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Review

Magnetic nanoparticles for environmental and biomedical applications: A review

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ABSTRACT

Engineered magnetic nanoparticles (MNPs) hold great potential in environmental, biomedical, and clinical applications owing to their many unique properties. This contribution provides an overview of iron oxide MNPs used in environmental, biomedical, and clinical fields. The first part discusses the use of MNPs for environmental purposes, such as contaminant removal, remediation, and water treatment, with a focus on the use of zero-valent iron, magnetite (Fe_3O_4), and maghemite (γ-Fe_2O_3) nanoparticles, either alone or incorporated onto membrane materials. The second part of this review elaborates on the use of MNPs in the biomedical and clinical fields with particular attention to the application of superparamagnetic iron oxide nanoparticles (SPIONs), which have gained research focus recently owing to their many desirable features such as biocompatibility, biodegradability, ease of synthesis and absence of hysteresis. The properties of MNPs and their ability to work at both cellular and molecular levels have allowed their application *in vitro* and *in vivo* including drug delivery, hyperthermia treatment, radio-therapeutics, gene delivery, and biotherapeutics. Physiochemical properties such as size, shape, and surface and magnetic properties as well as agglomeration of MNPs and methods to enhance their stability are also discussed.

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Introduction

Interest in nanotechnologies and nanoscale materials, particularly magnetic nanoparticles (MNPs), has grown recently and their applications have attracted the attention of both the research and industrial communities in the chemical, environmental and medical sectors. For example, MNPs have shown promising performance in pollutant removal or toxicity mitigation (Farmany, Mortazavi, & Mahdavi, 2016; Gavaskar, Tatar, & Condit, 2005; Grieger et al., 2010; Hu, Lo, & Chen, 2004; Hu, Chen, & Lo, 2005; Hu, Lo, & Chen, 2005; Li, Fan, et al., 2006; Li, Elliott, & Zhang, 2006b; Lu, Yu, & Cheng, 2015; Lu et al., 2016; Roth, Schwaminger, Schindler, Wagner, & Berensmeier, 2015; Roto, Yusran, & Kuncaka, 2016; Shen et al., 2009; Tratnyek & Johnson, 2006; Turcu et al., 2015; Wanna et al., 2016; Yantasee et al., 2007). Similarly, their effective application in membrane separation water treatment and purification processes has been demonstrated (Al-Hobaib, Al-Sheetan, & El Mir, 2016; Bagheripour, Moghadassi, Hosseini, & Nemati, 2016; Daraei et al., 2013; Ghaemi et al., 2015; Mukherjee & De, 2015; Ng, Lim, Ahmad, Ooi, & Low, 2015; Sabbatini et al., 2010; Yao, Choo, & Kim, 2009). In the medical fields, the inspiration for integrating nanotechnology has been expanding exponentially, particularly in the areas of drug delivery with the objective of directing the drug to the disease site with minimal side effects and reducing the dosage through more localized and efficient targeting. This involves magnetic drug targeting, whereby an external magnetic field gradient is applied at the target tissue to deliver the drug through active targeting using high-affinity ligand attachment, as well as therapeutic strategies (Bernkop-Schnurch & Walker, 2001; Chomoucka et al., 2010; Guduru et al., 2015; Li et al., 2016; Morrish, 2001; Pankhurst, Connolly, Jones, & Dobson, 2003; Qian et al., 2015; Rodzinski et al., 2016; Sun, Lee, & Zhang, 2008; Sun, Sun, Liu, Shen, & Jiang, 2016; Torchilin, 2006, 2009). This review will focus on the properties and recent development and applications of MNPs in the environmental and medical fields.

Magnetic nanoparticles

Structure and magnetic characteristics

Although there are many pure phases of iron oxide in nature, the most popular MNPs are the nanoscale zero-valent iron (nZVI), Fe_3O_4 and γ-Fe_2O_3. They possess different physicochemical properties originating from the difference in their iron oxidation states and their capability for contaminant removal. Among them, magnetite (Fe_3O_4), which is a ferromagnetic black color iron oxide of both Fe(II) and Fe(III), has been the most extensively studied. Magnetite is the preferred type because of the presence of the Fe^{2+} state with the potential of acting as an electron donor.

Fig. 1 shows the different magnetic states that occur during the crystallization of iron (Kodama, 1999; Teja & Koh, 2009). The paramagnetic crystal produces randomly aligned magnetic moments and the overall structure has zero net magnetization. When a paramagnetic state is subjected to an external magnetic field, the moments align to produce a small net crystal magnetization. At the ferromagnetic and antiferromagnetic states, the individual moments are randomly aligned without an external magnetic field.

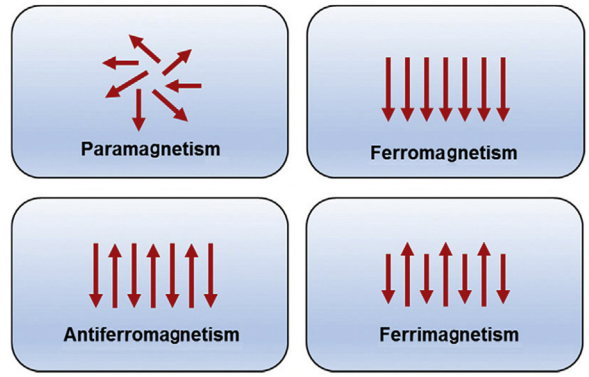

Fig. 1. Alignment of the magnetic moment of individual atoms of iron.

Bulk ferromagnets contain several magnetic domains in which uniformly magnetized regions exist. Each domain is separated by non-uniform magnetization distributions (domain walls) with different magnetization vectors. Because the vectors of each domain are not aligned, the net magnetization is low.

Many applications of magnetic nanoparticles rely on the use of magnetic fields to manipulate their properties, which depends on the effectiveness of the particle magnetic moment and the field gradient (Silva, Di Corato, Gazeau, Pellegrino, & Wilhelm, 2012). The force exerted upon single-core superparamagnetic nanoparticles is less effective owing to their small diameter and magnetic moment. However, in the case of multicore composites, the induced magnetic fields are high enough to allow magnetic targeting using moderate values of field intensity and gradient (Grześkowiak et al., 2015; Tombácz, Turcu, Socoliuc, & Vékás, 2015). The interaction between magnetic dipole–dipole and dipole–field may lead to clustering and formation of relatively large micrometer-sized linear aggregates with a drastic decrease in the specific surface area and potential clogging of blood capillaries (Socoliuc, Vékás, & Turcu, 2013; Tombácz et al., 2015).

Fabrication and modification methods

Fabrication and synthesis techniques of magnetic nanoparticle have been reviewed by many authors and there are excellent reviews available (Akbarzadeh, Samiei, & Davaran, 2012; Hajba & Guttman, 2016; Laurent, Bridot, Elst, & Muller, 2010; Reddy, Arias, Nicolas, & Couvreur, 2012). Although pure metals have favorable magnetic properties, their high toxicity and oxidative sensitivity make them unsuitable for biomedical use without proper treatment (Tran & Webster, 2010). The preparation methods used to produce MNPs can be divided into the following three categories (Reddy et al., 2012).

(1) Physical methods such as (a) size reduction to the nanometer range and dispersing in an aqueous medium using the classical colloidal routes and (b) condensation of the precursors from either a liquid or gaseous phase (Charles, 2002). The main drawback of the simple non-chemical "top-down" dispersion technique is the difficulty of producing the desired particle size and shape (DeCastro & Mitchell, 2002). However, a new laser

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