



Review article

Functional magnetic nanoparticle/clay mineral nanocomposites: preparation, magnetism and versatile applications



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ABSTRACT

Clay minerals and magnetic nanoparticles (MNP) combine to form a class of advanced nanocomposites that would possess exceptional magnetism, stability, adsorption, catalysis, and biocompatibility. This review summarizes and examines recent preparation strategies, properties and applications of magnetic nanoparticle/clay mineral (MNP/CM) nanocomposites. It is organized into five sections. The first section introduces the characteristics of magnetic nanoparticles, clay minerals and the scientific and technological necessity and significance of MNP/CM nanocomposites. The second section is concerned with the preparation of MNP/CM nanocomposites which involve the introduction of MNP into clay minerals via the coprecipitation of MNP and clay minerals, the combination of MNP and pillared clay minerals, the MNP-pillared clay minerals, the combination of surfactants coated MNP and clay minerals, and the intercalation of molecular magnetic compounds into clay minerals. In particular, great strides have been made in the integration of MNP with organo-clay minerals and the resultant nanocomposites can be assembled into the films of MNP/CM nanocomposite. The third focuses on discussion on the distinct magnetism, reactivity and stability of MNP/CM nanocomposites. The superparamagnetic MNP in MNP/CM nanocomposites show a fast response to external magnetic fields and allow MNP/CM nanocomposites to be readily manipulated, well functionalized and easily separated. The fourth section deals with the uses and potentials of MNP/CM nanocomposites in electromagnetic devices, magnetorheological fluids/ferrofluids, magnetic adsorbents, catalysts and biomaterials. The last section presents the view on the existing problems and challenges. Accordingly, it is suggested that future studies need place emphasis on narrowing the size distribution of the MNP/CM nanocomposites, endowing the MNP/CM nanocomposites with more functionalities, uncovering the preparation-modification-structure-magnetism-activity relationships of the MNP/CM nanocomposites, and advancing the practical applications.

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1. Introduction

Magnetic nanoparticles (MNP) have wide potential and practical applications in magnetic storage media (Frey et al., 2009), ferrofluid (Gao et al., 2010), magnetic hyperthermia (Laurent et al., 2011), catalysis (Leung et al., 2012), environmental remediation (Upadhyay et al., 2014), drug and gene delivery (Chourpa et al., 2005), cell separation (Xu et al., 2011), biomolecules targeting (Won et al., 2005), and magnetic resonance imaging (MRI) (Gupta and Gupta, 2005). Firstly, MNP possess a large specific surface on which a large proportion of atoms are exposed. Therefore, MNP have much higher surface energy than coarse particles. Secondly, the magnetic anisotropy energy significantly decreases when the dimension of the particles decreases to be on a nanometer scale. As a result, the energy of thermal motion of magnetic dipoles within MNP becomes larger than the magnetic anisotropy energy, until the thermal motion dominates the ordering of magnetic dipoles (Stavroyiannis et al., 1998). In other words, the energy of thermal motion of magnetic dipoles overcomes any preferential orientations of the magnetic moments of the nanoparticles. Consequently, MNP can exhibit superparamagnetic behavior which allows for a

reversible transition between a pseudoparamagnetic state and a pseudoferromagnetic state in an applied external magnetic field (Son et al., 2010). In addition, superparamagnetic MNP have a large constant magnetic moment and behave like a giant paramagnetic atom with a fast response to the applied magnetic field with negligible remanence and coercivity (Lu et al., 2007). Moreover, when the external magnetic field is removed, superparamagnetic MNP can retain negligible remanence and coercivity. These features allow MNP to be readily manipulated and separated.

However, naked MNP have some shortcomings in practice. For one thing, the aggregation of naked MNP is virtually unavoidable due to the high surface energy, van der Waals force and the dipole-dipole magnetic attraction among particles (Lu et al., 2007; Wang and Astruc, 2014). Even in an aqueous medium, the minimization of the Gibbs free energy and the hydrophobic surface of some MNP result in the aggregation of MNP (Durán et al., 2008; Pershina et al., 2014). When an external magnetic field is applied, the aggregation of MNP is aggravated (Lu et al., 2007). In addition, naked MNP is at the high risk of oxidation (McBain et al., 2008; Kalantari et al., 2014), acid/basic erosion (Pershina et al., 2014) and the release of metal ions (Singh et al., 2010). To tackle

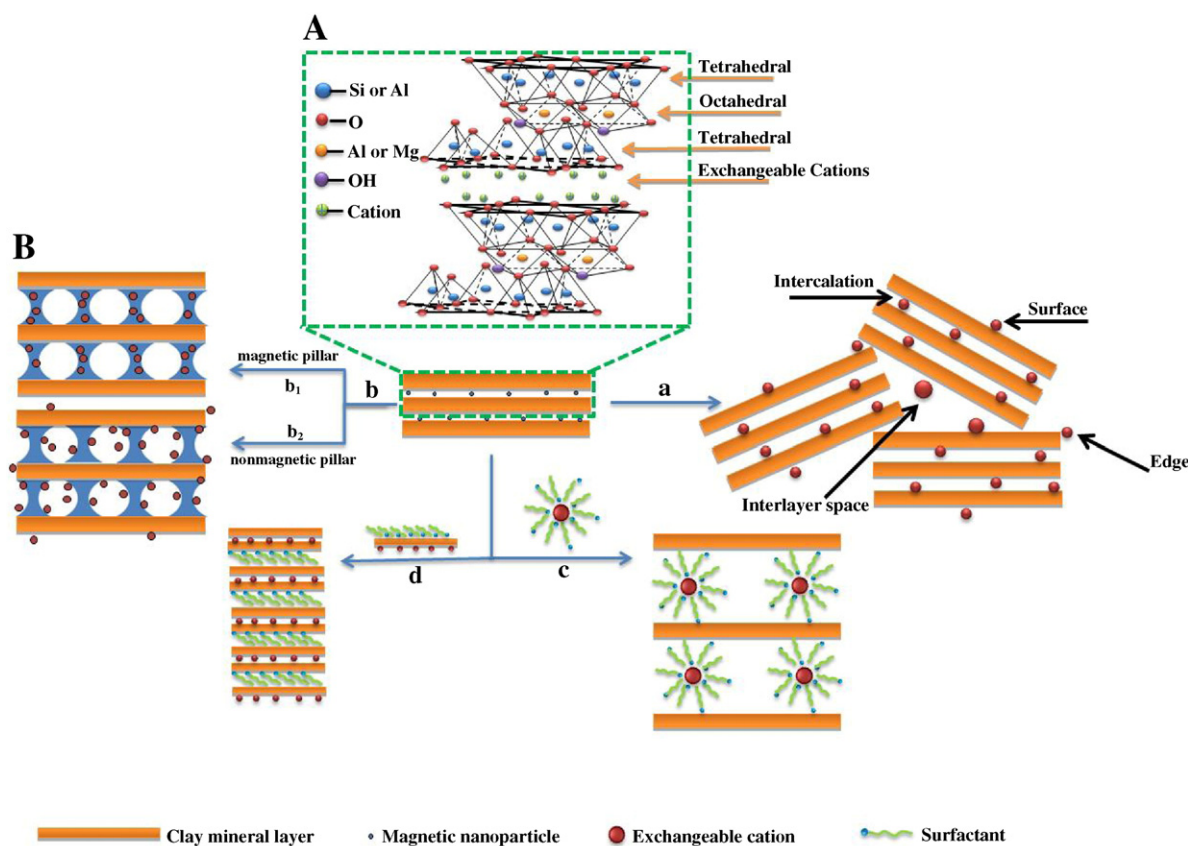


Fig. 1. (A) Schematic drawings of 2:1-type clay mineral. Depending on the clay mineral species, a small fraction of the tetrahedral Si atoms can be isomorphically substituted by Al and/or a fraction of the octahedral atoms (Al or Mg) can be substituted by atoms of lower oxidation number. (B) Typical routes to MNP/CM nanocomposites: (a) coprecipitation; (b) pillaring; (c) intercalation of surfactant modified MNP into clay mineral; (d) intercalation of MNP into surfactant intercalated clay mineral.

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