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# Chapter 1

## Introduction to nanoparticles and nanotechnology

Nanoparticles (NPs) or (zero-dimensional materials) hold a special place in nanoscience and nanotechnology, not only because of their particular properties resulting from their reduced dimensions, but also because they are promising building blocks for more complex nanostructures in nanotechnology. This chapter gives an overview on NPs and their presence in our daily lives. It provides examples of the use of NPs in nanotechnology to obtain different end-products in different economic activity sectors. In addition, a classification of NPs based on their dimension, morphology and chemical composition is presented. NP uniformity and agglomerations, with a special focus on superparamagnetic and magnetoplasmonic NPs and their nanocomposites are discussed.

### 1.1 Overview of nanoparticles and nanotechnologies

'Nano' is a prefix used to describe 'one billionth', or  $10^{-9}$ , of something. The concept of nanotechnology was introduced by physics Nobel laureate Richard P Feynman in his famous lecture entitled 'There's plenty of room at the bottom' at the December 1959 meeting of the American Physical Society [1]. Since then, there have been many revolutionary developments in physics, chemistry and biology that have demonstrated Feynman's ideas of manipulating matter at the atomic scale. In 1974, Norio Taniguchi (a professor at the Tokyo University of Science) invented the term 'nanotechnology' to describe extra-high precision and ultra-fine dimensions. He introduced the 'top-down approach' by predicting improvements and miniaturization in integrated circuits, optoelectronic devices, mechanical devices and computer memory devices. Approximately ten years later, K Eric Drexler introduced the 'bottom-up approach' when he discussed the creation of larger objects from their atomic and molecular components as the future of nanotechnology [2].

Nanotechnologies are now widely considered to have the potential to bring benefits in areas as diverse as drug development, water decontamination, information and communication technologies, and the production of stronger and lighter materials. Nanotechnologies involve the creation and manipulation of materials at the nanometre scale, either by scaling up from single groups of atoms or by refining or reducing bulk materials [3].

While the development of nanotechnologies is a modern multidisciplinary science involving the fields of physics, chemistry, biology and engineering, the production of NPs, both in nature and by humans, dates from the pre-Christian era. For example, the Romans introduced metals with nanometric dimensions in glass-making; the famous Lycurgus cup (currently exhibited at the British Museum), which displays a different colour depending on whether it is illuminated externally (green) or internally (red), contains NPs of silver and gold [4]. In 1857, Faraday reported the synthesis of colloidal gold (and other metals such as Cu, Zn, Fe and Sn) and its interaction with light [5]. For an overview and chronological table of nanotechnologies, see [6].

Another example of interest is the case of magnetic NPs. Krishnan [7], illustrated the role that magnetic materials play in biology and medicine. In the field of magnetic NPs, a noteworthy pioneering work was published by Blakemore in 1975 [8], where biochemically precipitated magnetite ( $\text{Fe}_3\text{O}_4$ ) was found in the tissues of various organisms including bacteria, algae, insects, birds and mammals. Many of these organisms use biogenic magnetite to sense the Earth's magnetic field for orientation and navigation. For more details on the development of magnetic NP synthesis and its presence in biomedicine and biotechnology see [7].

Throughout the last century, the field of colloid science has developed enormously and has been used to produce many materials, including metals, oxides and organic products [9, 10]. One of the first and most easily prepared magnetic colloidal systems was developed by Stephen Papell of the National Aeronautics and Space Administration in the early 1960s [11]. Papell's colloid consisted of finely divided particles of magnetite suspended in paraffin. To prevent particle-particle agglomeration or sedimentation, Papell added oleic acid as a dispersing agent. Subsequently, similar magnetic suspensions have also been synthesized with different nanometre sized particles of pure elements, such as iron, nickel and cobalt, in a wide range of carrier liquids [12, 13].

Ordinary materials, when reduced to the nanoscale, often exhibit novel and unpredictable characteristics such as extraordinary strength, chemical reactivity, electrical conductivity, superparamagnetic behaviour and other characteristics that the same material does not possess at the micro- or macroscale. A huge range of nanomaterials is currently being produced at an industrial scale, while others are being produced at smaller scales as they are still under research and development (table 1.1).

In summary, a number of examples of NPs with new magnetic, catalytic, magneto-optical or optical properties, among others, that differ from those of the bulk materials have been reported in the scientific literature. Size reduction has been found to be the reason behind many of these novel physical and chemical properties,

**Table 1.1.** List of nanomaterials commercially available [14].

Non-exhaustive list of nanomaterials either used in industry or under investigation.

Aluminum	Dendrimers	Platinum
Aluminum oxide	Dimethyl siloxide	Polyethylene
Aluminum hydroxide	Dysprosium oxide	Polystyrene
Antimony oxide	Fullerenes	Praseodymium oxide
Antimony pentoxide	Germanium oxide	Rhodium
Barium carbonate	Indium oxide	Samarium oxide
Bismuth oxide	Iron and iron oxides	Silanamine
Boron oxide	Lanthanum oxide	Silicon dioxide
Calcium oxide	Lithium titanate	Silver
Carbon black	Manganese oxide	Carbon nanotubes
Cerium oxide	Molybdenum oxide	Tantalum
Chromium oxide	Nanoclays	Terbium oxide
Cluster diamonds	Neodymium oxide	Titanium dioxide
Cobalt and cobalt oxide	Nickel	Tungsten
Colloidal gold	Niobium	Yttrium oxide
Copper (II) oxide	Palladium	Zinc oxide

**Table 1.2.** General classification and potential applications of NPs [14].

Product areas with end-products containing NPs	Sectors where nanotechnology is expected to have a considerable impact
<ul style="list-style-type: none"> <li>• Cosmetics and personal care products</li> <li>• Paints and coatings</li> <li>• Household products</li> <li>• Catalysts and lubricants</li> <li>• Sports products and textiles</li> <li>• Medical and healthcare products</li> <li>• Food and nutritional ingredients</li> <li>• Food packaging and agrochemicals</li> <li>• Veterinary medicines</li> <li>• Construction materials</li> <li>• Consumer electronics</li> </ul>	<ul style="list-style-type: none"> <li>• Medical and pharmaceutical sector</li> <li>• Bio-nanotechnology, bio-sensors</li> <li>• Energy sector, including fuel cells, batteries and photovoltaics</li> <li>• Environment sector including water remediation</li> <li>• Automotive sector</li> <li>• Aeronautics sector</li> <li>• Construction sector, including reinforcement of materials</li> <li>• Composite materials</li> <li>• Electronics and optoelectronics, photonics</li> </ul>

which allow a wide range of applications with economic benefits. In 2010, more than 1000 products containing NPs became commercially available (table 1.2) [15, 16].

## 1.2 Classification of nanomaterials

Typically, NPs are defined as an agglomeration of atoms and molecules in the range of 1–100 nm. They can be composed of one or more species of atoms (or molecules)

and can exhibit a wide range of size-dependent properties. Within this size range, NPs bridge the gap between small molecules and bulk materials in terms of energy states [17]. NPs are generally classified based on their dimensionality, morphology, composition, uniformity and agglomeration [18, 19]. However, nowadays, NP classification and categorization are still not well established. In the specific case of hybrid NPs (HNPs), the term ‘hybrid’ is commonly associated with organic–inorganic NPs and nanocomposites [20]. However, in this book the term ‘hybrid’ is used according to the Cambridge dictionary definition, where it refers to ‘something that is a combination of two different things, so it has qualities relating to both of them’ [21].

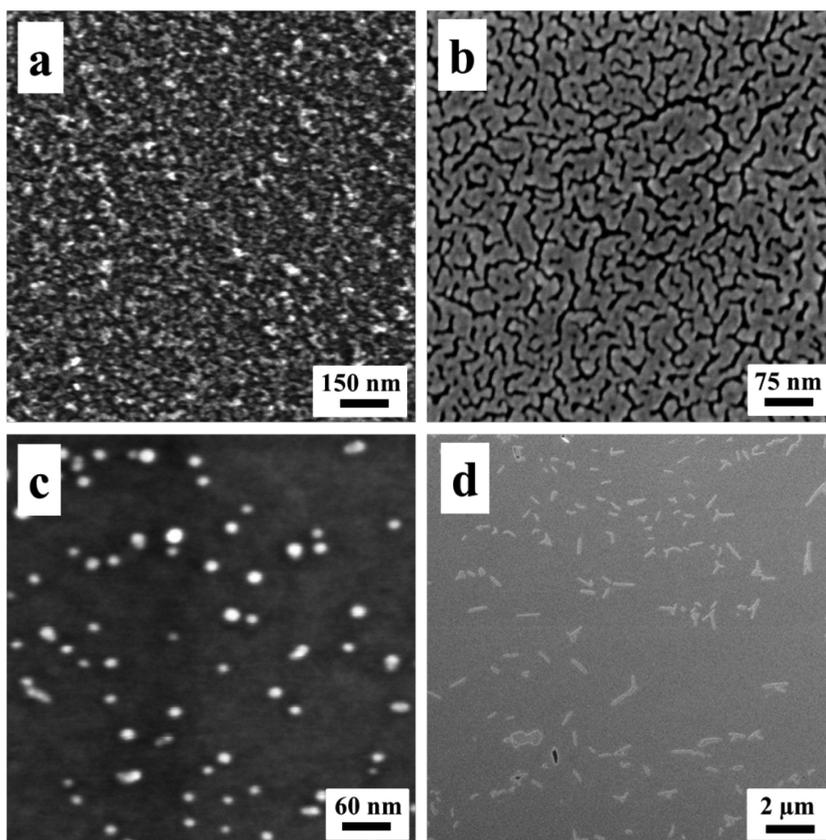
### 1.2.1 Dimensionality

- **Nanoscale in one dimension.** Materials with one dimension in the nanometre scale are typically thin films or surface coatings. Thin films have been developed and used for decades in various fields including electronics, information storage systems, chemical and biological sensors, fibre-optic systems, and magneto-optic and optical devices. Thin films can be deposited by various methods and can be grown controllably at the atomic level (monolayer) [22]. Those nanomaterials are known as 2D materials.
- **Nanoscale in two dimensions.** Nanomaterials having two dimensions in the nanometre scale. These include for example, nanotubes, dendrimers, nanowires, fibres and fibrils (known as 1D materials). Free particles with a large aspect ratio with dimensions in the nanoscale range are also considered 1D nanomaterials. The properties of 1D materials are less understood and manufacturing capabilities are less advanced.
- **Nanoscale in three dimensions.** Materials that are nanoscale in all three dimensions are commonly defined as 0D nanomaterials. These include quantum dots or nanocrystals, fullerenes, particles, precipitates, and colloids. Some 0D systems, such as natural nanomaterials and combustion products, metallic oxides, carbon black, titanium oxide (TiO<sub>2</sub>) and zinc oxide (ZnO) are well known, while others such as fullerenes, dendrimers and quantum dots represent the greatest challenges in terms of production and understanding of properties.

Figure 1.1 shows examples of nanomaterials with different dimensions. All the samples were deposited on a Si (111) substrate using the magnetron-sputtering-based inert-gas-condensation (MS-IGC) method as described in figures 2.1 and 2.2. The materials shown in figures 1.1(a) and (b) can be classified as 2D nanomaterials, while the Cu NPs shown in figure 1.1(c) are classified as 0D nanomaterials. The iron nanorods shown in figure 1.1(d) can be classified as 1D nanomaterials.

### 1.2.2 The morphology of NPs and nanocomposites

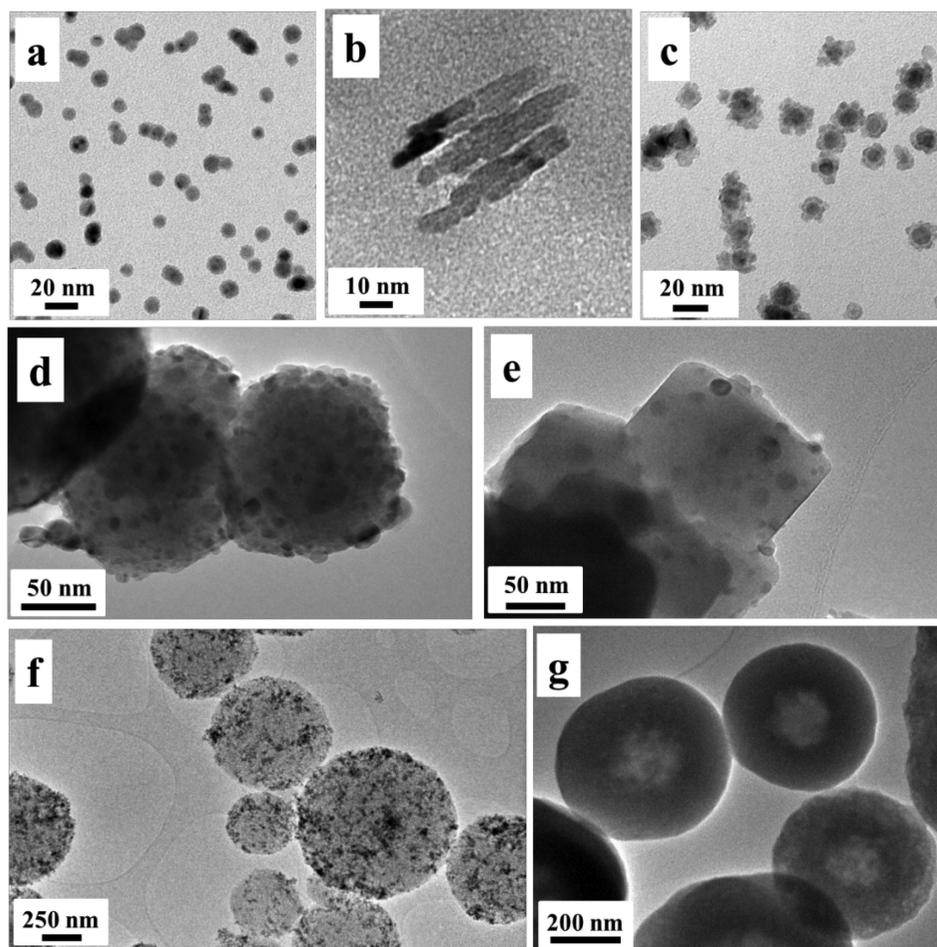
The morphological characteristics to be taken into account are the flatness, aspect ratio and spatial position of each element in the case of HNPs. A general



**Figure 1.1.** Scanning electron microscope (SEM) images showing (a) film of Ti NPs of 80 nm of thickness, (b) near-percolating Au film, (c) monodispersed Cu NPs, and (d) Fe nanorods (NRs).

classification exists between high and low aspect ratio particles. High aspect ratio NPs include nanotubes and nanowires. Low aspect ratio morphologies include spherical, oval, cubic, prism, helical and pillar shapes. Figure 1.2 shows examples of different morphologies of NPs and nanocomposites. Transmission electron microscopy (TEM) images of monodispersed Cu NPs, Fe nanorods and Cu core–Si shell NPs are shown in figures 1.2(a), (b) and (c), respectively. The details of the preparation methods for these NPs are presented in chapter 2. The TEM images in figures 1.2(d) and (e) show a porous magnetite NP and magnetite cubes decorated with Ni nanocrystals, respectively. These NPs were designed and synthesized using the hydrothermal process for purification of histidine-tagged proteins [23].

With regard to nanocomposites, substantial progress has been made in recent years in developing technologies in the fields of magnetic microspheres, magnetic nanospheres and ferrofluids. Nanospheres and microspheres containing a magnetic core embedded in a non-magnetic matrix are used in numerous biological applications [7]. They are used, for example, as carriers that can be targeted to a particular site by using an external magnetic field. In addition, the magnetic separation of



**Figure 1.2.** Transmission electron microscope (TEM) images of examples of NPs with different morphologies and compositions. (a) Monodispersed Cu NPs, (b) Fe nanorods, (c) Cu-Si core-shell NPs, (d) porous  $\text{Fe}_3\text{O}_4$  NPs, and (e)  $\text{Fe}_3\text{O}_4$  cubes decorated with Ni NPs. (f) Porous silica spheres with  $\gamma\text{-Fe}_2\text{O}_3$  NPs adsorbed on their surfaces, (g)  $\gamma\text{-Fe}_2\text{O}_3$  NPs embedded in porous silica spheres. For more details on the preparation and characterisation of these composites see [24, 25].

organic compounds, proteins, nucleic acids and other biomolecules and cells from complex reaction mixtures is becoming the most suitable method for large scale production in bioindustrial purification and extraction processes. For *in vivo* applications, it is imperative that well-defined biocompatible coatings surround the magnetic particles to prevent any aggregation and also to enable efficient protection of the body from toxicity. However, for *in vitro* applications, biocompatible coatings are not essential; particles can be coated with non-toxic materials inert to chemical and biological media. The particles employed in all these applications are mainly superparamagnetic colloids with appropriate coatings, guaranteeing the stability and biocompatibility of the solutions.

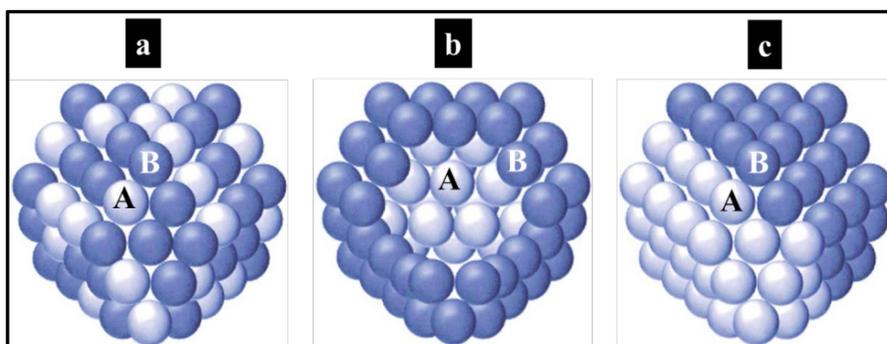
Superparamagnetic NPs exhibit magnetizations of magnitudes similar to those of ferromagnetic materials, however, they have neither coercivity nor remanence. This behaviour, which is of quantum origin, is limited to nanocrystals with sizes below the critical size [26]. Conversely, most applications require superparamagnetic colloidal dispersions with large magnetic responses. Because the magnetization of a particle is proportional to its volume, the maximum magnetization that one can achieve is limited by the critical size of the superparamagnetic transition, which depends on the material [7]. A well-established strategy to create superparamagnetic particles with larger superparamagnetic responses is using nanocomposites (see, for example, figures 1.2(f) and (g)). These superparamagnetic composites are typically made by embedding superparamagnetic nanocrystals in a non-magnetic matrix such as polystyrene or nanoporous silica [27–29]. The resulting colloidal particles retain the superparamagnetic response of their constituent nanocrystals and show larger magnetization when an external magnetic field is applied. Furthermore, neither coercivity nor remanence are observed at the working temperature. However, in addition to the intrinsic superparamagnetic behaviour of the constituent NPs, one must consider the interactions between the NPs inside the skeleton matrix due to their proximity and surface effects due to the coating; these can lead to changes in the overall magnetic response of the colloidal particle.

### 1.2.3 NP chemical composition

NPs can be composed of a single constituent material or be a composite of several materials. The NPs found in nature are often agglomerations of materials with various compositions, while pure single-composition materials can be easily synthesized using a variety of methods (see chapter 2).

There are three main types of chemical ordering in HNPs (figure 1.3) that describe the way in which the atoms of the elements are arranged within the same NP [30, 31]:

- **Mixed NPs:** can be either random or ordered (figure 1.3(a)). Randomly mixed alloys correspond to solutions of solids, whereas ordered nanoalloys correspond to ordered arrangements of A and B atoms.



**Figure 1.3.** Schematic images of binary NPs: mixed structure (a), core–shell structure (b), and layered structure (c) of A and B elements.

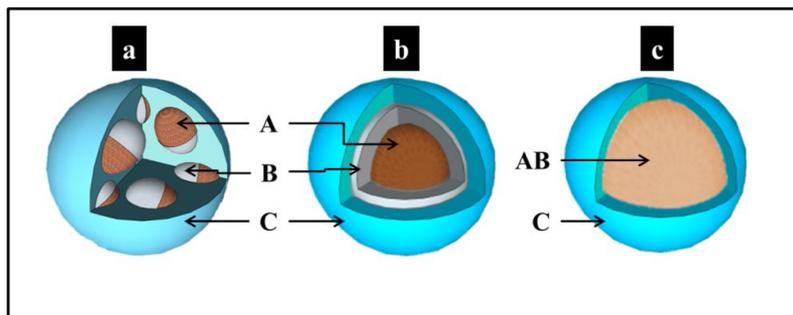
- **core–shell NPs**: consist of a shell of one type of atom (B) surrounding a core of another type of atom (A) (figure 1.3(b)). This pattern is generally denoted by  $A@B$  and is common for a large class of NPs. Various thermodynamic considerations, discussed further in chapters 3 and 4, lead to the segregation of materials within the core or shell. A subset of the core–shell category consists of multishell (or ‘onion-like’) NPs. These NPs have alternating A–B–A shells, or A–B–C in the case of ternary NPs as depicted in figure 1.4(b). The formation of these latter structures is discussed in chapter 4, where it is demonstrated that Fe–Ag–Si multishell structures are obtained by adjusting the experimental conditions.
- **Layered NPs** are commonly referred to in the literature as Janus (or ‘dumbbell-like’) NPs. They consist of two types of NPs (A and B) sharing a common interface (figure 1.3(c)). These types of NPs tend to minimize the number of bonds between elements A and B. This heterojunction structure facilitates phase separation.

Because of the increasing need for multifunctional NPs, other complex structures of NPs such as multicore–shell structures in which the cores can present either ‘dumbbell-like’ or ‘onion-like’ structures have been reported in the literature [32–36]. This type of NP is presented and discussed in chapter 4. Another multifunctional subset of the core–shell arrangement is an alloyed single core NP encapsulated in an inert shell (figure 1.4(c)). The case of  $\text{FeAl}@\text{Al}_2\text{O}_3$  NPs [37] is presented and discussed in section 3.2.

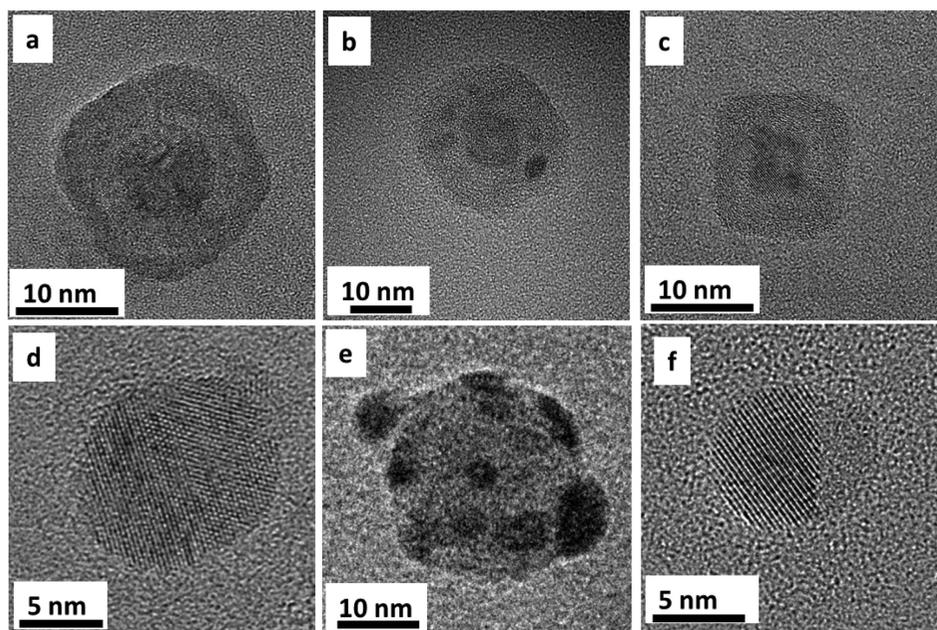
TEM images of NPs with various compositions and morphologies are shown in figure 1.5. These NPs were prepared using the MS-IGC method. Control over the composition and morphology of these NPs was achieved by adjusting the experimental conditions as explained in chapters 3 and 4. A detailed description of the deposition system is given in chapter 2.

### 1.3 NP uniformity and agglomeration

Based on their chemistry and electromagnetic properties, NPs can exist as dispersed aerosols, suspensions/colloids or in an agglomerate state. In fact, NPs tend to adhere



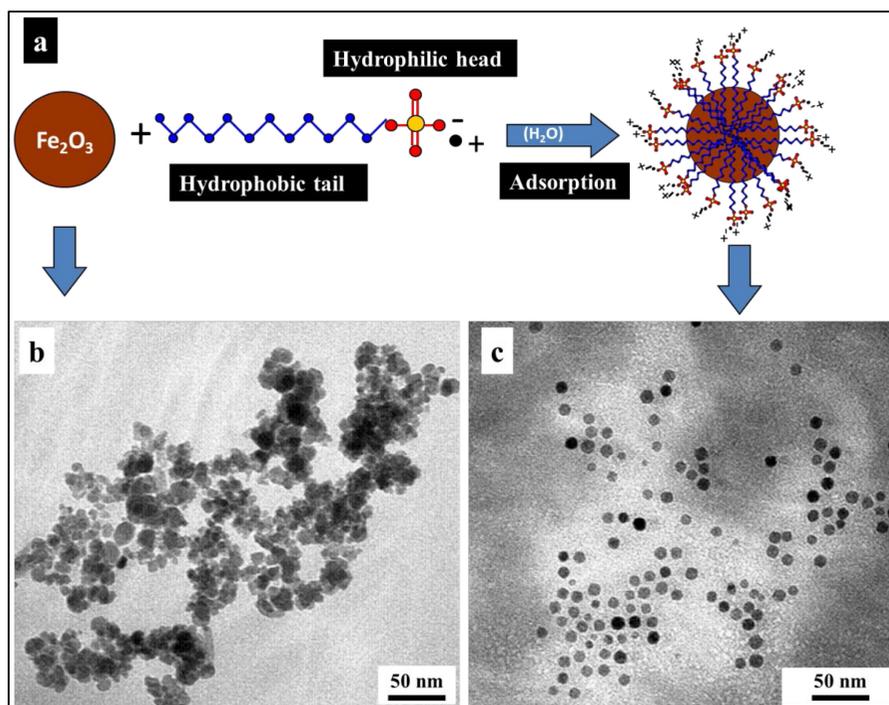
**Figure 1.4.** Schematic images of ternary NPs formed of elements A, B and C: (a) multicore@shell morphology (the cores present a dumbbell-like morphology), (b) core@multishell morphology, (c) alloyed-core@shell morphology.



**Figure 1.5.** (a) Cu@Ag core-shell NP, (b) Cu@Si multicore-shell NP, (c) Fe@Fe<sub>2</sub>O<sub>3</sub> core-shell NP, (d) CuAg mixed NP, (e) Si NP inoculated with Ag NPs resulting in a satellite morphology. (f) FeAg dumbbell-like NP; crystalline hemisphere corresponds to Ag.

to each other and to form agglomerates because of van der Waals forces that act over short distances, magnetic interactions, electrostatic forces present in the particles and adhesion forces related to the liquids adsorbed on their surfaces. Agglomeration due to Brownian motion is classified as ‘coagulation’.

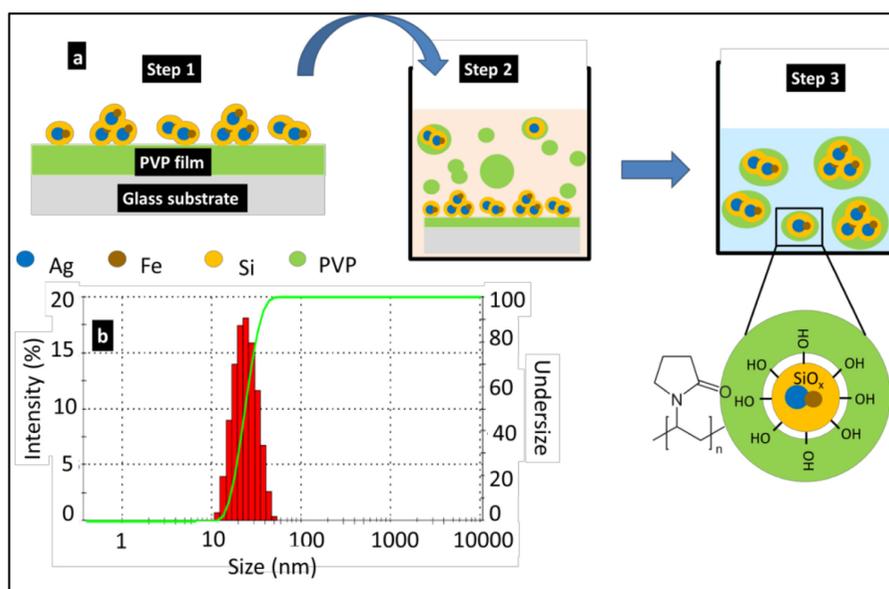
To avoid agglomeration, several processes include a post-synthesis stage to modify the particle surface by coating it with another organic or inorganic substance. In an agglomerate state, NPs may behave as larger particles, depending on the size of the agglomerate. For example, magnetic NPs tend to cluster, forming an agglomerate state, unless their surfaces are coated with a non-magnetic material. Figure 1.6 illustrates the typical process of stabilization of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs in an aqueous suspension. The molecules of the anionic surfactant sodium dodecyl sulfate (SDS) are adsorbed onto the surfaces of the nanocrystals providing a negative charge in water. Therefore, the nanocrystals in solution repel each other electrostatically resulting in a stable colloidal suspension. For more details on this procedure see [38]. Other methods commonly used for the stabilization of colloidal NPs consist in their surface functionalization with biological molecules such as oligonucleotides, resulting in strong electrosteric stabilization. In fact the oligonucleotides are negatively charged due to phosphate ( $PO_2^-$ ) groups along their backbones, inducing a stability based on electrostatic repulsions NP–NP. On the other hand, steric stabilization induced by the anchored oligonucleotides on the surface of the NPs is likely to contribute to the stability of the NPs [39].



**Figure 1.6.** (a) Illustration of the stabilization process applied to  $\gamma\text{-Fe}_2\text{O}_3$  NPs using SDS (sodium dodecyl sulfate) surfactant. (b) TEM image of the precipitated  $\text{Fe}_2\text{O}_3$  NPs without SDS. (c) TEM image of SDS-modified  $\text{Fe}_2\text{O}_3$  NPs (adapted from reference [38] by permission of The Royal Society of Chemistry).

In the case of NPs deposited using vapour phase methods, the NPs are generally deposited on a solid substrate. The transfer of these NPs to a stable suspension is still under investigation. For example, attempts were made to co-deposit NPs from the vapour phase with a beam of water vapour, methanol, or isopropanol onto a nitrogen-cooled substrate [40, 41]. However, the stability of the resulting suspensions was not reported. Recently, a simple and environmentally friendly method for harvesting NPs was developed using polyvinylpyrrolidone (PVP) as a stabilizer [34]. PVP was selected as a non-toxic polymer with good wetting properties. Figure 1.7 shows the procedure used to harvest the NPs to a stable and homogeneous colloidal suspension.

Other physical methods to produce dispersed and stable NPs consist in embedding the NPs in one-dimensional free-standing nanostructures such as ultra-thin films, also known as ‘nanosheets’ [42], so that the NPs are spatially fixed within the film (or matrix). For example, figure 1.8 shows an example of  $\text{Fe@Ag@Si}$  onion-like HNPs embedded in an amorphous carbon thin film. These HNPs were deposited using the MS-IGC system described in figure 2.2 [43]. The procedure consisted of the deposition of the HNPs on a Si substrate previously coated with a b-PEI and an amorphous carbon thin films, respectively. For more details see [42, 43].



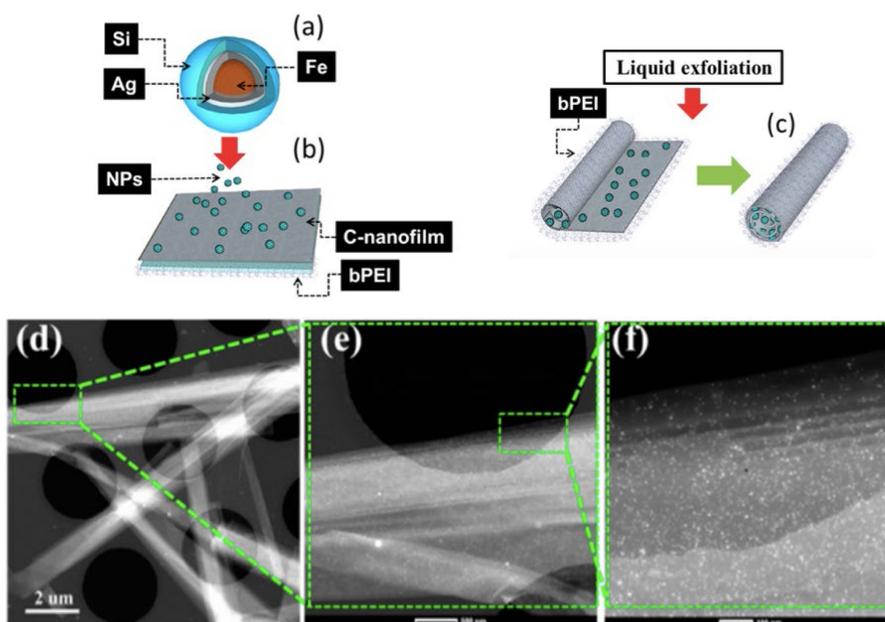
**Figure 1.7.** (a) Schematic of the exfoliation procedure of the NPs. (Step 1) multicore@shell NPs were deposited on a spin-coated PVP (polyvinylpyrrolidone) film on glass substrate. (Step 2) NPs/PVP/glass samples were immersed in methanol and sonicated for 15 min, then separated to remove excess PVP. (Step 3) After washing precipitated NPs with methanol, they were re-suspended in ultrapure water. (b) Dynamic light scattering histogram showing the size distribution of the hybrid NPs [34]. Reproduced by permission of The Royal Society of Chemistry.

## 1.4 NP characterization

Once NPs are synthesised, it is important to fully characterise and understand their structure. Over the years, many methods have been developed for a proper understanding of NP structure. In this section, the focus will be on the main techniques with relevance to this book, namely the EM including TEM, SEM and scanning TEM (STEM), electron energy loss spectroscopy (EELS); x-ray photoelectron spectroscopy (XPS); and atomic force microscopy (AFM).

TEM is a very powerful technique for the characterisation of NP size, composition and crystalline structure. When an electron beam interacts with a sample, the electrons can be either transmitted, scattered, backscattered or diffracted [44, 45]. TEM uses the transmitted electron signal to form an image of the sample. The transmitted electron beam is dependent on the sample thickness; for thin samples (a few nanometres), the transmitted electrons pass through without significant energy loss. STEM differs from TEM by focusing the electron beam into a narrow spot that is scanned over the sample in a raster.

Because the attenuation of the electrons depends significantly on the density and thickness of the sample, the transmitted electron beam forms a 2D image of the sample. In hybrid samples, STEM imaging allows the identification of different components based on intensity variation. This intensity variation is related to the



**Figure 1.8.** (a) Fe@Ag@Si NPs with ‘onion-like’ morphology are produced through a gas-phase condensation method. (b) NPs are *in situ* deposited on carbon nanofilms supported on bPEI film. (c) After the liquid exfoliation process, a self-scrolling process occurs, resulting in bPEI-functionalized CNS-NP nanocomposites. (d–f) STEM images with different magnifications of the CNS-NPs nanocomposites after the exfoliation process. The bright dots in (f) indicate the NPs embedded in the carbon film. Reproduced with permission from [43]. Copyright 2016 ACS.

difference in the atomic numbers of each component ( $Z$ -contrast). In addition, the rastering of the beam across the sample makes it possible to couple STEM with other characterization methods such as EELS [46], allowing direct correlation of image and quantitative data thus obtain details regarding the chemical composition of NPs.

General TEM analysis does not have sufficient resolution to determine the crystallinity of a nanomaterial. However, high resolution TEM (HRTEM) can be successfully employed for the characterisation of the crystallinity of a sample with atomic resolution, as well as for providing information regarding electron diffraction analysis. This approach helps in gaining an insight into the ordering of atoms in an NP. In addition, new generations of EM instruments such as the Titan-ETEM allow performing dynamic studies on the chemical reactions under the effects of the temperature changes and gas pressures at the atomic level. Combined with the image Cs corrector and monochromator technology, this system allows the study of the morphology, structure, composition and bonding of the nanostructures down to the atomic level. Other instruments, such as FEI Talos field emission gun (FEG) TEM, are equipped with highly sensitive Super-X EDS detectors for elemental analysis, and designed to enable the use of gas and liquid operating holders, making possible the study of nucleation and growth nanostructures in both gas and liquid phase.



**Figure 1.9.** TEM used for the characterization of NPs presented in this book. (Credit: OIST-Graduate University).

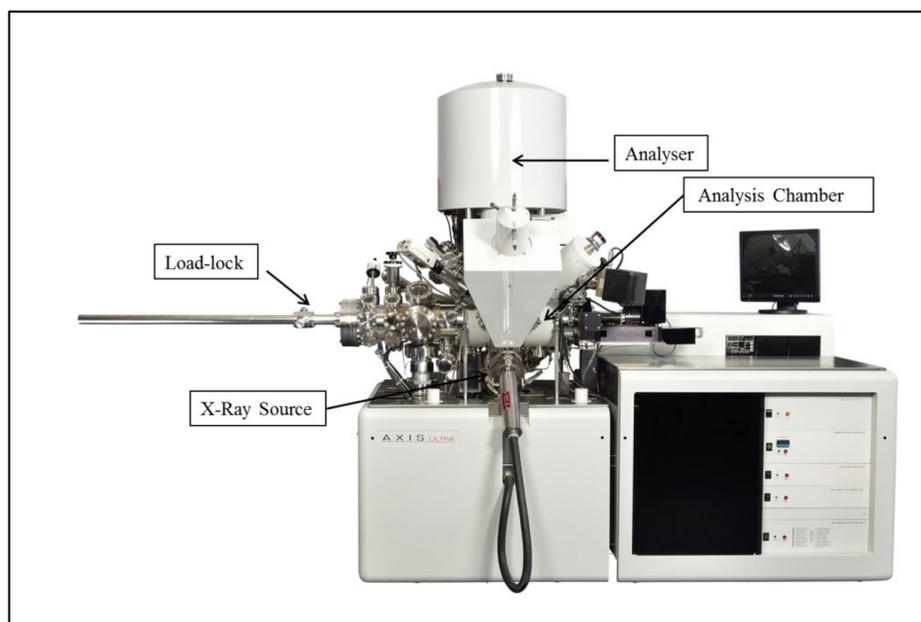
Figure 1.9 shows a photograph of the TEM used in the characterisation of the NPs presented in this book.

Regarding SEM characterisation, to create an SEM image, a source of electrons is focused into a beam, with a very fine spot (typically the spot size is  $\sim 5$  nm). The energy of the beam is ranging from a few hundred eV to 50 keV. The incident electron beam is rastered over the surface of the sample. As the electrons strike and penetrate the surface, a number of interactions occur resulting in the emission of electrons and photons from the sample. Three types of SEM images are generated by collecting the emitted electrons and photons: secondary electron (SE) images; backscattered electron (BSK) images; and elemental x-ray maps (EDX). The resolution of modern scanning electron microscopes is typically  $<10$  nm, and image resolution of about 0.5 nm can be achieved in the most recent generation field-emission-gun SEM.

While SEM allows the analysis of conducting and semiconducting samples, AFM is a versatile technique that works for almost any type of surface, encompassing composites, ceramics, oxides, polymers, and biological specimens. This technique was introduced by Binnig and Quate in 1986 [47] as an alternative to the earlier developed scanning tunneling microscopy (STM), which was limited to topographic imaging of the surface of conducting samples [48, 49]. Part of the scanning probe microscopy (SPM) family, AFM instrument consists of a nanoscale tip which is

scanned over a sample surface. The tip is placed on one side of a soft cantilever, while the opposite side is mounted on a positioning sample stage, which is usually made of an array of piezoelectrics, allowing the control of the distance between the tip and the sample. A laser is pointing at the end of the cantilever, and a mirror and a photodiode collecting the reflected laser beam. The main idea is to make use of a small force taking place between the tip and the atoms at the sample surface. This force depends on the distance between the tip and the sample, and causes the bending of the cantilever. The images are generated by scanning the tip on the surface of the sample, however, instead of adjusting the height of the tip to maintain a constant distance between the tip and the surface as in STM technique, the AFM measures the upward and downward deflections of the tip cantilever while maintaining a constant force of contact [50]. To keep the cantilever bending constant, a feedback loop must change the stage position during the scanning process of the sample. Therefore, a topographic image of the sample surface is obtained.

X-ray photoelectron spectroscopy (XPS), is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, chemical states, and electronic states of the elements within the material. XPS spectra are obtained by irradiating a material with a beam of x-rays while simultaneously measuring the kinetic energy of electrons that escape from the top 0 to 10 nm of the material being analysed. XPS requires high vacuum ( $P \sim 10^{-8}$  mbar) or ultra-high vacuum ( $P < 10^{-9}$  mbar) conditions. However, when used to analyse NPs, the importance of the coverage of the NPs must be kept in mind: high coverage leads to high-quality



**Figure 1.10.** X-ray photoelectron spectroscopy system used to analyse the NPs presented in chapters 3 and 4 of this book [51].

spectra. On the other hand, to quantify the composition of the NPs, an inert transfer of the sample to the analysis chamber is necessary to avoid contamination and oxidation of the NP surface. The system used to analyse the NPs presented in this book is shown in figure 1.10. Currently, this system is further developed to a fully automated system under the commercial name Axis-Nova [51].

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