

Chapter 1

The Nanoscience Paradigm: “Size Matters!”

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Abstract The essential feature of nanomaterials is that their physical and chemical properties are size dependent, making it possible to engineer the material properties not only by defining its chemical composition, but also by tailoring the size and shape of the nanostructures, and the way in which individual building blocks are assembled. This chapter addresses the origin of the size dependence of the properties of nanomaterials, which can be traced to two fundamental nanoscale effects: (a) the increase in the surface/volume ratio with decreasing size, and (b) spatial confinement effects. Furthermore, the definition and classification of nanomaterials is introduced, and the techniques used to fabricate and study them are briefly discussed, with emphasis on nanoparticles of inorganic materials.

1.1 What Is Different About the Nanoscale?

Most of the excitement about Nanoscience and Nanotechnology originates from the potential of nanomaterials to lead to a dazzling multitude of applications (e.g., solar energy conversion, optoelectronics, nanophotonics, spintronics, smart coatings, smart catalysts, biomedical applications, etc.). The essential feature of nanomaterials is that their physical and chemical properties are size dependent, making it possible to engineer the material properties not only by defining its chemical composition, but also by tailoring the size and shape of the nanostructures and the way in which individual building blocks (atoms or smaller nanoparticles) are assembled [1–3].

This may seem strange, as in our daily lives we experience the properties of materials as being completely independent from the dimensions of the objects they make. For example, the colour of a sheet of paper does not change if one cuts it into increasingly smaller pieces. However, when the dimensions of materials reach the nanoscale regime (≤ 100 nm), their intrinsic properties become size-dependent and

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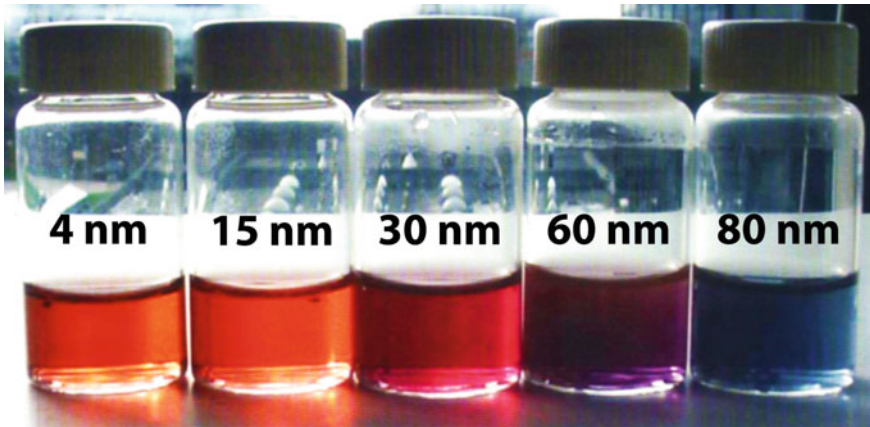


Fig. 1.1 Colloidal suspensions of gold nanoparticles in water. The nanoparticle diameters are indicated on the flasks (*courtesy* F.H. Reincke, Utrecht University)

may be strikingly different from those of their macroscopic (bulk) counterparts. This is clearly illustrated in Figs. 1.1 and 1.2 for two different materials: Gold (a noble metal) and CdSe (a semiconductor with a band-gap of 1.74 eV).

Let us consider the familiar metal Gold in more detail. If we would browse an encyclopaedia (or the internet) for the properties of Gold, we would probably find: “soft and ductile metal with a bright yellow color and luster, melting point 1,337 K, chemically inert...”. Strictly speaking, this definition is correct only in first approximation, since those are the properties of bulk Gold. As Fig. 1.1 eloquently demonstrates, Gold nanoparticles (NPs) are actually soluble (or, to be precise, easily form colloidal dispersions in solvents) and, when dispersed into transparent media (like water or glass), give rise to intense colours (orange, red, violet, blue, depending on the NP size). Moreover, gold NPs are chemically active, being very efficient catalysts [4], and melt at progressively lower temperatures as their size decreases below ~ 50 nm, reaching values as low as 600 K for 3 nm diameter NPs [5].

The origin of the size dependence of the properties of nanomaterials can be traced to two fundamental nanoscale effects [1–3, 5]: (a) the fraction of surface atoms (i.e., the surface/volume ratio) increases with decreasing size and becomes significantly large in NPs; and (b) the limited dimensions of the NP lead to spatial confinement effects that may affect a variety of different properties. These finite size effects will be discussed in detail in the following two subsections.

1.1.1 Finite Size Effects I: Spatial Confinement

Spatial confinement effects are a consequence of the quantum mechanical nature of matter, which is not immediately obvious for macroscopic objects since they consist of a very large number of atoms (for example, a Gold particle as small as 1 μm

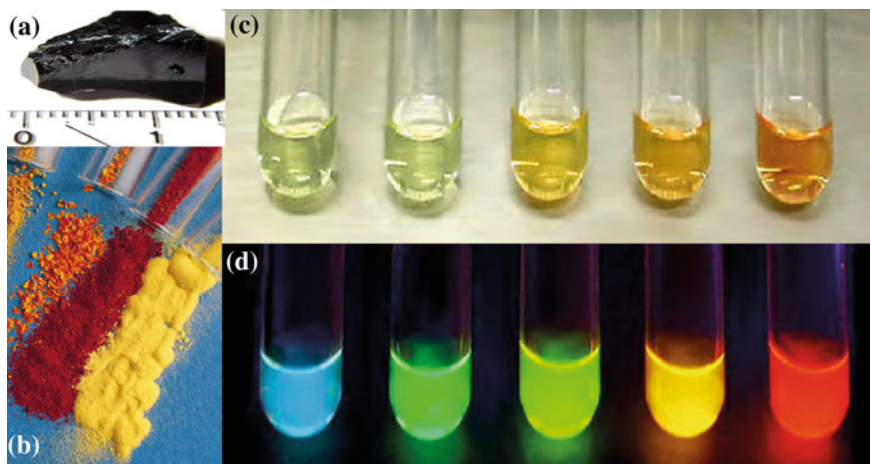


Fig. 1.2 **a** Fragment of a bulk CdSe single crystal (scale bar: 1 cm). **b** CdSe nanocrystals with diameters ranging from 2 nm (*yellow powder*) to 5 nm (*red powder*). Reprinted with permission from Ref. [31]. Copyright (1992) Scientific American, Inc. **c** Colloidal suspensions of CdSe nanocrystals with diameters ranging from 2 nm (*extreme left*) to 5 nm (*extreme right*) under ambient light illumination. Reprinted with permission from Ref. [32]. Copyright (2005) The Chemical Society of Japan. **d** The same suspensions shown in **c**, but under UV excitation. Reprinted with permission from Ref. [32]. Copyright (2005) The Chemical Society of Japan

already contains $\sim 10^{11}$ atoms). However, quantum effects become increasingly important as the size, and consequently the number of atoms, decreases below a certain critical limit. Interestingly, this critical length scale is not the same for different physical properties and different materials, as it depends both on the property under consideration and the exact nature of the chemical bonds in the material. The impact of spatial confinement is thus not the same for different materials and/or different properties. For example, confinement effects on the magnetic properties of NPs will only occur if the NP dimensions are comparable to or smaller than the critical magnetic single domain size of that particular material (20–100 nm, depending on the material) [6, 7].

The dramatic impact of spatial confinement on the optical properties of NPs is quite evident in Figs. 1.1 and 1.2 above. In the case of NPs of semiconductors, such as CdSe, the relevant length scale is the exciton Bohr radius (a_0), a dimension describing the spatial extension of excitons (i.e., electron-hole pairs) in solids, which ranges from ~ 2 to ~ 50 nm depending on the material [2]. As the size of the semiconductor NP approaches a_0 , confinement begins to affect the exciton wave function, inducing changes in the electronic states that are manifested in an increase of the band-gap energy with decreasing NP size. As a result, the optoelectronic properties of semiconductor NPs become strongly size- and shape-dependent, making it possible to tune the photoluminescence (PL) of semiconductor NPs through a wide spectral window by choosing the composition, size and shape of the NP. This effect is known as **quantum confinement**, and will be discussed in detail in Chap. 2.

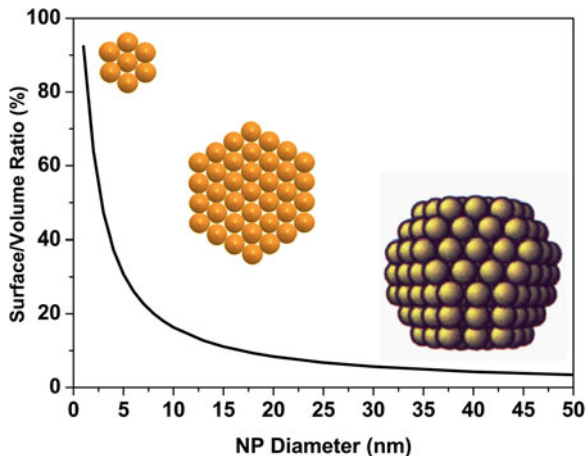


Fig. 1.3 Size dependence of the surface to volume ratio for spherical gold nanoparticles. For clarity, the evolution of the surface/volume ratio for diameters larger than 50 nm is not shown, since it decreases very slowly, reaching 2 % for 100 nm NPs and 0.8 % for 200 nm NPs. The calculations are based on the assumption that the nanoparticles are perfect spheres, regardless of the size. However, one should keep in mind that real nanoparticles are faceted and therefore can only in first approximation be described as spherical. A model for a 2 nm diameter gold NP (surface/volume ratio = 60 %) is shown at the extreme right of the figure. The cartoons at the centre and upper left show two-dimensional representations of NPs with surface/volume ratios equal to 50 and 86 %, respectively

In contrast, optical excitations in metals do not create excitons, but instead induce collective oscillations of the free electrons, which are known as plasmon resonances. Therefore, in the case of a metal the relevant length scale to observe spatial confinement effects on optical properties is the free electron mean free path, which in gold is ~ 50 nm [5]. Size effects on the plasmon resonance of metals will be addressed in Chap. 3.

1.1.2 Finite Size Effects II: Scaling

As the NP size decreases, the number of atoms is gradually reduced (e.g., 1×10^7 , 1×10^4 , and 100, for NP diameters of 100, 10, and 2 nm, respectively), while the fraction of atoms located at the surface increases (Fig. 1.3) [1–3]. This is essentially a scaling effect, since the surface to volume ratio of any object increases as its size decreases. For example, the surface of a sphere scales with the square of its radius r , while its volume scales with r^3 . Since the total number of atoms in the NP scales linearly with the volume, the fraction of atoms located at the surface of a spherical NP scales with the inverse of its radius.

The increase in the surface to volume ratio has a dramatic impact on several properties, since surface atoms are significantly different from those in the interior of the particle, as they have fewer neighbours and thus possess unsatisfied chemical bonds (i.e., dangling bonds). As a result, surface atoms have a higher free energy, higher reactivity, and increased mobility. Consequently, as the NP size gradually decreases, the contribution of the surface atoms to the total free energy and the properties of the NP progressively increases, causing a number of properties to change: melting and evaporation temperature decrease, and the reactivity, elasticity and plasticity increase. Moreover, this also increases the ability of the NPs to form stable colloidal dispersions, either by charge or steric stabilization. This has important consequences, one of them being that the NP becomes easily dispersible in solvents (Figs. 1.1 and 1.2 above), making fabrication and processing in solution possible.

The larger surface contribution may also lead to changes in interatomic spacings (either contraction or expansion) and bond angles, which may eventually stabilize crystal structures that are metastable for the bulk counterparts, or even lead to global structural reconstruction. It should also be noted that the dangling orbitals at the surface of a semiconductor NP give rise to energy levels within the band-gap [1]. As will be discussed in Chap. 2, this is detrimental to the photoluminescence quantum yield of the NP, because it favours non-radiative recombination of the exciton. For these reasons, it is essential to eliminate dangling bonds from the surface of semiconductor NPs, a process known as **surface passivation**. This can be achieved either by overgrowing a shell of a wider band gap semiconductor or by coating the surface with suitable organic ligands (see Chap. 6 for details).

1.2 Nanomaterials: Definition and Classification

1.2.1 *What Are Nanomaterials?*

The answer to this seemingly trivial question has been elusive for years, and it is only recently that scientists and other stakeholders (policy makers, funding agencies, etc.) reached a consensus on a general definition. The US National Nanotechnology Initiative (NNI) proposed in 2004 the following definition of Nanomaterials: “materials with dimensions of roughly 1–100 nm, where unique phenomena enable novel applications” [8]. A more specific definition was drafted by the European Commission (EC) in 2011: “Nanomaterial” means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm”; and/or “has internal or surface structures in one or more dimensions in the size range 1–100 nm”; and/or “has a specific surface area by volume greater than $60 \text{ m}^2 \text{ cm}^{-3}$, excluding materials consisting of particles with a size smaller than

1 nm” [9]. The EC definition may sound too elaborated and finicky, while the one proposed by the US-NNI is somewhat vague, but they both highlight an essential aspect of nanomaterials: “Size does matter, but only if it changes an intrinsic material property”. In other words, nanoscale size is a necessary but not sufficient condition. Basically, as clearly demonstrated in Sect. 1.1. above, the critical length scale defining the boundary between the “mesoscale” (i.e., the size range between macro- and nanoscale) and the “nanoscale” domains is not the same for different materials and/or different properties. Consequently, a meaningful and precise definition of “Nanomaterials” must take both aspects into account: “Nanomaterials are materials having at least one characteristic length scale in the range 1–100 nm, and with at least one property being considerably different from that of the bulk counterpart as a result of the nanoscale dimensions”.

1.2.2 Types of Nanomaterials

The definition above (Sect. 1.2.1) implies that Nanomaterials encompass a wide variety of different compounds and comprise many different categories. For instance, proteins, enzymes and DNA also fulfil the requirements mentioned above, and are therefore often referred to as **bionanomaterials**. This chapter (and the remainder of this book) deals only with inorganic nanomaterials, including carbon nanomaterials (viz., carbon nanotubes and nanostructured carbon materials, Chap. 4). Nanomaterials can also be larger objects that contain nanoscale structures, either internally or on their surfaces. These materials are typically referred to as **nanostructured materials**. An interesting example of nanostructured materials is provided by **nanoporous materials** [10]. In this case, the dimensions of the material body itself are much larger than 100 nm, but its pores are on the nanoscale. Nanoporous materials are addressed in detail in Chap. 4.

The concept of **dimensionality** is very useful in the classification of nanomaterials: **zero-dimensional (0-D)** nanomaterials are smaller than 100 nm in all directions (e.g., **nanoparticles**, **nanopores**), while **one-dimensional (1-D)** nanomaterials are smaller than 100 nm in 2 directions only (e.g., **nanorods**, **nanowires**, **nanotubes**), and **two-dimensional (2-D)** nanomaterials are smaller than 100 nm only in the thickness direction (e.g., **thin films**, **nanoplates**). However, one should keep in mind that, as discussed above (Sect. 1.1), the critical length scale is not necessarily 100 nm, as it depends on the material and property under consideration. For example, a CdSe nanoparticle of 50 nm in diameter will nevertheless be bulk-like (i.e., three-dimensional) from the point of view of the exciton, since the exciton Bohr radius of CdSe is only 3.5 nm (see Chap. 2 for details).

This book deals primarily with **nanoparticles**. Nanoparticles may be free-standing (both in colloidal suspension or as dry powders), supported on substrates, or embedded within a macroscopic matrix of a different material. **Colloidal nanoparticles** are addressed in detail in Chap. 6. It should be noted that not all colloidal particles are nanomaterials, since colloids span the size range from 1 nm

to 1 μm [11]. Therefore, colloidal nanoparticles are often referred to as “**nanocolloids**”. **Supported nanoparticles** are discussed in Chap. 5. Optical applications often require that the nanoparticle be embedded into a transparent matrix (e.g., polymer or glass), forming a **nanocomposite** [12]. Colloidal nanoparticles can also be used as building blocks for **nanoparticle solids or superlattices** [13–15], which are very promising for applications requiring thin-films [16].

1.3 The Nanoscale Tool Box

1.3.1 Techniques to Make Nanoparticles

Nanomaterials can be made using a wide variety of methods, which can be classified in two broad categories [17]:

- (a) **Top-down processes**, in which material is removed from a larger scale object to create nanostructures (e.g., lithography, either using electron beams, ion beams or X-rays). Lithography is heavily used in the semiconductor processing industry to fabricate integrated circuits and optoelectronic components. Alternatively, the material can be broken down into subsequently smaller particles, until the nanoscale is reached (high-energy ball milling). This process is widely used to fabricate nanomaterials in the form of powders.
- (b) **Bottom-up processes**, in which building blocks (atoms, molecules) are assembled together into progressively larger structures until the nanoscale is reached. Bottom-up processes can be carried out in numerous ways, yielding a wealth of different nanomaterials [17, 18]. A brief overview of some of the more common methods is presented below. For details the reader will be referred to the literature or subsequent chapters.

1.3.1.1 Bottom-up Approaches to Nanomaterials

Vapour phase deposition methods can be classified as physical vapor deposition (PVD) or chemical vapor deposition (CVD), and are widely used to fabricate thin-films, multilayers, nanotubes, or nanoparticles (either freestanding as powders or embedded into films of another material) [17]. CVD involves the reaction or thermal decomposition of gas phase species (precursors) at high temperatures (500–1,000 °C) followed by deposition on a substrate. A very important variation of this technique is the so-called Molecular Beam Epitaxy (MBE), in which the precursors are deposited directly on the substrate, allowing epitaxial, single atomic layers to be grown. Atomic layers can be sequentially grown on top of each other yielding thin-films with thicknesses that can be controlled with atomic precision. Depending on the nature of the precursor, this technique can also be termed

Chemical Beam Epitaxy (CBE), Metallorganic MBE (MOMBE) or Metallorganic CVD (MOCVD). MOCVD is used extensively to fabricate thin-films of compound semiconductors (e.g., AlGaAs). The chemical composition of subsequent layers can be changed, enabling the fabrication of complex multicomponent nanostructured thin-films, in which a smaller band-gap semiconductor is sandwiched between wider band-gap semiconductors, yielding a 2D-confined system (i.e., a quantum well) (see Chap. 2 for details), that can be readily integrated into devices (e.g., a quantum well laser). The technique can also be used to grow 0D-confined semiconductor nanoparticles (i.e., quantum dots, see Chap. 2 for details) embedded in a matrix of a wider band gap semiconductor, by using conditions that promote the Stranski-Krastanow growth mode [19].

The **Vapor-Liquid-Solid (VLS) method** is widely used to grow semiconductor (e.g., Si, GaAs, etc.) nanowires on substrates [20]. In this process, metal (e.g., Au) nanoparticles are deposited on a substrate and heated above the eutectic temperature for the metal-semiconductor system of choice, in the presence of a vapor-phase source of the semiconductor, resulting in a liquid droplet of the metal-semiconductor alloy. The continued feeding of the semiconductor into the liquid droplet supersaturates the eutectic, leading to the nucleation and growth of the solid semiconductor at the solid-liquid interface. This results in the growth of a nanowire with the alloy droplet on its top.

Liquid-phase methods make use of chemical precipitation reactions in solution [17, 18], and can be divided in:

- (a) **Colloidal Methods.** These methods rely on chemical reactions that lead to the nucleation and growth of nanoparticles (NPs) within a solvent, forming a colloidal sol. This process will be discussed in detail in Chap. 6. Colloidal methods are relatively inexpensive, facile and scalable. They are also highly versatile, and can be used to make nanoparticles of a plethora of different compositions: single compounds (metals, e.g. Au, semiconductors, e.g. CdSe, or insulators, e.g. SiO₂) [1, 5], alloys (e.g., FePt, Cd_{1-x}Zn_xS) [1], doped materials (e.g., ZnSe:Mn, NaYF₄:Yb,Er) [21–24], or combinations of two (or more) different materials joined by one or more interfaces in the same nanoparticle (i.e., heteronanocrystals, e.g., a CdSe core surrounded by a ZnS shell) [1] (see Chap. 6 for details).

It should be noted that the size and shape control offered by colloidal techniques are unmatched by epitaxial techniques (such as MBE and MOCVD), which typically yield nanostructures in the weak quantum confinement regime, owing to their relatively large lateral dimensions (> 10 nm). Moreover, colloidal NPs can easily be subjected to post-synthesis procedures, such as size-selection and surface functionalization (see Chap. 6 for details). They can also be solution-processed into **nanocomposites** with polymers [12], either by dissolving the NPs and polymers in a common solvent and subsequently drying out the mixture (ex situ method), or by carrying out the polymerization reaction in the presence of the NPs (in situ method). These nanocomposites are promising materials for devices that require optically active waveguides, such

as luminescent solar concentrators [25, 26], or optical switches [27]. Another attractive feature of colloidal NPs is that they can be used as building blocks for NP thin-films, either by directly depositing the colloidal NPs onto a substrate and evaporating the solvent, or by allowing the NPs to self-assemble into long-range ordered **superlattices** at air-liquid interfaces and subsequently transferring the superstructure to a suitable substrate [13–15, 28]. These superstructures are also referred to as NP arrays, NP solids, artificial solids or metamaterials [13–15]. Under certain conditions the NPs may also self-assemble into ordered three-dimensional superstructures known as supercrystals. NP thin-films hold immense promise for a variety of optoelectronic devices, such as light emitting devices, solar cells, photodiodes, photoconductors and field-effect transistors [16].

- (b) **Sol-gel methods** [17, 18]. In this case the metal precursors undergo hydrolysis and condensation reactions, forming colloidal sols that subsequently aggregate into a wet porous network (gel). Upon aging the gel undergoes a process of densification (syneresis) through which the pores contract and expel the solvent. The gels can then be dried yielding a nanoporous structure (xerogel or aerogel). Alternatively the dried gel can be thermally treated to yield a glass monolith. Sol-gel methods are also widely used to fabricate nanopowders, thin (50–500 nm) films, fibers, and also nanocomposites, if NPs are dispersed in the reaction medium prior to the onset of the hydrolysis reaction.
- (c) **Templated growth**. Liquid-phase growth can also be carried out inside templating or confining structures, which yield supported NPs. These methods will be discussed in detail in Chap. 5.

1.3.2 Techniques to Study Nanoparticles

The multi- and cross-disciplinary character of Nanoscience is also reflected in the multitude of techniques that are required to unravel and understand the properties of nanomaterials [1]. Given the extent of the subject, we will provide below only a brief overview of the essential techniques to study nanoparticles (NPs). For a more comprehensive treatment the interested reader will be referred to the literature or subsequent chapters.

Size, shape and crystal structure. Transmission Electron Microscopy (TEM) and High-Resolution TEM (HRTEM) are indispensable tools for the characterization of the size and shape of NPs. HRTEM may also yield information about the crystal structure and chemical composition of single NPs when associated to electron diffraction analysis and energy-dispersive X-ray spectroscopy (EDS), respectively. Electron microscopy techniques are addressed in detail in Chap. 7. X-Ray diffraction (XRD) can be used to determine the crystal structure of nanomaterials and may also yield information about the NP size (finite size effects lead to peak broadening in the XRD pattern).

Surface Characterization Techniques. Despite the large surface/volume ratio of nanoparticles, the NP surface has been scarcely investigated. Techniques commonly used for the surface characterization of bulk materials, such as X-Ray photoelectron spectroscopy (XPS) and Rutherford back-scattering spectroscopy (RBS), have penetration depths comparable to the typical dimensions of NPs and therefore yield information about the whole NP [1]. These techniques are thus useful to accurately determine the elemental composition of NPs, but cannot distinguish between surface and interior atoms. The degree of interior strain and disorder of NPs can be directly observed by combined small-angle X-Ray scattering (SAXS) and high-energy wide-angle X-ray scattering (WAXS) measurements, and also by extended X-Ray absorption fine structure (EXAFS) [1]. Solution Nuclear Magnetic Resonance (NMR) spectroscopy has been used to investigate in situ the composition of the surfactant layer of colloidal NPs and is discussed in detail in Chap. 10.

Optical spectroscopy. To unravel the optical properties and electronic structure of NPs a combination of spectroscopic techniques is needed [29, 30]. Absorption, photoluminescence (PL), and PL excitation (PLE) spectroscopy provide information about the energy level structure, and may also be used to identify radiative recombination at dopants or defects (Chap. 2). Time-resolved (TR) PL spectroscopy is well-established as a quantitative tool for the analysis of photoexcitation dynamics in colloidal NPs, yielding information about both radiative and non-radiative exciton recombination channels. TR spectroscopy is also essential to investigate energy transfer processes within or between NPs (Chap. 2). To probe the dynamics of fast processes, such as intraband relaxation, multiexciton generation and decay, and charge injection, a combination of ultrafast TR techniques must be used (viz., transient absorption, THz time-domain spectroscopy). These techniques provide complementary information regarding the fast relaxation of electrons and holes. The insights provided by optical spectroscopy on the photophysical properties of semiconductor and metals NPs are discussed in detail in Chaps. 2 and 3, respectively.

Scanning Tunneling Spectroscopy (STS). STS is a powerful technique to unravel the electronic energy levels of individual NPs and has been applied to both metallic and semiconductor NPs (see Chap. 8 for details).

Magnetic resonance spectroscopic techniques. NMR spectroscopy was already mentioned above, in the context of surface characterization techniques. Electron paramagnetic resonance (EPR) spectroscopy has been mostly applied to characterize paramagnetic ions (e.g., Mn^{2+}) in NPs, as it allows dopants at surface to be distinguished from those in the interior of the NP [1]. The technique can also be applied after photoexcitation of the sample, allowing the interaction between the exciton and paramagnetic impurities to be observed, as well as photoexcited carriers bound to impurities (i.e., donor and acceptor centres). These techniques will be addressed in Chap. 9.

1.4 Exercises

1. Why are nanomaterials different from macroscopic materials?
2. What is the dimensionality of a:
 - (a) spherical 200 nm Pd particle?
 - (b) spherical 2 nm Pd particle?
 - (c) 400 nm long Pd wire with a 4 nm diameter?
 - (d) 2 nm thick film of Pd on a flat substrate?
3. Assume you are heating 2 g of each of the materials mentioned in exercise 2. Which one would be the first to melt? Justify your answer.
4. (a) Explain the difference between the “top-down” and “bottom-up” methods of fabrication of nanomaterials. Provide one example of each.
5. The surface/volume ratio of a nanoparticle increases as its size decreases. This has both beneficial and deleterious consequences. Give one example of each, and comment on possible preparation strategies to minimize the negative consequences and take advantage of the beneficial ones.

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