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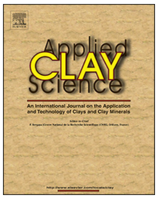

Research paper

Controllable synthesis of iron nanoparticles on polyethylenimine-modified montmorillonite: Dependence on the amine protonation extent

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ABSTRACT

This work looked at controllably synthesizing iron nanoparticles using borohydride solution reduction strategy with polyethylenimine-modified montmorillonite clay mineral as a host. In the hybridization process the protonation extent of polyethylenimine had vital but complex influence on the size, morphology, dispersion, distribution location, and even phase identity of the resultant iron particles. At the 90% protonation extent, optimized iron particles were obtained as nearly spherical smallest-sized core-shell entities (63 nm mean diameter) well dispersed on the external clay mineral surface, wherein the shell (amorphous iron oxide) preserved the core (polycrystalline metallic iron) from complete oxidation in air atomosphere. This regulation largely depended upon (a) the polymer interfacial conformation at clay mineral surface, (b) the relevant card-house-type pore feature, and (c) the complexation of the unprotonated polymer amino groups with the precursor ferric ions. The formation of the clay mineral card-house-type pore structure (in dry state) would be caused by washing and drying the electrostatic-steric stabilized polymer/clay mineral composite particles from the final dispersion under suitable conditions (with ethanol and acetone diluents and by vacuum-drying at 25 °C). In the hybridization system, besides the anticipated polymer-clay mineral electrostatic attraction, the hydrogen-bonding interactions of polyethylenimine with montmorillonite and iron particles were also detected.

1. Introduction

Montmorillonite, as a naturally occurring porous clay mineral material, has become an attractive host for various nanoparticles in terms of its unique layered structure, surface charge distribution, as well as cation-exchange, intercalation, and swelling properties (Bu et al., 2017; Fan et al., 2017). In an aqueous dispersion montmorillonite particles (arising from the uneven piling up of the clay mineral layers) possess permanent negative charges on the faces, while on the edges the charges are dependent on the dispersion pH (positive at acid pH and negative at basic pH) (Fan et al., 2017). Largely based on the surface charge heterogeneity, shape-anisotropic montmorillonite particles in colloidal systems present a rich phase behavior, of which the card-house assembly or floc as a porous host precursor has been attached special importance recently in the fields of organoclays, heterostructures, and nanocomposites (Yuan et al., 2006a, 2006b; He et al., 2010; Fan et al., 2011; Fan et al., 2017). As such, an in-depth insight into the structural property and formation mechanism of the card-house assembly is essential to optimize the related processes.

The isoelectric point of the edge is generally determined as pH 3.5–8 (Thomas et al., 1999; Lagaly and Ziesmer, 2003; Song et al., 2016). Thus, at the dispersion pH $<$ the edge isoelectric point the card-house is possible through the interparticle electrostatic attractions of the positively charged edges to the negatively charged faces (Van Olphen, 1951). But at the dispersion pH $>$ the edge isoelectric point all the particle surfaces are negatively charged and the interparticle electrostatic repulsions are dominant. The repulsions between neighboring particles force them to adopt more energetically favorable edge-to-face configurations, also leading to a card-house structure (Ginzburg et al., 2000). If the clay-clay interactions are mediated by introducing polymers, then the system tends to get complicated by additional clay-polymer and polymer-polymer interactions, of which the polymer induced bridging, electrostatic, steric, hydrophobic, and hydrogen-bonding effects are often involved. Generally, the electrostatic and/or steric repulsions between montmorillonite particles by the adsorbed polymer shells are favorable to the card-house formation; the repulsions are largely dependent on the polymer shell extension, which in practice can be adjusted by the adsorbed amount, molar mass, and chain conformation of polymers (Séquaris et al., 2000; Ramos-Tejada et al., 2001). Thus formed card-house structure is strongly featured by the

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position and orientation disorder of the clay mineral particles therein, typically in transmission electron microscopy images giving rise to disorganized dark bands that correspond to the particle edges facing up (Chatterjee et al., 2004). Besides, in the card-house structure the macro- and meso-porosities (mainly from the interparticle pores) are normally more enhanced than the micro-porosity (mainly from the intraparticle or interlayer pores), which would be an advantage for sorption and catalysis applications of the revelent products where mass transfer is important (Occelli et al., 1987).

Here, we extended our work about iron nanoparticles mediated by montmorillonite and polyvinylpyrrolidone (Fan et al., 2017) to a new iron nanoparticles/montmorillonite/polyethylenimine system for pursuing diversified and efficient manipulation strategy toward iron nanoparticle properties (mainly concerning the size, morphology, dispersion, distribution location, and phase identity), which would be very important to develop iron-based advanced composite materials and facilitate their theoretical and practical researches. Fundamentally, compared to the nonionic polyvinylpyrrolidone, the adopted polyethylenimine is a cationic polymer containing numerous amino groups that become increasingly protonated with decreasing pH (Wang et al., 2009). By the unprotonated amino groups with lone electron pairs on nitrogen, polyethylenimine is allowed to form complexes with a wide variety of transition metal cations (Dai and Bruening, 2002), and by the protonated amino groups with positive charges, polyethylenimine presents a strong electrostatic affinity to anionic materials including negatively charged inorganic solids (Chen and Kuo, 2006). In addition, the hydrogen-bond interaction between amino groups of polyethylenimine and other surface hydroxyls as well as the hydrophobic attraction between adsorbed polyethylenimine shells on solid particles in some cases cannot be ignored (Ramos-Tejada et al., 2006; Chen et al., 2016). Such that, a very different interaction fashion of polyethylenimine with montmorillonite and iron is expected from that of polyvinylpyrrolidone, which would profoundly affect the resultant materials in our new ternary system. With this system, we looked at growing and manipulating iron nanoparticles in a restricted environment provided by the amine-assisted clay mineral card-house-type pore structure. Specifically, the objectives of this work were to (1) synthesize Fe^0/Fe-oxide core-shell nanoparticles by reducing Fe^{3+} ions with $NaBH_4$ in solution adopting polyethylenimine-modified montmorillonite as a host, (2) derive a vital parameter (the polyethylenimine protonation extent) to facilitate the card-house-type assembling of montmorillonite particles and to achieve the property regulation of iron nanoparticles, and (3) elucidate the mechanisms behind the card-house formation and the nanoparticle regulation. To evaluate the resultant materials and explore the related mechanisms a combination of spectroscopic and microscopic techniques was used.

2. Materials and methods

2.1. Materials

The montmorillonite (Mt) used was purchased from Zhejiang Sanding Technology Co., China and the < 2 μm fraction was collected by sedimentation (about 96 mass% clay mineral and 4 mass% quartz by the auto-flushing method of Chung (1974)). Its composition from atomic emission spectrometric analysis was $Na_{0.82}Ca_{0.39}K_{0.12}(Si_{7.70}Al_{0.30})(Al_{2.84}Fe_{0.16}Mg_{0.79})O_{20}(OH)_4$ (ALS Chemex Guangzhou Laboratory, China) and the cation exchange capacity was 87 cmol(+)/kg determined by the ammonium acetate method (Fan et al., 2017). A branched polyethylenimine (PEI, molar mass 1800 g/mol, 99%) was supplied by Shanghai Aladdin Bio-Chem Technology Co., China and used as received. All other chemicals obtained from Shanghai Jiachen Chemical Co., China were of analytical grade, and deionized water was used throughout this work.

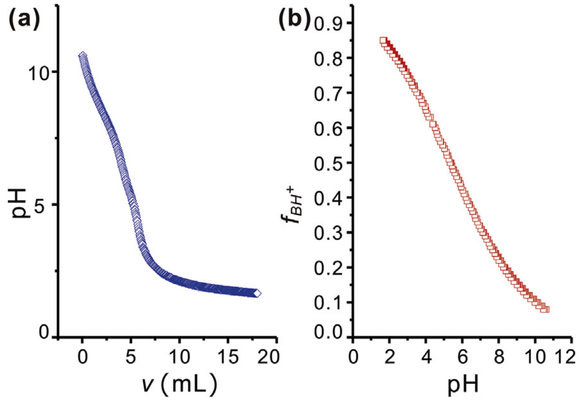

Fig. 1. Change of pH with the volume (v) of HCl titrated (a) and the dependence of the PEI protonation extent (f_{BH^+}) on pH (b).

2.2. Determination for protonation extent of PEI

The protonation extent of PEI (f_{BH^+}) at specific solution pH was determined by the potentiometric titration method of Suh et al. (1994) (Rex ZDJ-5 automatic potentiometric titrator using E-201-C pH combination electrode, INESA Scientific Instrument Co., China). In brief, the polymer (43 mg) was dissolved in water to 20 mL (initial pH 10.6), giving a concentration of 2.15 mg/mL or 0.05 resM (monomer residue molar concentration). Then, the solution was titrated with 0.1 mol/L HCl in small portions at 25 ± 0.5 °C controlled by a thermostatic waterbath pot (DK-S28, Shanghai Senxin Instrument Co., China). Fig. 1a shows the pH change with the added acid volume. After been treated by the following Eqs. (1)–(3), the titration data gave about the pH-dependent f_{BH^+} values (see Fig. 1b):

$$v = v_0 \frac{[H^+] + [P]_0/(1 + [H^+]^{-a}10^b) - K_W/[H^+]}{[HCl]_0 + K_W/[H^+] - [H^+]} \tag{1}$$

$$\log Q = a \times pH + b \tag{2}$$

$$f_{BH^+} = \frac{1}{1 + Q} \tag{3}$$

where v is the volume (in mL) of the HCl solution added to the amine, v_0 the initial volume (20 mL) of the amine solution, $[P]_0$ the initially added total amine concentration in resM (0.05), $[HCl]_0$ the concentration (0.1 mol/L) of the HCl solution, K_W the ionic product of water at 25 °C (1.01×10^{-14}), and Q the deprotonation quotient linearly related to pH. The values of a (0.203) and b (−1.087) were calculated by nonlinear regression of the data points performed with Eq. (1).

2.3. Synthesis of PEI-modified Mt

An amount of 5.0 g Mt was dispersed vigorously into 500 mL of water. Then to the dispersion partially protonated amine was added and kept stirring for 5 h. The amine was prepared by adjusting the pH (10.0, 7.2, 5.3, 3.6, or 1.6 corresponding to the protonation extent about 10, 30, 50, 70, or 90%, respectively, see Fig. 1b) of the polymer solution with 0.1 mol/L HCl (2.15 g PEI in 1000 mL final solution, initial acid-free solution pH 10.6). All the operations were carried out at 25 ± 0.5 °C with thermostatic waterbath. After that, the resultant slurry was separated by centrifugation, washed several times with water, and then vacuum dried overnight at 25 °C. Thus obtained binary composite was designated as Mt/PEI (n), where n denotes the protonation extent of the added amine. For instance, Mt/PEI (n = 10%) was from the 10% protonated polymer modified clay mineral.