Nanostructured advanced materials. Perspectives and directions*

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Abstract: A focus of frontline interdisciplinary research today is the development of the conceptual framework and the experimental background of the science of nanostructured materials and the perspectives of its technological applications. We consider some current directions in the preparation, characterization, manipulation, and interrogation of nanomaterials, in conjunction with the modeling of the unique structure–dynamics–function relations of nanostructures and their assemblies. The implications of quantum size and shape effects on the energetics, nuclear–electronic level structure, electric-optical response and dynamics, reveal new unique physical phenomena that qualitatively differ from those of the bulk matter and provide avenues for the control of the function of nanostructures. Current applications in the realm of nanoelectronics, nanooptoelectronics, and information nanoprocessing are addressed, and other directions highlighted. Chemical sciences make a central contribution to this novel and exciting scientific–technological area.

PROLOGUE

Nanoscience and nanotechnology pertain to the synthesis, characterization, exploration, interrogation, exploitation, and utilization of nanostructured materials, which are characterized by at least one dimension in the nanometer (1 nm = 10^{-9} m) range. Such nanostructured systems constitute a bridge between single molecules and infinite bulk systems. Individual nanostructures involve clusters, nanoparticles, nanocrystals, quantum dots, nanowires, and nanotubes, while collections of nanostructures involve arrays, assemblies, and superlattices of individual nanostructures [1,2]. Table 1 lists some typical dimensions of nanomaterials [1]. The chemical and physical properties of nanomaterials can significantly differ from those of the atomic-molecular or the bulk materials of the same chemical composition. The uniqueness of the structural characteristics, energetics, response, dynamics, and chemistry of nanostructures is novel and constitutes the experimental and conceptual background for the novel field of nanoscience. Suitable control of the properties and response of nanostructures can lead to new devices and technologies. The underlying themes of nanoscience and nanotechnology are dual: first, the bottom-up approach of miniaturization of the components, as advanced by Richard Feynman in his often-cited 1959 lecture stating that "there is plenty of room at the bottom" [3]; second, the top-down approach of the self-assembly of molecular components, where each molecular or nanostructured component plugs itself into a suprastructure. This approach was pioneered by Jean-Marie Lehn [4], revealing that "there is plenty of room at the top".

Table 1 Nanostructures and their assemblies.

Nanostructure	Size	Material

Clusters
Nanocrystals
Quantum dots
	Radius: 1–10 nm	Insulators,
		  semiconductors, metals,
		  magnetic materials

Other nanoparticles	Radius: 1–100 nm	Ceramic oxides
Nanobiomaterials Photosynthetic reaction center	Radius: 5–10 nm	Membrane protein
Nanowires	Diameter: 1–100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	Diameter: 1–100 nm	Carbon, layered chalcogenides
Nanobiorods	Diameter: 5 nm	DNA

2D arrays of
  nanoparticles
	Area: several nm^2–μm^2	Metals, semiconductors,
		  magnetic materials

Surfaces and
  thin films
	Thickness: 1–1000 nm	Insulators, semiconductors,
		  metals, DNA

3D superlattices of
  nanoparticles
	Radius: several nm	Metals, semiconductors,
		  magnetic materials

The IUPAC Conference on New Directions in Chemistry, the Workshop on Nanostructured Advanced Materials (WAM II), addressed the recent developments in the broad, interdisciplinary research field of nanoscience and nanotechnology, focusing on:

- Quantum structures, that is, nanoparticles and nanocrystals of metals and of semiconductors, nanostructures, nanowires, and nanobiological systems
- Assemblies of nanostructures (e.g., nanoparticles and nanowires) and the use of biological systems (e.g., DNA) as molecular nanowires, as well as templates for metallic or semiconducting nanostructures
- Theoretical and computational studies that provided the conceptual framework for structure, dynamics, response, and transport in nanostructures. Theory and simulations in chemical sciences are unique in the building of conceptual bridges with experiment.

This introductory chapter will highlight some significant aspects of the characterization, interrogation, and response of nanostructures, in conjunction with theoretical modeling of the unique structure, dynamics, and function of quantum structures and their assemblies. We focus on the current state of the art for the development of the conceptual framework and experimental background of nanoscience and nanotechnology.

QUANTUM STRUCTURES: SYNTHESIS, CHARACTERIZATION, MANIPULATION, AND ASSEMBLY

Impressive growth in nanoscience and technology in the last decade stems from new methods for the synthesis of nanomaterials in conjunction with the advent of tools for characterization and manipulation. The synthesis of nanomaterials spans inorganic, organic, and biological systems and manipulation with control of structure, size, and shape (Table 2). The subsequent assembling of the individual nanostructures into ordered arrays is often imperative for their functions. Uniqueness of properties of nano-

Table 2 Synthesis, characterization and description 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 Molecular dynamics Transport

<1–100 nm	Self-assembly
	  techniques
		SEM, TEM, SPM	Molecular dynamics
			  and mechanics

100 nm–1 µm	Processing,
	  modifications
		SEM, TEM	Coarse-grained models for
			  electronic interactions,
			  vibronic effects, and transport

structures originates from the combination of the individual nanosystems and their assembly methods. Notable examples for the synthesis of novel nanobuilding units are:

- Nanocrystals of metals, semiconductors and magnetic materials, involving the utilization of colloid chemistry methods [5–8]
- The use of physical and chemical methods for synthesis of nanoparticles of ceramic materials [1]
- Surface deposition of clusters and nanocrystals on graphite and other metallic or semiconducting surfaces provides novel 3-dimensional or 2-dimensional nanosytems [9]. Deposition of semiconducting clusters from a cluster beam provides novel and interesting systems of deposited fractal clusters [9], whose dimensionality is characterized by the Hausdorf fractal dimensionality, which is of considerable interest in the context of their response and chemistry.
- Single- and multi-walled carbon nanotubes [10], as well as nanotubes of layered metal chalcogenides (e.g., MoS_2, WS_2, $MoSe_2$, NbS_2, V_2O_5) [11–13]
- Nanowires of metals, semiconductors, oxides, nitrides, sulfides, and other materials [14,15]
- Utilization of quantum well superlattices for growing nanowires [16]
- New polymeric structures involving dendrimers and block copolymers [17]
- Nanobiological structures (e.g., bacterial and plant photosynthetic reaction centers [18] and segments of DNA [19,20]). Mutagenesis and chemical engineering of the protein structure and of the prosthetic groups in the reaction center, as well as chemical modifications of the DNA double strand, provide means of control of the response of these systems.

We now briefly address the characterization of nanostructures. In addition to the well-established techniques of crystallography and transmission electron microscopy and spectroscopy, the modern methods of scanning probe and tunneling spectroscopies [1] and of extended X-ray absorption fine structure (EXAFS) synchrotron radiation spectroscopy [21] have provided powerful tools for the characterization of nanostructures. Unique quantum nanostructures involve the familiar examples of scanning tunneling spectroscopy (STM) imaging of quantum dots (e.g., a germanium pyramid on a silicon surface) and of a quantum corral of 48 Fe atoms placed in a circle of 7.3 nm [1].

Perspectives of advances in the area of characterization and dynamic interrogation may involve time-resolved structural studies of nanostructures using synchrotron radiation sources. Temporal resolution on the ns time-scale was already achieved with the Grenoble ESRF synchrotron source for time-resolved structures of biomolecules (e.g., myoglobin) [22]. The interrogation of time-resolved structures for the dynamics and response of nanomaterials will be of considerable interest.

Self-assembly provides new ways to pattern a huge number (in the range of 10^6) of nanocrystals, nanowires, etc. to produce complex circuits for optical, magnetic, or electrical response. Examples for the self-assembly of individual nanosystems are:

- 2-dimensional and 3-dimensional structures of nanocrystals of semiconductors, metals, and magnetic materials being self-assembled using suitable organic solvents [23]
- Polymer-coated nanocrystals assembled to form giant nanoparticles [1]
- Self-assembled carbon nanotubes forming single crystals [24]
- Self-assembly of colloid nanostructures [25]
- Lithography-induced self-assembly [26]
- The utilization of the unique features of recognition, assembly, and specific binding of nucleobases in DNA duplexes for the construction of conductive blocks or as insulating/conducting templates for the assembly of other nanoelements [27]
- In the realm of biosystems, viral particles are decorated with metal nanoparticles, with the aim of allowing the viruses to assemble themselves into arrays to create networks of the nanoparticles [16]

THE NANOWORLD IS DIFFERENT

The conceptual framework and practice of nanoscience encompasses both nanostructures and their ensembles. In this broad context, the physical and chemical properties of nanostructures are distinct from both the single atom or the molecule and from the bulk matter of the same chemical composition. These fundamental differences between the nanoworld on the one hand, and the molecular and condensed phase worlds on the other hand, pertain to the spatial structures and shapes, phase changes, energetics, electronic–nuclear level structure, spectroscopy, response, dynamics, chemical reactivity, and catalytic properties of large, finite systems and their assemblies. Central issues in this broad, interdisciplinary research area of nanoscience pertain to size effects, shape phenomena, confinement of elementary excitations, level structure of elementary excitations, and the response to external electric and optical excitations of individual finite systems and of coupled finite systems. The ubiquity of these phenomena reflects on quantum effects in finite nanostructures.
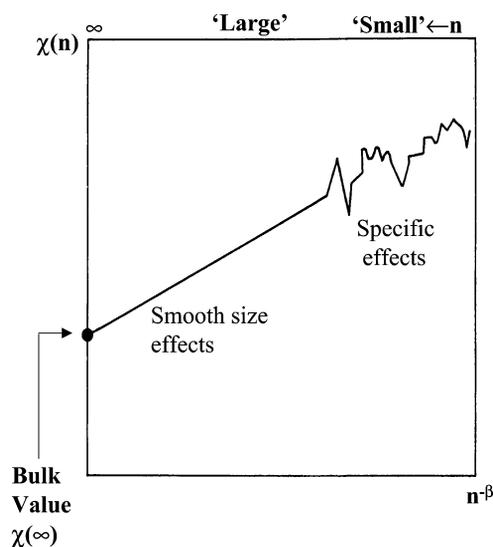
Size effects

A key concept for the quantification of the unique characteristics of individual nanostructures pertains to size effects [28–31]. These involve the evolution of structural, thermodynamic, electronic, energetic, spectroscopic, electromagnetic, dynamic, and chemical features of finite systems with increasing size (Fig. 1). This concept emerged from cluster chemical physics [28], but is applicable to other nanostructures [31] (e.g., nanocrystals or nanowires). Size effects fall into two categories (Fig. 1):

1. Specific size effects. These involve self-selection and existence of "magic numbers" for small and moderately sized clusters and nanostructures. An irregular variation of the relevant property $\chi(n)$ (where n is the number of constitutents), with increasing the size of the nanostructure, is manifested. Accordingly, $\chi(n)$ is not amenable to size-scaling.
2. Smooth size effects for "large" nanostructures. In this size domain, a quantitative description (Fig. 1) was advanced for the "transition" of the physical and chemical attributes of clusters to the infinite bulk system in terms of the size equation $\chi(n) = \chi(\infty) + An^{-\beta}$, where A is the constant and β ($\beta \geq 0$) is a positive exponent. For a spherical nanoparticle of radius R, the size equation is $\chi(n) = \chi(\infty) + \bar{A}n^{-3\beta}$. These size equations can be traced to two distinct physical origins: cluster packing and excluded volume effects [28–31]. Size equations constitute scaling laws for the nuclear-electronic level structure, energetics, and dynamics, providing the quantitative basis for the description of optical and electrical response of nanostructures.

When is such size-scaling partial and incomplete? Several examples come to mind in the context of energetics, nuclear dynamics, and cooperative effects. First, the structural characterization and specification of phase-like forms, for example, solid (rigid) and liquid (nonrigid) or solid (rigid) and solid (rigid) configurations and "smeared" (rounded-off) first-order [32–34] or second-order [33,34]

structural-phase changes between them in nanoparticles, as well as for second-order phase transitions (e.g., superfluidity in finite Boson systems) or onset of superconductivity in finite Fermion systems [32,33], may differ from the corresponding feature in bulk matter. Second, nuclear adiabatic dynamics of clusters manifests new collective excitations, (e.g., compression modes [29,30]), which do not have an analog in the bulk. Third, finite systems exhibit novel fragmentation patterns, such as cluster fission and Coulomb explosion [35–37], which are unique for finite systems and do not have an analog in the dynamics of the corresponding bulk matter. A striking example constitutes the dynamics of Coulomb explosion of multicharged single clusters, which may also prevail in nanostructures, whose energetics is characterized by a divergent scaling size equation [38].

Fig. 1 The cluster size dependence of a cluster property $\chi(n)$ on the number n of cluster constituents. The data are plotted vs. $n^{-\beta}$, where $\beta \geq 0$. "Small" clusters reveal specific size effects, while "large" clusters are expected to exhibit for many properties a smooth size dependence of $\chi(n)$, which converges for $n \to \infty$ to the bulk value $\chi(\infty)$.

Threshold size effects from a single particle to collective phenomena

An important variant of specific size effects pertains to the onset of a qualitatively new feature of the electronic or nuclear-level structure. For excess electron binding to atomic $(Xe)_n$ [39] or polar molecular $(H_2O)_n$, $(NH_3)_n$ clusters [28,40] the issue is: what is the minimal cluster size required for the localization of an excess electron? Experimental photoelectron spectroscopy, in conjunction with quantum mechanical calculations, established the threshold size of Xe_n^- for electron localization in the range $n_c = 4$–6 [39,41]. The threshold size for excess electron localization in polar clusters manifests a marked system specificity. For water clusters, both experiment and theory [28,40] reveal that an excess electron is bound by the dimer $(H_2O)_2$ forming a diffuse ($<r> \simeq 20$ Å) weakly bound ($E_b = -50$ meV), dipole bound state. In contrast, for ammonia clusters the "critical" cluster size is $n_c \simeq 35$, with the formation of a localized ($E_b = -0.5$ eV) solvated electron in the $(NH_3)_{35}^-$ cluster at the onset. Another significant area of many-particle threshold size effects pertains to the important problem of metal–nonmetal transition (MNMT) in clusters (in the section "Metal–nonmetal transition in finite systems").

Some fascinating novel collective phenomena in large finite systems pertain to the nuclear dynamics and phase changes of finite ultracold gases [42–46], which, in the temperature domain of $T = 100$ nk–100 μK, involve gases in magnetooptical traps, optical molasses, and Bose–Einstein con-

densates. While ultracold finite gases are macroscopic, some features of their optical response were already related to the dynamics of nanostructures [44]. These ultracold, finite systems may be of considerable interest in the context of superfluidity and superconductivity in nanostructures. An interesting example for the collective nuclear dynamics of an ultracold finite system pertains to the Bose–Einstein condensation of atoms with a negative scattering length (e.g., ^{7}Li atoms confined in a harmonic trap at $T \cong 100$ nK) [46]. A molecular description of the nuclear dynamics of this system [45] showed that the effective potential contains only metastable states subjected to macroscopic tunneling. For an assembly of ^{7}Li atoms, practical stability is insured for a critical size of $n_{CR} \simeq 1500$, manifesting some novel features of the collective nuclear tunneling of finite ultracold systems [46]. Of course, such instability, induced by macroscopic tunneling, cannot be described in terms of an algebraic size-scaling relation. In contrast, finite size effects on the critical temperature for Bose–Einstein condensation of a noninteracting Bose gas in a harmonic trap manifest the reduction of the condensate fraction and the lowering of the transition temperature, as compared to the infinite system [46]. In an n particles condensate, the shift of the critical temperature T_c, relative to that for the $n \to \infty$ limit, T_c^0, is given by the size-scaling relation $(T_c^0 - T_c)/T_c^0 \propto n^{-1/3}$. Alternatively, one can express the lowering of the critical temperature as $(T_c^0 - T_c) \propto L^{-1}$, where L is the characteristic length of the three-dimensional system [46]. The perspectives of exploring the response (e.g., optical excitations) of ultracold low-density nanosystems is of considerable future interest.

Metal–nonmetal transition in finite systems

The MNMT in bulk systems constitutes a quantum transformation driven by the effects of electron interactions, disorder, and temperature [47]. While the MNMT in the bulk is manifested by the combination of electron delocalization, localization, and electron-scattering phenomena [47], the corresponding effects in an atomic cluster (e.g., Na$_n$ or Hg$_n$) pertain to the implications of the discrete electronic-level structure in a finite system [48]. One approach to the visualization of the relevant electronic-level structure in a cluster or nanoparticle containing one valence electron per atom is to start with a bulk metal and gradually decrease its size to form smaller "metallic" particles. As the size of the particles is reduced, the electronic energy levels become discrete, with the energy spacing between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels being given by $\Delta \cong E_F/n$, where E_F is the Fermi energy of the bulk metal [48,49]. Kubo proposed [48] that the formation of a spatially filled "band" in the finite system can be realized at a finite temperature, when the spacing Δ is lower than the thermal energy. Under these circumstances, the electrical response of the nanostructure (e.g., held between nanoelectrodes) will result in gapless "metallic" conduction. Thus, the condition for an MNMT in a cluster of monovalent atoms is given by the Kubo relation [48] $\Delta \le k_B T$. For (Na)$_n$ sodium clusters ($E_F = 3.2$ eV) the Kubo condition for the MNMT is realized at $T > 5$ K for $n = 16000$ ($d = 10$ nm), at $T > 50$ K for $n = 2000$ ($d = 5$ nm), and at $T > 300$ K for $n = 125$ ($d = 2$ nm) [21]. For smaller Na cluster sizes ($n \lesssim 100$), this simple description breaks down, and a molecular description of these clusters is adequate [50].

For clusters containing two or more valence electrons per metallic atom, band-overlap effects induce the formation of the metallic state, for example, s–p band overlap in Hg$_n$ clusters [51–53]. While early ionization potential studies of (Hg)$_n$ clusters [51] predicted the MNMT and $n \simeq 10$, subsequent photoelectron spectroscopy data for Hg$_n^-$ clusters demonstrated s–p band closure for considerably larger clusters of $n = 400$ [52]. There is currently a discrepancy between the experimental result for s-p closure [52] and theory [53] for the MNMT in these finite systems. One expects that distinct relevant electrical or optical response properties, manifesting an MNMT in clusters, will be characterized by a different "critical size". This property dependence of the "critical" size reveals the generality, but not the universality of the MNMT in finite systems. The description of the MNMT in finite systems is general, but not universal.

Up to this point, we focused on clusters and nanocrystals of metallic elements. An interesting issue is the realization of metal clusters of nonmetallic elements, where metallic properties are induced by a melting-phase transition [34]. Some semiconducting solids (e.g., silicon or germanium) become metallic in the liquid state, owing to the change in the coordination number. There is a distinct possibility that "melting" (rigid–nonrigid transition) of Si or Ge clusters, which is exhibited at lower temperatures than that of the bulk, will result in metal clusters [21].

Finally, we move from individual nanostructures to their assemblies. The phenomena of the change of electronic structure and transport in an assembly of nanostructures (e.g., semiconducting or metal clusters) provides a means for controlling functionality of nanomaterials. A 2-dimensional array of Pd nanocrystals was induced to undergo a macroscopic MNMT by varying the spacer length or the cluster size [54]. The Mott–Hubbard model [55] is applicable to describe the MNMT induced in the nanomaterial by correlation effects between the nanoparticles, where the condition for the metal-insulator transition is $B/U \simeq 1.15$, where B is the bandwidth (without correlation) and U is the interparticle energy between nanoparticles.

Coulomb blockade

An important feature of electrical properties of finite systems refers to scaling relations for the charging energy of nanostructures, as manifested by the Coulomb blockade and the Coulomb staircase [56]. In a double-junction nanodevice, consisting of a cluster of nanocrystals confined between two metallic electrodes, which is subjected to an external voltage V, excess charges can accumulate on the nanoparticle, giving rise to a Coulomb blockade. The addition of a single electron to the nanoparticle of radius R results in the changing energy [56] $W = W(\infty) + b/R$, where $W(\infty)$ can be identified with the chang-
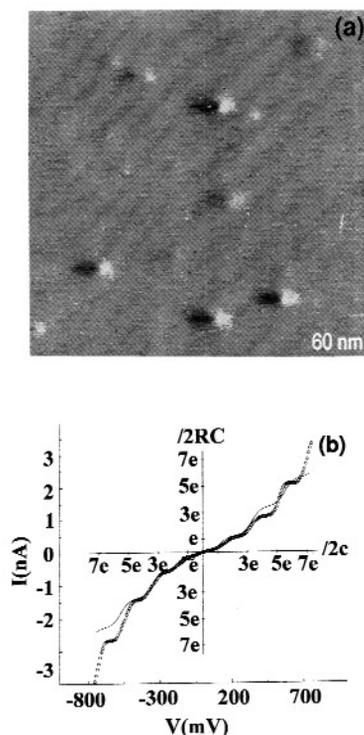
Fig. 2 Coulomb blockade for Pd nanoparticles [57]. (a) STM imaging of the nanoparticles on a graphite substrate. (b) The Coulomb staircase.
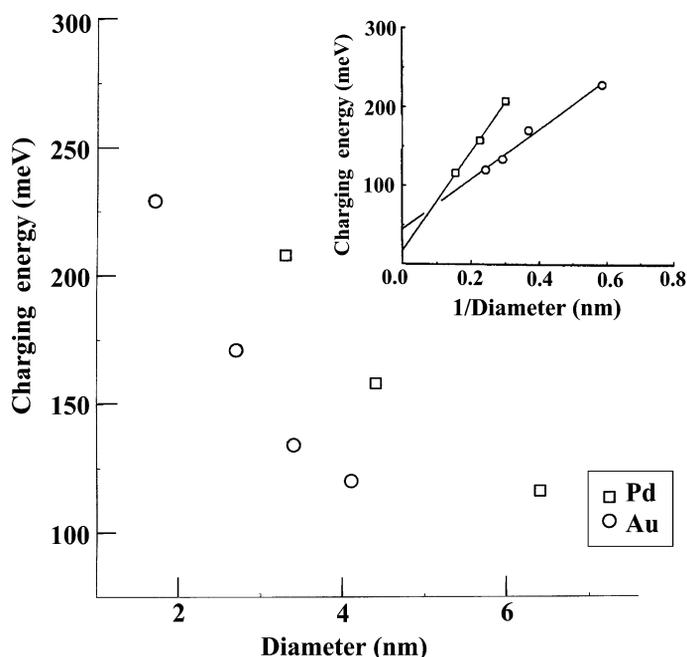
Fig. 3 Size dependence of the nonmetallic gap for Pd nanocrystals. The insert shows the dependence of the charging energy on the reciprocal nanocrystal diameter [57].

ing energy of the bulk. The minimal voltage $V_{MIN} = W/e$ required to inject an extra electron into the cluster, gives rise to the Coulomb blockade staircase, with the separation voltage steps exhibiting a size equation, i.e., $V_{MIN} = W(\infty)/e + b/eR$. The observation of the Coulomb staircase in the current voltage response is facilitated in nanocrystals [1,57] (Figs. 2 and 3). With a higher resolution, the observation of the eigenvalue staircase is facilitated, monitoring one-particle electronic excitations of the nanostructure [58]. The observation of the Coulomb staircase and the eigenvalue staircase in the electronic response of nanostructures provides a direct demonstration of the discreteness of the electronic-level structure in finite systems.

Confinement

Boundary effects on electrons or excitons in nanostructures result in the localization of these elementary excitations, provided that this interaction is repulsive. Characteristic examples are confinement of large-radius Wannier–Mott excitons (i.e., electron-hole pairs) in nanostructures [28,59–62] (Fig. 4). In this context, one encounters the interesting problem of the interplay between the attractive electron-hole interaction and the repulsive boundary repulsion. In the weak confinement limit, when the cluster size exceeds the exciton radius, the exciton energy is given by the size equation $E = E(\infty) + C/R^2$, where $E(\infty)$ is the bulk exciton energy, and $C = \pi^2 \hbar^2/2m^*$, with m^* being the exciton mass. The size effects describe confinement of an exciton in a spherical box. This scaling relation accounts well for the optical properties of clusters [28] and nanostructures [31,58–61], providing a central mechanism for the tuning of the optical response of nanostructures. For the case of a single charge carrier, boundary scattering affects the electronic-level structure. For a semiconducting nanowire of width (diameter) d, one expects that the band-gap, E_G, is given by energetics of a particle confined in a 2-dimensional box, $E_G = E_G(\infty) + B/d^2$, where $E_G(\infty)$ is the bulk gap value. Such a 2-dimensional confinement provides a control mechanism for the electrical properties of conducting nanowires [14].
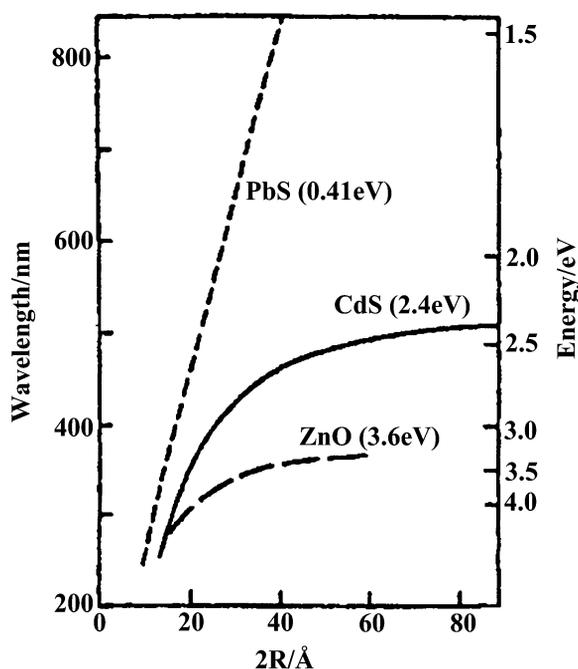
Fig. 4 Size dependence of the wavelength of the absorption threshold in semiconductors manifesting exciton confinement. [Reproduced by permission from A. Henglein, *Ber. Bunsen-Ges. Chem.* **99**, 903 (1995). Copyright VCH 1995.]

Size effects for transport in nanostructures

The ubiquity of quantum effects in finite systems reflects on unique transport properties of nanostructures. We have already considered the phenomenon of Coulomb blockade in nanoparticles. The electronic quantum size effects in nanowires are manifested when $d/\lambda_F \lesssim 1$, where λ_F is the electronic wavelength at the Fermi energy E_F. Accordingly, novel quantum effects in nanowires are expected to be exhibited when $d \lesssim 2\pi\hbar/(2mE_F)^{1/2}$, where $E_F \sim 1$ eV, i.e., when $d \lesssim 1$ nm. Under these conditions, quantized conductance is exhibited in nanowires, being given by the Landauer expression [56] $g = (2e^2/h)\sum_i T_i$ where T_i is the scattering matrix in channel i. When $T_i = 1$ for all the channels, the conductance is an integer multiple of the conductance quantum $2e^2/h = (12.9 \text{ k}\Omega)^{-1}$. This quantized conductivity (with $T_i = 1$) corresponds to ballistic transport in nanostructures. This transport quantization was experimentally demonstrated in carbon nanowires [15] (Fig. 5) and in metal nanowires [15]. In longer nanowires (>10 nm), heat dissipation effects may lead to instability.

Shape effects

The central question of the nanostructure shape analysis is: How do structural deformations affect the electronic–nuclear level structure, energetics, dynamics, and transport? The concept of spontaneous symmetry-breaking advanced by Anderson in 1984 pertains to the reduction of symmetry of the cluster or nanostructure driven by the instability thus acquired. Interesting implications to cluster and nanosystems involve spontaneous symmetry-breaking at zero and low magnetic fields in single quantum dots and quantum dot molecules in zero and low magnetic fields, which are reflected in the electronic charge density and spin densities [63]. These may involve Wigner crystallization, localization on individual electron puddles, as well as the formation of spin density waves without localization [63,64].
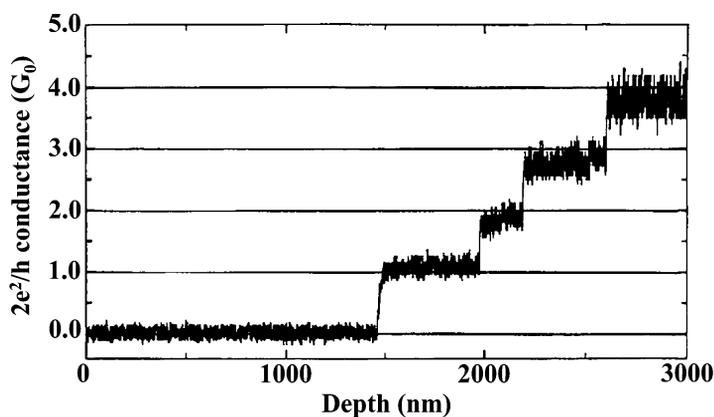
Fig. 5 Conductance of carbon nanotubes observed using the set-up in an AFM, showing the independence of the conductance of the depth into the liquid mercury in which the tip is being inserted. The second step is introduced as another nanotube touches the mercury [15].

Another class of shape effects involves nuclear collective excitations revealing shape deformation of spherical clusters. Such compressive modes are treated by the liquid drop model with the lowest excitation energy being given by [29,30] $\hbar\omega_B = \pi\hbar u/R$, where u is the velocity of sound and R the cluster radius. The size equation $\hbar\omega_B \propto n^{-1/3}$ was experimentally verified [65] by He scattering from Ar_n clusters. Coherent acoustic mode oscillations in supported silver nanoparticles ($R = 3$–20 nm) were experimentally demonstrated [66], and evidence for plasmon–collective vibration excitations was provided [66].

Another class of interesting, symmetry-breaking, dynamic–effects, involves fission of multicharged clusters [67–69]. The ubiquity of fission phenomena of charged droplets [70,71] and clusters [68,69] was described in terms of the celebrated liquid drop model [70,72], where a classically charged drop deforms through elongated shapes to form separate droplets. The fissibility parameter, advanced by Lord Rayleigh in 1882 [70], is $X = E$(Coulomb)$/2E$(surface) and characterizes the relative contribution of repulsive (Coulomb) and cohesive (surface) energies to the fission barrier. For $X < 1$, the spatially unisotropic fission limit prevails, with the formation of a small number of large nanostructures, as is the case for the Coulomb instability of nuclei, droplets, and metal clusters [67–72]. The Rayleigh limit is overcome by a marked enhancement of the Coulomb energy, which can be accomplished by multielectron ionization in intense laser fields. When $X > 1$, spatially isotropic Coulomb explosion of the cluster is exhibited [67]. The dynamics of symmetry-breaking and fragmentation of multicharged nanostructures may be of interest for structural processing of nanomaterials.

Nanoscale regime

The foregoing discussion of the novel implications of quantum size and shape effects on the energetics, level structure, electric and optical response, dynamics, and chemistry of nanostructures, addresses new physical and chemical phenomena, which are qualitatively different from those of the bulk matter and from those implied from scaling laws, which are based on "smooth" cluster size effects for large nanostructures. When one or more of the physical dimensions of the nanostructure becomes comparable to the microscopic length scale of some electronic or nuclear phenomenon, qualitatively different new effects (e.g., confinement energetics), and boundary scattering of elementary excitations are manifested, exhibiting new modes of optical or electronic response. Related to the above is the sensitivity of the properties of the nanosystem to shape, involving both static confinement of elementary excitations and

of dynamic structural distortions. Basic research on these fascinating issues provides avenues for the control of the function of nanostructures.

Nanoelectronics, nanooptoelectronics, and information nanoprocesing

One of the most important and far-reaching potential applications of nanomaterials will be in the field of nanoelectronics. While the field of molecular electronics [56] was fraught with some conceptual–practical difficulties in the context of connecting molecular devices to the "outside world", these issues were solved by nanodevice fabrication, the design of surface-nanodevice chemical contacts, and chemical engineering of molecular-nanoparticles or biomolecular-nanoparticle hybridization. This multidisciplinary research–technology area of nanoelectronics has dual goals:

(I)   The utilization of a single, individual nanostructure (e.g., cluster, nanoparticle, nanocrystal, quantum dot, nanowire, or nanotube) for the processing of optical, electrical, magnetic, chemical, or biological signals

(II)   Providing nanostructured materials, consisting of assemblies of nanostructures, for electronic, optoelectronic, chemical-catalytic, or biological-diagnostic applications

The distinction between classes (I) and (II) is always practical and sometimes also conceptual. While class (II) is aimed toward the miniaturization of electronic circuity and of catalytic and biological templates, class (I) is aimed toward the realization of single-electron nanodevices. There are already significant advances in the utilization of single nanostructures for single-electron memory devices based on Coulomb blockade [57] and on a single-electron transistor [73] (Fig. 6). Progress for the class (II) system involves scanning probe tips in arrays [1], LED and laser diodes of semiconductor nanostructures, arrays of semiconductor quantum dots, and nanowires [74]. Nanocircuits making use of carbon nanotubes were described [75]. Metallic and semiconducting properties of multiwalled nanotubes have been constructed by the stepwise burning of layers and by chirality control [76]. These approaches
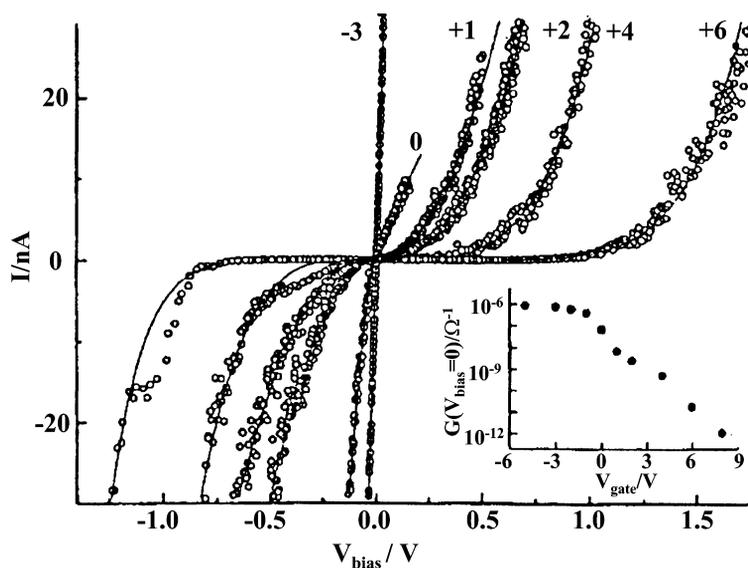
Fig. 6 Current-potential characteristics at different gate voltages of a field-effect transistor based on a single-walled nanotube. [Reproduced by permission from S. J. Tans, A. R. M. Verscheuren, C. Dekker, *Nature* **393**, 49 (1998). Copyright *Nature* 1998.]

allow for the use of nanotubes in nanocircuitry, with special potential advances in the use of Y junction nanotubes. Another significant area involves nanomaterials for optoelectronics, where functional devices, based on confinement, show potential for photonic switching and optical communication.

The miniaturization of electronic circuitry will allow for the advent of novel information storage, reading, retrieval, and programming systems. Both classes (I) and (II) of nanoelectronics show great potential for nanoscale information processing. The information paradigm in nanostructures may involve two alternative routes. First, the bottom-up approach, starting from a single nanostructure being based on nanofabrication, miniaturization, and assembly of nanostructures to produce a nanostructured computer. Resonant tunneling devices deserve special mention in this context, since they have already demonstrated success in multivalued logic and memory circuits [1]. Second, the top-down approach will utilize and apply the conceptual framework of supramolecular chemistry and self-assembly of nanostructures to produce organized suprastructures for information processes. Spintropic memory based on magnetic, semiconducting nanoparticles, provides a promising direction.

Perspectives in nanoscience and nanotechnology

The emerging nanoworld encompasses entirely new and novel means of investigating structures and systems. Species as small as single atoms and molecules will be manipulated and even exploited as atomic switches [77,78]. Computer-controlled scanning probe microscopy enables real-time, hands-on nanostructures manipulation. Nanomanipulators have been designed to operate in scanning and transmission electron microscopes as well. A nanomanipulator gives virtual telepresence on the surface, with a scale factor of a million to one. Optical tweezers provide another approach to hold and move nanometer structures, a capability specially useful in investigating dynamics of molecules and particles [79]. 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 [80]. 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 operation requiring parallel tip arrays is now being explored in several laboratories.

Novel potential developments in the realm of nanotechnology pertain to nanomaterials, molecular and biological nanomachines, biological and medical applications, and environmental protection and improvement.

Consolidated nanostructures employing both ceramic and metallic materials are being increasingly recognized as important in creating new generations of ultra high-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. Several nanostructured alloys of high strength have been discovered and are in an advanced stage for use. Besides high-strength materials, dispersions and powders, as well as large bodies of novel morphologies, are being discovered. Coatings with highly improved features resulting from the incorporation of nanoparticles are being developed.

Nanoelectrochemical systems (NEMS) are likely to augment the already established microelectromechanical systems (MEMS). A related aspect pertains to molecular motors. In wiring systems, molecular motors are responsible for DNA transcription, cellular transport and muscle contraction. New fabricated tools enable us to understand and exploit these motors as actuators in nanoelectromechanical systems. These may lead to artificial biological devices that are powered by adenosine 5′-triphosphate (ATP) [81]. Besides the naturally occurring nanomachines (e.g., molecular motor protein F1-ATPase), 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 is an aspect of great interest.

DNA chips and microarrays represent a technology with immediate 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 chip devices [82] will be useful in genomic research, drug discovery, gene expression analysis, forensics, and various types of detection and diagnostics. Electronically active DNA microarrays and electronically directed DNA self-assembly technology hold promise in various areas including photonic and electronic devices.

Since genetic medicine appears to be emerging as a part of future health care, gene and drug delivery assume importance. 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.

Semiconductor nanocrystals have been used as fluorescent biological labels [83]. It is likely that sensors based on nanotechnology will revolutionize health care, climate control, and detection of toxic substances. Integrated nanoscale sensors could monitor the condition of a living organism, the environment, or nutrient supply. It is altogether 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 not only useful for understanding transport and other aspects of those materials, but also helps 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 fairly well documented. The design of environmentally benign nanocomposites, the use of nanomaterials (e.g., nanoparticles of TiO_2) for various environmental cleansing processes and of nanoporous solids (e.g., MCM41) for sorption, are typical examples of the applications of nanotechnology for the protection and improvement of the environment. The use of nanoporous polymers for water purification [84] and purification of fluids by photocatalysis using nanostructural TiO_2 [85] are two other examples.

CONCLUDING REMARKS

The preceding overview serves to provide a glimpse of the current status and future prospects of nanostructured materials. Clearly, there is a great vitality in this area of immense opportunities. While it is truly an interdisciplinary area covering physics, chemistry, biology, materials, and engineering, chemists have a major role to play. Synthesis, self-assembly, manipulation, simulation, and theory require dedicated efforts of chemists, and there is every reason to believe that nanoscience will become an integral part of chemical science. Interaction among scientists with different backgrounds will undoubtedly create new materials and new science with novel technological possibilities.

Nanoscience and technology are likely to benefit various industrial sectors, including chemical and electronic industries, as well as manufacturing. Health care and medical practice will undoubtedly benefit from nanoscience, as will environmental protection. One of the difficult problems facing the design of nanostructures-based systems is in understanding how they are to be interconnected and addressed. There is much to be learnt about the preferred architectures of systems and the design and fabrication of devices. Developing techniques for fabricating a large number of nanostructures also requires substantial effort. The eventual success of nanoscience will depend on the development of new manufacturing technologies. There is every reason to believe that there will be much progress in the coming decade.

There is considerable effort in nanotechnology in a large number of academic and industrial laboratories all over the world, and it is becoming imperative that we establish dedicated centers with the required infrastructure and experimental facilities for nanomaterials research. The subject has caused excitement not only in the advanced countries but also in the developing nations, and international cooperation would certainly be most beneficial.

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