Science and technology of nanomaterials: current status and future prospects

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The science and technology of nanomaterials has created great excitement and expectations in the last few years. By its very nature, the subject is of immense academic interest, having to do with very tiny objects in the nanometer regime. There has already been much progress in the synthesis, assembly and fabrication of nanomaterials, and, equally importantly, in the potential applications of these materials in a wide variety of technologies. The next decade is likely to witness major strides in the preparation, characterization and exploitation of nanoparticles, nanotubes and other nanounits, and their assemblies. In addition, there will be progress in the discovery and commercialization of nanotechnologies and devices. These new technologies are bound to have an impact on the chemical, energy, electronics and space industries. They will also have applications in medicine and health care, drug and gene delivery being important areas. This article examines the important facets of nanomaterials research, highlighting the current trends and future directions. Since synthesis, structure, properties and simulation are important ingredients of nanoscience, materials chemists have a major role to play.

Introduction

Nanotechnology is the term used to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials, with at least one dimension

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in the nanometer range ($1 \text{ nm} = 10^{-9} \text{ m}$). Table 1 lists typical nanomaterials of different dimensionalities. The properties of materials with nanometric dimensions are significantly different from those of atoms or bulk materials. Suitable control of the properties of nanometer-scale structures can lead to new science as well as new products, devices and technologies. The underlying theme of nanotechnology is miniaturization, the importance of which was pointed out by Feynman¹ as early as 1959 in his often-cited lecture entitled "There is plenty of room at the bottom". The challenge is to beat Moore's law² and accommodate 1000 CDs in a wristwatch.³

There has been explosive growth of nanoscience and technology in the last decade, primarily because of the availability of new methods of synthesizing nanomaterials, as well as tools for characterization and manipulation (Table 2). Several innovative methods for the synthesis of nanoparticles and nanotubes, and their assemblies, are now available. There is a better understanding of the size-dependent electrical, optical and magnetic properties of individual nanostructures of semiconductors, metals and other materials. Besides the established techniques of electron microscopy, crystallography and spectroscopy, scanning probe microscopies have provided powerful tools for the study of nanostructures. Novel methods of fabricating patterned nanostructures, as well as new device and fabrication concepts, are constantly being discovered. Nanostructures have also been ideal for computer simulation and modelling, their size being sufficiently small to accommodate considerable rigour in treatment. In computations on nanomaterials,4 one deals with a spatial scaling from 1 Å to

Table 1 Typical nanomaterials

	Size (approx.)	Materials
(a) Nanocrystals and clusters (quantum dots) Other nanoparticles (b) Nanowires Nanotubes (c) 2-Dimensional arrays (of nano particles) Surfaces and thin films (d) 3-Dimensional structures (superlattices)	diameter 1–10 nm diameter 1–100 nm diameter 1–100 nm diameter 1–100 nm several nm ² –µm ² thickness 1–1000 nm Several nm in all three dimensions	Metals, semiconductors, magnetic materials Ceramic oxides Metals, semiconductors, oxides, sulfides, nitrides Carbon, layered metal chalcogenides Metals, semiconductors, magnetic materials Various materials Metals, semiconductors, magnetic materials

Table 2 Different methods of synthesis and investigation of nanomaterials

Scale (approx.)	Synthetic methods	Structural tools	Theory and simulation
0.1–10 nm	Covalent synthesis	Vibrational spectroscopy NMR Diffraction methods Scanning probe microscopies (SPM)	Electronic structure
< 1–100 nm 100 nm–1 μ m	Self-assembly techniques Processing, modifications	SEM, TEM, SPM SEM, TEM	Molecular dynamics and mechanics Coarse-grained models, hopping <i>etc</i> .

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1 μm and temporal scaling from 1 fs to 1 s, the limit of accuracy going beyond 1 kcal mol⁻¹. There are many examples which demonstrate the current achievements and paradigm shifts in this area; STM images of quantum dots (e.g., a germanium pyramid on a silicon surface) and of the quantum corral of 48 Fe atoms placed in a circle of 7.3 nm radius being familiar ones. Ordered arrays or superlattices of nanocrystals of metals and semiconductors have been prepared by several workers. Nanostructured polymers formed by the ordered self-assembly of triblock copolymers and nanostructured high-strength materials (e.g., Cu/Cr nanolayers) are other examples. Prototype circuits involving nanoparticles and nanotubes for nanoelectronic devices have been fabricated. Quantum computing⁶ has made a good start and appropriate quantum algorithms have been developed.

Not everything in nanoscience is new; many existing technologies employ nanoscale processes, catalysis and photography being well-known examples. Our capability to synthesize, organize and tailor-make materials at the nanoscale is, however, of very recent origin. The immediate goals of the science and technology of nanomaterials must be to fully master the synthesis of isolated nanostructures (building blocks) and their ensembles and assemblies with the desired properties, to explore and establish nanodevice concepts and systems architecture, to generate new classes of high-performance materials, including biologically-inspired systems, to connect nanoscience to molecular electronics and biology, and to improve known investigative methods while discovering better tools for the characterization of nanostructures.^{4,5} Some of the potential applications of nanotechnology which will have the greatest societal and economic impact are in the production of novel materials and devices, in nanoelectronics and computer technology, as well as in medicine and health care. These wide-ranging applications may indeed usher in a new direction in manufacturing and in the electronics, space, chemical and energy industries.

In this article, we will present the important highlights in the field of nanomaterials related to their synthesis and assembly, experimental tools for their investigation, modelling and simulation, and their potential applications. We have endeavoured to make the article concise and illustrative rather than encyclopedic, and have cited key, representative references to help describe the present status of the subject.

Synthesis and assembly

The synthesis of nanomaterials spans inorganic, organic and biological systems, all with control of size, shape and structure. Assembling the nanostructures into ordered arrays is often necessary to render them functional and operational. It is by a combination of novel nanobuilding units and strategies for assembling them that nanostructured materials and devices with new capabilities can be generated. In the last decade, nanoparticles (powders) of ceramic materials have been produced on a large scale by employing both physical and chemical methods. In addition, there has also been considerable progress in the preparation of nanocrystals of metals, semiconductors and magnetic materials by employing colloid chemical methods.^{7–10} Nearly monodisperse nanocrystals of materials with narrow size distributions have been prepared by several workers, with control of the shape in some instances. To illustrate this aspect, transmission electron microscopy (TEM) images of CdSe nanorods are shown in Fig. 1. The availability of such nanocrystals has enabled better studies of sizedependent properties such as size-controlled light emission properties of semiconductor nanocrystals, the nonmetallic gap in metal nanocrystals, size-dependent Coulomb blockade and the associated scaling laws. Fig. 2 and 3 illustrate some typical size-dependent properties of materials. Size-dependent

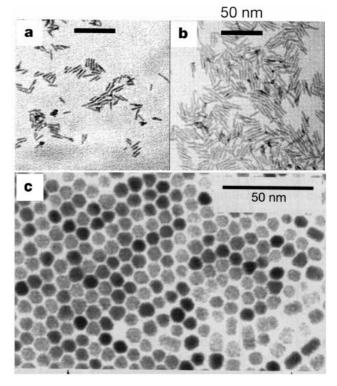


Fig. 1 TEM images of CdSe quantum rods: (a), (b) low-resolution images of quantum rods of different aspect ratios; (c) 3-dimensional orientation. (Reproduced by permission from ref. 10, X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59. Copyright Nature 2000.)

properties have been exploited for biological tagging, for example using semiconductor nanocrystals as fluorescent biological labels. ¹¹ There is a qualitative change in some facets of synthesis, the preparation of thin films being one such. For example, it is now possible to carry out atomic layer-by-layer deposition of films, thereby affording new heterostructures and metastable phases. ¹²

Since the discovery of carbon nanotubes, ¹³ much has been achieved in the synthesis of multiwalled and single-walled nanotubes and bundles of aligned nanotubes. ¹⁴ Fig. 4 shows an electron microscopy image of aligned multiwalled nanotubes. Carbon nanotubes have been doped with nitrogen and boron. Especially noteworthy is the recent synthesis of Y-junction carbon nanotubes (Fig. 5), which can act as vital components in nanoelectronics ¹⁵ since, unlike ordinary nanotubes which can be metallic or insulating, kinks or bends will act as metal–insulator junctions. Nanotubes of other inorganic materials, in particular those of layered metal chalcogenides (*e.g.* MoS₂,

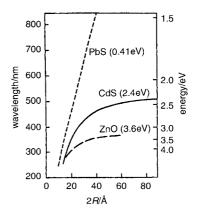


Fig. 2 Size-dependence of the wavelength of the absorption threshold in semiconductors. (Reproduced by permission from A. Henglein, *Ber. Bunsen-Ges. Phys. Chem.*, 1995, **99**, 903. Copyright VCH 1995.)

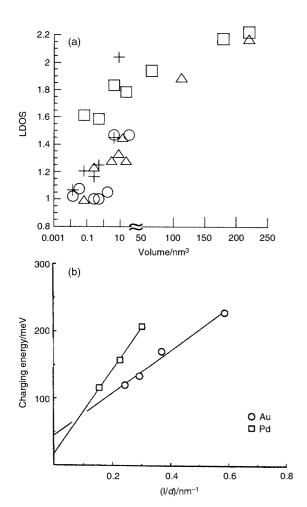


Fig. 3 (a) Size-dependence of the nonmetallic gap (local density of states) with the volume of metal nanocrystals. (Reproduced by permission from C. P. Vinod, G. U. Kulkarni and C. N. R. Rao, *Chem. Phys. Lett.*, 1998, **289**, 329. Copyright Elsevier 1998.) (b) Size-dependence of the charging capacity (Coulomb blockade) in metal nano crystals. (Reproduced by permission from P. J. Thomas, G. U. Kulkarni and C. N. R. Rao, *Chem. Phys. Lett.*, 2000, **321**, 163. Copyright Elsevier 2000.)

WS₂, MoSe₂, NbS₂), have been synthesized.^{14,16,17} These materials are likely to possess interesting and useful properties. Nanowires of metals, semiconductors, oxides, nitrides, sulfides and other materials have been prepared by various methods.^{14,18} In the area of polymers, the engineering of new polymeric structures by using dendrimers and block copolymers deserves special mention¹⁹ (see Fig. 6, for example). Nanosized polymers of different shapes could have many applications.

The construction of ordered arrays of nanostructures by employing organic self-assembly techniques provides alternative strategies for the production of nanodevices. Two- and three-dimensional arrays of nanocrystals of semiconductors, metals and magnetic materials have been assembled by using suitable organic reagents.²⁰ Strain-directed assembly of nanoparticle arrays (e.g., of semiconductors) provides the means to introduce functionality into the substrate that is coupled to that on the surface. 21 Fig. 7 shows a TEM image of Pd nanocrystals containing 1415 atoms. By varying the spacer length (or crystal size), arrays of metal nanocrystals can be made to undergo a metal-non-metal transition of the Mott-Hubbard type. Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices have been described recently² (Fig. 8). Spin-dependent tunnelling has been observed in selfassembled cobalt nanocrystal superlattices.²² Nanocrystals of uniform size suitably coated with a polymer are found to assemble to form giant nanocrystals with magic nuclearity.²³ It

is noteworthy that self-assembly of objects of varying sizes (nm to mm) occurs through weak interactions.²⁴ Single crystals of single-walled carbon nanotubes (Fig. 9) have been formed by self-assembly.²⁵ Lithography-induced self-assembly (LISA) is likely to open up new possibilities in the near future.²⁶

The area of nanoporous solids has witnessed many major advances. There has been a constant quest for crystalline solids with giant pores and several have been synthesized recently.²⁷ It has become possible to control pore size in zeolites and other nanoporous materials, and the shape-selective catalysis afforded by nanoporous solids continues to motivate much of the work in this area. Since the discovery of mesoporous MCM 41 by Mobil chemists, a variety of mesoporous inorganic solids with pore diameters in the 2–20 nm range have been prepared and characterized.²⁸ Mesoporous fibers and spheres of silica and other materials have also been prepared. A variety of inorganic, organic and organic-inorganic hybrid openframework materials with different pore architectures have been synthesized in the last few years, particularly noteworthy being the large variety of open-framework metal phosphates.² Equally interesting are the macroporous solids (pore diameters 100–1000 nm) prepared by templating crystalline arrays of silica or polymer spheres.³⁰

Many new nanostructured systems will undoubtedly be built in the next few years using a variety of nanobuilding units, and there is considerable scope for the discovery of newer and better methods of synthesis, assembly and processing. Robotic self-assembly of nanostructures may be employed more commonly. It is also likely that in the next few years, more effective interfaces with biology will emerge. There is already evidence to show that DNA-directed assembly has the potential for nanofabrication. ³¹ DNA chips and microarrays have imminent applications in diagnostics and genetic research. Preparation of nanoparticles of therapeutic drugs would directly help in drug targeting. Similarly, gene delivery may become possible through the use of nanoparticles of lipid/polymer–DNA complexes.

Experimental tools

As mentioned earlier, the rapid pace of progress in the area of nanomaterials has been made possible in part because of improved methods of measurement, characterization and manipulation. While standard methods of measurement and characterization are routinely employed for investigation, the increasing use of scanning probe microscopies (spatial resolution 1 nm), combined with high-resolution electron microscopy, has enabled direct images of structures to be obtained and aided the study of properties. Thus, scanning tunnelling spectroscopy provides important information on electronic structure and properties. Scanning probe microscopies are now employed at low temperatures, under vaccum or in a magnetic field. Computer-controlled scanning probe microscopy is useful for nanostructure manipulation in real time, and nanomanipulators are being used with scanning and transmission electron microscopes. ³² Newer versions of nanomanipulators will have to be developed by using technologies such as nanoelectromechanical systems (NEMS).

Techniques such as magnetic force microscopy and surface force microscopy are of great value in specific situations. While magnetic force microscopy directly images magnetic domains, magnetic resonance microscopes can detect nuclear or electron spin resonance with submicron spatial resolution. Near field scanning optical microscopy allows optical access to subwavelength scales (50–100 nm) by breaking the diffraction limit.³³

Nanomechanics performed in the atomic force microscope enables the study of single molecules, and is valuable in understanding folding and related problems in biological

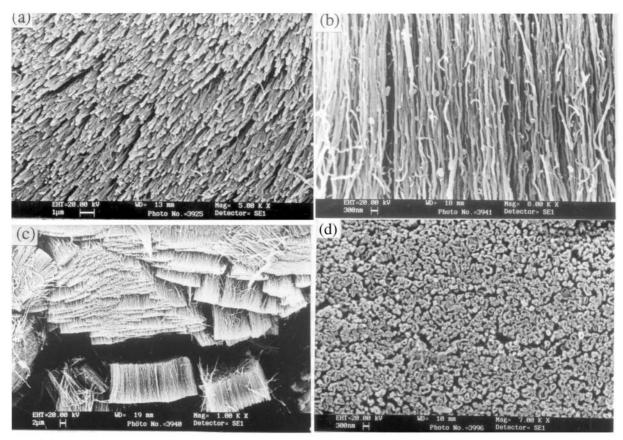


Fig. 4 TEM images of aligned multi-walled carbon nanotubes; (a), (b) and (d) show nanotubes in different orientations, (c) shows several bunbles. (Reproduced by permission from C. N. R. Rao, A. Govindaraj, R. Sen and B. C. Satishkumar, Mater. Res. Innovations, 1998, 2, 128. Copyright

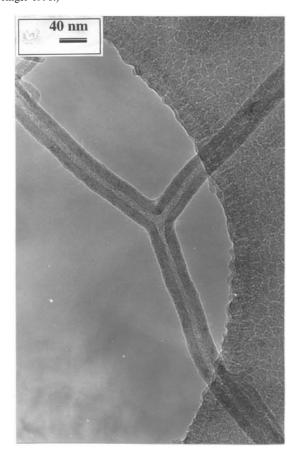


Fig. 5 TEM image of a Y-junction nanotube. (Reproduced by permission from ref. 15, B. C. Satishkumar, P. J. Thomas, A. Govindaraj and C. N. R. Rao, Appl. Phys. Lett., 2000, 77, 2530. Copyright AIP 2000.)

molecules. In order to circumvent the limitations of scanning probe microscopy, cantilever probes have been developed to enable high-speed nanometer scale imaging.³⁴ Clearly, there is much scope for the development of miniaturized instruments for the study of individual molecules and nanounits.

Optical tweezers provide an elegant means to investigate the dynamics of particles and molecules.³⁵ Thus, force measurement of complementary DNA binding provides a selective and sensitive sensor.³⁵

Microfabricated chips for DNA analysis and polymerase

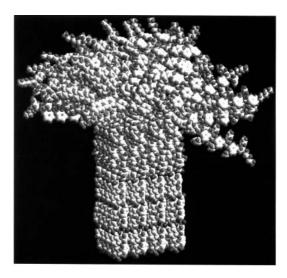


Fig. 6 Supramolecular nanostructure formed by the self-assembly of triblock copolymers. (Reproduced by permission from ref. 19, S. I. Stupp, V. LeBouheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser and A. Amstuz, Science, 1997, 276, 384. Copyright AAAS 1997.)

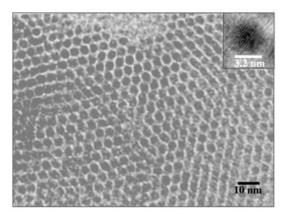


Fig. 7 TEM image of a two-dimensional array of Pd₁₄₁₅ nanocrystals (diameter 3.2 nm). (Reproduced from ref. 8, C. N. R. Rao, G. U. Kulkarni, P. J. Thomas and P. P. Edwards, *Chem. Soc. Rev.*, 2000, **29**, 27.)

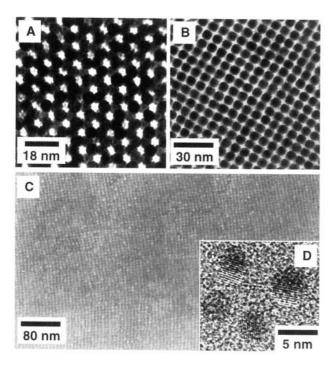


Fig. 8 (A) TEM image of a 3-D assembly of $Fe_{50}Pt_{50}$ nanocrystals (diameter 6 nm). (B) TEM image after replacing the capping oleic acid with hexanoic acid. (C) High-resolution scanning electron microscopy (HRSEM) image of 180 nm thick $Fe_{52}Pt_{48}$ nanocrystals (diameter 4 nm). (D) HRTEM image of $Fe_{52}Pt_{48}$ nanocrystals. (Reproduced by permission from ref. 22*a*, S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989. Copyright AAAS 2000.)

chain reactions have been developed.³⁶ It would be of great benefit if appropriate tools for 3-D imaging and microscopy as well as for chemical analysis of materials in nanometric dimensions become available.

Simulation and modelling

A variety of computational techniques have been employed to simulate and model nanomaterials. Since the relaxation times can vary anywhere between picoseconds to hours, it becomes necessary to employ Langevin dynamics besides molecular dynamics in the calculations. Simulation of nanodevices as a whole, through the optimization of the various components and functions, is challenging, as in the simulation of large systems and coupled phenomena. There are many instances where simulation and modelling have yielded impressive

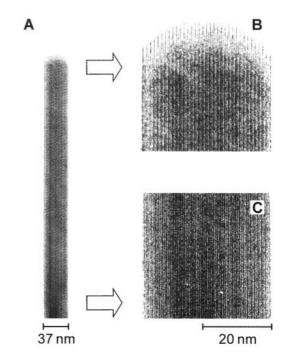


Fig. 9 (A) HRTEM image of a single-walled nanotube crystal (diameter 37 nm). (B) and (C) Lattice resolution of the crystal. (Reproduced by permission from ref. 25, R. R. Schlittler, J. W. Seo, J. K. Gimzewski, C. Durkan, M. S. M. Saifullah and M. E. Welland, *Science*, 2001, **292**, 1136. Copyright AAAS 2001.)

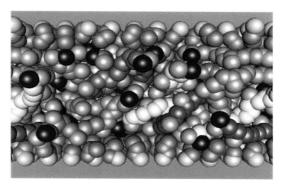


Fig. 10 Snapshot of squalane under shear flow confined between two walls with tethered butane chains. (Reproduced by permission from A. Gupta, H. D. Cochran and P. T. Cummins, *J. Chem. Phys.*, 1997, **107**, 10327. Copyright AIP 1997.)

results, nanoscale lubrication being one such example (Fig. 10). Simulation of the molecular dynamics of DNA has met with some success³⁷ and quantum dots and nanotubes have been modelled satisfactorily. Nevertheless, first principles calculations of nanomaterials can be problematic if the clusters are too large to treat by Hartree–Fock methods and too small for density functional theory.

Applications

By employing sol-gels and aerogels, high-surface area inorganic oxide materials with improved absorption and other properties are being produced. The preparation of superadsorbents for toxic chemicals is becoming possible by these methods. Ocnsolidated nanocomposites and nanostructures will yield ultrahigh-strength, tough structural materials, strong ductile cements and novel magnets. Significant developments will occur in the sintering of nanophase ceramic materials and in textiles and plastics containing dispersed nanoparticles, the latter being useful in the design of miniature lithium-ion batteries; nanostructured electrode materials would improve

the capacity and performance of Li-ion batteries. Nanostructured tin oxide also appears to attain higher reversible capacities.⁴¹ Shipway *et al.*⁴² have recently reviewed nanoparticle-based applications.

Both known and new types of nano-, meso- and macroporous materials will be put to use for inorganic synthesis and industrial catalysis. Porous films (e.g. mesoporous silica) can be used as molecular sieving membranes and in catalysis. The chemical industry may indeed get involved to a greater extent in the design of catalysts containing different types of nanometric particles, since nanoscale catalysis could provide greater selectivity. Nanocatalysis by gold illustrates how nanoparticles can have entirely different catalytic properties. Electron transfer in nanostructures can also be exploited for applications. There is a good possibility that nanomaterials such as carbon nanotubes will be used for storage of hydrogen and other gases. 14,43 It has been reported that carbon nanotubes can store hydrogen up to ca. 4 wt% or more and that the stored hydrogen is released easily without fatigue, but some doubts have been raised about these findings.⁴³ Nanoporous polymers are useful for water purification, while MoS2 nanotubes and fullerenes are good solid lubricants.

The techniques of nanoimprint-lithography and soft lithography are sufficiently developed⁴⁴ and a combination of self-assembly with patterning tools could enable new nanolithographic patterns to be obtained.⁴⁵ Examples of nanoimprint lithography and the LISA process are shown in Fig. 11. Thin-film electrets patterned with trapped charge provides another method of patterning which may be useful in

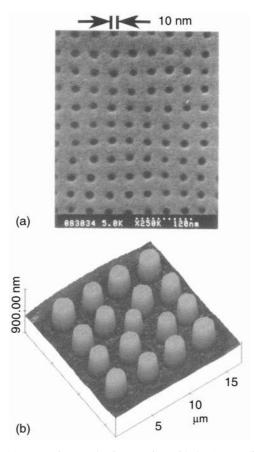


Fig. 11 (a) SEM micrograph of a top view of holes (10 nm diameter, 40 nm period) imprinted into poly(methyl methacrylate) (PMMA) (60 nm deep). (Reproduced by permission from S.-Y. Chou, P. R. Krauss, W. Zhang, L Guo and L. Zhuong, *J. Vac. Sci. Technol., B*, 1997, 15, 2897. Copyright Slack 1997.) (b) AFM image of a PMMA/LISA pillar array formed under a square pattern. (Reproduced by permission from ref. 26, S.-Y. Chou and L. Zhang, *J. Vac. Sci. Technol., B*, 1999, 17, 3197. Copyright Slack 1999.)

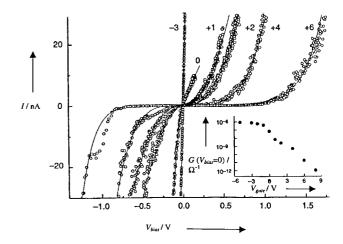


Fig. 12 Current–potential characteristics at different gate voltages of a field-effect transistor based on a single-walled nanotube. (Reproduced by permission from S. J. Tans, A. R. M. Vercsheuren and C. Dekker, *Nature*, 1998, **393**, 49. Copyright Nature 1998.)

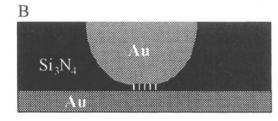
high-density charge-based data storage and high-resolution printing. 46

Carbon nanotubes are being used as tips in scanning microscopes and also as efficient field emitters for possible use in display devices. Nanotubes have been shown to act as field-effect transistors, as illustrated in Fig. 12. Newer properties of nanotubes continue to be discovered. For example, nanotubes have been found to exhibit optical limiting properties. Hodulated chemical doping of individual nanotubes yields an intramolecular wire electronic device, And magnetic clusters deposited on single-walled nanotubes exhibit the Kondo effect.

Colloidal gold particles attached to DNA strands can be employed to assay specific complementary DNAs. 49 The technology of DNA microchip arrays, involving lithographic patterning, which has been used effectively for mapping genetic information in DNA and RNA, is bound to see further improvement. Similarly, drug and gene delivery will be rendered more effective with the use of nanoparticles and nanocapsules. New miniaturized devices could become useful not only in drug delivery,50 but also in diagnostics and other applications. Molecular motors, such as the protein F₁-AT phase, are already known, but it may become practical to power an inorganic nanodevice with such a biological motor.⁵¹ Other areas in biology where nanomaterials can have an impact are in the monitoring of the environment and living systems by the use of nanosensors and in the improvement of prosthetics used to repair or replace parts of the human body. Water-based ferrofluids, prepared by using organic templates, are useful as coloured magnetic inks. Soft materials can also be used for nanofabrication.52

The most important and far-reaching applications of nanomaterials will be in nanodevices and nanoelectronics. There are already significant advances in these areas to justify greater expectations. Typical of the advances to date are the demonstration of single electron memory, Coulomb blockade and quantum effects, scanning probe tips in arrays, logic elements and sensors. The number of applications for semiconductor nanostructures, in particular those of the group III-V nitrides (e.g. InGaN) as LEDs and laser diodes, 53 are impressive, and quantum dots and wires of these materials will have a great number of uses. In Fig. 13, the essential features of nanodevice fabrication are shown schematically. A noteworthy development is the possible design of defect-free molecular electronics involving chemically fabricated systems, wherein an electronically addressable molecular switch operates.⁵⁴ Electron transport studies have been carried out on





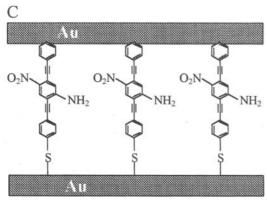


Fig. 13 Schematics of nanodevice fabrication: (A) cross-section of a silicon wafer with a nanopore etched through a silicon nitride membrane; (B) gold-self-assembled monolayer-gold junction in the pore area; (C) enlargement of the active self-assembled monolayer region with the molecules sandwiched in the junction. (Reproduced by permission from J. Chen, M. A. Reed, M. A. Rawlett and J. M. Tour, Science, 1999, 286, 1550. Copyright AAAS 1999.)

molecular-scale systems employing advanced microfabrication and self-assembly techniques.5

Nanocircuits and nanocomputers making use of carbon nanotubes have already been described. 14 Recently, metallic and semiconducting properties of multi-walled nanotubes have been engineered by stepwise burning of layers or by tailoring the chirality.⁵⁶ Such strategies directly help in the use of nanotubes in nanocircuitry. Use of Y-junction nanotubes may help to make further advances in this direction.

Resonant tunnelling devices in nanoelectronics deserve special mention, since they have already demonstrated success in multivalued logic and memory circuits. Functional devices based on quantum confinement would be of use in photonic switching and optical communications.

It is altogether likely that chips for chemical analysis, nanorobotic systems, spintronic memory based on magnetic semiconductors and a variety of other technologies will become realities in the next few years. Our ability to carry out studies of nanometer-scale objects will be effectively improved by integrating nanometer-scale control electronics into micro/ nanomachines.

Concluding remarks

The preceding discussion of the current status and future prospects of the science and technology of nanomaterials should suffice to demonstrate the great vitality of the subject and the immense opportunities it offers. It is a truly interdisciplinary area, encompassing physics, chemistry, biology, materials science and engineering. Interaction amongst

scientists with different backgrounds will undoubtedly create new science, and in particular new materials, with unforeseen technological possibilities. While there is already considerable effort being devoted to nanotechnology in various academic and industrial laboratories, there is certainly a need to establish dedicated centres with the required infrastructure and experimental facilities. The subject has caused excitement in the advanced as well as the developing nations, and is one where international cooperation would be fruitful. What is also noteworthy is that nanotechnology will benefit not only the electronics industry, but also the chemical and space industries, as well as medicine and health care. Materials chemists have a major role to play in developing the various facets of nanoscience, such as design, synthesis, assembly and catalysis. They can also make valuable contributions to theory, modelling and computer simulation.

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