Chapter 10

NANOSCALE PROCESSES IN THE ENVIRONMENT

Contact persons: R. Flagan, California Institute of Technology; D.S. Ginley, National Renewable Energy Laboratory

10.1 VISION

Nanotechnologies have the potential to significantly impact the generation and remediation of environmental problems through understanding and control of emissions from a wide range of sources, development of new "green" technologies that minimize production of undesirable by-products, and remediation of existing waste sites and polluted water sources. Removal of the finest contaminants from water supplies (less than 300 nm) and air (under 20 nm), and continuous measurement and mitigation in large areas of the environment, are envisaged.

However, nanoscale materials also potentially pose occupational and ambient health risks from both existing sources, such as diesel engines, and new systems involved in the production of nanoscale materials. In many cases, these systems are new technologies, and their environmental hazards will need to be carefully assessed.

Interdisciplinary research on molecular/nanoscale processes that take place in natural systems is important for understanding the environmental consequences of generation and transport of contaminants in the environment. Research needs include studies of interfaces between organic and inorganic structures, with focus on specific processes characterized by small length scales.

10.2 CURRENT SCIENTIFIC AND TECHNOLOGICAL ADVANCEMENTS

Nanoscale Processes in the Environment

Complex physical and chemical processes involving nanoscale structures are essential to phenomena that govern the sequestration, release, mobility, and bioavailability of nutrients and contaminants in the natural environment. Processes at the interfaces between natural physical and biological systems have relevance to health and biocomplexity issues. Increased knowledge of the dynamics of processes specific to nanoscale structures in natural systems not only will improve understanding of transport and bioavailability but also lead to development of nanotechnologies useful in preventing or mitigating environmental harm.

Pollution by Nanoparticles and Mitigation

Nanoscale materials occur naturally in the atmosphere, in minerals, in the ocean, and in biological systems. The risks to human health for particles on this length scale have not been assessed. In some cases, as for silica and asbestos fibers, the hazard potential is clear; in others, it appears that the hazard potential may be lower. Nanoscale aerosol particles are constantly involved in complex chemical processes in the atmosphere.

The considerable attention paid in recent years to the presence of fine particles in the atmosphere has led to the PM-2.5 ambient air quality standard. However, part of the difficulty of assessing the impact of nanoscale materials on biological systems is finding analytical techniques suitable for monitoring both their presence and their impact. Efforts to understand the nature of the particles at the fine end of the size spectrum have led to the development of a number of instruments that are facilitating determination of the health and environmental impacts of nanoparticles. Nanoparticles can be grown to detectable sizes by vapor condensation in an instrument called a condensation particle counter. Over the past decade, the detection capability of such instruments has been extended to as small as 3 nm in atmospheric pressure air. Additional information on the nature of nanoparticles can be obtained by differential mobility analysis, a technique in which particles are charged (typically with one positive or negative charge), caused to migrate across a particle-free stream by an applied electric field, and discharged as a monodispersed aerosol. Over the past decade, the time required to measure particles over a wide range of sizes has been reduced from tens of minutes to a fraction of a minute in commercially available instruments, and measurements within a few seconds have been demonstrated in the laboratory. As interest in nanotechnology has increased, the sizing capability of the differential mobility analysis has been extended to 1 nm and below.

Environmental Technologies

A number of environmental and energy technologies have already benefited substantially from nanotechnology.

- *Reduced waste and improved energy efficiency*. Catalysis presents a major success story. It has also been demonstrated in some cases that catalytic efficiency (rate and turnover) is substantially altered by the use of nanoscale reagents in homogeneous or heterogeneous applications. Nanoscale materials for Li battery cathodes such as aerogel or zerogel V_2O_5 can substantially increase capacity, cell life, and charge-discharge rates.
- *Environmentally benign composite structures*. The ability to incorporate nanoscale inclusions in composites has the potential to produce materials with improved properties and tailored to specific applications such as improved filtration systems. This can produce systems with increased environmental robustness, resulting in longer service life and reduced overall system costs and replacement needs, and reduced environmental impact. It also can produce lighter, smaller structures, resulting in systems with reduced energy consumption. Use of nanoscale materials in composites can range from the use of oxide- or nitride-based inclusions in steels to the development of fully engineered heterogeneous composites.
- *Waste remediation*. Nanostructured materials have an increasingly important role in the remediation of wastes. This can take many forms, from using TiO_2 particles to oxidize organic contaminates, to employing nanoscale scavengers to capture heavy metals in contaminated waste sites. In many cases, illuminated particles can be oxidizing agents, active either in solution or in aerosols. Recent work has shown that

UV-illuminated nanoscale TiO_2 can be employed to clean atmospheric contaminates, including hazardous organic chemicals, cells, and viruses, as well as to sequester hazardous chemicals. Nanoscale particles with suitable surface derivatization (ligands or reagents) can also be used to sequester heavy metals or bond to and passivate contaminated surfaces. In addition, it is clear that the more efficient chemical processes are, the less direct waste is produced. One interesting possibility is that as the surface chemistry of nanostructured materials is better understood, it will be possible to tailor the surface in nanostructured material-mediated reactions to minimize the generation of wastes.

More recently, the discovery of the ordered mesoporous material MCM-41 has extended the pore size range that is attainable in structured inorganic materials to the 10 to 100 nm size ranges. It took nearly a decade to take these materials from the initial discovery to a commercial product. One of the uses of this product is in waste remediation of heavy metals at nuclear power sites. The ability to tailor the nanostructured materials for specific ions is important both in being able to remove all the waste and segregate it, and in lowering the cost of the process.

- *Energy conversion*. Use of energy, indirectly as electricity and as fuel for transportation, is responsible for an enormous and adverse impact on the environment. Nanoscale systems offer the potential for renewable energy conversion systems with much less waste production; when this potential is coupled with improved batteries or fuel cells having nanoscale or mesoscale electrodes for energy storage in transportation, the positive impact on the environment could be tremendous. Chapter 9 of this report includes additional details on these energy-related applications.

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

Nanoscale Processes in the Environment

IWGN workshop participants agreed that there is an urgent need to encourage interdisciplinary research that involves novel approaches and that adopts newly developed experimental, theoretical, and computational methods for characterizing nanostructures. If interaction is increased between the community of scientists and engineers studying the fundamental properties of nanostructures and the community attempting to understand complex processes in the environment, this will hasten both communities gaining an integrated understanding of the environmental role of nanoscale phenomena. Overall, there exist opportunities in a number of areas:

- Replacement of waste-generating technologies with “green” technologies
- Improvement of process efficiency and manufacturing of smaller and lighter materials in order to reduce material and energy use
- Better understanding and control of natural phenomena and pollution through use of nanosensors and nanoelectronics

Pollution by Nanoparticles and Mitigation

The key to avoiding or remediating pollution by nanoparticles is understanding the basic science of the interaction of nanoparticles and nanostructured materials with the environment, especially with biological systems. Little is known of the key factors governing size, shape and surface chemistry. There are no effective predictive models. Before these are developed, the pollution potential of nanoparticles can only be assessed empirically, and in many cases that is quite difficult.

Nanoparticles have the potential to be “micro-reactors” that can be employed in a wide variety of circumstances to convert energy, remediate waste, and provide sensing. There are a tremendous number of uses for these microreactors. The prerequisite knowledge of the basic materials science of these systems includes fully understanding principles of synthesis, surface chemistry/derivatization, and incorporation into macro systems; as this understanding is developed, it should be possible to design microreactors for specific applications. An example of this might be use of nanoscale sensors for direct monitoring of environmental quality as well as associated process monitoring to assure optimum efficiency and minimize energy consumption of equipment. Direct environmental sensors will be important to almost all production process lines (chemical, electronic, automotive, etc.), as well as consumer use of vehicles and heating and cooling systems. As we move to smarter and smarter appliances, the need for active sensing and feedback becomes increasingly important to facilitate the “greenest” performance. In many cases, sensing can only be accomplished at the nanoscale.

Synthesis and stabilization of small nanostructures from a materials science point of view is of environmental concern. It has been demonstrated that very complex crystalline nanoparticles can be synthesized and stabilized by novel chemical and physical deposition approaches. The ability to prepare stable, isolatable particles provides the first major building block towards entirely new important technological areas: the use of nanostructured materials both as precursors to conventional and new materials and as discrete entities in larger passive and active arrays.

Environmental Technologies

Although structural nanocomposites have begun to make an impact already, over the next 5-10 years there is a tremendous opportunity to make smarter, environmentally friendly composites. The current thrust has been primarily to develop composites that have the equivalent strength at much lighter weight through incorporation of nanoparticles in polymer matrices. The objective is to nanoengineer the polymer and nanoparticles to optimize strength and weight while simultaneously adding new functionality such as chemical inertness or reactivity, conductivity, or optical properties. An example might be corrosion-resistant colored panels for automobiles.

Sorbents, membranes, and catalysts are already ubiquitous in a wide variety of systems for waste remediation, emission prevention, and “green” and energy efficiency technologies. Many active membranes, sorbents, and catalysts operate on the nanoscale. The ability to tailor these active elements at the nanoscale can significantly improve their performance and functionality. There is an increasingly critical need to proactively and continuously preserve water and air purity. Nanoscale sorbents, membranes, and catalysts have the potential to selectively target waste atoms or molecules and sequester or destroy them while not adversely affecting the remainder. Likewise, nanotechnology has the potential to create green technologies through active intervention in a wide variety of process streams, by increasing the efficiency of a process, eliminating waste, or actively treating waste as it is produced.

10.4 SCIENTIFIC AND TECHNOLOGICAL INFRASTRUCTURE

Nanotechnology spans many disciplines and suffers from the lack of common terminology and nomenclature and standards for measurement. It also suffers from researchers' lack of access to equipment. Many of the instruments and tools required for nanotechnology research are very expensive. Mechanisms are needed that will provide researchers with efficient access to the tools that they require. This is often accomplished by establishment of centers around core facilities such as universities and government laboratories, but individual investigators and small groups also need access to state-of-the-art instrumentation. By establishing mechanisms for appropriate sharing of capital-intensive facilities with researchers from other institutions, this access can be improved. Agreements to allow reasonable access to such facilities, at cost, might become an alternative to cost sharing in the acquisition of major facilities and instrumentation. For this approach to work within the typical academic laboratory, mechanisms would have to be developed for training users and controlling risk to facilities.

10.5 R&D INVESTMENT AND IMPLEMENTATION STRATEGIES

Environmental applications of nanotechnologies demonstrate their potential to revolutionize entire industries and displace major existing technologies. In spite of the few examples to the contrary, the costs and risks of transitioning from discovery to commercialization are too great and the benefits too ill-defined for large companies to undertake the wide range of development projects required to bring nanotechnologies into practice. There is a need for government-sponsored mechanisms to facilitate this development.

An increased knowledge of the dynamics of processes specific to nanoscale structures in natural systems can improve understanding of complex processes occurring in the environment and lead to development of approaches for mitigating environmental harm.

Collaboration between universities, national laboratories, and industry is also essential to the development of nanotechnology with application to the environment. This could be accomplished by establishing cross-disciplinary fellowships to support researchers for extended visits to institutions in the other sectors.

10.6 PRIORITIES AND CONCLUSIONS

Several themes should be considered priorities in developing nanoscale processes related to environmental management:

- Develop understanding and control of relevant processes, including protein precipitation and crystallization, desorption of pollutants, stability of colloidal dispersions, micelle aggregation, microbe mobility, formation and mobility of nanoparticles, and tissue-nanoparticle interaction. Emphasis should be given to processes at phase boundaries (solid-liquid, solid-gas, liquid-gas) that involve mineral and organic soil components, aerosols, biomolecules (cells, microbes), biotissues, derived components such as biofilms and membranes, and anthropogenic additions (e.g., trace and heavy metals).

- Carry out interdisciplinary research that initiates novel approaches and adopts new methods for characterizing surfaces and modeling complex systems to problems at interfaces and other nanostructures in the natural environment, including those involving biological or living systems. New technological advances such as optical traps, laser tweezers, and synchrotrons are extending examination of molecular and nanoscale processes to the single-molecule or single-cell level. Meanwhile, mathematicians are developing more effective ways to describe systems that are dynamic, multiscale, multicomponent, and exhibit emergent or aggregate behavior.
- Integrate understanding of the roles of molecular and nanoscale phenomena and behavior at the meso- and/or macroscale over a period of time. Model nanostructures should be studied, but in all cases, research must be justified by its connection to naturally occurring systems or to environmentally beneficial uses. Environments for investigation are not limited and might include terrestrial locations (e.g., acid mines), subsurface aquifers, polar environments, or the atmosphere.

10.7 EXAMPLES OF CURRENT ACHIEVEMENTS AND PARADIGM SHIFTS

10.7.1 From Discovery to Application: A Nanostructured Material (MCM-41)

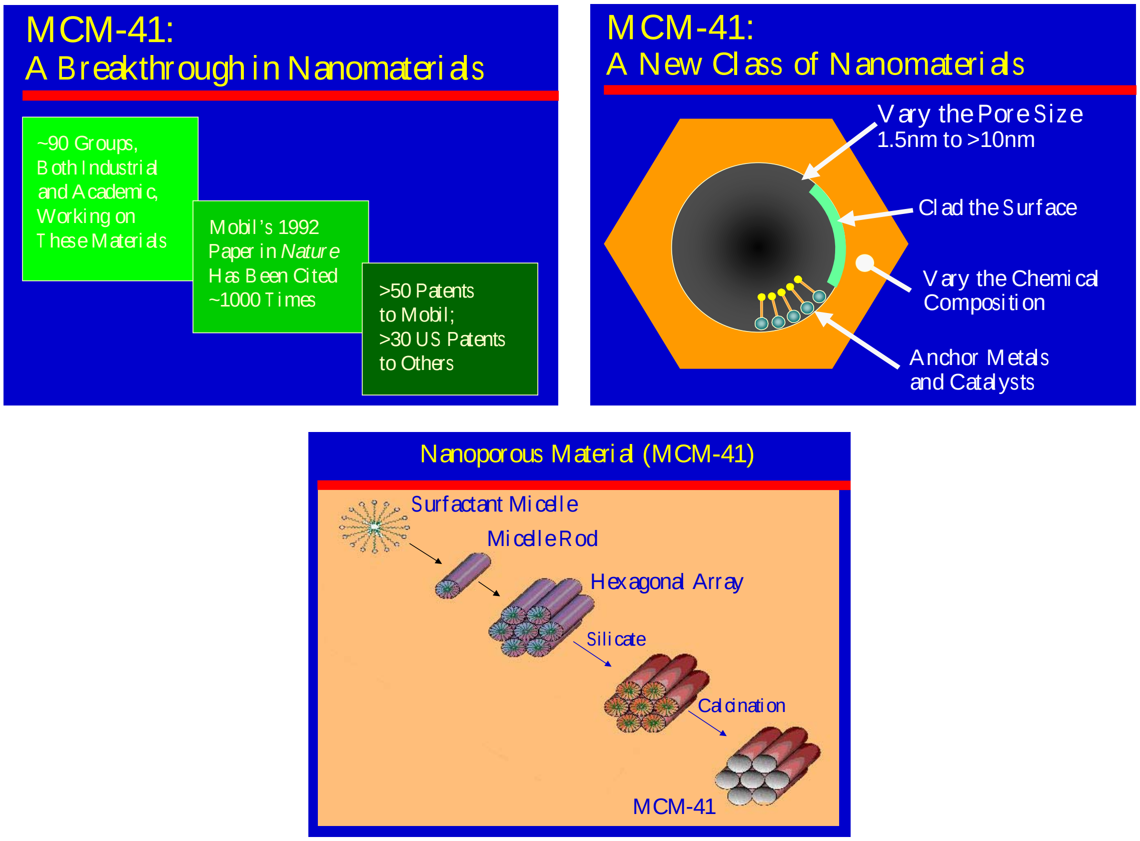
Contact person: J.J. Wise, Mobil (ret.)

At a time when amorphous metal oxide supports for catalysts were well established within the chemical industry, visionary researchers within Mobil Oil Corporation undertook a long-term research program into the use of crystalline materials as catalyst supports (Figure 10.1). That program has revolutionized catalysis, displacing conventional catalyst supports for many applications (see more details in Chapter 9). In particular, the program focused on zeolites, porous materials with well-defined shapes, surface chemistry, and pore sizes smaller than 1 nm. The zeolites Y and ZSM-5 are now used widely around the world in several major catalytic processes in the petroleum and petrochemical industries, generating billions of dollars in additional revenues.

10.7.2 Nanoparticles in the Environment

Contact person: A. Navrotski, University of California, Davis

Nanoparticles—iron oxides, clays, and other colloids—are the major transporting agents of both pollutants and nutrients in soil, water, and air. Understanding these modes of transport can help distribute desirable organic and inorganic constituents and immobilize undesirable ones. Control could be achieved of morphology, agglomeration, and coatings on natural nanoparticles to have the desired enhancement or retardation effect. Examples currently in use or under development are (1) zeolites and other porous soil conditioners, especially for the controlled storage and release of water; (2) use of clay and zeolites as part of radionuclide barriers at the Yucca Mountain proposed nuclear waste repository; (3) controlled release of iron, phosphorus, and other nutrients from fertilizer; (4) additions of aluminosilicates to food as texturizing agents (e.g., in non-dairy creamer) and of zeolites to animal feed (claimed to make pigs grow faster); (5) use of zeolites as ion exchangers in water purification and in detergents; and (6) use of silica gel and other nanophase solids as desiccants. Many of these are currently low-technology products; fine-tuning them may lead to more sophisticated applications, for example, drug delivery, and environmental regeneration systems in spacecraft and other confined spaces.



MCM-41:
A Breakthrough in Nanomaterials

~90 Groups, Both Industrial and Academic, Working on These Materials

Mobil's 1992 Paper in *Nature* Has Been Cited ~1000 Times

>50 Patents to Mobil; >30 US Patents to Others

MCM-41:
A New Class of Nanomaterials

Vary the Pore Size 1.5nm to >10nm

Clad the Surface

Vary the Chemical Composition

Anchor Metals and Catalysts

Nanoporous Material (MCM-41)

Figure 10.1. From discovery to application: a nanostructured material (MCM-41) (courtesy Mobil Oil).

The ability to identify, characterize, and analyze nanoparticles quickly and in detail with respect to composition, trace elements, atomic-level structure, and morphology will lead to better understanding of their role in pollution and to better, more unambiguous, identification of the sources of pollution. For example, the definition of "asbestos," currently based solely on shape (aspect ratio >10), needs to be modified to take into account the growing body of data indicating that chemically different particles have very different toxicity. Indeed, the mechanisms of toxicity of nanoparticles are still poorly understood, and nanotechnology-based sensors are likely to play a role in developing such understanding. Similarly, nanotechnology will provide sensors for the detection of low levels of contaminants in air and water.

10.7.3 Nanoporous Polymers and their Applications in Water Purification

Contact person: D. Li and T.C. Lowe, Los Alamos National Laboratory

A completely new class of organic nanoporous polymers with narrow pore-size distribution (0.7-1.2 nm) has been synthesized using cyclodextrins as basic building blocks. These processable nanoporous polymers (Figure 10.2) exhibit superior inclusion forces and molecular transport properties towards organic guest molecules at water-solid interfaces. In fact, the formation constants of polymeric cyclodextrins and organic guest molecules are over 8 orders of magnitude larger than molecular cyclodextrins in water, and yet the process is completely reversible in organic solvents such as ethanol. The significant potential of these results is that hazardous organic contaminates may be reduced to parts-per-trillion levels in water by these polymers.

Figure 10.2. Nanoporous polymer samples in pure form (white), absorption of 4-nitrophenol (yellow), and absorption of 4-nitrothiolphenol (orange) (reprinted from Li and Ma 1999; published 1999 American Chemical Society).

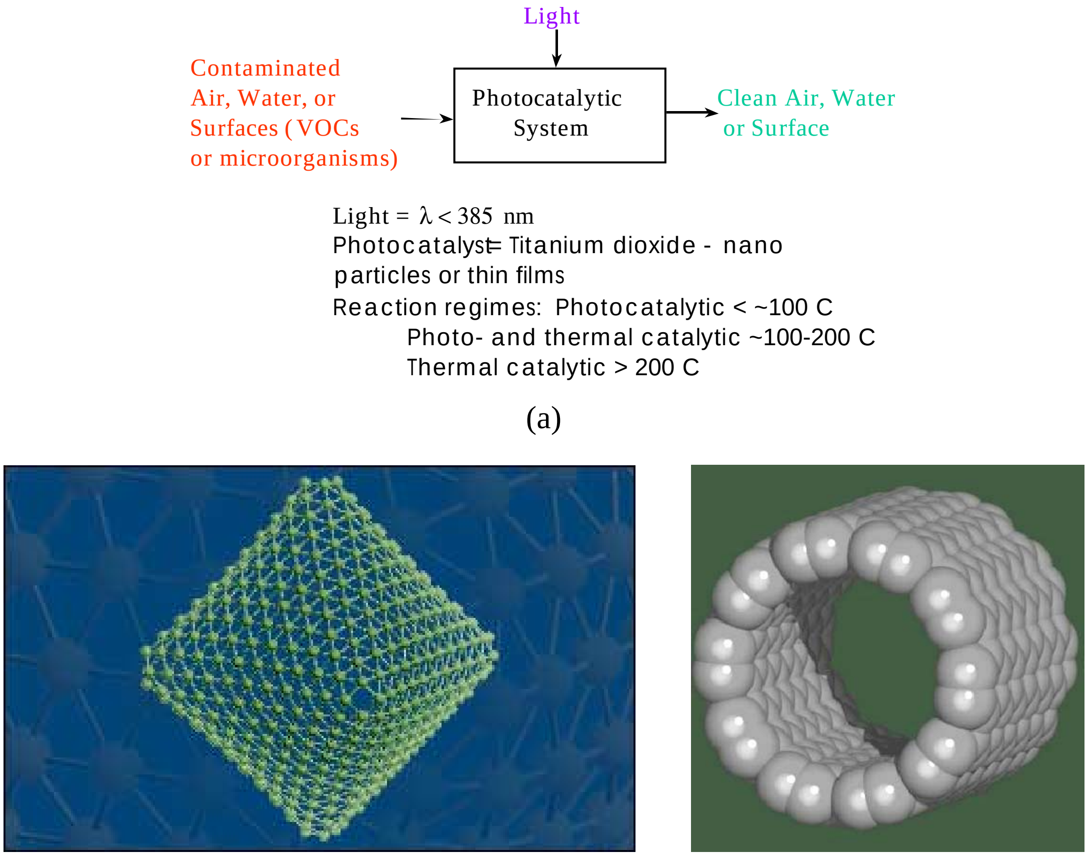
10.7.4 Photocatalytic Fluid Purification

Contact person: D.S. Ginley, National Renewable Energy Laboratory

Nanoparticles have been demonstrated to have considerable environmental potential as active remediation agents. Key to the remediation of existing wastes and the prevention of new waste streams is the development of active agents that can function to remove waste where it is located or where it is generated. Figure 10.3 shows schematically how this could work and illustrates two new materials that could significantly impact this area.

Figure 10.3a illustrates how nanostructured TiO_2 can be employed as a photocatalyst to clean up a variety of waste streams (Bauer et al. 1999). The process can oxidize organic wastes and biological contaminates. It is currently being tested in operating rooms and elsewhere. This approach is illustrative of a number of approaches where a nanomaterial is inserted into a waste stream, where it reacts with or sequesters the contaminant, producing an environmentally benign process stream.

Along the lines of evolving improved materials for these applications are two new materials, illustrated in Figure 10.3b and c. In the middle of Figure 10.3b is a schematic illustration of a new inorganic fullerene composed of Mo and S (Parilla et al. 1999). This regular structure may have only relatively inert Van der Waals surfaces. With an optical bandgap in the visible region, this may be ideal species for the photooxidation of waste streams. Figure 10.3c shows a schematic of a single-wall carbon nanotube. As discussed in Chapter 9, these structures have the potential to be employed in gas purifiers and as hydrogen storage media (Kappes 1999, Dresselhaus et al. 1999). They may also have extensive use to purify air streams and to act as an agent for adsorbing heavy metals and other contaminates. Both the inorganic fullerenes and the nanotubes represent new structures that can potentially be tailored to provide specific chemical functionality.



(a)

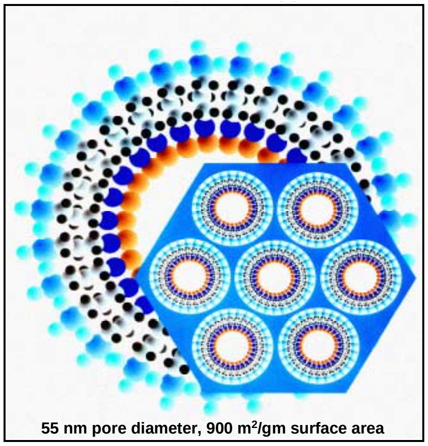
(b) (c)

Figure 10.3. Photocatalytic fluid purification: (a) process concept; (b) inorganic MOS fullerene; and (c) single-wall carbon nanotube, each of which has photocatalytic potential.

10.7.5 Hierarchical Self-Assembled Nanostructures for Adsorption of Heavy Metals

Contact persons: G. Exarhos, Pacific Northwest National Laboratory and G. Samara and S.T. Picraux, Sandia National Laboratories

Figure 10.4 is a schematic drawing of a functionalized mesoporous nanocomposite consisting of a silicate framework of cylindrical pores that give the material a honeycomb appearance, with concomitant large surface area and nanometer porosity. The pores function as templates for the attachment of molecules of specific size and chemical functionality to form dense monolayers on the wall surfaces. The molecules bind strongly at one end to the ceramic support, leaving the free end available for interaction/reaction with targeted chemical species. These nanocomposites, referred to as self-assembled monolayers on mesoporous supports, or SAMMS (work performed at Pacific Northwest National Laboratory), are very effective at sequestering heavy metal ions from waste streams and are expected to find numerous other applications in energy storage, separations, catalysis, and environmental restoration technologies.



- **Chemically selective surfactant molecules self-assemble within the interstices of a mesoporous silica matrix derived through solution processing routes.**
- **Resulting material shows high adsorption capacity for mercury and other heavy metals.**
- **Numerous environmental and commercial applications.**

Figure 10.4. Hierarchical self-assembly for 3-D nanostructured materials: self-assembled monolayers on mesoporous supports (Pacific Northwest National Laboratory).

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