Preface

Understanding the size and shape dependence of physical properties in nanoscale particles is a fundamental step towards the design, the fabrication, and the assembly of materials and devices with predictable behavior. In recent years, there has been a remarkable advancement in the ability to fabricate shape-controlled nanoparticles, for example rods, wires, and nanoparticles with branched shapes, especially via synthetic approaches in solution. Shape-controlled inorganic nanoparticles are among the most promising candidates as building blocks in nanoscale materials and devices, both because their physical properties are modified considerably compared to those of spherical nanoparticles and because their intrinsic geometry opens many new opportunities for their assembly into organized super-structures. In this book, we have decided to review the physical properties of elongated inorganic nanoparticles, with particular emphasis on the transition in these properties when the shape of the nanoparticles evolves from a sphere to a rod, but we will consider in many cases also nanowires. From the point of view of specific properties and materials, we have decided to cover the optical properties of semiconductors and noble metals, the electrical properties of semiconductors, the magnetic properties of various metals and metal oxides, the catalytic properties of various classes of materials, and the mechanical properties of metals and metal alloys.

Chapter 1 will give an introduction into some basic quantum physics concepts, specifically tailored to the following Chaps. 2 and 3 that are devoted to the optical and electrical properties of semiconductor nanorods. Semiconductor nanocrystals are among the most studied materials in nanoscience nowadays, due to the large number of potential applications employing these materials, for example, in optical devices (lasers [1–3], light emitting diodes [4, 5], photo-detectors [6], solar cells [7–9]), or biological labeling [10, 11], to cite a few. Elongated, rod-shaped semiconductor nanocrystals possess interesting physical properties which depend on their size, aspect ratio, and chemical composition, and these nanoparticles have been proposed as active materials in light emitting devices [12], photocatalysis [13], optically induced light modulation [14], photovoltaics, [7–9, 15] wave-function engineering [16–18], and optical memory elements exploiting the exciton storage process [19]. More in general, these nanoparticles have been considered as replacement for spherical nanocrystals (the so-called "quantum dots") in all those studies in which the elongated shape could in principle add new or improved properties.

Chapter 4 will deal with optical properties of elongated metal nanocrystals. Metallic nanocrystals have been proposed in a wide range of applications in various fields, among them sensing, biosensing, photodynamic therapy, photovoltaics, optics (light emitting diodes, photo detectors, lasers, imaging techniques beyond the diffraction limit), nano-optics, and nano-electronics (for example plasmonic waveguides) [20–32]. Metal nanostructures can interact strongly with light in the visible and near infrared region of the spectrum, due to the presence of free electrons, which can be promoted both to empty energy levels in the same band or to levels of an empty overlapping band. An incident electromagnetic field can elicit collective oscillations of these free electrons [20–23], which cause a displacement of the electrons from the nuclei, leading to the formation of various possible distributions in the surface charges. This creates Coulomb interactions between positive and negative charges, which induce restoring oscillating forces acting on free electrons. Each type of surface charge distribution is characterized by a collective oscillation mode, also termed as localized surface plasmon resonance. Various factors influence the possible types of SPRs in nanostructures and the frequencies at which they are observed and the shape of metal nanoparticles is certainly one of them. As an example, in rod-shaped nanoparticles the plasmon mode is split into two modes, a longitudinal one and a transverse one. There are many other physical effects connected with an elongated shape which differ from the spherical case, and these will be covered in detail in Chap. 4.

In Chap. 5 we will review the magnetic properties of elongated nanoparticles. Many of the applications of magnetic nanoparticles are in life sciences and biomedicine [33–35]. Superparamagnetism is the term used for describing the absence of coercivity and remanent magnetization in particles that still maintain a considerable amount of polarizable spins under the effect of an external magnetic field [36, 37]. These magnetic nanocrystals, also known as superparamagnets, combine their reduced sizes with their magnetic field responsive character even if no residual magnetization is observed in the absence of an external magnetic field. For this reason they have been proposed as vectors for both in vitro and in vivo transport of different drugs or biomolecules attached to their surfaces, thereby providing selective access to cellular or molecular levels which are inaccessible to conventional therapeutic approaches. In the same way, they can also be used in biodetection and bioseparation techniques since once the target molecule has been attached to the nanocrystals, the application of an external magnetic field will allow their recovery [38, 39]. Iron oxide is clearly the most suitable material for such purposes due to its high chemical stability, biocompatibility, and superparamagnetic properties and iron oxide nanoparticles are being already used in several diagnostic and therapeutic techniques [40].

The achievement of higher coercivity values in particles with reduced size for information storage devices, or faster magnetic responses for smaller biomedical vectors, could be possible if one considers not only the finite size effects of spherical nanocrystals but also the additional phenomena arising from the shape anisotropy of particles such as nanorods. Nanorods or other one-dimensional nanosystems could also be capable of widening the temperature range of applications of a certain magnetic material compared to its bulk form (as will be shown later). The uniaxial shape anisotropy of metallic and oxide nano-objects will probably become a key factor for the development of improved devices. This chapter will also present an overview of various classes of magnetic materials that have been synthesized in nanorod shapes.

Chapter 6 will deal with the catalytic properties of elongated nanoparticles. Today, there is an increasing demand for catalytic materials, in terms of catalytic efficiency, cost of production, specificity, durability, and environmental sustainability [41–44]. This demand is driving research towards the exploitation of new nanoscale catalyst particles, in which the individual components have specific size, shape, exposure of specific reactive surfaces, and suitable combination of materials [45, 46]. Micro- and nanoparticles of various materials have been used as catalysts for many years [47–50], and experimental evidence has been collected so far demonstrating that the catalytic activity of particles is strongly related to their size, and in particular that nanosized particles exhibit increased catalytic activity with respect to larger particles, due to their higher surface to volume ratio [51, 52]. With recent advances in the synthesis of inorganic nanoparticles with controlled size and morphology [53–56], interest has grown towards the understanding of how the catalytic performance of these materials is dependent on shape. In terms of catalytic properties, there are several reasons why an elongated morphology is often preferable over a spherical morphology, and these will be described in Chap. 6, along with several case studies of nanorod-shaped catalysts.

Chapter 7 deals mainly with the mechanical properties of elongated nanoparticles. The miniaturization of micro electromechanical devices and the fabrication of thin films in the electronic industry have started to raise questions already decades ago about the mechanical behavior of confined systems. Early experiments on tensile testing of metal whiskers with micrometer transverse sides have evidenced strengths much higher than the bulk value [57], and recently pure metals and alloys with at least one dimension in the micro- and nanoscale range have been investigated, thanks to advances in the fabrication of new generations of samples suitable for mechanical testing (for example micro pillars prepared by focused ion beam) and in various techniques for studying their stress and deformation properties. Those studies have revealed a marked deviation in the mechanical properties of samples from bulk-like behavior already when their size is of the order of a few micrometers, which is comparable to the length scale of many plasticity mechanisms based on dislocation nucleation and propagation. The increased strength of single nanocrystals could be useful for applications of these materials as active probes in nano-indentation, scanning probe microscopy, and field emission [58–60], to cite a few. Chapter 7 ends with a paragraph on melting studies on nanorods.

Finally, we conclude this book with some remarks and an outlook on the future directions in this field.

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