

Nanotechnology in the Life Sciences

Kamel A. Abd-Elsalam
Mohamed A. Mohamed
Ram Prasad *Editors*

Magnetic Nanostructures

Environmental and
Agricultural Applications

 Springer

Nanotechnology in the Life Sciences

Series Editor

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Nano and biotechnology are two of the 21st century's most promising technologies. Nanotechnology is demarcated as the design, development, and application of materials and devices whose least functional make up is on a nanometer scale (1 to 100 nm). Meanwhile, biotechnology deals with metabolic and other physiological developments of biological subjects including microorganisms. These microbial processes have opened up new opportunities to explore novel applications, for example, the biosynthesis of metal nanomaterials, with the implication that these two technologies (i.e., thus nanobiotechnology) can play a vital role in developing and executing many valuable tools in the study of life. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale, to investigating whether we can directly control matters on/in the atomic scale level. This idea entails its application to diverse fields of science such as plant biology, organic chemistry, agriculture, the food industry, and more.

Nanobiotechnology offers a wide range of uses in medicine, agriculture, and the environment. Many diseases that do not have cures today may be cured by nanotechnology in the future. Use of nanotechnology in medical therapeutics needs adequate evaluation of its risk and safety factors. Scientists who are against the use of nanotechnology also agree that advancement in nanotechnology should continue because this field promises great benefits, but testing should be carried out to ensure its safety in people. It is possible that nanomedicine in the future will play a crucial role in the treatment of human and plant diseases, and also in the enhancement of normal human physiology and plant systems, respectively. If everything proceeds as expected, nanobiotechnology will, one day, become an inevitable part of our everyday life and will help save many lives.

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Preface

Recently, magnetic nanostructures have gained a remarkable interest in the last several years both for basic research and applied studies. Because of their low cost, ease of manufacture, and modification, they have great potential for agricultural, medical, and environmental applications. The use of magnetic nanostructures has been proven in a wide range of fields including catalysis, biotechnology, biomedicine, magnetic resonance imaging, agriculture, biosensors, and removal of environmental pollutants, among others.

The book title *Magnetic Nanostructures: Environmental and Agricultural Applications* indicates that this book in 16 chapters has collected the knowledge, discoveries, and the fruitful findings of magnetic nanostructures and their application in agriculture and environment as well. The potential applications of magnetic nanomaterials in the agriculture and food sectors are manifold: from the development of sensors and monitoring the environment to the treatment of wastewater and the remediation of contaminated soils and from increasing crop yield (e.g., nanopesticides or nanofertilizers) to biosecurity (e.g., sensors for detecting pathogens along the whole food chain from the farm to fork). The current book is, therefore, most welcome, as it brings together various sources of expertise on different aspects related to the application of those magnetic nanostructures in the agri-food sector and environmental remediation. The magnetic nanostructures have also a great potential in biotechnological processes taking into account that they can be utilized as a carrier for enzymes during different biocatalytic transformations. Novel magnetic nanomaterials can be used for detection and separation of pesticides from environmental and biological samples. The excellent adsorption capacity of the modified magnetic nano-adsorbent together with other advantages such as reusability, easy separation, environmentally friendly composition, and freedom of interferences of alkaline earth metal ions makes them suitable adsorbents for removal of heavy metal ions from environmental and industrial wastes. One of the most important environmental applications of magnetic nanostructures has been in the treatment of water, whether in the remediation of groundwater or through the magnetic separation and/or sensing of contaminants present in various aqueous systems. The integrated combination of those 16 chapters written by experts with considerable

experience in the area of research provides a comprehensive overview on the synthesis, characterization, application, environmental processing, and agriculture of engineered magnetic nanostructures. For the application of any materials anywhere, we should have a clear-cut know-how, such as how it can be applied and what are the different ways.

Hence, in this book, Chap. 1 clearly lays out the foundation of the book by providing the overview of the concepts, strategies, techniques, and tools of nanomagnetism and its promises in the future prospects. We believe that, before using any material, we should know firstly its physical and chemical properties to decide the precise use of those materials in different applications. Hence, Chap. 2 deals with the bio-based synthesis of magnetic nanoparticles and their applications. Chapter 3 is devoted to plant-mediated synthesis, applications, and challenges of magnetic nanostructures. Microbially synthesized biomagnetic nanomaterials have been deliberated in Chap. 4. In Chap. 5, we are discussing an overview of nanotechnology and nanobiotechnology for environmental remediation. Chapter 6 highlighted using magnetic nanoparticles in gene delivery system in plant science. Chapter 7 highlighted the application of magnetic nanoparticles in biofuel production. The next three chapters deal with the concerns of hazards of nanomaterials to water treatment, human health, and environment and also critical views on compliances. Magnetic material in adsorption removal of heavy metals from wastewater is discussed in Chap. 8. Chapter 9 describes the water purification using magnetic nanomaterials. Also, Chap. 10 includes more information related to metal ferrites and their graphene-based nanocomposites: synthesis, characterization, and applications in wastewater treatment. Utilization of magnetic nanostructures in environmental and agricultural applications has been deliberated in Chap. 11. On the other side, magnetic nanoparticle applications in plant protection were explained in Chap. 12. Shrivastava et al. discuss the application of magnetic nanoparticles for removal of pesticides from environmental samples prior to instrumental analysis in Chap. 13. We have another chapter (Chap. 14) to discuss the impact of iron-based nanomaterials on soil microbes and soil health. Finally, Chaps. 15 and 16 intend to highlight the antimicrobial propensity of magnetic nanoparticles with a special emphasis on the role of nanoparticle interface in determining the antimicrobial propensity, their antimicrobial mechanism, factors affecting the antimicrobial activity, benefit limitations of magnetic nanoparticles as an antimicrobial agent, and methods used for testing antimicrobial activity. The 16 chapters of this book have been authored mostly by different expert teams of scientists dealing with various aspects related to the concepts, strategies, techniques, and tools of nanosciences focusing on the application potential and also on concern for nontoxicity.

We wish to thank Springer officials, particularly William F Curtis, Eric Schmitt, Eric Stannard, and Sowmya Thodur, for their generous support and efforts in accomplishing this volume. We are highly delighted and thankful to all our contributing authors for their vigorous support and outstanding cooperation to write altruistically these authoritative and valuable chapters. We especially thank our families for their consistent support and encouragement. The editors convey their heartfelt gratitude

to all the contributors for their excellent, informative, and up-to-date contributions and for their consistent support and cooperation.

Hence, we believe this book will lead to a better understanding of the interdisciplinary field of functional biology and nanosciences. The purpose of writing this book was to bring together all possible approaches to tackle the target of the improvement of agriculture applications by introducing crop plants into areas not currently being used for cultivation without environmental risks. Future perspectives and challenges are discussed to make magnetic nanostructure green nanotechnology technically more feasible and economically sustainable. We have tried our best to realize these goals in bringing out this book, and now we want the readers to evaluate how far we have been successful in this aim.

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Chapter 1

Nanoparticles: Magnetism and Applications



Abd El-Moez A. Mohamed and Mohamed A. Mohamed

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1.1 Introduction

Nanoparticles (NPs) are small particles with diameter range of 1–100 nm. The nanoscale materials, in particular magnetic NPs, have attracted the attention in several applications as magnetic fluids (Jordan et al. 1999), magnetic energy storage (Jordan et al. 1999), and biomedicine (Vallejo-Fernandez et al. 2013) due to their unique properties in comparison with the bulk material. The unique properties include low Curie temperature, superparamagnetism, and high magnetic susceptibility. The technological implementations of magnetic NPs depend on their size, morphology, and chemical composition. The magnetic properties of magnetic NPs can be tuned to match the desired applications by size (Baldi et al. 2007), shape (Song and Zhang 2004), or doping (Mohapatra et al. 2013). For example, iron oxide NPs over than 28 nm are ferrimagnetic and used in magnetic separation as ferrofluids (Scherer and Neto 2005), iron oxide NPs below 28 nm are superparamagnetic and used for biomedical applications (Gazeau et al. 2008), and iron oxide below 4 nm are primarily paramagnetic and can be used as a magnetic resonance imaging (MRI) contrast agent (Mihyun et al. 2011). However, magnetic NPs have several challenges as agglomeration that occurs to reduce the surface energy and chemical activity. Therefore, it was important to protect the NPs from oxidation using a coating protective layer, forming a core-shell structure. In spite of the interesting idea of the core-shell structure, it is associated with a loss in the magnetic properties of the NP.

NPs are widely used in nanotechnology, which is a recent technology related to the nanoscale. The nanotechnology term is used to describe the ultrahigh precision and the ultrafine dimensions. Norio Taniguchi introduced the top-down approach by predicting some improvements in the integrated circuits. Later, K. E. Drexler introduced the bottom-up approach through building up large objects from atoms (Cullity and Graham 2008).

1.2 NP Structure and Features

NPs have a core-shell structure with high surface area to volume ratio. Therefore, the surface is expected to show a different chemistry from the core. For example, the core of silica NPs shows the SiO_2 structure, which is different from the surface that is very close to the $\text{Si}(\text{O})_{2-x}\text{OH}_{2x}$ (Paparazzo et al. 1992). This shows the different compositions of the outer layer that have 7% more Si atoms on the surface. It means a significant contribution of the surface chemistry where the NP surface is the first contact with the external environment or media. It is worth to mention that the surface chemistry can be adjusted according to the desired application. But surface functionalization is a challenge because almost all the NP properties are lost during precipitation process. That is why, it is important to protect the NP surface during synthesis by several ways such as coating. Thus, it can be said that the NP is

a three-layered structure of the core material, the surface, and the added shell. However, the core is the most important part that has the key role of the NP properties.

The NP surface can be coated by different kinds of media as polymers, metal ions, and surfactants. Although the charged surface NPs are the best ones to disperse in aqueous media, several materials do not have a good surface for charge localization or stabilization. To stabilize these NPs, a small molecule with chargeable group is stuck to the NP surface with a covalent bond; gold and silver are good examples for that (Henglein and Giersig 1999). Another different method to produce stable NPs is using a surfactant (Qiu et al. 1999), where the NP is formed in a micelle. The difference between these two methods is that, in the surfactant method, the surfactant is in equilibrium in a media (Shawd 1992). The shell is the outer layer of the core and sometimes it is a different structure of the core as the cadmium selenide core with zinc sulfide shell (Malik et al. 2002). Sometimes this outer layer is formed spontaneously without any penetration to the core, leading to a core-shell structure. This is like the iron oxide shell layer that is formed around the iron NP core where the core plays the key role in the properties.

Magnetic NPs show important features as chemical stability, superparamagnetism, and high surface area. Superparamagnetism is the most important character of magnetic NPs that appears below a certain critical size (Kolhatkar et al. 2013). Superparamagnetic NPs show a high resistance of externally applied magnetic fields with high magnetization, which is greater than the observed in paramagnetic materials (Faraudo and Camacho 2010). Moreover, their magnetic moments are randomly distributed in the absence of magnetic field without any tendency of particle accumulation (Lam et al. 2013). In addition, the small size of NPs leads to a change in the material properties where the periodic boundary conditions are destroyed, changing melting point and coercive force and leading to magnetic disorder. The change in melting point with size reduction refers to the increase in surface atoms, this is because of the surface energy contribution to Gibbs energy, and this change is inversely proportional with the particle size (Christian et al. 2008).

1.3 Synthesis

NPs are produced via different methods and techniques; however, not all methods work for different kinds of NPs. Two main approaches are used to prepare the NPs, the top-down and the bottom-up. The top-down approach is cutting a large-scale material until the nanoscale is reached. This may be achieved by etching or lithography techniques, for example (Dai et al. 2005). On the other hand, the bottom-up approach is used to grow the NPs from simple molecules. Despite the various techniques using these two approaches, in this part, we will present examples for the most commonly used methods in NP fabrication.

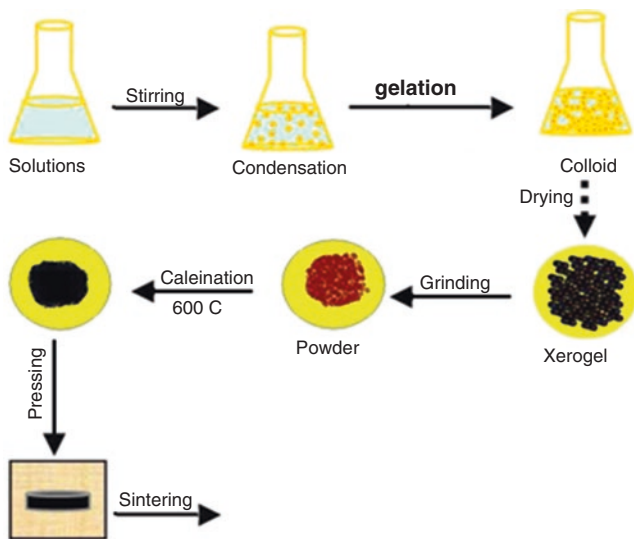


Fig. 1.1 Schematic diagram for the sol-gel method

1.3.1 Sol-Gel Method

The sol-gel method is suitable for the synthesis of nanostructured metal oxides (Dai et al. 2005). It is a formation of inorganic compounds via polycondensated interactions in liquids. Sol is a colloidal dispersion of particles in a solution and condenses in a gel form. The starting raw materials are usually metallic salts, dissolved in distilled water or other solvents together and stirred to homogenize the dispersion. The sol particles interact via van der Waals forces; sometimes it is required to add an organic complex agent as ethylene glycol and increase the interaction temperature by heating on a hot plate. Then, the gel needs drying and heating at minimum 400 °C for several hours to make sure that all organic compounds are completely evaporated. Then the obtained resultant is ready to use or can be subjected to another treatment according to the prepared material. A schematic summary is presented in Fig. 1.1 for the sol-gel method. The advantages of this method are preventing the coprecipitation problems, and it is suitable for various nanostructures as nanoporous materials, thin films, and powder.

1.3.2 Ball Milling

This is a simple mechanical method that depends on decomposition of the coarse-grained structures to fine ones. In this method, the powder is enclosed in a small container with steel balls in a shaker. There is an energy transfer from balls to powder that depends on several factors as ball to powder ratio, ball size, vibration speed, and milling time. The NPs are produced due to the shear action via milling,

however, several disadvantages are observed in that method as plastic deformation and contamination in the produced materials. However, this method is restricted to oxide NPs, specially, amorphous alloy.

1.3.3 Gas-Phase Condensation

This is a general method that contains several techniques. The main principle of this method is the production of small clusters that can be aggregated to form NPs. However, the condensation occurs only when the vapor is saturated.

1.3.4 Direct Evaporation in Furnace

This is an old technique to produce NPs by heating up the material in inert or active gas. Evaporated hot atoms make direct collisions with gas cold atoms, losing energy and condensing as small clusters that keep growing in the supersaturated area. It is worth mentioning that the cluster size and distribution depends on gas flow, condensation, and evaporation rates. One disadvantage of this method is that it is only suitable for high vapor pressure materials.

1.3.5 Gas-Phase Processing

The material is evaporated in an inert gas and the clusters are formed from the gas phase due to nucleation. It was found that the NP size increases with increasing vapor and gas pressure. In this method, NPs are collected using a cooled rotating cylinder and deposited on the wanted collection media. Several modifications have been updated for the collection device as corona discharge, which is better in the larger scale synthesis of NPs. Despite the precise control in NP size in that method, it is more suitable for gas flowing systems.

1.4 Magnetic Properties

Magnetism has drawn the attention since its discovery in magnetite natural mineral. It plays an important role in several modern technological implementations as magnetic sensing (Giri et al. 2015), magnetic refrigeration (Giri et al. 2015), and tumor treatment (Ikeda et al. 1994). Faraday, Oersted, and Ampere investigated the origin of magnetism. They used the basics of electromagnetics, especially Ampere, who suggested the circular electric current, introducing the concept of magnetic moment, which is responsible for the macroscopic magnetic properties of materials.

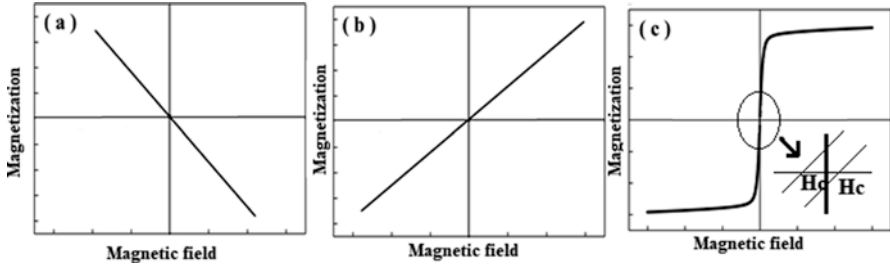


Fig. 1.2 Characteristic hysteresis loops of (a) diamagnetic, (b) paramagnetic and (c) ferromagnetic materials, the inset in (c) shows the hysteresis behavior and coercivity (H_c)

To discuss in brief the origin of magnetism, let us recall the electron motion in a free atom around a nucleus. The electron moves around the nucleus in an orbital motion, being a moving charge in a current loop. This generates a small magnetic field, showing up an orbital magnetic moment parallel to the rotation axis. Simultaneously, electron rotates around itself in a spin motion, leading to a spin magnetic moment pointing up or down with spin = 1/2. The paired electrons show opposite orbital and spin moments, cancelling each other and showing a zero net magnetic moment. Therefore, atoms with the fully filled electronic shells do not show a permanent magnetization as inert gases (Cullity and Graham 2008). Alternatively, materials with unpaired electrons show a net magnetic moment and interact with external magnetic fields. When a material is exposed to an external magnetic field, the electron magnetic forces are affected and the magnetic response is quite different among materials. The magnetic susceptibility term (χ) is usually used as a measurement of material response to the applied magnetic field (H), where χ is the ratio between the magnetization (M) to the applied magnetic field, $\chi = M/H$, and M is the number of aligned magnetic moments per unit volume. According to the degree of interaction between electrons and the applied magnetic field, magnetic materials are classified into several categories, but ferromagnetism, paramagnetism, and diamagnetism are the most common types, where each type of these categories has different origin. Diamagnetism arises in the completely filled electronic shells where electrons are an even number, such as in copper. In such case, electrons pair with opposite magnetic moments, showing up a zero net magnetic moment. Diamagnetic materials are characterized by a negative χ , as seen in Fig. 1.2a, where they show a negative linear behavior for M vs H curve without any hysteresis. Paramagnetism and ferromagnetism are quite similar. They show a positive χ (see Fig. 1.2a, b); however, M increases linearly with the applied magnetic field over the whole range in paramagnetic materials, which is in contrast with the ferromagnetic materials where M tends to saturation at the relatively high magnetic fields.

In principle, both paramagnetism and ferromagnetism can be found in materials with odd number of electrons that means one or more unpaired electrons. However, both materials are different in origin, magnetic structure, and behavior when they are exposed to an external magnetic field. Paramagnetism origins from orbital and spin electron motions, meanwhile ferromagnetism origins mainly from the electron spin

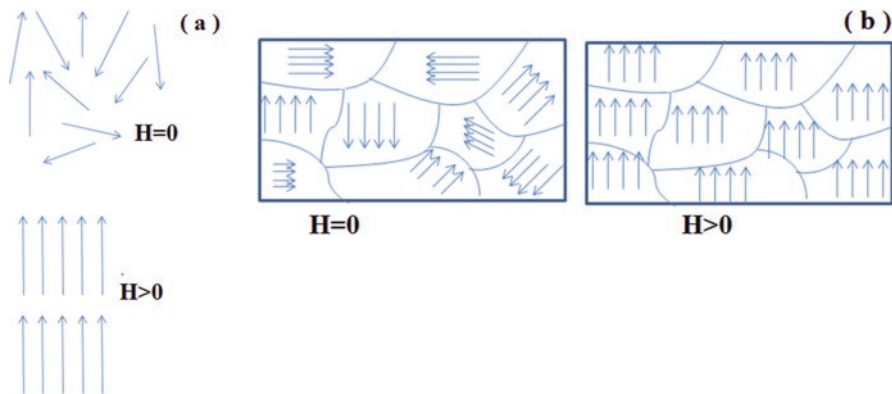


Fig. 1.3 Magnetic structure and spin orientation in the presence and absence of external magnetic field ($H = 0$ and $H > 0$, the magnetic field direction points to up) for (a) paramagnetic and (b) ferromagnetic materials

motion. Regarding the magnetic structure and the magnetic ordering, in the absence of magnetic field, the magnetic moments of the paramagnetic material are randomly distributed (see Fig. 1.3a), meanwhile in the ferromagnetic material, the spins are aligned in blocks called domains, which are separated from each other by boundaries called Bloch wall (see Fig. 1.3b). When a ferromagnetic/paramagnetic material is exposed to an external magnetic field, the magnetic moments are aligned parallel with the magnetic field direction. When the external magnetic field is removed, the magnetic moments of the paramagnetic material are randomly distributed again, in contrast with the ferromagnetic material that has some oriented magnetic moments, which are called residual magnetization (M_r). This reveals the spontaneous magnetization of the ferromagnetic materials and the hysteresis behavior that requires a coercive field (H_c) to remove that M_r (see the inset of Fig. 1.2c). It is worth mentioning that most of magnetic technological implementations are called ferromagnetism that has different properties when it goes to the nanoscale. Therefore, let us highlight in brief the effect of low dimension scale on magnetism.

Recently, nanomagnetism has been investigated in several materials, where the material should have at least one dimension of 100 nm as the one-dimensional surface thin films, the two-dimensional fibers, or the three-dimensional particles. Domain structure plays a vital role in the ferromagnetic behavior, whereas the ferromagnetic material goes below a critical size, it becomes very close to the single domain structure. It is worth mentioning that the magnetism of fine particles arises from the size effect that is affected by domain structure. According to the magnetic domain theory, the critical size of single domain is affected by several factors as crystal anisotropy, domain wall energy, and particle shape. Moreover, it was found that the magnetic properties are size dependent, for example, the coercivity increases with reducing the particle size and decreases again reaching a zero value when the single domain size goes below a critical size, which is the case of superparamagnetism (see Fig. 1.4). Superparamagnetic particles have no hysteresis,

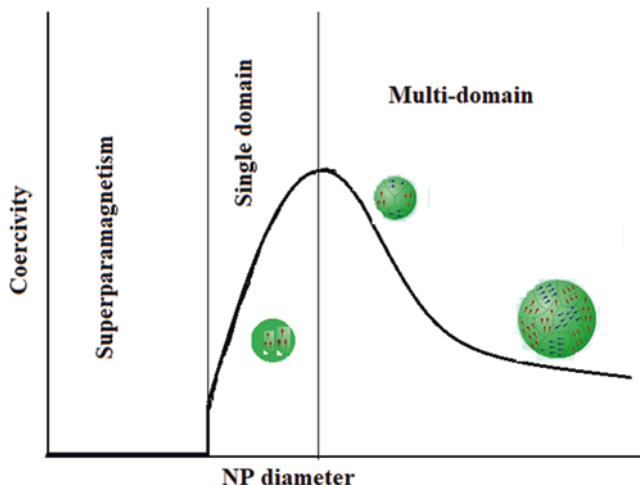


Fig. 1.4 Relation between the particle size and coercivity

meaning that zero coercivity due to the strong thermal fluctuation that demagnetizes any previous magnetic spin memory. This leads to thermal relaxation of the residual magnetization (M_r), $M_r = M_r(t=0)e^{(t/t_N)}$, where t_N is the Neel relaxation time. This introduces the fascinating property of the superparamagnetic NPs of losing magnetic memory after removing the external applied magnetic field, which give them the advantage of being introduced in biological systems. In some cases, small superparamagnetic particles are collectivized forming a cluster, where we can see a ferromagnetic behavior with hysteresis in the presence of magnetic field that is called superferrimagnetism, which is common in the multicore particles.

1.5 Applications

Magnetic NPs are promising in biomedical applications as magnetic hyperthermia, magnetic resonance imaging, drug delivery, etc. In this part, we will discuss in brief some of these applications.

1.5.1 Magnetic Hyperthermia

Hyperthermia is a type of treatment, where the body tissue is exposed to high temperatures that damage cancer cells, where tumor cells die at elevated temperatures from 42 °C to 46 °C. It is an efficient method in cancer treatment as it introduces a local heat and does not need surgery (Stauffer et al. 1982). Several methods have

been employed in hyperthermia as water baths and radiator applicators. However, these methods do not provide a precision of the supplied heat to the target area. The most common method is the capacitive heating using a radio-frequency electric field (Ikeda et al. 1994). This method is difficult in use due to the impact of released heat by tumor size and electrode position. Another efficient method in hyperthermia treatment is using magnetic NPs. Magnetic hyperthermia is a term used to describe the released heat by magnetic NPs due to application/removal of alternating magnetic field. The treatment starts with injection of the coated NPs in the blood stream near the tumor, where the NPs can stick (Montet et al. 2006). Then the NPs are exposed to an external alternating magnetic field for 15–60 minutes to maintain the temperature in the range of 42–46 °C (Shido et al. 2010). The released heat in case of magnetic NPs is described by the hysteresis loss (Andra et al. 1999). In detail, when ferromagnetic NPs are exposed to an alternating magnetic field, the particles are aligning themselves to match the magnetic field direction, and the energy used in the alignment is released during magnetic moment relaxation.

1.5.2 Magnetic Resonance Imaging

Traditional imaging modules, such as ultrasound, optical imaging, and X-ray tomography, lack the high resolution that is offered by the magnetic resonance imaging (MRI) (Estelrich et al. 2015). MRI is reconstructed due to the stimulation and the relaxation of hydrogen protons. It depends on the radio frequency of the applied magnetic field and records the relaxation time of protons in biomolecules for producing high resolution and contrast (Lam et al. 2013). To understand the concept of MRI, it is important to recall that human body consists of several hydrogen protons that spin around their axis. When there is an external applied magnetic field, the spin of these protons aligns themselves in the direction of the applied magnetic field. The sum of these magnetic moments forms a magnetization vector with two components with respect to the magnetic field direction, a parallel M_z component and a perpendicular M_{xy} component. It is worth to mention that not all spins are in the same phase but precess around the magnetic field axis (B_0) with Larmor frequency of $\omega_0 = \gamma B_0$. In radio frequency magnetic fields, protons are excited to higher levels due to energy absorption. Removing the radio frequency magnetic field relaxes protons to lower energy states. There are two types of relaxations, spin-lattice relaxation (T_{SL}) and spin-spin relaxation (T_{SS}). These two relaxations are constructed as gray scale images, and the contrast enhancement can be expressed as $R_i = 1/T_i = {}^0R_i + r_i C$, where R_i is the relaxation rate with a contrast agent, T_i is the relaxation time, 0R_i is the relaxation rate without a contrast agent, r_i is the relaxation constant, and C is the concentration of the contrast agent (Bjernerud 2008). Iron-based NPs are the most common NPs used as contrast agents in MRI because of several advantages as load ability and high magnetization with strong shortening effect on transverse relaxation time that leads to high contrast at low concentrations, where the relaxation of hydrogen protons can be affected by magnetic NPs.

1.5.3 Drug Delivery

Due to the high stability, magnetic NPs are widely used in drug delivery. Using magnetic NPs provides effective and safe way in drug delivery, where it avoids the side effects of the traditional chemotherapy (Wang et al. 2017). Drug transporter NPs interest with small size and large surface area, which protect them from degradation and increase the sedimentation time. However, several challenges are being faced by magnetic NPs in drug delivery to the target tissue in vivo systems such as the ability of crossing biological barriers of the vascular endothelium. Therefore, the efficiency of magnetic NPs depends on size, morphology surface chemistry, and charge. Large NPs with size greater than 200 nm can be prevented by the splenic macrophage cells, and small NPs with size less than 10 nm are easily removed by extravasation and renal clearance. Meanwhile, particles with size 10–100 nm are the optimum for injection. New incorporated doped and coated NP cores are modified to improve drug delivery and detection. Moreover, using new surface coating as gold or silica shell allows using some toxic NPs that have high magnetic moment. In addition, hollow structure microspheres as Fe_3O_4 coated by SiO_2 can load large amount of drug and it can be controlled by an external magnetic field.

1.5.4 Antimicrobial Agents

Silver NPs show antibacterial, antiviral, and antifungal properties (Aziz et al. 2015, 2016). For instance, they show inhabitation of negative and positive Gram bacteria as well as yeasts (Peiris et al. 2017), where silver NPs change the membrane permeability of the bacterial cell wall (Marambio-Jones and Hoek 2010) and the interaction of Ag NPs with the intercellular proteins leads to cell death (Chen and Schluesener 2008) and the bacterial replication is stopped due to the Ag release.

1.6 Conclusion

Magnetic nanoparticles are synthesized based on two approaches, the bottom-up and the top-down approaches, using different methods and techniques as the sol-gel and the ball milling. The magnetic properties of nanoparticles are sensitive to size, shape, morphology, and chemistry. Where the large-scale ferromagnetic material has a multidomain structure, but with decreasing size, it approaches the single domain structure with a change in magnetic properties. Any decrease in size below the single domain size leads to the superparamagnetism, where the nanoparticle shows high magnetization with zero coercivity that is suitable for magnetic

hyperthermia treatment. Magnetic nanoparticles have several applications as cancer treatment, magnetic resonance imaging, and drug delivery; however, the magnetic properties of nanoparticles can be tuned to suit the desirable application.

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Chapter 2

Bio-Based Synthesis of Magnetic Nanoparticles and Their Applications



Siavash Iravani

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2.1 Introduction

Green nanoscience and nanotechnology include different approaches which decrease or eliminate toxic substances to restore the environment. Green synthesis of nanoparticles (NPs) makes use of environmentally friendly, non-toxic, and safe components. The development of reliable, nontoxic, and eco-friendly methods for the synthesis of NPs is of extreme importance to develop their biomedical applications. Recently, industrial demands for magnetic NPs have increased due to their impact in many fields of applications, including drug delivery, magnetic resonance imaging (MRI), cell separation, antimicrobial activities, and hyperthermia treatment for cancer (Iravani 2011; Iravani et al. 2014a, b; Iravani and Zolfaghari 2013; Korbekandi et al. 2013; Korbekandi and Iravani 2013; Korbekandi et al. 2009, 2012). Many scientific types of research focus their attention on the biosynthesis and optimization of magnetic NPs (Sastry et al. 2003). Biological methods of nanoparticle preparation using microorganisms, enzymes, fungi, and plants or plant extracts have been reported as possible eco-friendly substitutes to chemical and physical methods (Prasad 2014; Prasad et al. 2016, 2018) (Fig. 2.1). For instance, one of the most well-known biological methods for the production of magnetic NPs is through magnetotactic bacteria. Magnetotactic bacteria are known to synthesize

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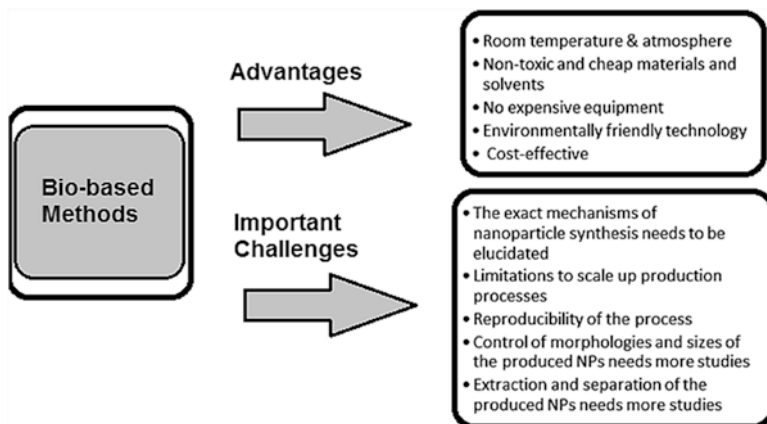


Fig. 2.1 Important advantages and challenges of bio-based methods

magnetite (Fe_3O_4) by a direct mechanism of mineralization. They produce intracellular magnetite (magnetosomes) of high purity and crystallinity, which shows consistent morphologies and narrow grain-size distribution that are within single domain size ranges. Moreover, green bio-based synthesis of magnetic NPs using inactivated plant tissue, plant extracts, exudates, and other parts of living plants has been reported (Biehl et al. 2018).

Important challenges associated with biosynthesis of NPs are tedious purification steps and poor understanding of the exact mechanistic aspects. In fact, in the bio-based synthesis of NPs, control of the morphologies of the NPs and monodispersity of the produced NPs in the solution phase are very critical. Technical challenges should be addressed before these approaches can be a successful and competitive alternative for industrial synthesis of NPs. Mechanistic aspects are necessary for the economic and rational development of nanoparticle biosynthesis. The important aspects which might be considered in the process of producing well-characterized NPs are as follows: (1) selection of the best organisms; (2) selection of the biocatalyst state; (3) optimal conditions for cell growth and enzyme activity; (4) optimal reaction conditions; (5) stabilization, extraction, and purification processes; and (6) scaling up the laboratory process. In fact, there are many scientific investigations carried out at research laboratories in small scale, but unfortunately, there are few reports on industrial-scale production of NPs using bio-based methods. Industrial-scale synthesis of metal NPs using biomass needs some processes, including seed culture, inoculation, harvesting the cells, synthesis of NPs by adding metal ions to the cells, separation of cells by filtration, homogenization of the cells to isolate the produced NPs, stabilization of the biosynthesized NPs, product formulation, and quality control. It should be noted that the rate at which particles are produced, size reproducibility, and ease of recovery are the key aspects for the mass production of magnetic NPs (Iravani 2011; Iravani et al. 2014a, b; Iravani and Zolfaghari 2013; Korbekandi et al. 2013; Korbekandi and Iravani 2013; Korbekandi et al. 2009, 2012).