1
Nanomaterials – An Introduction

C. N. R. Rao, A. Müller, and A. K. Cheetham

The term nanotechnology is employed to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials, with at least one dimension in the nanometer range ($1\ \text{nm} = 10^{-9}\ \text{m}$). In Table 1.1, we list typical nanomaterials of different dimensions. Properties of materials of nanometric dimensions are significantly different from those of atoms as well as those of bulk materials. Suitable control of the properties of nanometer-scale structures can lead to new science as well as new devices and technologies. The underlying theme of nanotechnology is miniaturization. The importance of nanotechnology was pointed out by Feynman 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 law, according to which the size of microelectronic devices shrinks by half every four years. This implies that by 2020, the size will be in the nm scale and we should be able to accommodate 1000 CDs in a wristwatch, as predicted by Whitesides.

There has been an explosive growth of nanoscience and technology in the last few years, primarily because of the availability of new strategies for the synthesis of nanomaterials and new tools for characterization and manipulation (Table 1.2). There are many examples to demonstrate the current achievements and paradigm shifts in this area. Scanning tunneling microscope (STM) images of quantum dots (e.g. 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 (Figure 1.1). Several methods of synthesizing nanoparticles, nanowires and nanotubes, and their assemblies, have been discovered. Thus, nanotubes and nanowires of a variety of inorganic materials have been discovered, besides those of carbon. Ordered arrays or superlattices of nanocrystals of metals and semiconductors have been prepared. Nanostructured polymers formed by the ordered self-assembly of triblock copolymers and nanostructured high-strength materials are other examples.

Besides the established techniques of electron microscopy, diffraction methods and spectroscopic tools, scanning probe microscopies have provided powerful means for studying nanostructures. Novel methods of fabrication of patterned nanostructures as well as new device and fabrication concepts are constantly being

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Tab. 1.1. Examples of nanomaterials.

	Size (approx.)	*Materials*
Nanocrystals and clusters (quantum dots)	diam. 1–10 nm	Metals, semiconductors, magnetic materials
Other nanoparticles	diam. 1–100 nm	Ceramic oxides
Nanowires	diam. 1–100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	diam. 1–100 nm	Carbon, layered metal chalcogenides
Nanoporous solids	pore diam. 0.5–10 nm	Zeolites, phosphates etc.
2-Dimensional arrays (of nano particles)	several nm2–μm2	Metals, semiconductors, magnetic materials
Surfaces and thin films	thickness 1–1000 nm	A variety of materials
3-Dimensional structures (superlattices)	Several nm in the three dimensions	Metals, semiconductors, magnetic materials

discovered. Nanostructures are also ideal for computer simulation and modelling, their size being sufficiently small to accommodate considerable rigor in treatment. In computations related to nanomaterials, one deals with a spatial scaling from 1 Å to 1 μm and a temporal scaling from 1 fs to 1 s, the limit of accuracy going beyond 1 kcal mol^{-1}. Prototype circuits involving nanoparticles and nanotubes for nanoelectronic devices have been fabricated. Quantum computing has made a beginning and appropriate quantum algorithms are being developed.

Let us not forget that 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 recent origin. Novel chemistry has been generated by employing nanoparticles, nanowires and other nanostructures. This includes electrochemical, photochemical, catalytic and other aspects. The immediate objectives of the science and technology of nanomaterials are: (i) to fully master the synthesis of isolated nanostructures (building blocks) and their assemblies with the desired properties, (ii) to explore and establish nanodevice concepts and systems architectures, (iii) to generate new classes of high performance materials, (iv) to connect

Tab. 1.2. Methods of synthesis and investigation of nanomaterials.

Scale (approx.)	*Synthetic Method*	*Structural Tool*	*Theory and simulation*
0.1 to ~10 nm	Covalent synthesis	Vibrational spectroscopy NMR Diffraction methods	Electronic structure
<1 to ~100 nm	Techniques of self-assembly	Scanning probe microscopies	Molecular dynamics and mechanics
100 nm to ~1 μm	Processing, modifications	SEM, TEM	Coarse-grained models etc.

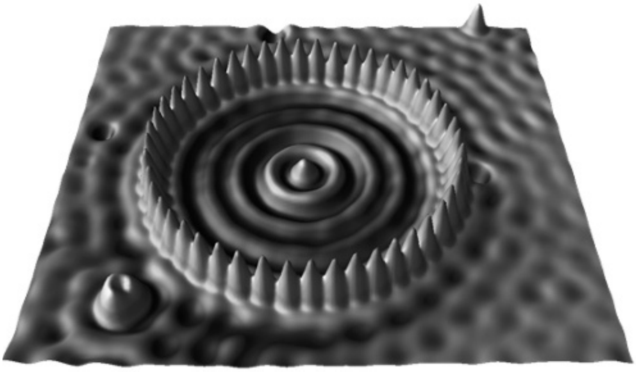

Fig. 1.1. STM image of a quantum corral of 48 Fe atoms placed in a circle of 7.3 nm [IBM Research].

nanoscience to molecular electronics and biology, and (v) to improve known tools while discovering better tools of investigation of nanostructures.

1.1
Size Effects

Size effects constitute a fascinating aspect of nanomaterials. The effects determined by size pertain to the evolution of structural, thermodynamic, electronic, spectroscopic, electromagnetic and chemical features of these finite systems with increasing size. Size effects can be classified into two types, one dealing with specific size effects (e.g. magic numbers of atoms in metal clusters, quantum mechanical effects at small sizes) and the other involving size-scaling applicable to relatively larger nanostructures. The former includes the appearance of new features in the electronic structure. In Figure 1.2, we show how the electronic structures of metal and semiconductor nanocrystals differ from those of bulk materials and isolated atoms. In Figure 1.3, we show the size-dependence of the average energy level spacing of sodium in terms of the Kubo gap (E_F/N) in K. In this figure, we also show the effective percentage of surface atoms as a function of particle diameter. Note that at small size, we have a high percentage of surface atoms.

Size affects the structure of nanoparticles of materials such as CdS and CdSe, and also their properties such as the melting point and the electronic absorption spectra. In Figures 1.4 and 1.5, we show such size effects graphically. It should be noted that even metals show nonmetallic band gaps when the diameter of the nanocrystals is in the 1–2 nm range. Hg clusters show a nonmetallic band gap which shrinks with increase in cluster size. It appears that around 300 atoms are necessary to close the gap. It is also noteworthy that metal particles of 1–2 nm diameter also exhibit unexpected catalytic activity, as exemplified by nanocatalysis by gold particles.

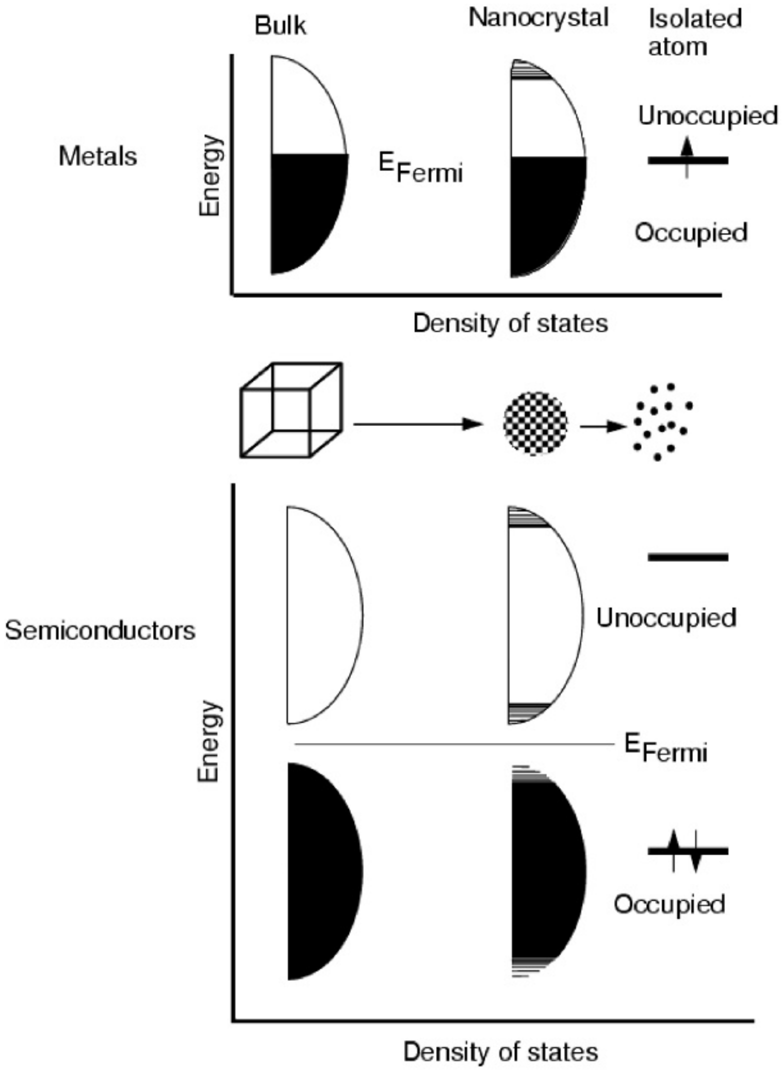

Fig. 1.2. Density of states for metal and semiconductor nanocrystals compared to those of the bulk and of isolated atoms [from C. N. R. Rao, G. U. Kulkarni, P. J. Thomas, P. P. Edwards, *Chem-Euro J.*, **2002**, *8*, 29.].

1.2
Synthesis and Assembly

The synthesis of nanomaterials and assembling the nanostructures into ordered arrays to render them functional and operational are crucial aspects of nanoscience. The materials/structures include nanoparticles, nanowires, nanotubes,

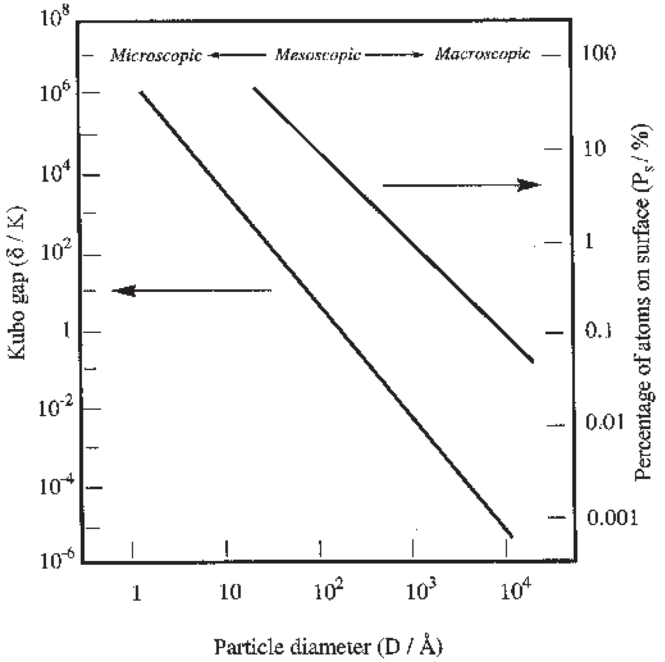

Fig. 1.3. A plot of the average electronic energy level spacing (Kubo gap, δ) of sodium as a function of the particle diameter. Also shown is the percentage of sodium atoms at the surface as a function of particle diameter [From P. P. Edwards, R. L. Johnston and C. N. R. Rao, in *Metal Clusters in Chemistry*, ed. P. Braunstein et al., John Wiley, 1998.].

nanocapsules, nanostructured alloys and polymers, nanoporous solids and DNA chips. What is also noteworthy is that chemists have synthesized molecular entities of nanometric dimensions. In Figure 1.6, we show a two-dimensional crystalline array of thiolized metal nanocrystals to illustrate self-assembly.

1.3
Techniques

The emerging nanoworld encompasses entirely new and novel means of investigating structures and systems, besides exploiting the well known microscopic, diffraction and spectroscopic methods. Species as small as single atoms and molecules are manipulated and exploited as switches. Computer-controlled scanning probe microscopy enables a real-time, hands-on nanostructure manipulation. Nanomanipulators have also been designed to operate in scanning and transmission electron microscopes. A nanomanipulator gives virtual telepresence on the

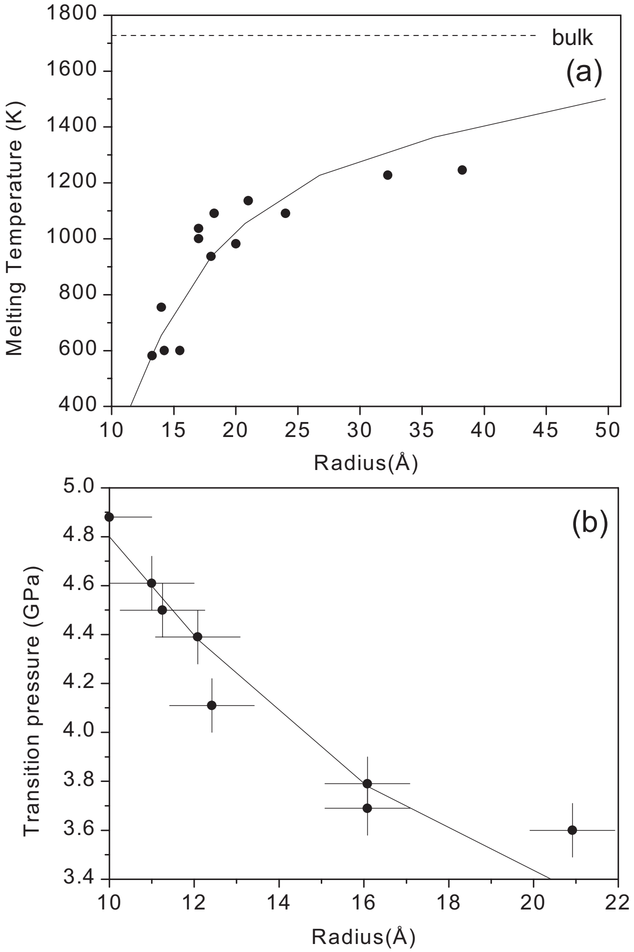

Fig. 1.4. (a) Size dependence of the melting temperature of CdS nanocrystals. (b) Size dependence of the pressure-induced wurtzite–rock salt transformation in CdSe nanocrystals [from A. P. Alivisatos, *J. Phys. Chem.*, **1996**, *100*, 13226.].

surface, with a scale factor of a million to one. Optical tweezers provide another approach to holding and moving nanometer structures, a capability especially useful in investigating the dynamics of molecules and particles. Questions such as, how does a polymer move, generate force, respond to an applied force and unfold, can be answered by the use of optical tweezers. It is noteworthy that the positioning of nanoparticles accurately and reliably on a surface by using the tip of an atomic force microscope as a robot has already been accomplished. Large-scale operations requiring parallel tip arrays are being explored in several laboratories.

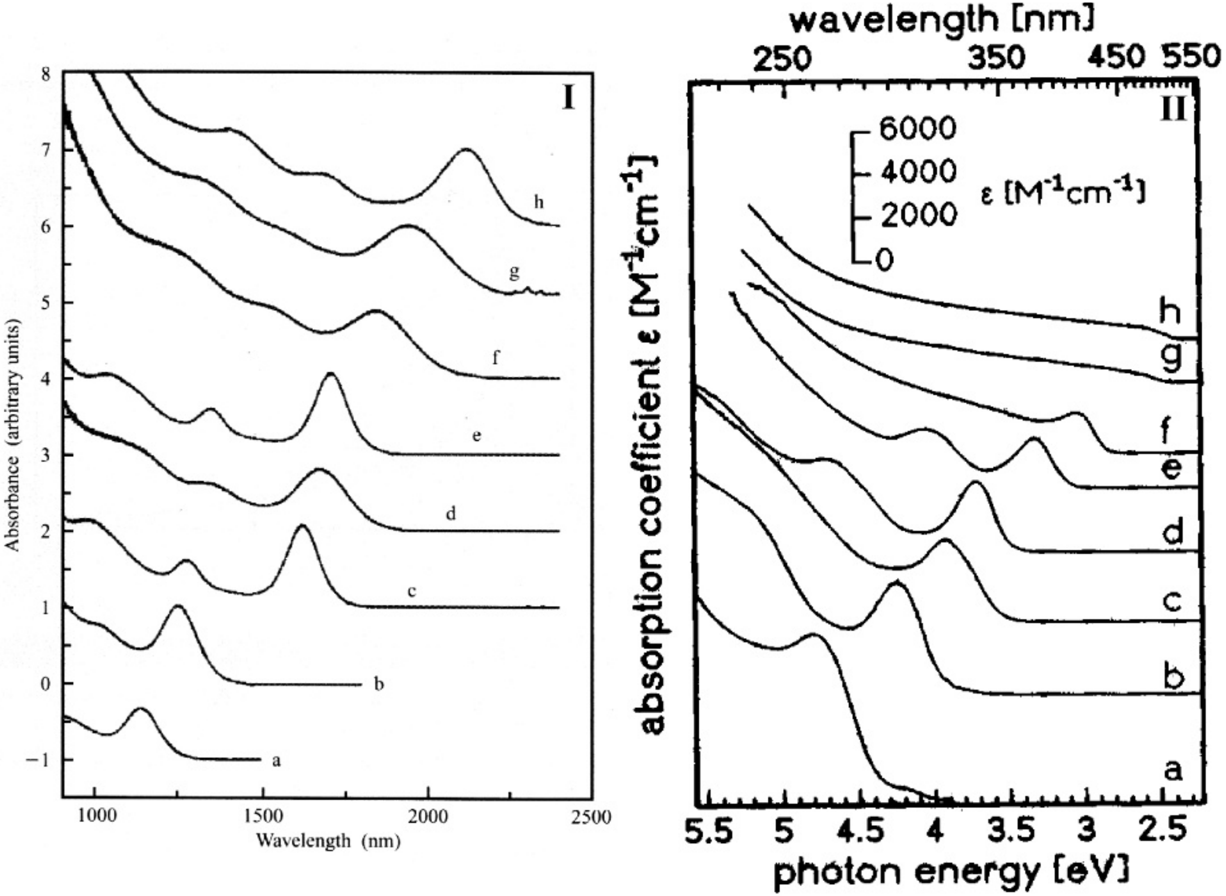

Fig. 1.5. Electronic spectra of (I) PbSe nanocrystals (a. 3.0 nm, b. 3.5 nm, c. 4.5 nm, d. 5.0 nm, e. 5.5 nm, f. 7 nm, g. 8 nm, h. 9 nm) and (II) of CdS nanocrystals (a. 0.64 nm, b. 0.72 nm, c. 0.8 nm, d. 0.93 nm, e. 1.94 nm, f. 2.8 nm, g. 4.8 nm) [from T. Vossmeyer et al. *J. Phys. Chem.*, **1994**, *98*, 7665 and R. W. Murray et al., *IBM J. Res. Dev.*, **2001**, *45*, 47.].

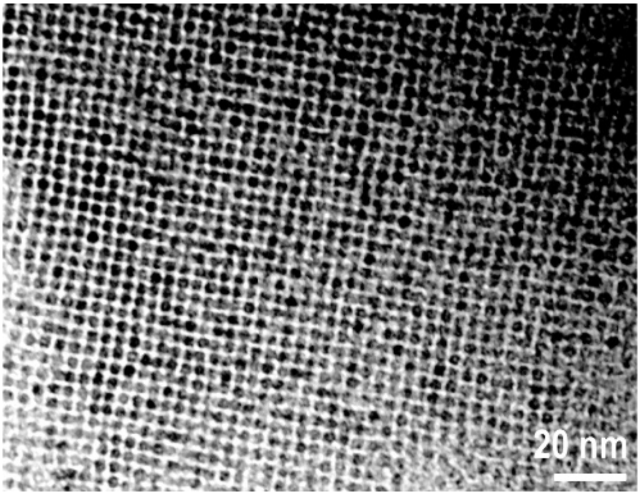

Fig. 1.6. Two-dimensional array of thiolized $Pd_{561}Ni_{561}$ nanocrystals [from P. J. Thomas, G. U. Kulkarni, C. N. R. Rao, *J. Nanosci. Nanotechnol.*, **2001**, *1*, 267.].

1.4
Applications and Technology Development

Some of the important applications and technologies based on nanomaterials are the following: (i) Production of nanopowders of ceramics and other materials, (ii) nanocomposites, (iii) development of nanolectrochemical systems (NEMS), (iv) Applications of nanotubes for hydrogen storage and other purposes, (v) DNA chips and chips for chemical/biochemical assays, (vi) gene targeting/drug targeting and (vii) nanoelectronics and nanodevices. The last one, which is probably the most challenging area, includes new lasers, nanosensors, nanocomputers (based on nanotubes and other materials), defect-free electronics for future molecular computers, resonant tunneling devices, spintronics and the linking of biological motors with inorganic nanodevices.

1.5
Nanoelectronics

The multidisciplinary area of nanoelectronics has two objectives: (i) utilization of a single nanostructure (e.g. nanocrystal, quantum dot, nanotube) for processing electrical, optical or chemical signals, and (ii) utilization of nanostructured materials involving assemblies of nanostructures for electronic, optoelectronic, chemical and other applications. While it is often difficult to make distinctions between the two, the first category is specifically intended to obtain single-electron devices and the second category is for the purpose of miniaturization in information storage etc. Typical examples of single nanostructure devices are those employing Coulomb blockade or a single-electron transistor. Arrays of quantum dots, scanning probe tips and nanotubes are examples of the second category. In Coulomb blockade, the addition of a single electron to a nanoparticle of radius R gives rise to the charging energy, $W = W(\infty) + [b/R]$ where $W(\infty)$ relates to the charging energy of the bulk. The minimum voltage, $V_{\min}$, required to inject an extra electron into the nanoparticle gives rise to the Coulomb staircase with voltage steps, $V_{\min} = [W(\infty)/e] + [b/eR]$. The observation of the staircase provides a direct demonstration of the discrete electronic structure in such finite (nano) systems. In Figure 1.7, we show the I–V characteristics of an isolated 3.3 nm Pd nanocrystal, exhibiting the Coulomb staircase phenomenon. The dependence of the charging energy on particle size is also shown in Figure 1.7.

1.6
Other Aspects

Consolidated nanostructures employing both ceramic and metallic materials are considered important in creating new generations of ultrahigh-strength, tough structural materials, new types of ferromagnets, strong and ductile cements, and new biomedical prosthetics. Typical of the nanostructured hard materials are Co/WC and Fe/TiC nanocomposites. Nanoparticle-reinforced polymers are being considered for automotive parts. Besides high strength materials, dispersions and powders as well as large bodies of novel morphologies are being produced. Coatings with highly improved features resulting from the incorporation of nanoparticles are being developed.

Nanoelectrochemical systems (NEMS) are likely to augment the already established micro analogue, MEMS. A related aspect pertains to molecular motors. Molecular motors are responsible for DNA transcription, cellular transport and muscle contraction. New fabrication tools enable us to understand and exploit these motors as actuators in nanoelectromechanical systems. These may lead to artificial biological devices that are powdered by ATP. Organic chemists are synthesizing molecules (e.g., rotaxanes) capable of various kinds of motions at the nanolevel. Using molecular motors as nanomachines and interfacing them with inorganic energy sources and other nanodevices would be of great interest.

DNA chips and microarrays represent a technology with applications in diagnostics and genetic research. DNA chips and arrays are devices wherein different DNA sequences are arrayed on a solid support, the arrays generally having 100 to 100,000 different pixels (DNA sites) on the chip surface. The chips will be useful in genomic research, drug discovery, forensics and different types of detection and diagnostics. Electronically active DNA microarrays and electronically directed DNA self-assembly technology could be of value in photonic and electronic devices and other areas. Appropriate nanoparticles containing DNA may indeed provide viable means of delivery in the near future. The gene gun is already being used to deliver genetic materials to transfect plant and animal cells.

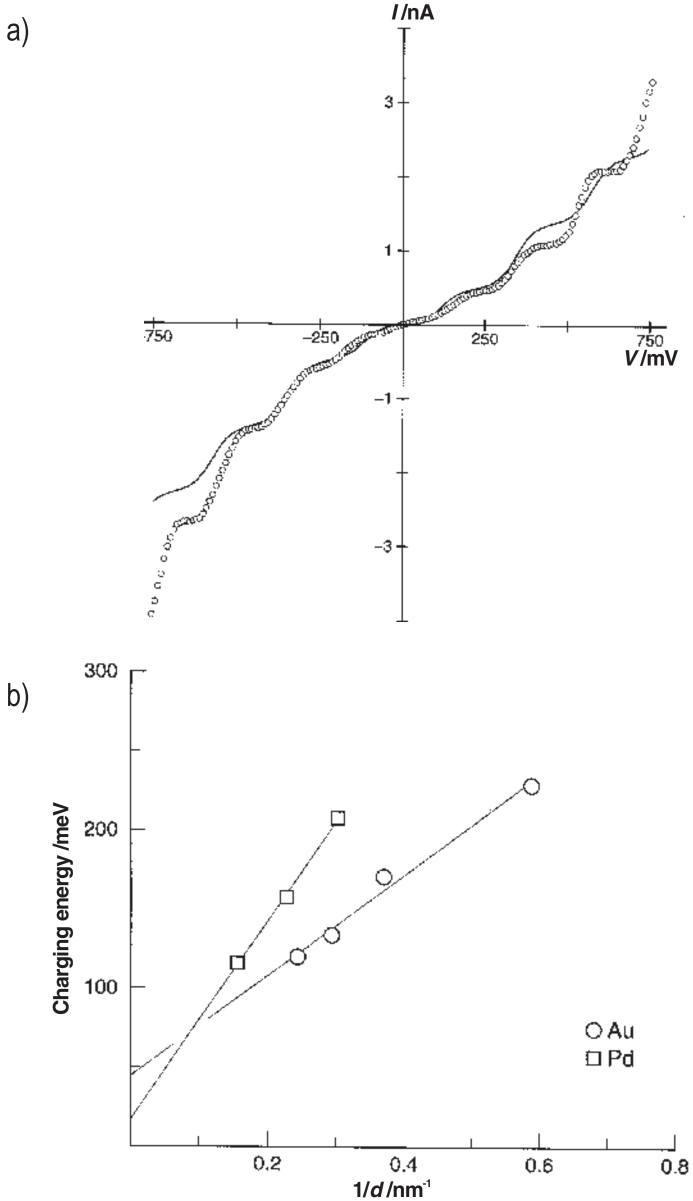

Fig. 1.7. (a) *I–V* characteristics of an isolated 3.3 nm Pd nanocrystal (dotted line) and theoretical fit (solid line) obtained at 300 K using a semiclassical model. (b) The size dependence of the charging energy [from P. J. Thomas, G. U. Kulkarni and C. N. R. Rao, *Chem. Phys. Lett.*, **2000**, *321*, 163.].

Semiconductor nanocrystals are being used as fluorescent biological labels. It is likely that sensors based on nanotechnology will revolutionize health care, climate control and detection of toxic substances. It is quite possible that we will have nanochips to carry out complete chemical analysis. Such nano-total analysis systems will have to employ new approaches to valves, pipes, pumps, separations and detection.

A knowledge of the processes related to nanoscale structures, natural as well as man-made, is useful in understanding transport and other aspects of these materials, and in developing technologies for preventing or minimizing harm to the environment. The use of homogeneous and heterogeneous catalysis (including nanocatalysis) for improving energy efficiency and reducing waste is well documented. The design of environmentally benign nanocomposites, the use of nanoparticles of TiO_2 and other nanomaterials for environmental cleansing processes and of nano-porous solids for sorption, are examples of the applications of nanotechnology for the protection and improvement of the environment. The use of nanoporous polymers for water purification and purification of liquids by photocatalysis of nanoparticles of TiO_2 are two other examples.

1.7
Concluding Remarks

The subject of nanomaterials is of great vitality and offers immense opportunities. It is truly interdisciplinary and encompasses chemistry, physics, biology, materials and engineering. Interaction amongst scientists with different backgrounds will undoubtedly create new science, and in particular new materials, with unforeseen technological possibilities. What is noteworthy is that nanotechnology is likely to benefit not only the electronics industry, but also the chemical and space industries, as well as medicine and health care. Chemistry has much to contribute to most aspects of the science and technology of nanomaterials.

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