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Chapter 9

APPLICATIONS: ENERGY AND CHEMICALS INDUSTRIES

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9.1 VISION

The trend to smaller and smaller structures, that is, miniaturization, is well known in the microelectronics industry, evidenced by the rapid increase in computing power through reduction of the area and volume needed per transistor on chips. In the energy and chemicals areas, this same trend towards miniaturization, i.e., control of function and/or structure at the nanoscale, also is occurring, but for different reasons. Smallness in itself is not the goal. Instead, it is the realization or now even the expectation that new properties intrinsic to nanostructures will enable breakthroughs in a multitude of different technologically important areas. Nanoengineering is expected to lead to significant improvements in solar energy conversion and storage; better energy-efficient lighting; stronger, lighter materials that will improve transportation efficiency; use of low-energy chemical pathways to break down toxic substances for remediation and restoration; and better sensors and controls to increase efficiency in manufacturing and processing.

9.2 CURRENT SCIENTIFIC AND TECHNOLOGICAL ADVANCEMENTS

What is it about the concept of nanoscale science and technology that is leading to such emphasis and excitement in a multitude of disciplines and areas of research around the world? The fundamental driving force towards efforts to exploit the nanoscale or nanostructure comes from two realizations: (1) the macroscopic bulk behavior with which we are most familiar is significantly different from quantum, or nanoscale, behavior, and (2) materials with some aspect of quantum behavior can now be synthesized and studied in the laboratory. Obviously, quantum behavior becomes increasingly important as the controlling parameter gets smaller and smaller.

Exploiting the Properties of Quantum Behavior

The following are examples where quantum behavior differs from bulk behavior:

- Nanoparticles (metal, carbon, metal oxide, etc.) exhibit novel electronic, chemical, magnetic, and structural properties.

- Molecular diffusivity through molecular sieve materials such as zeolites cannot be predicted or explained by hard sphere molecular properties or fixed wall apertures.

- Catalysts with one, two, or three dimensions in the nanometer size range exhibit unique catalytic or chemical activities.

- Electron/photon charge and transfer is different in nanostructures.

Understanding atom-to-atom interactions at the fundamental level is becoming increasingly important in materials science research efforts. There are now numerous instances where materials with some aspect of quantum behavior are actually being fabricated and studied:

- Clusters consisting of pure metals, mixed metals, metal oxides, metal carbides, metal sulfides, carbon clusters, and organic molecular clusters
- Molecular sieve materials with precisely controlled pore sizes
- Carbon nanotubes of differing helicity, diameter, and shells
- Single layer few molecular layer thin films
- Catalysts with at least one dimension at the nanoscale
- Extremely high surface area materials for use as sorbents or as catalyst supports
- Battery materials with nanoscale porosity
- Energy conversion with Gratzel cell-type devices employing dyes absorbed on nanoscale inorganic oxides
- Electronic devices where at least one device dimension is on the nanoscale

Understanding and control of nanostructure are expected to become increasingly important in many diverse areas of current and future academic and industrial activity in the chemical and energy industries, as well as in related materials endeavors:

- *In petrochemical processing*, a key goal is to promote catalytic reactions that have high selectivity with high yield. It is anticipated that this goal will be more closely approached through tailoring a catalyst particle via nanoparticle synthesis and assembly, so that it performs only specific chemical conversions, performs these at high yield, and with greater energy efficiency. Such precise control will impart opportunities for more efficient usage of our limited natural resources.

- *In energy applications,* some new nanostructured materials with well-defined pore sizes and high surface areas are currently being fabricated and tested in the laboratory for potential use in energy storage, chemical separations, and battery technologies. The use of nanoscale materials for energy generation and storage may allow for higher capacities, higher rates of charge and discharge, and far greater control over the absorption and charge transfer processes. Materials with significantly increased H_2 (or CH_4) storage capacity in small volume containers could be the enabling feature for lower-cost, more efficient, less polluting fuel-cell-powered vehicles or fuel cell power generation units for local business applications. Similarly, removal of H_2S, H_2O, CO, and/or CO_2 from natural gas near well heads would enable more efficient transport of natural gas from the well head to the end user. The relatively recent discovery that continuous channels of nanocrystalline tin aggregates are formed during the electrochemical reduction of tin oxide is opening opportunities for greatly improved rechargeable lithium-ion batteries. It has also been demonstrated that such nanostructured anode materials such as V_2O_5, $LiCoO_2$ and MnO_2 have improved capacities, lifetimes, and charge/discharge rates.

- *In the construction materials area,* novel materials are being fabricated in which improved bonding and strength dependent upon the surface area and morphology of nanoscale constituents are leading to materials with enhanced strength and toughness for use in the construction and steel industries. The use of nanostructured tungsten carbide/cobalt composites gives a two-fold increase in abrasion resistance and hardness, increasing the lifetime of drill bits. Incorporation of nanoscale carbon fibers or nanotubes into concrete not only increases strength but also offers the opportunity to continually monitor the structural integrity of the structure via electrical resistivity measurements. Proper control of the number and size of grain boundaries in steels is expected to lead to improved strength and performance. For example, smaller-diameter but stronger pipes can operate at higher pressures, which may allow more cost-effective distribution of high-pressure gases.

- *In other materials areas,* the potential is being investigated for creation of novel materials, devices, and processes, including thermal barrier materials and highly selective sensors, and also for development of molecular replication technologies for rapid scale-up and manufacturing. These are being pursued actively in laboratories worldwide.

Ultimately, of course, no matter how much is learned about the nanoscale and its properties, the industrial use of such materials will only come about if and when there is a definitive cost advantage for the end user.

The chemical and energy industries are already benefiting from the nanoscale technology revolution. Since the late 1970s, the scientific community has experienced enormous progress in the synthesis, characterization, and basic theoretical and experimental understanding of materials with nanoscale dimensions, that is, small particles, clusters, or nanocrystalline materials (Prigogine and Rice 1988; Averback et al. 1991). Such materials are groups of atoms or molecules that display properties different from both the smaller individual atoms or molecules and the larger bulk materials. Many techniques have been developed to produce clusters, beams of clusters, and clusters in a bottle (Hu and Shaw 1999, 15) for use in many different applications, as will be discussed below.

The properties of such materials have opened a third dimension to the periodic table, that is, the number of atoms (N) (Rosen 1998). N now becomes a critical parameter by which the properties for these "nanoscale" systems are defined. As a simple example, for metals, we have known for decades that the atomic ionization potential (IP) is typically about twice the value of the bulk work function. It is only relatively recently that experiments have shown that the ionization potential and electron affinity for clusters containing specific number N of (metal) atoms varies dramatically and non-monotonically with N for clusters containing less than 100-200 atoms (Taylor et al. 1992; Rohlfing et al. 1984). Other properties such as chemical reactivity, magnetic moment, polarizability, and geometric structure are also found to exhibit a strong dependence on N. The expectations for new materials with properties different from the atom or the bulk material have been realized. The opportunity is now open to precisely tailor new materials through atom-by-atom control of the composition to generate the clusters or particles of precise design for use in their own right or as building blocks in larger-scale materials or devices—that is, nanotechnology fabrication at its ultimate.

As an example of the unique properties of nanoparticles that make them of interest to energy and chemicals researchers, nanocrystalline materials composed of crystallites in the 1-10 nm size range possess very high surface-to-volume ratios, owing to their fine grain size. These materials are characterized by a very high number of low-coordination-number atoms at edge and corner sites, which can provide a large number of catalytically active sites. Nanostructured materials exhibit chemical, catalytic, and physical properties characteristic of neither the isolated atoms nor the bulk material. One of the key issues in applying such materials to industrial problems involves discovery of techniques to stabilize small nanocrystallites in the shape and size desired. This is an area of active fundamental research (Ying and Sun 1997; Trudeau and Ying 1996), and if successful on industrially interesting scales, is expected to lead to materials with novel properties specific to the size or number of atoms in the crystallite.

Nanoscale Catalysis

A key objective of nanoscale catalyst research is to produce a material with exceedingly high selectivity at high yield in the reaction product or product slate, that is, chemicals or fuels by design; with the option of altering the product or product slate simply by changing the surface functionality, elemental composition, or number of atoms in the catalyst particle. For instance, new catalysts with increasing specificity are now being fabricated in which the stoichiometry may be altered due to nanometer size restrictions in one, two or three dimensions.

Recent examples where nanocrystalline metallic and ceramic materials have been successfully investigated for catalytic applications are discussed briefly below:

- Nanostructured gold catalysts fabricated by a group at Osaka National Research Institute display novel catalytic properties (Haruta 1997a; Haruta 1997b). Bulk gold is unreactive under the same conditions. Highly selective catalytic activity at or even below room temperature is observed to switch on for gold particles smaller than about 3-5 nanometers in diameter. Accompanying this turn-on in catalytic activity is the discovery that these nanoscale gold particles (crystals) have an icosahedral structure and not the fcc structure of bulk materials. Several issues appear to be key in fabricating these novel catalytic materials. For instance, the Osaka group has shown that the preparation method is crucial to fabricating gold catalysts with high catalytic activity and selectivity; that the catalytic activity, selectivity, and temperature of operation are critically dependent on the choice of catalyst support; and that water (moisture) even in ppm levels dramatically alters the catalytic properties. Examples of novel catalytic behavior of nanoscale gold particles demonstrated to date are (a) CO oxidation at temperatures as low as -70°C, and (b) very high selectivity in partial oxidation reactions, such as near-room-temperature reduction of nitric oxide with H_2 using alumina-supported gold nanoparticles. Nanoscale gold catalysts supported on Fe_2O_3 have recently been commercialized and are being used as "odor eaters" for bathrooms in Japan.

- The importance of controlling at least one dimension on the nanoscale size range has been demonstrated for the industrially important hydrodesulfurization (HDS) reaction (Chianelli et al. 1994; Chianelli 1998). For catalysts based on the layered compound MoS_2, maximum HDS activity is obtained only on well crystallized nanosized

materials, while the HDS selectivity is determined by the number of layers or "stack height" of the nanocrystalline MoS_2. In the hydrodesulfurization reaction, cyclohexylbenzene occurs only on the MoS_2 "rim" sites or those around the "edges" of the stack, whereas the pathway to biphenyl requires both "rim" and "edge" sites. Thus, the reaction selectivity is controlled by controlling the aspect ratio of MoS_2 nanoparticles. Such control of one-dimensional and two-dimensional nanostructures for selective chemical advantage is an exciting new area of research. Of course, a major industrial challenge will be to fabricate such nanocrystals in a cost-effective and commercializable form.

- Tschope et al. (1995) have demonstrated that nanocrystalline, non-stoichiometric cerium oxide (CeO_{2-x}) catalysts give rise to a substantial reduction in the temperature of selective SO_2 reduction by CO and exhibit excellent poisoning resistance against H_2O and CO_2 in the feed stream compared to that for conventional high surface area cerium oxide. Such catalysts are produced by controlled post-oxidation of cerium nanoclusters generated via inert gas condensation synthesis. The CeO_{2-x} materials were found to possess a significant concentration of Ce^{3+} and oxygen vacancies, even after high temperature (500°C) calcination.

- Electrochemical reduction of metal salts is yet another option used to control the size of nanoscale catalyst particles (Reetz et al. 1995). This has been successfully used to prepare highly dispersed metal colloids and fix the metal clusters to the substrate. Control of current density during the electrochemical synthesis process allows control of the size of the transition metal particles at the nanoscale. A combination of scanning tunneling microscopy (STM) and high-resolution transmission electron microscopy (TEM) was used to visualize surfactant molecules attached to nanostructured palladium clusters.

Hydrogen Storage

Discovery of materials with higher hydrogen storage per unit volume and weight is an active area of research in several laboratories around the world and is considered by many to be an enabling technology for vehicular fuel cell applications. Researchers at Los Alamos National Laboratory (Schwarz 1998, 93) are studying one approach that enables materials such as magnesium to be used for hydrogen storage. Magnesium is of interest because it can store about 7.7 wt% hydrogen but the adsorption/desorption kinetics are slow compared to that of metal hydrides. High surface area (nanoparticle) mixtures of Mg and Mg_2Ni are produced by ball milling of bulk materials. The addition of Mg_2Ni catalyzes the H_2 dissociation such that the rate of hydrogen adsorption increases to that comparable to $LaNi_5$ and exhibits a low pressure adsorption plateau at about 1500 torr pressure. Experiments show that the pressure plateau can be tailored through alloying. Studies with other catalysts such as FeTi and $LaNi_5$ are presently ongoing to improve both the capacity and charge/discharge rate of hydrogen storage.

A second approach to new hydrogen storage materials involves the use of nanoporous carbon fibers and carbon nanotubes. The carbon fiber materials are produced via catalytic decomposition of hydrocarbon vapors and are reported to exhibit exceptionally high hydrogen storage capacity (Baker 1998, 172). This approach also has the potential

advantage of being able to reduce the total system weight, since the sorbent, in this case carbon, is (on an atom-to-atom basis) significantly lighter than a metal or metal hydride.

Rechargeable Batteries

Discovery of the ability to intercalate alkali metal ions such as lithium into a transition metal oxide crystal framework led directly to Sony's introduction of the rechargeable lithium-ion battery into the commercial market in 1991 (Nagaura and Tozawa 1990; Bubala 1997). The Li-ion battery has several advantages over the nickel-cadmium (Ni-Cd) and nickel metal hydride (Ni-MH) batteries. The Li-ion structures are extremely lightweight and compact, making them more useful for battery packs. The Li-ion battery also provides a higher nominal voltage (approximately three times that of Ni-Cd or Ni-MH) and a higher capacity (approximately two times that of Ni-Cd or Ni-MH) for the same weight of active material (Sony 1999).

Recently, it has been discovered at Fuji that the nanostructure created in the amorphous tin oxide-based system gives significantly higher reversible capacities than the commercial systems using carbon electrodes (Brousse et al. 1998; Idota et al. 1997; Idota et al. 1995). The novelty of the tin oxide-based system is the electrochemical reduction of tin oxide to form continuous channels of nanocrystalline tin aggregates held together by the amorphous clusters of inactive oxide ions. However, the insertion and removal of lithium from the intermetallic system is accompanied by significant volume expansion (~300%), leading to disintegration and cracking of the electrode during cycling (Courtney and Dahn 1997).

Researchers at Fuji developed an ingenious solution to this problem, wherein they used a glass-forming composition primarily composed of tin, along with glass formers from group III, IV, or V of the Periodic Table. In-situ electrochemical reduction of the glass resulted in the formation of nanocrystalline tin precipitates (~7-10 nm) within the amorphous matrix phase (Li et al. 1998). The large volume fraction of the nanocrystalline tin islands enclosed by the amorphous oxide network was sufficient to form continuous channels and thereby maintain the necessary electrical conductivity within the electrode. The open structure of the glass helped to accommodate the strain associated with the volume expansion during insertion and removal of lithium from tin. The volumetric strain was also largely reduced due to the formation of nanocrystalline regions of tin.

It is believed that the nanocrystalline nature of tin precludes the formation of bulk phases of Li-Sn alloys, and the ratio of Li:Sn is therefore varied continuously, minimizing the deleterious influence of the large-volume expansion-related strain. This nanocomposite has been described by many as an active-inactive composite; the inactive matrix is the oxide glass enclosing the cluster of the active phase of tin. The realization of this concept has led to stable reversible capacities of almost twice that of carbon, and it is presently an active area of research, particularly in identification of synthetic processes and methods to stabilize the cathode structures so that the irreversible lithium loss can be eliminated.

A novel particulate sol-gel approach has been developed at Carnegie Mellon University that leads to the formation of intermixed nanophase reactants of Li_2CO_3 (less than ~20

nm) and NiO (~30-50 nm) that directly react almost instantaneously in a single step to form the desired nanocrystalline (~100-500 nm) oxide (Chang 1999; Chang et al. 1997). The nanocrystalline oxide exhibits less than 1% antisite defects. Such fine-scale perfect crystals also exhibit one of the highest first discharge capacities. Advances in materials processing and increased understanding of the materials chemistry, nanoscale structure, and electrochemical reactions will play a pivotal role in dictating the future of this prominent energy storage technology. Carbon nanotubes have been demonstrated to store Li efficiently. Their use could improve anode performance as well.

Self-Assembled Nanostructures

Chemical self-assembly of nanostructured materials such as zeolites or carbon materials occurs when a large molecular or crystalline structure results from the precise organization of a large number of molecules or atoms into a given and reproducible structure. Typically, organization through chemical self-assembly occurs because of specific interactions of the molecules or atoms among themselves with (or without) a template. The interaction of the different bonding mechanisms involved in self-assembly is an area of strong fundamental research interest. For this document, only two areas will be highlighted: zeolites and carbon materials. Both of these materials exhibit desirable characteristics of self-assembly; namely, that they are novel and reproducible structures that can be fabricated in industrially significant quantities.

Zeolitic Materials

Aluminosilicates (e.g., zeolites) are crystalline porous nanostructures with long-range crystalline order with pore sizes that can be varied from about 4 Å to 15 Å in conventional zeolites. A zeolite may exhibit a three-dimensional zeolite cage structure consisting of intersecting straight and ziz-zag channels or a simpler two-dimensional zeolite configuration. The size of the window is determined by the number of oxygens in the ring. Table 9.1 gives approximate window dimensions for zeolites as a function of the number of oxygens in the ring.

Table 9.1. Zeolite Channel "Window" Dimensions for Number of Oxygens in Ring

Number of Oxygens in Ring	Ring Diameter (Å)
4	1.2
5	2.0
6	2.8
8	4.5
10	6.3
12	8.0

As can be seen by examination of Table 9.1, molecules can pass through or be blocked from transport through or into the zeolite, depending on the size of the window of the channel in the zeolite. For example, normal hexane with a kinetic molecular diameter of about 5.1 Å can easily pass through a 10 ring or larger, whereas cyclohexane with a kinetic molecular diameter of 6.9 would pass through a 10 ring only with great difficulty. Thus, all other things being equal, a 10-ring zeolite could be used to separate mixtures of

normal hexane and cyclohexane. It is this property, together with the ability to chemically modify the acidity of zeolitic materials, that makes zeolites extremely valuable as highly selective catalysts, selective sorbents, and membranes. The zeolite catalyst area alone is the basis for an industry that exceeds $30 billion annually.

In 1992, a new family of aluminosilicates (M-41S) with pore sizes between 20 and 100 Å in diameter was reported by Mobil researchers (Beck et al. 1992; Kresge et al. 1992). One of particular interest is MCM-41, which consists of hexagonal arrays of uniform 2 to 10 nanometer cylindrical pores. Not only can such materials be synthesized, but also novel structures such as "tubules-within-a-tubule" have been fabricated as mesoporous molecular sieves in MCM-41 (Lin and Mou 1996). Of particular interest is the possibility to expand the so-called "liquid crystal templating" mechanism (Huo et al. 1994; Sun and Ying 1997) to non-aluminum dopants within the silicate MCM-41 framework and to derive non-siliceous MCM-41 type of materials (Braun et al. 1996).

Another approach to synthesizing large pore and large single crystals of zeolitic materials is being pioneered by Ozin and his group at Toronto, who have demonstrated that crystals as large as 5 mm can be synthesized (Kupperman et al. 1993). The ability to synthesize such large crystals has important implications for discovery of new sensors (selective chemical adsorbents) and membrane devices (selective transport of molecular species), since large single crystals can now be available to the laboratory researcher to carry out fundamental studies of adsorption and diffusion properties with such materials.

Such materials are expected to create new opportunities for applications in the fields of separations science for use directly as molecular sieves or as new molecular sieving sorbent materials; in catalysis as heterogeneous catalysts and as supports for other catalyst materials; as well as other novel applications (Brinker 1996). The ability to synthesize zeolitic materials of precise pore size in the range between 4 Å and 100 Å continues to expand the possibilities for novel opportunities for research and technological innovation in the catalytic, separations, and sorption technologies.

Carbon Materials

The carbon-based materials considered here include fullerenes and their relatives such as endohedral fullerenes, metal-coated fullerenes, carbon nanotubes, carbon nanoparticles, and porous carbons. Since 1990 with the discovery of techniques to produce soluble carbon in a bottle, research on and with carbon materials has skyrocketed (Dresselhaus et al. 1996; Dresselhaus and Dresselhaus 1995). Not only can the molecular forms of carbon, the fullerenes, and their derivatives be synthesized, characterized, and studied for applications, but many other new carbon materials such as multi- and single-walled carbon nanotubes can now be produced in macroscopic quantities. A rich literature now exists on these new carbon materials; the following section of this report will only highlight some recent examples of particular interest in the area of high surface area materials.

Of particular interest for future catalytic applications is the recent report that not only can C_{60} be coated with metal atoms, but also the metal coating can consist of a precise number of metal atoms. For example, $C_{60}Li_{12}$ and $C_{60}Ca_{32}$ have been identified mass spectroscopically (Martin, Naher, et al. 1993; Martin, Malinowski et al. 1993;

Zimmerman et al. 1995). C_{60} has been coated with a variety of different metals, including Li, Ca, Sr, Ba, V, Ta, and other transition metals. Interestingly, addition of more than 3 Ta atoms to C_{60} breaks the C_{60} cage. Replacement of one carbon atom in C_{60} by a transition metal atom such as Co or Ir is being studied for possible catalytic applications. The future technological challenge will be to discover techniques to fabricate large quantities of such materials so that we can put such catalyst materials in a bottle and not just in molecular beams.

Carbon nanotubes have the interesting property that they are predicted to be either semiconducting or conducting (metallic) depending on the chirality and diameter of the nanotube. Such materials are being studied as conductive additives to plastics and for use in electrochemical applications (Dresselhaus 1998) where the uniformity of the nanotube diameter and length is not overly critical. Another approach is to use the carbon nanotube as a template for a nanotube of an inorganic oxide. Hollow nanotubes of zirconia and yttria-stabilized zirconia have been prepared by coating treated carbon nanotubes with a zirconium compound and then burning out the carbon template (Rao et al. 1997). Finally, many groups around the world have recently demonstrated large-scale production of single-walled nanotubes, so one may anticipate a strong upsurge in the characterization and potential usage of single-walled carbon nanotubes in the future.

Porous carbons are of interest as molecular sieve materials, both as sorbents and as membranes or as nanostraws for filtration. A major research objective is to develop materials or structures with exceedingly high storage capacity per unit volume and weight for gases such as H_2 or CH_4. These could become an economic source of combustion fuel or as the means to power fuel cells for ultralow-emission vehicles or for electric power generation. Microporous hollow carbon fibers have exhibited high permeance and high selectivity as hydrogen selective membranes; development is now underway to scale up production of these membranes to commercial levels (Soffer et al. 1987; Jones and Koros 1994; Rao and Sircar 1993). As discussed earlier, carbon fiber materials produced via catalytic decomposition of hydrocarbon vapors have also recently been reported (Baker 1998, 172) to exhibit exceptionally high hydrogen adsorption capacity.

More mundane uses of nanotubes as nanometer reinforcing rods in polymers, both for structural and electrical properties, or even in concrete are being contemplated because of the "super strength" of the individual fibers (Lourie et al. 1998). Also, the substantially larger quantities of nanotubes now commercially available allows larger-scale testing of materials fabricated with nanotubes. Incorporation of conducting carbon nanotubes in construction materials such as concrete or structural plastics will allow for real-time, continual, and remote monitoring of material integrity and quality.

Thin Films

Another approach to self-assembly involves the fabrication of microporous and dense ultrathin films. Research and development of microporous thin films for use as molecular sieving membranes using inorganic crystalline materials such as zeolites or porous silica is yet another area of active research around the world. For molecular sieving membranes, one critical challenge is to discover ways to create large-scale, thin,

nearly defect-free membranes. These films have potential applications in energy conversion, batteries, catalysis, and fuel cells.

One recent example of these types of thin films is the fabrication of mesoporous conducting thin films grown from liquid crystal mixtures (Attard et al. 1997). TEM reveals an ordered array of 2.5 nm diameter cylindrical holes in a 300 nm thick Pt film. The hole diameter can be varied either by changing the chain length of the surfactant molecule or by adding an alkane to the plating solution. It is interesting that this technique produces a continuous thin film with nanoscale porosity in an electrically conducting material.

Thin films of specialized coatings for corrosion, thermal, and/or chemical stability are valuable in the chemical and energy industries. The ability to coat existing reactors, tubing and other equipment exposed to harsh environments is somewhat mundane but can save on replacement capital and processing costs in both industry and research.

Novel chemical sensors may be anticipated through use of ultrathin films composed of specialized clusters. Nanoparticles provide high surface area, which allows one to detect the state of a chemical reaction, selectively and sensitively detect chemical leaks for both safety and reduction of waste, and improve the quality of the detection signals. Demonstration of the synthesis of oriented films of mesoporous silica on mica is an important step for generation of new materials (Yang et al. 1996).

9.3 GOALS FOR THE NEXT 5-10 YEARS: BARRIERS AND SOLUTIONS

Over the last two decades, the development and improvement of new techniques to fabricate and characterize nanoscale materials has fueled much of the enormous growth in nanoscale science and technology. Breakthroughs in synthesis have not only made nanoscale materials more readily available for scientific study and characterization, but also in some instances, have opened the door to large-scale industrial testing and use.

For example, atomic force microscopy and scanning tunneling microscopy are two techniques that have become major workhorses for characterization of the structural and electronic properties of nanoscale materials. The strong upsurge in interest and funding in nanoscale materials must to a large degree be credited to the recent development of these two techniques. Combined with X-ray spectroscopy, high-resolution transmission electron microscopy, and low-energy, high-resolution scanning electron microscopy, researchers now have the means to physically characterize even the smallest structures in ways impossible just a few years ago. Not only can the structure be precisely examined, but the electronic and, in some instances, the magnetic character of the nanostructures also can be mapped out.

Using the scanning probe devices, scientists not only can image individual atoms and molecules but can also manipulate and arrange them one by one in ordered arrays. Atomic manipulation to build structures is just in its infancy, but one can imagine a route to the ultimate goal of atomically tailored materials, built up atom by atom by a robotic synthesizer. The "abacus" of C_{60} molecules produced at the IBM laboratories in 1997 is an excellent example of possibilities that may lie ahead for manipulation at the atomic

scale. The Angstrom Technology Partnership project in Japan is now in its second 5-year program to push the frontiers of atom manipulation closer to the commercial sector.

Of the fundamental properties that control the stability of atoms, clusters, and particles on a surface or support, particularly critical are the adsorption and adhesive energies of a metal atom or particle on a solid metal or oxide surface. An understanding of these properties that determine the stability of materials can impact applications ranging from oxide-supported metal catalysts and bimetallic catalysts to metal-ceramic interfaces used in microelectronics. With knowledge of such parameters, scientists can predict the relative strengths of the metal–metal and metal atom–support interaction energies and infer relative stabilities as a function of the composition and size of the metal cluster. Recently, it has become possible to experimentally measure the metal atom–surface bond strength on a per-atom basis using adsorption microcalorimetry on ultrathin single crystal metal or metal oxide surfaces (Stuckless et al. 1997). The technique for direct calorimetric measurement of metal adsorption energies developed at the University of Washington is based in part on earlier work first developed by King and colleagues at Cambridge University (Yeo et al. 1995). The technique, which probes interactions on an atom-by-atom or molecule-by-molecule basis, can be thought of as another "atomic probe"—one that can be expected to substantially advance our database and understanding at the ultimate nanoscale for materials: single atoms.

Similarly, new techniques are being developed to allow chemical and catalytic reactions to be followed in-situ in real time. As an example, an infrared and nuclear magnetic resonance (NMR) spectroscopic technique is being developed at the Max Planck Institute in Muelheim, Germany (Siegel et al. 1999, NTSC Report, Appendix B) to monitor kinetics of CO adsorption on 1-3 nm diameter metal colloid particles (typically Pt, Rh, or Pd) in liquids and to follow in real time the way CO organizes itself on the particles while in liquid suspension. Such techniques will allow scientists to begin to understand the metal particle properties in solution and thus infer how they might behave in real reaction mixtures. Extension of such techniques to real catalytic reactions in solution for catalyst particles of different sizes and compositions is likely in the not too distant future.

The application of combinatorial techniques for screening the multitude of reactions occurring in many chemical processes will become exceedingly valuable in the future. One can envision nanoliter reactors injecting nanoliters of reagents on nanometer catalysts arranged in an indexed array for rapid screening of hundreds if not thousands of reactions. Alternatively, arrays of nanometer catalysts selectively prepared with a known but different number of atoms (the same or different atom) could be prepared on supports and then screened for specific reactions. The use of such combinatorial techniques to determine catalytic and chemical reactions, although in its infancy, is one of the most rapidly growing areas of research interest in industry.

The area where nanoscale materials may have the greatest future impact in the energy and chemicals industries is difficult to predict, but some signs point to possibilities of substantial advancement in the areas of adsorption/separations, particularly in gas sorption and separations, and in novel chemical catalysis using nanoscale catalyst particles.

At least two major challenges must be faced before utilization and generation of nanoscale materials can become commonplace. The first is achieving *critical dimensional control* of the nanoscale structure over long times and varying conditions. In nanoscale catalyst materials, the critical chemical selectivity is likely to be intimately associated with the local environment around what is termed the "active" site. This suggests that the size, type, and geometry of the atoms making up the active site will play a critical role in defining the conditions under which this active site will be able to carry out its designed function. Fabrication of materials with exactly the same structure and composition at each active site has been and will continue to be a major challenge to materials and catalytic scientists.

The second challenge is achieving *thermal and chemical stability control* of the fabricated nanostructure. It is generally accepted that the smaller the nanostructure (active site) the more likely it becomes that the structure may move, aggregate, be poisoned, decompose, or change its shape, composition, or morphology upon exposure to thermal and/or chemical cycling. The identification of windows of stable operation in which the specific structure or material will be able to retain the desired (and designed) behavior is critical for commercial applications.

It is important to recognize that the use of nanostructuring or nanostructures to generate, fabricate, or assemble new materials, devices, or processes is at an embryonic stage. The effects of the nanostructure on materials properties and our ability to measure them will be increasingly important for future progress in development of nanotechnology-based materials for the marketplace.

9.4 SCIENTIFIC AND TECHNOLOGICAL INFRASTRUCTURE

It is important to recognize that nanoscale science and technology is not a "stand alone" field of endeavor, but rather is more of a "generic" area that is expected to have a critical impact and overlap in many areas of science and technology. The breadth of the issues covered in this document is illustrative. The fields, disciplines, and areas of expertise that fall under the nanotechnology umbrella are many and diverse. This diversity offers both an opportunity and a challenge to the scientific, technological, educational, and funding communities.

Many of the tools and instruments required for nanotechnology research are state-of-the-art, very expensive, and inaccessible to a large fraction of researchers. Progress is most apparent in this field within collaborative undertakings that combine complementary equipment and skills. A single researcher cannot do it all in this particular field. Mechanisms are needed that will provide researchers with easy access to the tools or expertise they require. One approach is to establish centers around core facilities such as universities and government laboratories. This should suffice for researchers associated with the center but does not provide close support for individual researchers or small groups located at a distance from such a center.

9.5 R&D INVESTMENT AND IMPLEMENTATION STRATEGIES

In the energy and chemical industries, long-term R&D has come under increasing pressure. Addressing the technical challenges of supporting existing technologies and improving technology in a company typically requires a disproportionate fraction of the total resources available. As a result, over the last twenty or so years, fundamental or basic research in industrial laboratories has declined significantly. The apparent expectation by many industrial R&D managers is that much of this fundamental work will be picked up by academic or national laboratory research initiatives; however, in an ever tightening financial environment, basic research has declined in those quarters as well.

If the United States is to remain the world's technology leader, mechanisms must be established first to identify critical research areas and then to ensure long-term funding for these critical research areas. One approach is to make it simpler to establish collaborative efforts between universities, national laboratories, and industry. This will not be an easy task to accomplish, because the goals of each organization are different and in some instances even conflicting; for example, academe's need to publish conflicts with industry's need to keep material proprietary.

9.6 PRIORITIES AND CONCLUSIONS

In the energy and chemical industries, nanotechnology is still at a nascent stage: significant opportunities are available and great strides forward may be anticipated. We see that even "mature" technologies such as catalysis, dispersions and coatings, microporous materials, and structural materials are already being impacted. In many industries where nanoscale approaches are critical, specific opportunities have already been identified and in many instances, the nanoscale approach to research is ongoing. Examples include the following:

- Higher selectivity catalysts through nanoscale fabrication
- Novel sorbent materials through chemical self-assembly
- High-capacity, low-volume, lightweight nanostructured materials for hydrogen and natural gas storage
- High-selectivity, high-permeance gas separations using molecular sieving membranes
- New approaches to combinatorial chemistry through nanoscale reactors and nanoscale mixing
- Improved thermal barrier coatings using nanoscale fabrication
- Strengthened construction materials using nanoscale binders
- Higher strength polymeric fibers and pipes using nanoscale fibers
- New energy conversion employing nanoscale materials for improved light gathering and higher efficiency
- Improved rechargeable batteries using nanoscale anodes and cathodes
- Improved process efficiency through the application of smart sensors

The challenges that must be faced are twofold. First, there are the scientific and technical challenges specific to nanoscale materials and approaches. Dimensional control and stability of the nanostructure or material fabricated by nanostructuring approaches must be maintained for long times and under varying conditions and environments; self-disassembly must not be allowed to occur. The efforts in this area generally encompass and depend on many different scientific disciplines. Thus, mechanisms for collaboration and interaction appear to be a necessity for substantial progress. For ultimate success, most nanotechnology requires identifiable scale-up options to produce macroscopic materials, devices, and processes.

Second, there are the challenges of allocating sufficient time and funding to build the fundamental database that will be required for new commercial technologies based upon nanoscale approaches. Since fundamental advances cannot be anticipated, basic science should not be slighted in a shortsighted approach to funding development of what we already know.

9.7 EXAMPLES OF CURRENT ACHIEVEMENTS AND PARADIGM SHIFTS

9.7.1 Towards Artificial Photosynthesis – Gratzel Cell
Contact person: D. Ginley, National Renewable Energy Laboratory

Figure 9.1 illustrates two of the approaches under investigation that could lead to systems resembling artificial photosynthesis. In photosynthesis, light is harvested by an array of collectors, and then the excited state energy is funneled to a reaction center where this excited state energy is converted into stored chemical energy. Although light harvesting is not readily attainable at present, there are a number of approaches employing composite structures that might be enabling toward this goal.

Figure 9.1a (top) illustrates work that is being done at Lawrence Berkeley Laboratories by Alivisatos (Huynh et al. 1999, Alivisatos and Katari 1995). In this case, absorbing or emitting (if you want to make an LED, you can run a solar cell in reverse) nanoparticles (CdSe) are in a conductive organic matrix. If there is an external field present between the back metallization and the transparent front contact, then when an electron/hole pair is created on the nanoparticle absorbers, they are separated and transmitted to the contacts, and current flows in the device. Conceptually, it is possible to get excited state transfer between nanoparticle absorbers.

Figure 9.1b (bottom) illustrates the Gratzel cell, as investigated by a number of laboratories (Gratzel et al. 1999). In this case, optically excited dyes inject negative charge into nanoparticle TiO_2 and photooxidize a reversible couple in the solution. Cells with this configuration have demonstrated solar conversion efficiencies of 10% and extended stability.

In both of these approaches, the nanomaterials are critical in the processes whereby light is adsorbed, charged carriers are generated and separated, and current flows in the device. Engineering the nanostructured materials and the interfaces in the devices is critical to their eventual practical application.
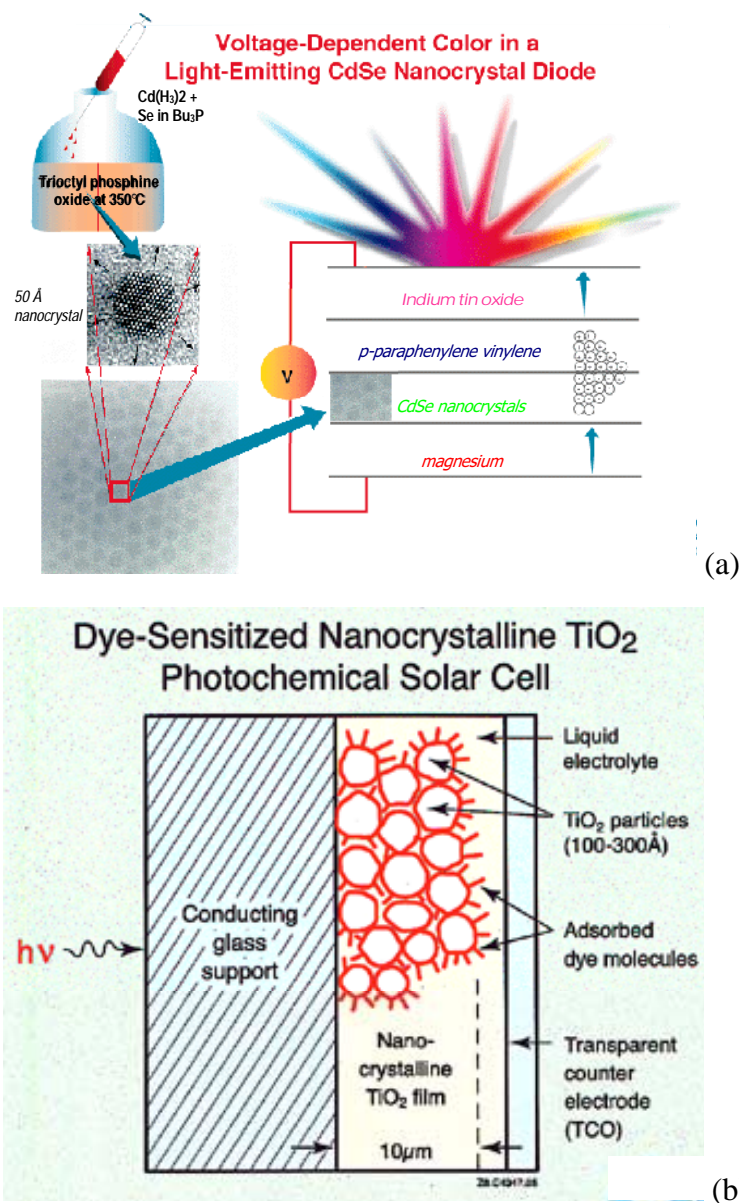
Figure 9.1. Two concepts for solar energy conversion: nanomaterials leading to direct conversion or chemical production: (a) light-emitting nanocrystal CdSe diode in a conducting organic matrix; (b) photochemical Gratzel cell of optically excited charged dyes.

9.7.2 Energy Storage: Fuel Cells, Carbon Nanotubes for Storage and Li Batteries
Contact person: D. Ginley, National Renewable Energy Laboratory

Figure 9.2 illustrates some of the new approaches under investigation for the storage of energy. These systems could be coupled to renewable energy generation systems or employed in hybrid vehicles, etc. Figure 9.2a illustrates a fuel cell that would use hydrogen and oxygen as the active couple and have only water as a product (Swartz et al. 1999). Key to the successful development of such cells is the ability to store the hydrogen effectively, to have appropriately selective membranes, and to have catalysts that readily promote the recombination of hydrogen and oxygen to produce water.
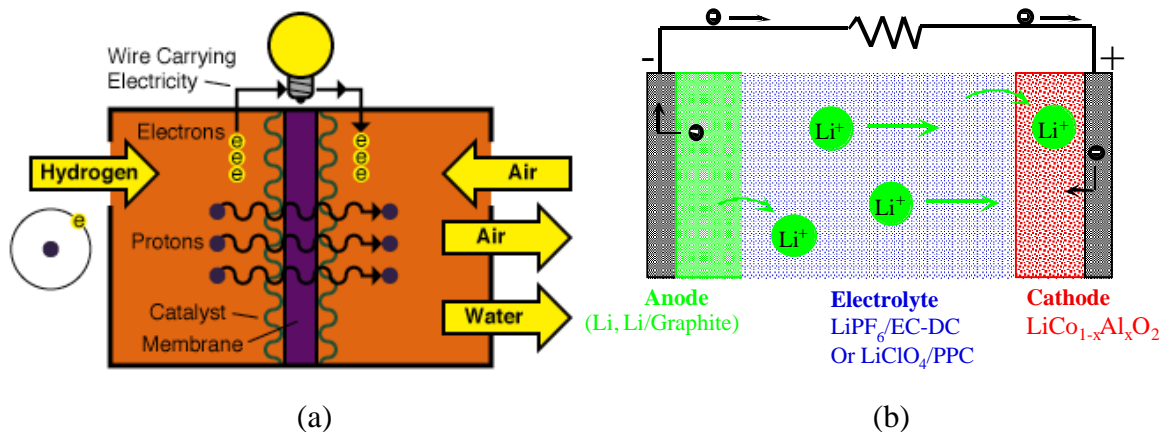
Figure 9.2. Fuel cells and Li batteries for energy storage.

In addition, it is becoming clear that the membrane and catalysts will need to be nanostructured to be the most effective in a fuel cell. Figure 9.2b shows the typical structure for a rechargeable secondary Li battery. In this case, both the anode and cathode can benefit substantially from engineering at the nanoscale. Because diffusion processes are so important in these battery materials, electrodes that are mezo/nanostructured can have improved charge/discharge rates and may have greater stability (Whitehead et al. 1999). Recent work on cathodes has demonstrated that aerogels of V_2O_5 or nanoparticulate $LiCoO_2$ or MnO_2 can have improved properties as a cathode (McGraw et al. 1999). Recent work on carbon nanotubes and on Li/Sn alloys have shown that the true structure of the anode may be at the nanoscale; thus, it is critical to understand the materials science and electrochemistry (diffusion) at this length scale.

9.7.3 Improved Energy Efficiency

Contact person: S.T. Picraux, Sandia National Laboratories

Nanotechnology will have a significant influence on energy efficiency. The left side of Figure 9.3 illustrates how nanostructuring can lead to dramatic advances in magnetic materials. Here fabrication of so-called "exchange spring magnets" consisting of alternating nanometer-thick layers of hard (e.g., SmCo) and soft (e.g., Fe) magnetic materials gives dramatic increases in the performance of permanent magnets (work performed at Argonne National Laboratories). For example, a decrease in the SmCo layer thickness from 20 nm to ~2 nm for a given Fe layer thickness increases the maximum energy product $(BH)_{max}$ by over three times.

Improvements in the performance of motors due to advances in magnets will increase energy efficiency. Material structuring at the nanometer scale can also greatly increase the strength and hardness of metals and alloys, allowing the use of lighter materials (e.g., Al) and greatly reducing energy loss by friction and wear. The right side of Figure 9.3 illustrates the greatly increased yield strength of Ni by ion-implanting Al and O into the near surface (work performed at Sandia National Laboratories). The implantation produces a dispersion of nanometer-sized Al_2O_3 in the Ni, which is responsible for the increased strength. Similarly, O implantation turns Al into a material with strength and wear resistance exceeding those of the best bearing steels.
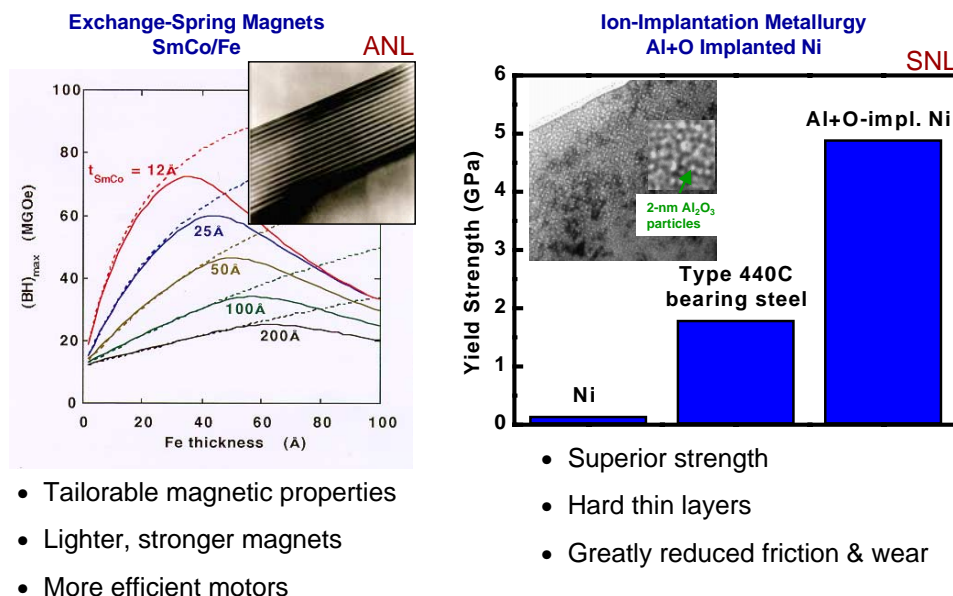
Figure 9.3. Nanoscience will lead to improved energy efficiency (DOE National Laboratories).

9.7.4 Nanoscale Catalysis

Contact person: D. Cox, Exxon Research and Engineering Co. (ret.)

The energy and chemical industries have greatly benefited from nanotechnology. Catalysis represents a major success story, both in the use of oxide-supported, highly dispersed metal (nanoscale active sites) catalysts and in the use of crystalline materials (zeolites) as highly selective catalysts. The latter case has come about most recently and is due in large part to the discovery by Mobil researchers of how to synthesize large quantities of zeolites such as ZSM5. This availability of unlimited commercial quantities of zeolites has led to a modern revolution in catalysis. Zeolite catalysts now are used to process over 7 billion barrels of petroleum and chemicals annually, forming the basis of an industry that exceeds many tens of billions of dollars a year in revenues. A multitude of commercial processes have been developed that exploit size exclusion and selective molecular diffusivity properties based upon the nanosize pore and channel structure of zeolites (Figure 9.4). This, together with the ability to tailor the acidic character of the zeolite through ion exchange processes, has opened up a myriad of research and development opportunities in the energy, chemical, and environmental industries.

One of the most important zeolite catalyzed processes in which selective molecular diffusion is the controlling aspect is the isomerization of C8 aromatics using H-ZSM5 catalysts. The demand for two C8 isomers, paraxylene and orthoxylene, is much greater than that for the C8 isomers metaxylene and ethylbenzene. H-ZSM5 with its 0.6 nm pore size has the unique ability to isomerize xylenes with little cracking of the feedstock. A second crucial property is that paraxylene has a much higher diffusivity in H-ZSM5 than do the other xylene isomers. This means that the paraxylene molecules can more easily diffuse out of the zeolite crystal, whereas the ortho and metaxylene isomers are effectively trapped within the pores.
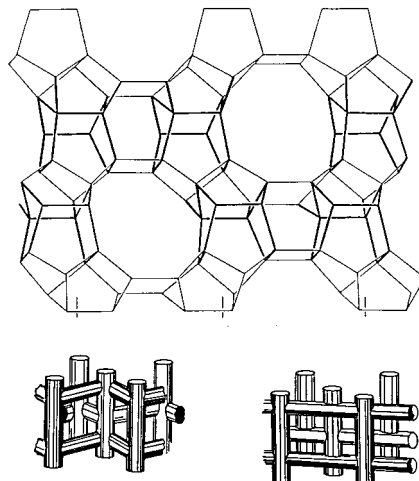
Figure 9.4. Drawing of the three dimensional channel structure of ZSM-5 (reprinted by permission from Siegel et al. 1999; ©1999 Kluwer Academic Publishers, printed version, and Loyola College in Maryland, electronic versions).

A commercial process "Parex" based upon this unique nanoscale property was developed and is in commercial use through licensing agreements in many refineries around the world. Parex is but one example of many commercial processes based upon zeolite catalytic processes used in the chemical and energy industries. Substantial industrial and academic research is ongoing to synthesize new zeolites (the recent discovery of larger pore zeolites such as MCM-41 by Mobil researchers is but one example) and develop new sorption and separation processes to exploit the molecular or nanoscale selectivity inherent in such crystals.

9.7.5   Hydrogen Storage in Carbon Nanotubes: Research Promise for Fuel Cell Applications

Contact persons: M. Dresselhaus, Massachusetts Institute of Technology, and
A. Brecher, Department of Transportation, Volpe Center

The Department of Energy Hydrogen Program Plan (1992, DOE/CH10093-147) indicates that a hydrogen storage capacity of about 63 kg H_2/m^3, or 6.5 wt%, hydrogen in carbon must be achieved for advanced fuel cell power storage and generation applications. Research findings indicate that carbon nanotubes have unique structural and morphological properties that permit both a relatively large volumetric storage capacity for hydrogen gas and effective adsorption and desorption.

Carbon nanotubes are a single layer of the hexagonal lattice graphite, wrapped into a single-walled cylindrical tube of about 1 nanometer diameter (with about 20 atoms around the cylinder), but up to several microns long. This gives an aspect (or length-to-diameter) ratio in excess of 10,000. Adsorption of a hydrogen gas monolayer on a graphite surface can occur at low temperature under dense packing conditions to yield an uptake of 4.1 wt% hydrogen. H_2 molecules are considered to be spheres with a dynamic radius of 2.89 Å. Nanotubes are, however, more useful as a practical storage vessel for hydrogen, because they will retain the hydrogen even at room temperature, and because the cylinder wall curvature increases the binding energy of the hydrogen molecules to the

surface carbon atoms relative to that of the free graphite surface. Furthermore, when single-wall carbon nanotubes are prepared, they form "ropes." These are a triangular, close-packed lattice of parallel cylinders with an intertube separation of 3.4 Å, the same as the separation between adjacent graphite layers. The triangular stacking of nanotubes permits additional storage of hydrogen molecules in the interstitial space.

Geometrical packing of hydrogen inside single-walled carbon nanotubes yields a storage fraction of about 3.3 wt%. Hydrogen stored in the interstitial volume would adsorb another 0.7 wt%, thus resulting in a total of 4 wt%. This theoretical prediction has indeed been experimentally confirmed by Dillon et al. as published in *Nature* in 1997 (Dillon et al. 1997) and in more recent work by the same group. Prigogine and Rice (1988) and Averback et al. (1991) discuss several materials design approaches to increasing the uptake of hydrogen and the H/C storage ratio in nanocylinders, fullerenes, or in specially designed carbon fibers. A more recent summary of presently available results (Dresselhaus and Eklund 1999) paints a promising picture for the use of carbon nanotubes for storage of hydrogen and other gases through variation of gas pressure and nanotube diameter. Efforts are being pursued to increase the hydrogen-to-carbon storage ratio to achieve the levels considered practical for multiple energy generation and storage applications, such as fuel cells for transportation and for small and medium stand-alone power sources.

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