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Core–shell structured iron nanoparticles well dispersed on montmorillonite

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ABSTRACT

Iron nanoparticles have been successfully synthesized using sodium borohydride solution reduction of ferric trichloride hexahydrate in the presence of montmorillonite as an effective protective reagent and support as well. A combination of characterizations reveals the well disperse of these obtained iron nanoparticles supported on the external surface of clay with roughly spherical morphology and mean diameter of 55 nm. The particles are oxidation resistant well with iron core–iron oxide shell structure. The shell thickness of 3 nm remains almost invariable under ambient conditions. Discernable hysteresis loop reveals ferromagnetic behavior of the iron nanoparticles, which make them easy for magnetic separation and potential in some practical applications.

1. Introduction

Novel quantum size-dependent physicochemical properties make metallic iron nanoparticles of great potential in a wide range of applications including magnetic recording media [1], ferrofluids [2], magnetic resonance imaging contrast agents [3], heterogeneous catalysts [4], and environment remediation [5–7]. Different strategies have been so far reported for synthesizing iron nanoparticles. Chemical reduction of iron salts with borohydrides in solution among these reported methods shows some prominent advantages such as safety, simplicity, low cost, and feasibility in most laboratories. However, a disadvantage of this method is that the iron product strongly depends on the preparation conditions. Almost any changes in the preparation procedure might have obvious influences on the resultant product. In addition, this method is prone to introduce impurity of boron into iron product. For example, some previous studies have revealed the occurrence of the invasion of boron invading into iron crystal lattice [8,9]. The borohydride reduction method is also limited by ease to oxidize and addiction to aggregate of iron nanoparticles.

The oxidation of iron nanoparticles is conventionally minimized under vacuum condition or in inert atmosphere. Attempts to form shell coating iron core have also been applied to protect the iron core from further oxidation. The shell can be composed of different materials, among which the native iron oxide is attractive and intensively studied for its almost unavoidable formation and high efficiency to suppress oxidation of iron core [10–13]. The aggregation of iron nanoparticles can be largely inhibited by dispersing them with organic or inorganic protective reagents. Compared with polymer or surfactant protective reagents, inorganic chemically inert ones such as clay minerals are more cost-effective and environment-friendly. Furthermore, they can also act as supports to facilitate reuse and recycling of nanoparticles. Of such clay minerals, montmorillonite (Mt) is often used as an effective protective reagent and support as well. Mt is a naturally occurring 2:1 type layered alumonosilicate with turbostratic structure [14], in which each layer comprises an alumina octahedral sheet sandwiched between two silica tetrahedral sheets, and the layer has a permanent negative charge resulting from isomorphous substitution occurring mainly in the octahedral sheet. Such layers are stacked by weak dipolar or Van der Waals forces, leading to the intercalation of charge compensating cations into the interlayer space and causing Mt to be easily expanded along the *c*-direction. Therefore, not only adsorption on the external surface but also intercalation into the interlayer space can occur [15]. Accordingly, in the case of nanoparticles generation using the borohydride reduction method, two reaction sites from the external surface and the interlayer space are available in Mt. Many efforts for synthesizing nanoparticles by borohydride

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reduction resort to Mt to inhibit particle agglomeration and to act as a support. However, might be due to the complications of the borohydride reduction method itself, few studies as we know are available related to the generation of iron nanoparticles using borohydride solution reduction in the presence of Mt.

Here we present our results obtained from synthesizing nanoscale metallic iron nanoparticles well dispersed on Mt using sodium borohydride reduction in solution. The iron core–iron oxide shell structure of the resultant particles and their magnetic behavior are also investigated.

2. Experimental

Raw Mt sample obtained from Inner Mongolia, China was purified by sedimentation and the fraction less than 2 μm was collected. The Mt fine fraction was then ion-exchanged with NaCl solution to obtain Na^+–montmorillonite (Na^+–Mt). Some Mt fine fraction (6 g) was dispersed in 400 ml aqueous acetone solution (50% v/v) and then treated with 600 ml aqueous NaCl solution (0.2 M) at 80 °C for 24 h according to the literature method [15] with some modifications. The cationic exchange capacity (CEC) of these obtained Na^+–Mt was determined according to the ammonium acetate saturation method [16] and was found to be 111.1 mmol/100 g. The Na^+–Mt was used as protective reagent and support for the synthesis of iron nanoparticles. $FeCl_3 \cdot 6H_2O$ and $NaBH_4$ available locally were all of analytical grade and used as received. Distilled water was used throughout this work.

Iron nanoparticles were synthesized using the modified version of Wang and Zhang [5]. Typically, Na^+–Mt (1.0 g) was stirred in 50 ml water for 24 h, then $FeCl_3 \cdot 6H_2O$ (corresponding to 6 CEC of Na^+–Mt) was added to the aqueous clay suspension. The mixture was stirred for another 24 h and then 50 ml freshly prepared $NaBH_4$ solution was dropwise added under stirring. The molar ratio of borohydride to ferric iron was 4:1. After $NaBH_4$ was added the solution turned to black, indicating the reduction of ferric iron. All the experiments were carried out at room temperature and no precautions were taken to eliminate oxygen from the reaction vessel. After several centrifugation/redispersion cycles in 50% v/v aqueous ethanol solution then in acetone, the final product was vacuum dried at 60 °C for 24 h. Reference iron particles were prepared with the same procedure mentioned above except the absence of clay.

Element analyses were performed on a Varian Vista-Pro inductively coupled plasma optical emission spectrometry (ICP-OES). Crystal phases were identified by X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer using CuKα radiation. Microstructure characterization and particle size determination were carried out by a combination of a 100 kV JEOL JEM-100CXII transmission electron microscope (TEM) attached an electron diffractometer, a 200 kV JEOL JEM-2100 high-resolution transmission electron microscope (HRTEM), and a 5 kV FEI-Sirion 200 field emission scanning electron microscope (FESEM) attached an Oxford INCA energy dispersive X-ray spectroscopy (EDX). Magnetic behavior was measured using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

The reference iron nanoparticles generated in homogeneous solution in the absence of Mt are roughly spherical and connected in chains of about 80 nm in width as shown in Fig. 1a. The chain-like morphology of iron particles caused by magnetostatic attraction are also reported in literature [17,18]. The α-Fe phase present in the XRD pattern (Fig. 2a) reveals the metallic nature of the particles, and the existence of iron oxide is also observed. This indicates the existence of the iron core–iron oxide shell structure of the reference particles. The iron oxide might be magnetite and/or maghemite. The two oxides have similar lattice constants. So, they are not easily distinguished by XRD. Exact identification of the two oxide phases by Mössbauer spectroscopy is being conducted.

No boron is detected by EDX analysis as shown in Fig. 1b. The absence of boron signal may be due to the trace amount or the separating state of the element. The lattice constant of the reference iron $a = 2.866$ Å, refined by least square fit following the TREOR algorithm, shows negligible variation to the reported value of bcc structured α-Fe (JCPDS No. 06-0696). This coincidence prefers that boron segregates in a separating state from the iron product. Similar result has also been reported by Corrias et al. [19]. As mentioned above, some previous studies have revealed the possibility of boron invading into the crystal lattice of iron [8,9]. The difference between this study and the previous ones might be attributed to the different experimental conditions adopted, respectively. In particular, we adopted the borohydride to iron molar ratio of 4:1 as recommended by Wang and Zhang [5], which is suitable for generating iron nanoparticles. The ratio of 4:1 adopted in this study is less than that adopted by Zhang and Manthiram [8]. In their study a borohydride to iron molar ratio of about 12:1 was adopted, if the Mt CEC value could be considered as 100 mmol/100 g typical for this type of clay. The decrease of the ratio indicates less borohydride used in this study, which might reduce the chance of boron incorporating into iron crystal lattice. The iron and oxygen signals in the EDX analysis are from the

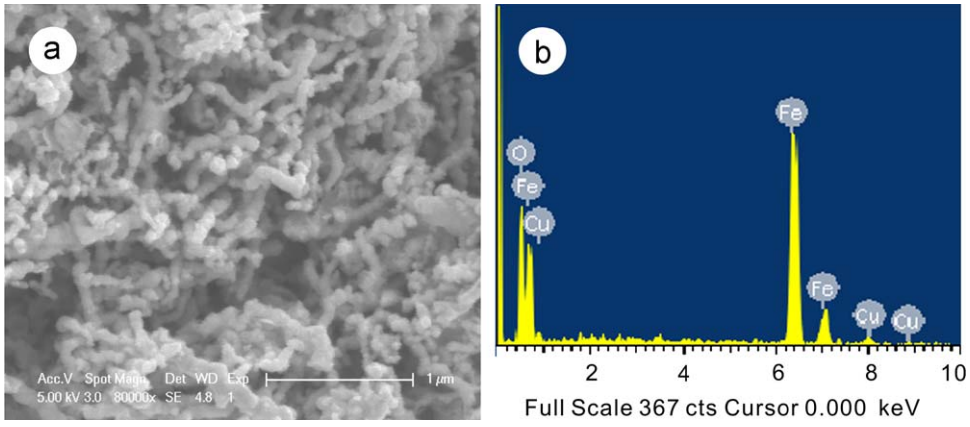

Fig. 1. (a) FESEM image of iron nanoparticles obtained using borohydride solution reduction of ferric iron salt in the absence of montmorillonite. Chain-like morphology from magnetostatic attraction of the particles is clearly revealed. EDX result is shown in (b).