Chapter 1

# NANOPOROUS MATERIALS - AN OVERVIEW

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## 1 Introduction

In recent years, nanomaterials have been a core focus of nanoscience and nanotechnology – which is an ever-growing multidisciplinary field of study attracting tremendous interest, investment and effort in research and development around the world. Nanoporous materials as a subset of nanostructured materials possess unique surface, structural, and bulk properties that underline their important uses in various fields such as ion exchange, separation, catalysis, sensor, biological molecular isolation and purifications. Nanoporous materials are also of scientific and technological importance because of their vast ability to adsorb and interact with atoms, ions and molecules on their large interior surfaces and in the nanometer sized pore space. They offer new opportunities in areas of inclusion chemistry, guest-host synthesis and molecular manipulations and reaction in the nanoscale for making nanoparticles, nanowires and other quantum nanostructures.

To provide a comprehensive overview of the area of nanoporous materials, this chapter will begin with a brief introduction to nanoscience and nanotechnology, and the importance of nanomaterials. The basic concepts and definitions in relation to porous materials and nanoporous materials will be given to understand the context of nanoporous materials. Following this introduction, a systematical classification of the types and scope of nanoporous materials will be presented. The properties and their characterisation and measurement methods will be briefly described before major applications in various fields are reviewed. Finally in this chapter, key scientific and engineering issues and future directions are identified as challenges and opportunities to researchers in this field.

## *1.1 Nanotechnology and nanomaterials*

Nanoscale is fascinating because it is on this scale that atoms and molecules interact and assemble into structures that possess unique properties, which are dependent on the size of the structures. It is at this scale that molecular interactions, processes, and phenomena can be controlled and directed to form the desired geometries of the materials building blocks with desirable properties. Nanoscale phenomena and objects have, of course, been utilized for some time. Small metal or metal oxide crystallites supported on a ceramic material, for example, are mostly nanoscale particles that have been used to crack crude oil into fuels for many years. However, what distinguishes cutting-edge nanoscience is the degree of understanding, deliberate control, and precision that new nanostructuring techniques afford. Instead of discovering new materials by serendipity or by trial-and-error, we can now design them systematically.

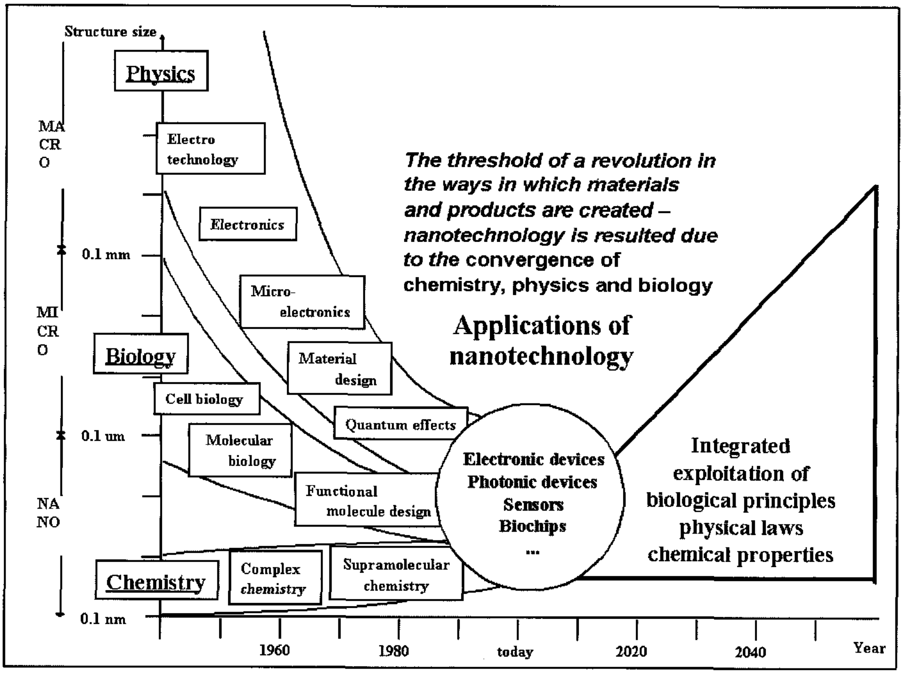


**Figure 1.** Threshold of nanotechnology as basic sciences converges to the nanoscale (adapted from [1])

What makes nanoscale building blocks interesting is that by controlling the size in the range of 1-100 *nm* and the assembly of such constituents, one could alter and prescribe the properties of the assembled nanostructures. As Professor Roald Hoffmann – the Chemistry Nobel Laureate put it,"*Nanotechnology is the way of ingeniously controlling the building of small and large structures, with intricate properties; it is the way of the future, with incidentally, environmental benignness built in by design*". Nanostructured materials may possess nanoscale crystallites, long-range ordered or disordered structures or pore space. Nanomaterials can be designed and tailor-made at the molecular level to have desired functionalities and properties. Manipulating matter at such a small scale with precise control of its properties is one of the hallmarks of nanotechnology. The potential and importance of nanoscale science and technology has clearly been recognized worldwide as evidenced by significant investments in nanotechnology R&D in the USA, Europe, Japan and other Asia-Pacific countries since 2000 when the US Nation Nanotechnology Initiative was announced.

## *1.2 Definitions of pores and porous materials*

Porous materials are like music: the gaps are as important as the filled-in bits. The presence of pores (holes) in a material can render itself all sorts of useful properties that the corresponding bulk material would not have [2]. Generally porous materials have porosity (volume ratio of pore space to the total volume of the material) between 0.2-0.95 [3]. Pores are classified into two types: open pores which connect to the surface of the material, and closed pores which are isolated from the outside. In functional applications such as adsorption, catalysis and sensing, closed pores are not of any use. In separation, catalysis, filtration or membranes, often penetrating open pores are required. Materials with closed pores are useful in sonic and thermal insulation, or lightweight structural applications. Pores have various shapes and morphology such as cylindrical, spherical and slit types. There are also pores taking more complex shapes such a hexagonal shape. Pores can be straight or curved or with many turns and twists thus having a high tortuosity.

The definition of pore size according to the International Union of Pure and Applied Chemistry (IUPAC) is that micropores are smaller than 2 nm in diameter, mesopores 2 to 50 nm and macropores larger than 50 nm. However this definition is somewhat in conflict with the definition of nanoscale objects. Nanoporous materials are a subset of porous materials, typically having large porosities (greater than 0.4), and pore diameters between 1- 100 nm. In the field of chemical functional porous materials, it is better to use the term "nanoporous" consistently to refer to this class of porous materials having diameters between 1 and 100 nm. For most functional applications, pore sizes normally do not exceed 100 nm anyway. It is noted that nanoporous materials actually encompass some microporous materials to all mesoporous materials.

So what are the unique properties of those materials? Nanoporous materials have specifically a high surface to volume ratio, with a high surface area and large porosity, of course, and very ordered, uniform pore structure. They have very versatile and rich surface composition, surface properties, which can be used for functional applications such as catalysis, chromatography, separation, and sensing. A lot of inorganic nanoporous materials are made of oxides. They are often non-toxic, inert, and chemically and thermally stable, although in certain applications the thermal stability requirement is very stringent so you have to have a very highly thermal stable catalyst.

## 2 Classification of Nanoporous Materials

Porous materials can be classified according to their materials constituents (such as organic or inorganic; ceramic or metal) or their properties. Table 1 summarizes the available nanoporous materials according to their chemical compositions and their technical characteristics.

**Table 1.** Classification of nanoporous materials

| | Polymeric | Carbon | Glass | Alumino-silicate | Oxides | Metal |
|---|---|---|---|---|---|---|
| Pore size | Meso-macro | Micro-meso | Meso-macro | Micro-meso | Micro-meso | Meso-macro |
| Surface area / Porosity | Low >0.6 | High 0.3-0.6 | Low 0.3-0.6 | High 0.3-0.7 | Medium 0.3-0.6 | Low 0.1-0.7 |
| Permeability | Low-medium | Low-medium | High | Low | Low-medium | High |
| Strength | Medium | Low | Strong | Weak | Weak-medium | Strong |
| Thermal stability | Low | High | Good | Medium-high | Medium-high | High |
| Chemical stability | Low-medium | High | High | High | Very high | High |
| Costs | Low | High | High | Low-medium | Medium | Medium |
| Life | Short | Long | Long | Medium-long | Long | Long |

## 3 Properties and characterization of nanoporous materials

Nanoporous materials possess a unique set of properties that the bulk correspondent materials do not have such as high specific area, fluid permeability and molecular sieving and shape-selective effects. Different nanoporous materials with varying pore size, porosity, pore size distribution and composition have different pore and surface properties that will eventually determine their potential applications. For different applications there are different sets of performance criteria that would require different properties.

For example, the performance criteria for a good adsorbent include

(1) High adsorption capacity. Fundamental properties that affect this parameter are specific surface area, surface chemical nature, and pore size. These parameters determine how much adsorbates can be accumulated by per unit mass of adsorbents.

(2) High selectivity. For multicomponent mixture, selectivity is highly desired for separation. The selectivity of an adsorbent will depend on the pore size, shape and pore size distribution as well as the nature of the adsorbate components.

(3) Favorable adsorption kinetics. Adsorption kinetics is determined by the particle (crystallite) size, the macro-, meso and microporosity of the adsorbent. Sometimes, binder type and amount would also affect the interparticle transport thus the global adsorption process kinetics. A favorable kinetics means that the adsorption rate is fast or controllable depending on the requirement of a particular application.

(4) Excellent mechanical properties. Obviously, adsorbents need to be mechanically strong and robust enough to stand attrition, erosion and crushing in adsorption columns or vessels. High bulk density and crushing strength, and attrition resistance are desirable.

(5) Good stability and durability in use. Adsorbents are often subject to harsh chemical, pressure and thermal environments. Good stability in those environments is essential in ensuring long life or durable utilization. As synthesized nanoporous materials may or may not have all these desirable properties depending on the synthesis systems, methods and processing conditions. Obviously the practical challenges in making good adsorbent materials will be to obtain high-adsorption-capacity adsorbents in a simple and cost effective manner, to make sure the above requirements/criteria are met as much as possible. In many cases, post-synthesis modification is required to impart certain functionality or

improve certain property due to the inability of the synthesis route to achieve them during the process of synthesis. There are many research efforts devoted to this area.

If used as catalyst support or catalysts, nanoporous materials involved are required to have not only the above properties but also suitable surface chemistry characteristics such as acidity or basicity, and shape selectivity is often important.

## 4 Major opportunities in applications

There are ever expanding applications for nanoporous materials besides the traditional areas of adsorption separation, catalysis and membranes. This chapter is not intended to cover the details of applications of nanoporous materials but will provide an overview of the main application opportunities and market potentials. Many promising applications and processes are dealt with in the subsequent chapters in this book by the contributing authors.

### *4.1 Environmental separations*

As the regulatory limits on environmental emissions become more and more stringent, industries have become more active in developing separation technologies that could remove contaminants and pollutants from waste gas and water streams. Adsorption processes and membrane separations are two dominating technologies that have attracted continuous investment in R&D. Adsorbent materials and membranes (typically nanoporous) are increasingly being applied and new adsorbents and membranes are constantly being invented and modified for various environmental applications such as the removal of $SO_2$, $NO_x$, and VOCs emissions [4]. Adsorbents of the traditional types such as commercially available activated carbons, zeolites, silica gels, and activated alumina have estimated worldwide market exceeding US$1.5 billion per year [5].

New adsorbent materials with well defined pore sizes and high surface areas are being developed and tested for potential use in energy storage and environmental separation technologies. Table 2 lists some examples of new adsorbents for energy and environmental applications as identified by Yang [5].

**Table 2.** Examples of emerging processes for environmental separations

| Energy and Environmental Applications | Adsorbents and technology |
|---|---|
| $CH_4$ storage for on-board vehicular storage | Super-activated carbon and activated carbon fibers; Near or meeting DOE target storage capacity |
| $H_2$ storage for on-board vehicular storage | Carbon nanotubes possible candidate |
| $N_2/CH_4$ separation for natural gas upgrading | Clinoptilolite, Sr-ETS-4 by kinetic separation |
| Sulfur removal from transportation fuels (gasoline, diesel and jet fuels) | $\pi$-complexation sorbents such as Cu(I)Y, AgY |
| CO removal from $H_2$ to <10 ppm for fuel cell applications | $\pi$-complexation sorbents such as CuCl/$\gamma$-$Al_2O_3$, CuY, and AgY; silica molecules sieve membranes |
| NO*x* removal | Fe-Mn-Ti oxides, Fe-Mn-Zr oxides, Cu-Mn oxides |
| Removal of dienes from olefins (to<1 ppm) | $\pi$-complexation sorbents such as Cu(I)Y, AgY |

### *4.2 Clean energy production and storage*

Future energy supply is dependent on hydrogen as a clean energy carrier. Hydrogen can be produced from fossil fuels, water electrolysis and biomass. However, the current debates on the hydrogen economy are intimately linked to the clean production of hydrogen from fossil fuels such as natural gas and coal. Due to the low cost and wide availability of coal, coal gasification to syngas and then to hydrogen through the water gas shift reaction is a promising route to cheap hydrogen. The success of such a hydrogen production route will be only possible provided that carbon dioxide is sequestered safely and economically. Key to the cost-effective conversion of coal to hydrogen and carbon capture is nanomaterials development such as catalyst for the WGS reaction and inorganic membranes for hydrogen/$CO_2$ separation.

In the future hydrogen economy, hydrogen will be the dominant fuel, and converted into electricity in fuel cells, leaving only water a product. Fuel cell development has been very rapid in recent year. However, there are many technological challenges before fuel cells become commercially viable and widely adopted. Many of the problems are associated with materials notably related to electrocatalyst, ion-conducting membranes and porous supports for the catalyst. Certain nanoporous materials such as carbon nanotubes and zirconium phosphates have already shown promise for application in fuel cells.

Hydrogen storage will be also essential in hydrogen economy infrastructure. Currently there are no optimal systems for hydrogen storage. Hydrogen can be stored in gaseous, liquid or more recently in solid forms. Nanostructured materials such as carbon nanotubes again show promise as an adsorbent. Despite many controversial reports in the literature, hydrogen storage in carbon nanotubes may one day become competitive and useful. Another type of nanostructured carbons is templated by using 3-D ordered mesoporous silicates. It has been shown that this type of carbons exhibit interesting and superior performance as supercapacitor and electrode materials for Li-ion battery applications [6]. The clean energy market is a huge one already and according to the Austin Business Journal [7] the worldwide "clean energy" market is expected to grow from US$9.5 billion in 2002 to US$89 billion by 2012. Fuel cell products will expand from a U$500 million business in 2002 to US$12.5 billion by 2012.

### *4.3 Catalysis and photocatalysis*

Heterogeneous catalysis has had a major impact on chemical and fuel production, environmental protection and remediation, and processing of consumer products and advanced materials [8]. A survey of U.S. industries revealed that the annual revenue from chemical and fuel production topped all other industrial sectors at $210 billion. The survey also showed that over 60% of the 63 major products and 90% of the 34 process innovations from 1930-80 involved catalysis, illustrating the critical role of this field in the fuel and chemical industry. The significance of catalytic processes can be further demonstrated by the value of their products, which amounted to $1 trillion in the United States alone in 1989 [9].

More efficient catalytic processes require improvement in catalytic activity and selectivity. Both aspects will reply on the tailor-design of catalytic materials with desired microstructure and active site dispersion. Nanoporous materials offer such possibilities in this regard with controlled large and accessible surface area of catalyst but avoiding standalone fine particles. The traditional methods of impregnation of metal ions in nanoporous supports are not as effective in achieving high dispersion of active centers, whereas incorporation in template synthesis or intercalation are more advanced techniques rendering high activity owing high surface area of the active components and selectivity due to the narrow pore size distribution.

Transition metal oxides exhibit a wide range of physical, chemical and optical properties. One of the most widely studied metal oxides is semi-conducting $TiO_2$. Titania in anatase form exhibits strong photocatalytic effect, which generates electron-hole pairs. As a result the material can harvest photos in the near UV region (<410nm) to render its surface strong oxidizing power to decompose organic molecules. Photocatalysis is a rapid growing field of study that has attracted intense attention of chemical and materials researchers in recent years. It is estimated that the $TiO_2$ photocatalyst market in Japan along could exceed US$5billions [10].

### *4.4 Sensors and actuators*

Nanoparticles and nanoporous materials possess large specific surface areas, and high sensitivity to slight changes in environments (temperature, atmosphere, humidity, and light). Therefore such materials are widely used as sensor and actuator materials. Gas sensors reply on the detection of electric resistivity change upon change in gas concentration and their sensitivity is normally dependent on the surface area. Gas sensors based on nanoporous metal oxides such as $SnO_2$, $TiO_2$, $ZrO_2$, and ZnO are being developed and applied in detectors of combustible gases, humidity, ethanol, and hydrocarbons. Zirconia is typically a good sensor material for oxygen. According to the market projection by Freedonia group [11], the market demand for chemical sensors is forecast to grow 8.6% per year to $3.4 billion in 2006.

### *4.5 Biological applications*

Nanomaterials that are assembled and structured on the nanometer scale are attractive for biotechnology applications because of the potential to use material topography and the spatial distribution of functional groups to control proteins, cells, and tissue interactions, and also for bioseparations. Bionanotechnology is all about creating nanomaterials or biomaterials for biological applications [12]. Many studies are underway in fundamental understanding and exploiting the nature of nanoscale systems and processes to

- Develop improved chemical separations and isolation media using nanoporous materials
- Integrate engineered and self-assembled materials into useful devices ranging from biosensors to drug delivery systems
- Develop new products and biomedical devices by manipulating biomolecules enzymes, other proteins, and biochemical processes at the nanoscale.

Proteins have been used by nature for billions of years to create the incredibly complex nanoscale structures within a living cell. Molecular scale scaffolding, cables, motors, ion pores, pumps, coatings, and chemically powered levers composed primarily of proteins are all found in nature. Proteins provide superior catalytic abilities over traditional inorganic type catalysts and the simplified reaction conditions of enzymes require less complex engineering than catalytic reactors. Nanoporous materials being porous and some often found bio-compatible afford the capability to build enzymatic nanomaterials that mimic natural biological reactions. Immobilizing recombinant enzymes into nanoporous materials can be used for long-lifetime biological reactors for a variety of applications. The possibilities for using enzymes in small-scale reactors for producing drugs, energy, decontaminating wastes, and creating complicated synthetic reactions are limitless [13].

Nanopores embedded in an insulating membrane fabricated by using a physical method has been demonstrated useful to examine biomolecules one by one, achieving single-molecule analysis [14]. Li et al. [14] are able to use an ion beam to shrink a pore of micrometer size in a silicon nitride membrane down to nanoscale dimensions for measuring the motion of single DNA molecules through the nanopores. The most supervising result of the work is that the DNA molecules do not thread meekly through these nanopores like a noodle of spaghetti that one sucks up, but instead come through the pores in several configurations. This is an important breakthrough towards DNA sequencing, demonstrating the potential applications of nanoporous materials in bioengineering.

Another area of applications that is exciting as far as nanoporous materials is concerned, is biosensors. Piezoelectric biosensors utilizing high surface area nanoporous coatings exhibit increased sensitivity in detection. Immobilized biological molecules on the surface of nanoporous silica can serve as biological detection systems [15, 16]; microscale piezoelectric cantilevers serve as the transducer. There is a shift in resonance frequency of the cantilever when molecules adsorb onto its surface. The shift in frequency results from the change in mass of the cantilever; and the sensitivity is directly related to the ratio of the mass of the adsorbed analyte to the mass of the cantilever. Thus by incorporating nanoporous silica, between the transducer and biological detection system, the increased surface to volume ratio of the cantilever increases the sensitivity of the resonant frequency of the oscillator to changes in mass [17]. Biosensors have major potential in the healthcare industry where, for example, real-time *in vivo* sensing could be used for insulin pumps, drug detection in emergency situations. Rapid methods for detecting pathogens in food products and animal feed could save billions of dollars in medical costs. It is estimated that the world market for biosensors in 2001 was US$1.44 billion [11]. The estimated market for bionanotechnology products in 2003 is US$930 m, and is expected to reach over US$3 billion in 2008 (http://www.frontlinesmc.com/nano/Nano PressRelease.pdf).

### *4.6 Other applications*

Besides the above applications, there are also tremendous opportunities for nanoporous materials in the following areas [18].

(1) high efficiency filtration and separation membranes
(2) catalytic membranes for chemical processes
(3) porous electrodes for fuel cells
(4) high efficiency thermal insulators
(5) electrode materials for batteries
(6) porous electronic substrates for high speed electronics

## 5 Concluding remarks

Nanomaterials will have a profound impact on many industries including microelectronics, manufacturing, medicine, clean energy, and environment. In these industries, there are already many examples of applications of microporous zeolites and molecular sieves as nanoscale catalysts and gas separation membranes. Expanding the pore dimensions to mesopores range will increase the scope of their applications in these fields. In particular, mesoporous materials will have wider applications into biological separation, biosensors, and nanoreactors for conducting multiple and controlled biological reactions on microchips. In the fields of clean energy production and storage, nanoporous materials as catalysts and storage media and electrode materials will have tremendous potential in enabling process innovations in areas such as gas to liquid conversion, hydrogen production, alterative solar cells, fuel cells and advanced batteries. In the environmental filed, nanoporous and nanocrystalline semiconductors are the key to cost-effective photocatalytic purification of water and air, economic removal and recovery of organic vapors, greenhouse gas reduction and utilization. In health care, biomaterials for orthopedic, and cardiovascular applications, tissue repair, biosensors, and controlled drug delivery are likely to be developed and applied in the near future, all of which will depend on the development of new nanoporous substrates or coatings one way or the other.

In the science of nanoporous materials, there are many challenges and opportunities ahead of us. For example, in catalysis, one of the key goals is to promote reactions to have a high selectivity with a high yield. To meet this goal, tailoring a catalyst particle via nanoparticle synthesis and self-assembly so that it catalyzes only a specific chemical conversion with a higher yield a greater energy efficiency is imperative. For adsorption and catalysis selectivity, a relatively narrow pore size distribution is desirable. Traditional amorphous nanoporous materials such as silica gels, alumina, and activated carbons are limited in shape selectivity because of their broad pore size distribution and fixed pore geometries. Microporous zeolites and pillared clays are the only class of nanocrystalline materials with uniform pores. However, their pore sizes are limited to below 1.0-1.2nm. The mesostructured molecular sieves and oxides that have been developed since the invention of MCM-41 by Mobil scientists [19] have shown great promises for separation, catalysis and biological applications where large molecules are involved. The supramolecular templating techniques and processing have revolutionized the synthesis and application opportunities of nanoporous materials. There are many templating pathways in making mesostructured materials. New synthesis strategies are constantly being revealed and trailed for improving the pore size range, chemical composition, thermal and hydrothermal stabilities. Structural modification either via isomorphous substitution or post-synthesis grafting can improve the surface chemistry characteristics and thermal stability [20]. Surface functionalization is particularly important for selective adsorption, and biomolecular immobilization and separation. All these topics are exciting and scientifically challenging, which are well addressed in the subsequent contributions in this book.