of dye molecules to harvest sunlight can lead to highly efficient DSSCs. To take advantage of the enhanced electron transport and the surface area offered by these devices, Prof. Zhong Lin Wang has created an optical fiber–nanowire hybrid based on 3D DSSC by introducing solar light internally along the fiber.¹⁴ Such a structure is effective for enhancing efficiency because it allows light to have multiple interactions with the dye molecules adsorbed on the nanowire surface without increasing the electron-transport distance. In comparison with light illumination from the outside of the device that is normal to the fiber axis, internal axial illumination enhances the energy conversion efficiency by a factor of up to six for the same device. Most recently, Prof. Wang's group has presented a new approach for the fabrication of 3D DSSC by integrating planar optical waveguides and nanowires.¹⁵ The ZnO nanowires are grown normal to the quartz slide. The 3D cell is constructed by alternately stacking the slide and a planar electrode. The slide serves as a planar waveguide for light propagation. The 3D structure effectively increases the light absorbing surface area without increasing the electron path length to the collecting electrode due to internal multiple reflections. This results in an average improvement in energy conversion efficiency of a factor of 5.8 compared to planar illumination. The 3D design allows the solar cell to be concealed, smaller, and more efficient.

Nanostructured Materials for Clean Fuel Applications and CO₂ Capture. In 1992, Prof. Reshef Tenne of the Weizmann Institute of Science, Israel, discovered inorganic fullerene-like nanospheres and nanotubes, a new class of nanomaterials.¹⁶ Since this discovery, other inorganic nanotubes (INTs) have been reported.^{17,18} Many applications of INTs have been exploited, including uses in solar cells, photocatalytic hydrogen production,¹⁹ piezoelectric nanogenerators,²⁰ and hydrogen storage.²¹ At the ACS symposium, Prof. Tenne presented recent progress in the synthesis of core–shell INTs (CSNTs) via the use of

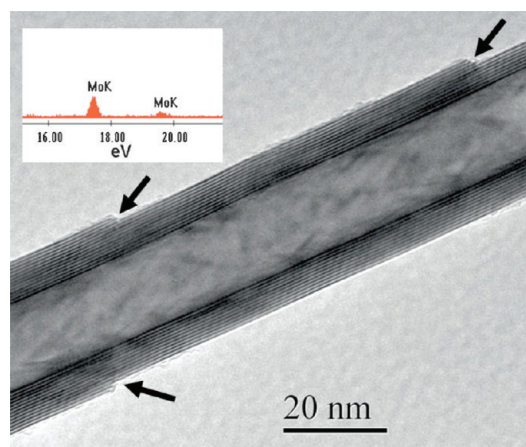


Figure 3. TEM image of a CSNT-WS₂@MoS₂ prepared via a gas-phase reaction. Arrows represent MoS₂ layers. The inset is a part of the EDS spectrum taken from the INT, exhibiting molybdenum peaks. Reproduced with permission from ref 22. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.

another INT template, for example, INT-WS₂. Three different schemes were reported for the production of CSNTs. The first is the capillary-filling technique that uses INT-WS₂ as filling vessels for a molten salt. The second method involves a conformal coating of the INT-WS₂ from the gas phase. In this case, the MoS₂ layers (resulting from reacting MoCl₅ and S) most often cover the INT-WS₂, resulting in CSNT-WS₂@MoS₂ (see Figure 3).²² The third scheme employs an *in situ* wetting process within the transmission electron microscopy (TEM) chamber. The highly energetic electron irradiation causes local melting or evaporation of the layered compound, which in turn is deposited on the inner and outer surfaces of the nearby template INT-WS₂. This deposition was shown to result in tubular layers atop the INT-WS₂ or within their hollow core. Wetting processes are also used for the production of metal-coated INT-WS₂. Such novel materials have also shown promising activity for hydrosulfurization with clean fuel production, according to a joint study performed by Prof. Tenne and Dr. Uwe Burghaus of North Dakota State University.^{23,24} Ni- and Co-doped MoS₂ and WS₂ nanotubes, which are under investigation, should result in even higher activities. Future directions include exploring other applications of the materials such as Fischer–Tropsch related chemistry.

Dr. Jun Liu and his co-workers from Pacific Northwest National Laboratory have exploited the preparation of

metal–organic framework (MOF) based materials for CO₂ capture through the combination of self-assembly and controlled crystallization. By carefully selecting the molecular ligands and the cosolvent, the detailed micro- and mesoscale porosity can be tuned in MOFs. The shape selective synthesis of MOF nanocrystals can also be achieved by controlling crystallization behavior. These materials have shown good shape selective catalytic properties and good selectivity and kinetics for CO₂ absorption.²⁵ In addition, Dr. Liu and his colleagues are studying how to extend two-dimensionally controlled nucleation and growth methods to 3D functional nanocomposite materials. This strategy involves the integration of controlled nucleation and growth and 3D self-assembly processes. Rather than using a hard substrate or functionalized surface to make supported thin films and coatings, they use a soft molecular template to control the crystallization and 3D organization simultaneously. High-surface-area stable crystalline mesoporous materials of different transition metal oxides, which have greatly enhanced thermal stability for catalytic applications in CO oxidation and water-gas shift reaction, have been obtained.²⁶

Prof. Noritatsu Tsubaki from the University of Toyama, Japan, reported on novel preparations of core–shell and bimodal Fischer–Tropsch (FT) catalysts based on self-assembly of nanomaterials. Conventional FT catalysts and zeolite are assembled to form a

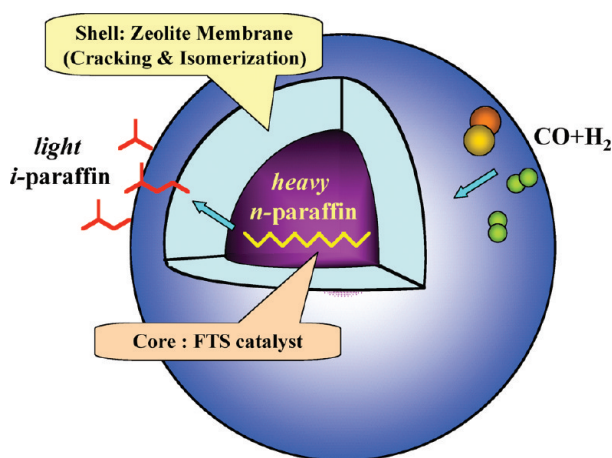


Figure 4. Scheme of the core-shell catalyst. Reproduced with permission from ref 27. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

core-shell structure (Figure 4). The core, the FT-active site, converts syngas into linear hydrocarbons, which then migrate to the acidic sites of zeolite where they undergo further hydrocracking and isomerization to form branched hydrocarbons, realizing a one-step production of isoparaffin from syngas. To deal with the trade off between the dispersion of active sites and the diffusion efficiency of the reactants and products, Prof. Tsubaki and his co-workers made a bimodal catalyst structure with both large and small pores. The large pores lead to high diffusion rates of the reactants and products whereas the small pores provide large surface areas and high metal dispersions. They employed oxide as building blocks to produce small pores inside the large pores of the homo- or heteroatom support. The idea can be used for the combination of two or more sequential reactions with many synergistic effects.²⁷

Nanotechnology for Fuel Cells. Fuel cells are attractive power sources but several challenges still exist for practical applications. A major limitation of current proton-exchange membrane fuel cells is related to the catalyst at the cathode. Instead of platinum catalysts, better and less-expensive catalysts are needed to make the widespread use of low-temperature fuel cells viable.²⁸ Bimetallic or trimetallic alloys with controllable size, shape, composition (e.g., M_1M_2 , $M_1M_2M_3$, where $M(1 \text{ or } 2) = \text{Pt, Co, Ni, V, Fe, Cu, Pd, W, Ag, Cr, Au, etc.}$), and morphology (e.g., alloy, core@shell structures, nanocubes,

etc.)²⁹ provide a particularly exciting possibility for tuning the reactivity of catalysts. Chun-Yaung Lu, a graduate student of Dr. Graeme Henkelman of the University of Texas at Austin, presented their theoretical study on the effect of bimetallic nanoparticles on the oxygen reduction reaction (ORR). Their study showed that the structural deformation induced by atomic oxygen binding can energetically stabilize the oxidized states and thus reduce the catalytic activity. They indicated that when the metal particle is small (fewer than 100 atoms), the geometric relaxation induced by oxygen binding becomes significant for soft metals such as Pt and Au. The overall oxygen binding energy is thus the balance between the intrinsic oxygen affinity and the geometric relaxation. Because geometric relaxation will stabilize the particle energetically, the ORR activity may be reduced accordingly. One possible way to fine-tune the binding energy is to employ an alloy. Introducing hard metals that have mild oxygen affinity, such as Pd or Cu, will not dramatically change the overall oxygen affinity. Instead, the binding energy can be adjusted by suppressing the structural relaxation. This study suggests an effective method for the rational design of nanometallic ORR catalysts, in addition to manipulating the electronic structure.

Nanogenerators for Converting Mechanical Energy into Electricity. Developing wireless nanodevices and nanosystems is of critical importance for sensing, medical science, environmental/infrastructure

monitoring, defense technology, and even personal electronics. It is highly desirable for wireless devices to be self-powered without requiring a battery. The search for sustainable self-sufficient power sources for micro/nanosystems is a new initiative in today's energy research.³⁰ It is essential to explore innovative nanotechnologies for converting mechanical energy, vibrational energy, and hydraulic energy into electrical energy that will be used to power nanodevices. Prof. Zhong Lin Wang's group has developed an approach for converting nanoscale mechanical energy into electrical energy by piezoelectric zinc oxide nanowire arrays.³¹ The operation mechanism of the nanogenerator relies on the piezoelectric potential created by an external strain. A dynamic straining of the nanowire results in a transient flow of the electrons in the external load due to the driving force of the piezopotential. Prof. Wang and colleagues have been involved in the development of the nanogenerator from the initial design from fundamental science to engineering integration and now to technological scale-up.³²⁻³⁵ Currently, a mild strain can output 1.2 V from an integrated nanogenerator,³⁵ from which a self-powered nanosensor has been demonstrated. A commercial LED has been lit up using this power source.³⁶ This is a key step for developing a complete nanowire-based nanosystem.³⁵

Developing wireless nanodevices and nanosystems is of critical importance for sensing, medical science, environmental/infrastructure monitoring, defense technology, and even personal electronics

Nanotechnology for Energy-Storage

Systems. In addition to challenges in creating highly efficient energy-production systems, another hurdle facing the scientific community is energy storage. It is a significant challenge to prepare materials with hierarchical structural control (materials with controlled porosity and structures on multilength scales) and multifunctionality for Li-ion batteries and other materials. In this regard, Dr. Jun Liu and his group are currently exploring a new approach involving a combination of self-assembly and controlled crystallization, in order to produce a new class of nanocomposite materials with well-controlled architectures on the nano- and microscales and with high capacity (or activity) and stability for energy storage and electrocatalysis.³⁷ The emphasis in the studies by Dr. Jun Liu is the understanding of crystallization in self-assembled materials to control both the porosity and spatial distribution of the components in these materials on multiple length scales. For example, Dr. Liu reported that they have employed extended graphene sheets solubilized in the hydrophobic domains as the fundamental building blocks for the self-assembly of three-dimensionally ordered architectures (Figure 5). The graphene sheets and metal oxide precursors self-assemble into ordered 3D composite structures. The metal oxides are then crystallized between the graphene sheets as controlled by the functional head groups of the surfactants.

Prof. Guozhong Cao from the University of Washington has successfully developed nanostructured materials for Li-ion batteries.³⁸ He reported their recent achievement in intentionally introducing defects in the nanostructured electrodes for enhanced Li-ion intercalation capacity. The surface defects were introduced through annealing at elevated temperatures in controlled reactive gases, whereas the bulk defects were introduced through doping. Prof. Cao presented three examples to illustrate the impact of surface and bulk defects on Li-ion intercalation. The first example compared acid-anodized TiO₂ nanotube arrays annealed in nitrogen and carbon monoxide. TiO₂ nanotubes annealed in

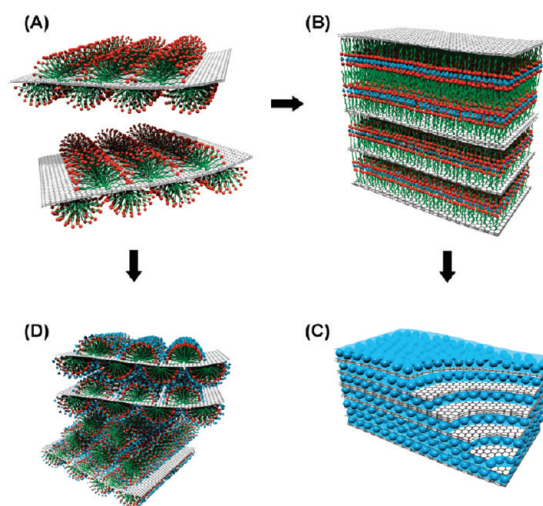


Figure 5. Schematic representations of the ternary self-assembly approach to ordered metal oxide–graphene nanocomposites: (A) Graphene or graphene stacks are used as the substrate instead of graphite. Adsorption of surfactant hemimicelles on the surfaces of the graphene or graphene stacks causes its dispersion in surfactant micelles in an aqueous solution; (B) the self-assembly of the anionic sulfonate surfactant on the graphene surface with an oppositely charged metal cation (e.g., Sn²⁺) species and the transition into the lamella mesophase toward the formation of SnO₂–graphene nanocomposites, where hydrophobic graphenes are sandwiched in the hydrophobic domains of the anionic surfactant; (C) metal oxide–graphene layered nanocomposites composed of alternating layers of metal oxide nanocrystals and graphene/graphene stacks after the crystallization of metal oxide and removal of the surfactant; (D) self-assembled hexagonal nanostructure of the metal oxide precursor (e.g., silicate) with nonionic surfactants (e.g., Pluronic P123) on graphene stacks. Reproduced with permission from ref 37. Copyright 2010 American Chemical Society.

carbon monoxide with detectable trivalent titanium ions and carbon species possessed Li-ion intercalation capacity exceeding the theoretical limit of bulk TiO₂. The second example described sol–gel derived nanostructured V₂O₅ film electrodes annealed in nitrogen and then air that demonstrated significantly different intercalation capacity and cyclic stability. The last example was a sol–gel derived V₂O₅ film doped with Mn, which demonstrated appreciable improvement in Li-ion intercalation cyclic stability. The presence of surface and bulk defects in electroactive materials introduced through annealing in controlled gases or controlled doping leads to demonstrably enhanced Li-ion intercalation capacity, improved intercalation and extraction rates, and better cyclic stability. It is believed that the surface defects promote the phase transition accompanied with the Li-ion intercalation process and that the bulk defects may improve the transport properties. Figure 6 shows the scanning electron microscope (SEM) images of mesoporous V₂O₅ nanofibers prepared using electrospinning.

Dr. Seung M. Oh from Seoul National University, Republic of Korea, discussed the effects of defects on amorphous MoO₂ electrodes. Amorphous MoO₂ was obtained by the reduction of a molybdate solution with borohydride. The electrochemical performance of the amorphous MoO₂ was compared with crystalline MoO₂ when used as the anode material in Li-ion batteries. The crystallinity of MoO₂ is closely related to its electrochemical performance. Amorphous MoO₂ features a high energy density with a four-electron reduction, whereas crystalline MoO₂ is restricted to only a one-electron reduction. Amorphous MoO₂ shows high reversibility that is close to the theoretical four-electron capacity. These amorphous materials can have additional Li⁺ storage sites and higher lithiation kinetics. That is, the defect sites and disorders in these less crystalline materials are the storage sites for additional Li⁺. In addition, solid-state Li⁺ diffusion can be facilitated through the defects and disordered atomic arrays.

However, nanosized metal oxides are expected to improve the high-rate

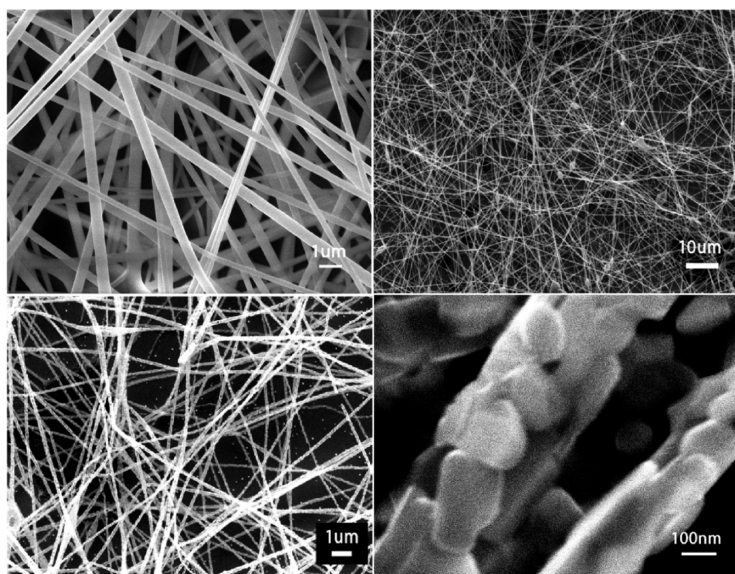


Figure 6. SEM images of mesoporous V_2O_5 nanofibers under different magnifications: (a) prior to annealing; (b–d) after annealing at 500 °C in air for 1 h.

capability of cathode materials for Li-ion batteries because of the considerably higher effective interfacial area between the nanosized metal oxide and the electrolyte, and its shorter Li diffusion length during charge/discharge cycles. Since nanosized metal oxides tend to agglomerate, good dispersion and improved conductivity of an electrode composed of nanosized oxides is important for achieving high-rate capability. Prof. Kwang-Bum Kim from Yonsei University, Republic of Korea, reported on metal oxide/carbon nanotube (CNT) nanohybrid materials ($LiMn_2O_4/CNT$, $LiCoO_2/CNT$ and $Li_4Ti_5O_{12}/CNT$ nanocomposites) with excellent high-rate capability and good structural reversibility for energy-storage applications. These hybrid materials were synthesized through selective heterogeneous nucleation and growth of the oxides on a CNT surface using microwave-hydrothermal processes. Carbon nanotubes serve here as substrates to support nanosized metal oxide and to connect the nanoparticles along the one-dimensional conduction path.^{39,40}

Nanotechnology for Hydrogen-Storage Materials. Hydrogen is considered to be a promising clean energy carrier. A major challenge in a future “hydrogen economy” is the development of a safe, compact, robust, and efficient means of hydrogen storage, in particular, for mobile applications. Thomas Kollin Nielsen,

a Ph.D. student of Prof. Torben R. Jensen and Prof. Flemming Besenbacher at the Interdisciplinary Nanoscience Center (iNANO), Aarhus University, reported on a concept for hydrogen storage using nanoconfined reversible chemical reactions. In this scheme, nanoparticles of the reactive hydride composites system, $LiBH_4$ and MgH_2 , are embedded in nanoporous carbon aerogel scaffolds with pore size $D_{max} \approx 21$ nm. They react during the release of hydrogen and form MgB_2 and LiH , as shown in Figure 7.⁴¹ For this system, the hydrogen desorption kinetics are significantly improved in comparison with traditional bulk conditions. Moreover, the nanoconfined system has enhanced reversibility and stability and may also improve thermodynamic properties. The recent results from the iNANO group confirmed that nanoconfinement sig-

nificantly mediates enhanced hydrogen desorption kinetics and stability compared to the bulk samples. The nanocomposite system was found to be capable of storing 3.9 wt % H_2 , of which 72% is still available after four hydrogen uptake and release cycles. The same iNANO group reported another innovative study at the ACS symposium on anion substitution (e.g., Ca_2) in metal borohydrides (e.g., $Ca(BH_4)_2$) that leads to hydrogen absorption under more moderate temperature conditions.

Characterization of Energy-Related Nano- or Nanostructured Materials. To design, to synthesize, and to apply nanomaterials, we need to understand the reaction mechanisms and processes occurring on the surface of nano or nanostructured materials, not only under ultrahigh vacuum (UHV) conditions but under real conditions. Fortunately, progress in vacuum technology and surface-science techniques has led to significant progress in our ability to characterize nanomaterials and especially surface processes. A suite of surface-sensitive techniques such as AES, ion scattering spectroscopy (ISS), UV and X-ray photoemission spectroscopy (UPS and XPS), metastable impact electron spectroscopy (MIES), high-resolution electron energy loss spectroscopy (HREELS), infrared reflection absorption spectroscopy (IRAS), low energy electron diffraction (LEED), and scanning probe microscopies (e.g., scanning tunneling microscopy, STM, and atomic force microscopy, AFM) have been developed.^{42–45} To gain insight into the fundamental steps involved in surface reactions, Prof. Gerhard Ertl developed the so-called “surface science approach”⁴⁶ to simplify

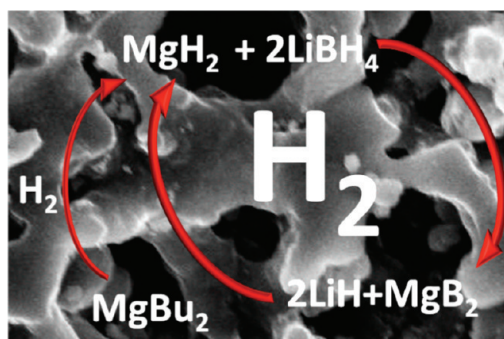


Figure 7. $LiBH_4$ and MgH_2 are embedded in nanoporous carbon aerogel scaffolds with pore size $D_{max} \approx 21$ nm. They react during release of hydrogen and form MgB_2 and LiH . Reproduced from ref 41. Copyright 2010 American Chemical Society.

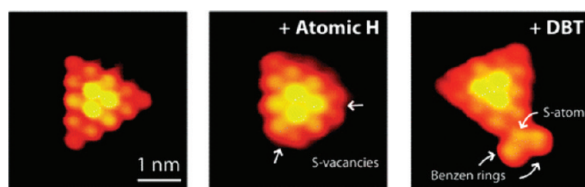


Figure 8. STM analyses on size threshold of dibenzothiophene adsorption on MoS₂ nanoclusters. Reproduced from ref 48. Copyright 2010 American Chemical Society.

the considerations of reactions on surfaces; model systems consisting of either flat, single-crystal surfaces or well-defined nanoclusters on surfaces are studied under clean and well-controlled, often UHV, conditions. With this approach, an impressive amount of detailed insight into fundamental processes on surfaces has been obtained. This has contributed substantially to our understanding of the processes involved in catalysis.

Recently, Prof. D. Wayne Goodman's group at Texas A&M University used the acetoxylation of ethylene to vinyl acetate (VA) to investigate the mechanism of the promotional effect of Au in a Pd–Au alloy catalyst.⁴⁷ The combination of kinetic data and the IRAS characterization revealed that the critical reaction site for VA synthesis consists of two noncontinuous, suitably spaced, Pd monomers. The role of Au on the Pd–Au bimetallic surface is to isolate single Pd sites that facilitate the coupling of critical surface species to produce the product, while at the same time inhibiting the formation of undesirable reaction byproduct. At the ACS symposium, Dr. Jeppe V. Lauritsen and Prof. Flemming Besenbacher demonstrated how STM can reveal atomic-scale insight into catalysis, including quantitative information on surface diffusion of adatoms and molecules. The use of time-resolved, high-resolution STM movies yields information on the diffusion of adatoms, vacancies, interstitials, and molecules (e.g., water molecules on oxide surfaces), sintering and diffusion of nanoclusters on oxide surfaces, and diffusion of intermediate species. It was also shown the fast-scanning STM can be used to identify active sites and to determine new nanostructures with novel catalytic properties. Figure 8 is an example of an STM image of dibenzothiophene adsorption on MoS₂ nano-

clusters.⁴⁸ In certain cases, the atomic-scale information obtained may even lead to the design of new and improved catalysts.⁴⁸

In hydrodesulfurization (HDS) of fossil fuels, the sulfur levels are reduced by sulfur extraction from hydrocarbons through a series of catalyzed reaction steps on low-coordinated sites on MoS₂ nanoclusters. By means of STM, Dr. Jeppe V. Lauritsen, Prof. Flemming Besenbacher, and their students have shown how the adsorption and reaction of MoS₂ nanoclusters toward the HDS-refractory dibenzothiophene (DBT) vary dramatically with small changes in the size of the MoS₂ nanocluster. High-resolution STM images reveal that MoS₂ nanoclusters that are larger than a critical size of 1.5 nm react with hydrogen to form so-called sulfur vacancies, predominantly located at the edges of the MoS₂ nanoclusters. These edge vacancies are not capable of binding DBT directly. In contrast, smaller MoS₂ nanoclusters below the critical size of 1.5 nm are much more reactive and perform remarkably better. Here, sulfur vacancies form predominantly at the corner sites, and these corner vacancy sites show a high affinity for DBT. The results thus indicate that very small MoS₂ nanoclusters may have unique catalytic properties for the production of clean fuels.⁴⁸

Outlook of Nanomaterials for Sustainable Energy Production. Nanomaterials have large surface areas, and we are approaching an era in which nanomaterials can be synthesized with unique, functional properties for applications in the areas of energy conversion and storage. No matter what form of energy is used, low-cost nanomaterials will be required for highly efficient energy production and conversion and for the development of efficient and inexpensive energy storage systems. Nanomaterials serve as energy carriers, absorbents,

media for energy transfer, catalysts, converters, and energy pools or vessels for reactions. In all of these applications, the core technology to be developed is the preparation of novel nanomaterials with controllable sizes, shapes, and/or structures. However, it may not be easy to reach the goal of size, shape, and/or structural control because of thermodynamic limitations. There is no question that the route forward is to exploit a truly multidisciplinary approach combining competences from physics, chemistry, materials science, and biology in order to synthesize, to characterize, and to model new and novel functional nanomaterials with unique properties. Conventional methods, such as doping, impregnation, and ion exchange, will continue to be used, but there is great opportunity to learn from and try to mimic the nanomaterials and nanomachinery in nature.^{8,49} The visionary biomineralization pathways⁸ (*via virus template*) developed by Prof. Belcher's group is a promising route for the manufacture of nanomaterials with the desired properties in an environmentally friendly and sustainable way. Many properties of living systems could potentially be harnessed, and methods based on nonequilibrium characteristics will have interesting applications in the future. For example, nonequilibrium cold plasma preparations with high electron temperatures (as high as 10⁴ K) and very low gas temperatures (as low as room temperature) can generate materials similar to the virus template.⁵⁰ With such high electron temperatures, nucleation and growth kinetics vary substantially from that of the conventional thermal method. Moreover, the development of new characterization techniques for nanomaterials is extremely important. In particular, techniques that can be used for *in situ* analyses under high pressure and high temperature conditions will be of utmost importance for the future developments. Results based on molecular modeling are also extremely important and will be helpful in the design of the next generation of nanomaterials for energy applications. For example, a density functional theory study revealed that Ga₂O₃ is excellent for activating

CO₂,⁵¹ which led to the design and synthesis of a Ga-doped Ni/SiO₂ catalyst that showed excellent properties for CO₂ reforming.⁵² The results of molecular modeling are also important for interpreting STM data.⁴⁸

Nanotechnology for sustainable energy production is now one of the fastest growing research fields in the world and will hopefully head to the development of a renewable energy economy in which fossil fuel resources will only be used to produce more valuable chemicals. This vision is that energy, environmental, and security problems created by the consumption of fossil fuels will be solved once and for all.

Acknowledgment. The organizers acknowledge funding of their research from the US Department of Energy (U. Burghaus via DE-FG02-08ER15987), the National Natural Science Foundation of China (C. J. L. via 20990223), the Danish Research Agency, The Villum Kann Rasmussen, and the Carlsberg Foundation and European Research Council. The assistance of Dr. Jeanne Wynn in Department of Chemistry of Tianjin University is appreciated. Financial support from McAllister Technical Services (USA) and SPECS (Germany), particularly for this symposium, is gratefully acknowledged.

REFERENCES AND NOTES

- Serrano, E.; Rus, G.; García-Martínez, J. Nanotechnology for Sustainable Energy. *Renewable Sustainable Energy Rev.* **2009**, *13*, 2373–2384.
- Somorjai, G. A.; Frei, H.; Park, J. Y. Advancing the Frontiers in Nanocatalysis, Biointerfaces, and Renewable Energy Conversion by Innovations of Surface Techniques. *J. Am. Chem. Soc.* **2009**, *131*, 16589–16605.
- Komarneni, M.; Kadossov, E.; Justin, J.; Lu, M.; Burghaus, U. Adsorption of Thiophene on Silica-Supported Mo Clusters. *Surf. Sci.* **2010**, *604*, 1221–1229.
- Tuxen, A.; Kibsgaard, J.; Gøbel, H.; Lægsgaard, E.; Topsøe, H.; Lauritsen, J. V.; Besenbacher, F. Size Threshold in the Dibenzothiophene Adsorption on MoS₂ Nanoclusters. *ACS Nano* **2010**, *4*, 4677–4682.
- Christopher, P.; Ingram, D. B.; Linic, S. Enhancing Photochemical Activity of Semiconductor Nanoparticles with Optically Active Ag Nanostructures: Photochemistry Mediated by Ag Surface Plasmons. *J. Phys. Chem. C* **2010**, *114*, 9173–9177.
- Trimm, D. L. Coke Formation and Minimisation During Steam Reforming Reactions. *Catal. Today* **1997**, *37*, 233–238.
- Zhu, X.; Huo, P.; Zhang, Y.-P.; Cheng, D.-G.; Liu, C.-J. Structure and Reactivity of Plasma-Treated Ni/Al₂O₃ Catalyst for CO₂ Reforming of Methane. *Appl. Catal., B* **2008**, *81*, 132–140.
- Neltner, B.; Peddie, B.; Xu, A.; Doenlen, W.; Durand, K.; Yun, D. S.; Speakman, S.; Peterson, A.; Belcher, A. Production of Hydrogen Using Nanocrystalline Protein-Templated Catalysts on M13 Phage. *ACS Nano* **2010**, *4*, 3227–3235.
- Ruan, C. M.; Paulose, M.; Varghese, O. K.; Mor, G. K.; Grimes, C. A. Fabrication of Highly Ordered TiO₂ Nanotube Arrays Using an Organic Electrolyte. *J. Phys. Chem. B* **2005**, *109*, 15754–15759.
- Liu, M.; de Leon Snapp, N. P.; Park, H. Water Photolysis with a Cross-Linked Titanium Dioxide Nanowire Anode, in press.
- Wang, Y. L.; Jiang, X. C.; Xia, Y. N. A Solution-Phase, Precursor Route to Polycrystalline SnO₂ Nanowires that Can Be Used for Gas Sensing under Ambient Conditions. *J. Am. Chem. Soc.* **2003**, *125*, 16176–16177.
- Ratanatawanate, C.; Xiong, C. R.; Balkus, K. J. Fabrication of PbS Quantum Dot Doped TiO₂ Nanotubes. *ACS Nano* **2008**, *2*, 1682–1688.
- Roy, P.; Kim, D.; Lee, K.; Spiecker, E.; Schmuki, P. TiO₂ Nanotubes and their Application in Dye-Sensitized Solar Cells. *Nanoscale* **2010**, *2*, 45–59.
- Weintraub, B.; Wei, Y. G.; Wang, Z. L. Optical Fiber/Nanowire Hybrid Structures for Efficient Three-Dimensional Dye-Sensitized Solar Cells. *Angew. Chem., Int. Ed.* **2009**, *48*, 8981–8985.
- Wei, Y.; Xu, C.; Xu, S.; Li, C.; Wu, W.; Wang, Z. L. Planar Waveguide-Nanowire Integrated Three-Dimensional Dye-Sensitized Solar Cells. *Nano Lett.* **2010**, *10*, 2092–2096.
- Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. Polyhedral and Cylindrical Structures of WS₂. *Nature* **1992**, *360*, 444–446.
- Guimaraes, L.; Enyashin, A. N.; Frenzel, J.; Heine, T.; Duarte, H. A.; Seifert, G. Imogolite Nanotubes: Stability, Electronic, and Mechanical Properties. *ACS Nano* **2007**, *1*, 362–368.
- Park, H. G.; Holt, J. K. Recent Advances in Nanoelectrode Architecture for Photochemical Hydrogen Production. *Energy Environ. Sci.* **2010**, *3*, 1028–1036.
- Zhang, J.; Bang, J. H.; Tang, C. C.; Kamat, P. V. Tailored TiO₂-SrTiO₃ Heterostructure Nanotube Arrays for Improved Photoelectrochemical Performance. *ACS Nano* **2010**, *4*, 387–395.
- Xi, Y.; Song, J. H.; Xu, S.; Yang, R. S.; Gao, Z. Y.; Hu, C. G.; Wang, Z. L. Growth of ZnO Nanotube Arrays and Nanotube-Based Piezoelectric Nanogenerators. *J. Mater. Chem.* **2009**, *19*, 9260–9264.
- Bhattacharya, S.; Majumder, C.; Das, G. P. Hydrogen Storage in Ti-Decorated BC₄N Nanotube. *J. Phys. Chem. C* **2008**, *112*, 17487–17491.
- Kreizman, R.; Enyashin, A. N.; Deepak, F. L.; Albu-Yaron, A.; Popovitz-Biro, R.; Seifert, G.; Tenne, R. Synthesis of Core-Shell Inorganic Nanotubes. *Adv. Funct. Mater.* **2010**, *20*, 2459–2468.
- Goering, J.; Burghaus, U.; Arey, B. W.; Eidelman, O.; Zak, A.; Tenne, R. Reactive and Non-Reactive Interactions of Thiophene with WS₂ Fullerene-Like Nanoparticles: An Ultra-High Vacuum Surface Chemistry Study. *Catal. Lett.* **2008**, *125*, 236–242.
- Komarneni, M.; Sand, A.; Nevin, P.; Zak, A.; Burghaus, U. Adsorption and Reaction Kinetics of Small Organic Molecules on WS₂ Nanotubes: An Ultrahigh Vacuum Study. *Chem. Phys. Lett.* **2009**, *479*, 109–112.
- Fernandez, C. A.; Thallapally, P. K.; Motkuri, R. K.; Nune, S. K.; Sumrak, J. C.; Tian, J.; Liu, J. Gas-Induced Expansion and Contraction of a Fluorinated Metal–Organic Framework. *Cryst. Growth Des.* **2010**, *10*, 1037–1039.
- Wang, D. H.; Ma, Z.; Dai, S.; Liu, J.; Nie, Z. M.; Engelhard, M. H.; Huo, Q. S.; Wang, C. M.; Kou, R. Low-Temperature Synthesis of Tunable Mesoporous Crystalline Transition Metal Oxides and Applications as Au Catalyst Supports. *J. Phys. Chem. C* **2008**, *112*, 13499–13509.
- Bao, J.; He, J. J.; Zhang, Y.; Yoneyama, Y.; Tsubaki, N. A Core/Shell Catalyst Produces a Spatially Confined Effect and Shape Selectivity in a Consecutive Reaction. *Angew. Chem., Int. Ed.* **2008**, *47*, 353–356.
- Menning, C. A.; Chen, J. G. Regenerating Pt-3d-Pt Model Electrocatalysts Through Oxidation–Reduction Cycles Monitored at Atmospheric Pressure. *J. Power Sources* **2010**, *195*, 3140–3144.
- Zhong, C.-J.; Luo, J.; Njoki, P. N.; Mott, D.; Wanjala, B.; Loukrakpam, R.; Lim, S.; Wang, L.; Fang, B.; Xu, Z. Fuel Cell Technology: Nano-Engineered Multimetallic Catalysts. *Energy Environ. Sci.* **2008**, *1*, 454–466.
- Wang, Z. L. Towards Self-Powered Nanosystems: From Nanogenerators to Nanopiezotronics. *Adv. Funct. Mater.* **2008**, *18*, 3553–3567.
- Wang, Z. L.; Song, J. H. Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays. *Science* **2006**, *312*, 242–246.
- Wang, X. D.; Song, J. H.; Liu, J.; Wang, Z. L. Direct Current Nanogenerator Driven by Ultrasonic Wave. *Science* **2007**, *316*, 102–105.
- Qin, Y.; Wang, X. D.; Wang, Z. L. Microfiber-Nanowire Hybrid Structure for Energy Scavenging. *Nature* **2008**, *451*, 809–813.
- Yang, R. S.; Qin, Y.; Dai, L. M.; Wang, Z. L. Flexible Charge-Pump for Power Generation using Laterally Packaged Piezoelectric-Wires. *Nat. Nanotechnol.* **2009**, *4*, 34–39.
- Xu, S.; Qin, Y.; Xu, C.; Wei, Y. G.; Yang, R. S.; Wang, Z. L. Self-Powered Nanowire Devices. *Nat. Nanotechnol.* **2010**, *5*, 366–373.
- Zhu, G.; Yang, R.; Wang, S.; Wang, Z. L. Flexible High-Output Nanogenerator Based on Lateral ZnO Nanowire Array. *Nano Lett.* **2010**, *10*, 3151–3155.
- Wang, D. H.; Kou, R.; Choi, D.; Yang, Z. G.; Nie, Z. M.; Li, J.; Saraf, L. V.; Hu, D. H.; Zhang, J. G.; Graff, G. L. Ternary Self-Assembly of Ordered Metal

- Oxide–Graphene Nanocomposites for Electrochemical Energy Storage. *ACS Nano* **2010**, *4*, 1587–1595.
38. Wang, Y.; Cao, G. Z. Developments in Nanostructured Cathode Materials for High-Performance Lithium-Ion Batteries. *Adv. Mater.* **2008**, *20*, 2251–2269.
39. Ma, S. B.; Nam, K. W.; Yoon, W. S.; Bak, S. M.; Yang, X. Q.; Cho, B. W.; Kim, K. B. Nano-Sized Lithium Manganese Oxide Dispersed on Carbon Nanotubes for Energy Storage Applications. *Electrochem. Commum.* **2009**, *11*, 1575–1578.
40. Kim, J. Y.; Kim, K. H.; Park, S. H.; Kim, K. B. Microwave-Polyol Synthesis of Nanocrystalline Ruthenium Oxide Nanoparticles on Carbon Nanotubes for Electrochemical Capacitors. *Electrochim. Acta*, published online April 18, 2010, <http://dx.doi.org/10.1016/j.electacta.2010.04.047>.
41. Nielsen, T. K.; Bsenberg, U.; Goslawit, R.; Dornheim, M.; Cerenius, Y.; Besenbacher, F.; Jensen, T. R. A Reversible Nanoconfined Chemical Reaction. *ACS Nano* **2010**, *4*, 3903–3908.
42. Tao, F.; Dag, S.; Wang, L. W.; Liu, Z.; Butcher, D. R.; Bluhm, H.; Salmeron, M.; Somorjai, G. A. Break-Up of Stepped Platinum Catalyst Surfaces by High CO Coverage. *Science* **2010**, *327*, 850–853.
43. Baber, A. E.; Tierney, H. L.; Sykes, E. C. H. Atomic-Scale Geometry and Electronic Structure of Catalytically Important Pd/Au Alloys. *ACS Nano* **2010**, *4*, 1637–1645.
44. McClure, S. M.; Lundwall, M.; Zhou, Z.; Yang, F.; Goodman, D. W. Characterization of Pt/SiO₂ Model Catalysts at UHV and Near Atmospheric Pressures. *Catal. Lett.* **2009**, *133*, 298–306.
45. Temel, B.; Tuxen, A. K.; Kibsgaard, J.; Topsøe, N. Y.; Hinnemann, B.; Knudsen, K. G.; Topsøe, H.; Lauritsen, J. V.; Besenbacher, F. Atomic-Scale Insight into the Origin of Pyridine Inhibition of MoS₂-Based Hydrotreating Catalysts. *J. Catal.* **2010**, *271*, 280–289.
46. List of Publications of Gerhard Ertl. *J. Phys. Chem. B* **2004**, *108*, 14197–14215.
47. Chen, M.; Kumar, D.; Yi, C.-W.; Goodman, D. W. The Promotional Effect of Gold in Catalysis by Palladium-Gold. *Science* **2005**, *310*, 291–293.
48. Tuxen, A.; Kibsgaard, J.; Gøbel, H.; Lægsgaard, E.; Topsøe, H.; Lauritsen, J. V.; Besenbacher, F. Size Threshold in the Dibenzothiophene Adsorption on MoS₂ Nanoclusters. *ACS Nano* **2010**, *4*, 4677–4682.
49. Zhou, H.; Li, X. F.; Fan, T. X.; Osterloh, F. E.; Ding, J.; Sabio, E. M.; Zhang, D.; Guo, Q. X. Light Harvesting: Artificial Inorganic Leaves for Efficient Photochemical Hydrogen Production Inspired by Natural Photosynthesis. *Adv. Mater.* **2010**, *22*, 951–956.
50. Wang, Z.-J.; Xie, Y. B.; Liu, C.-J. Synthesis and Characterization of Noble Metal (Pd, Pt, Au, Ag) Nanostructured Materials Confined in the Channels of Mesoporous SBA-15. *J. Phys. Chem. C* **2008**, *112*, 19818–19824.
51. Pan, Y. X.; Liu, C.-J.; Mei, D. H.; Ge, Q. F. Effects of Hydration and Oxygen Vacancy on CO₂ Adsorption and Activation on Beta-Ga₂O₃(100). *Langmuir* **2010**, *26*, 5551–5558.
52. Pan, Y. X.; Kuai, P. Y.; Liu, Y.; Ge, Q. F.; Liu, C.-J. Promotion Effects of Ga₂O₃ on CO₂ Adsorption and Conversion over a SiO₂-Supported Ni Catalyst. *Energy Environ. Sci.* **2010**, *3*, 1322–1325.