Monodisperse single-crystal mesoporous magnetite nanoparticles induced by nanoscale gas bubbles

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Abstract Monodisperse single-crystal mesoporous magnetite nanospheres with particle size of \( \sim 100 \) nm and pore size of 7.6 nm were synthesized through a solvothermal process. Transmission electron microscopy images clearly show the mesoporous structure of the products. Nitrogen adsorption–desorption data confirmed that the pore size is in the range of mesoscale. Based on the evolution experiments, a plausible mechanism was proposed including a gas bubble induced mesoporous structure formation process. The mesoporous magnetite nanospheres show high magnetization value, which resulted from the single crystalline structure, as confirmed by the high-resolution transmission electron microscopy data. By simply decreasing the concentration of ammonium acetate, magnetite hollow spheres or aggregated nanoparticles could be obtained. This work may provide new advances in the approaches to fabricate magnetite with different interior structures.

Keywords Nanobubbles · Magnetite · Mesoporous · Single-crystal

Introduction

Synthesis and assembly of porous materials has attracted considerable attention for their applications in the fields of sensors, catalysis, and drug delivery (Lou et al. 2008; Zeng 2006; Trewyn et al. 2007; Tiemann 2007; Zhang et al. 2009). Most of the porous structures are based on silicon-containing materials. However, some important transition metal oxides (such as \( \text{Fe}_3\text{O}_4 \), \( \text{Co}_3\text{O}_4 \), \( \text{TiO}_2 \), etc.) have also been fabricated in the past decade (Lu and Schuth 2006; Tian et al. 2004; Li et al. 2009; Liu et al. 2009a; Dong et al. 2011). To date, various interior porous architectures including simple hollow spheres, core–shell and mesoporous structures for metal oxide have already been constructed (Liu et al. 2004; Suh et al. 2006, Sun et al. 2011).

Designing nanoscale pores into magnetic materials has attracted intense interest for enhanced performance in the field of absorbent, efficient catalysis, magnetic driven drug delivery system, etc. (Caruso et al. 2001; Andersson et al. 2007; Cao et al. 2008). In particular, mesoporous \( \text{Fe}_3\text{O}_4 \) have been prepared by different methods in recent years. Jiao and co-workers fabricated the mesoporous iron oxide using three-dimensional mesoporous silica (KIT-6) as a hard template (Jiao et al. 2006). Xia et al. fabricated the magnetite porous materials with polymer surfactants as soft templates (Xia et al. 2009). Kwak group recently reported mesoporous magnetite using triblock copolymer (PEO100-PPO65-PEO100) micelles as...
pore-forming template (Yu and Kwak 2010). Guo et al. (2009) prepared mesoporous magnetite particles with a similar-surfactant structure worked as soft template. These template methods usually include some complicated processes such as repeat treatments with corrosive solution or calcinations at high temperatures to remove the template.

Gas bubble induced porous structure has been emerged as a facile and environment-friendly method to introduce pores into materials (Craig 2011). N₂, Ar, or N₂/CO₂ have been used as the gas bubble to induce the formation of expected hollow structured from ZnSe, Fe₃O₄, or CaCO₃ materials, respectively (Peng et al. 2003; Lynch et al. 2011; Han et al. 2009). In this study, ammonia gas produced from our reaction system was used as a template to fabricate mesoporous Fe₃O₄ nanospheres. By simply adjusting the concentration of the reaction materials (ammonium acetate), appropriate amount of ammonia gas could be released and worked as the templates to form the mesopores in the magnetite spheres. Compared with the conventional template method, this simple gas-bubble template approach may be more convenient. Magnetite hollow spheres or magnetite nanoparticles could also be fabricated by decreasing the ammonium acetate concentration.

**Experimental**

Preparation of magnetite nanoparticles

Ferric chloride hexahydrate (FeCl₃·6H₂O, extra pure) was purchased from Junsei Chemical Co., Ltd. Ammonium acetate (NH₄Ac, >98 %) and ethylene glycol (EG, >99 %) were purchased from Aldrich. All chemicals were used as received. Magnetite products were prepared through a solvothermal reaction. For a representative synthesis, 5 mmol of FeCl₃·6H₂O was dissolved in 60 mL of ethylene glycol with stirring to form a clear homogeneous solution, followed by the addition of 0.1 mol of NH₄Ac (1.67 mmol/L). The mixture was stirred vigorously until it became homogeneous and then was sealed in a Teflon-lined stainless steel autoclave (100 mL capacity). The autoclave was heated to 200 °C and maintained 12 h, and then it was cooled to room temperature. The black precipitate was collected by magnetic separation and sequentially rinsed for five times with ethanol and five times with water under ultrasonication to remove the solvent thoroughly, and then dried in a vacuum oven at 60 °C for 12 h.

Sample characterization

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 2010 microscope operating at 200 kV accelerating voltage. Scanning electron microscopy (SEM) images were taken by a field emission scanning electron microscope (FE-SEM; Philips XL30SFE and Hitachi S-4800). A thin gold film was sprayed on samples before measurements. For the particle size estimation, over 100 particles on the SEM images were averaged. Nitrogen adsorption measurements were performed on an ASAP 2010 volumetric adsorption analyzer (Micromeritics, Norcross, GA, USA) at 77 K. Brunauer-Emmett-Teller (BET) method was utilized to determine the surface area. Pore size distribution was calculated using the adsorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. Powder X-ray diffraction (XRD) patterns were recorded using a Philips diffractometer with a Geiger counter. The X-ray tube was operated at 40 kV and 30 mA (Cu Kα radiation with Ni filter, λ = 1.5406 Å). Magnetization of nanoparticles was measured using a superconducting quantum interference device (SQUID, MPM5-XL-5). XPS spectrum was obtained using a VG Scientific ESCALAB 250 XPS spectrometer with a monochromatic Al Kα source including charge compensation at Korea Basic Science Institute (KBSI) (Busan, S. Korea).

**Results and discussion**

Mesoporous Fe₃O₄ was synthesized using FeCl₃·6H₂O as iron source, ammonium acetate as alkalinity source, and ethylene glycol (EG) as reductant agent and reaction medium. TEM images (Fig. 1a, b) show a clear heterogeneous phase, which was associated with the porosity of the analyzed particles. More detailed information was acquired using high-resolution TEM images. The parallel lattice fringes across the whole particle are clearly visible (Fig. 1c), which confirmed perfectly oriented attachment from Fe₃O₄ nanocrystals and the high crystallinity of the materials (Oskam et al. 2003). The lattice fringes observed in the image
are about 0.48 nm, which agrees well with the separation between the (111) lattice planes (Deng et al. 2005). High crystallinity of the as-prepared product was further confirmed by the XRD pattern with sharp and intense peaks (Fig. 2a). The nature of Fe₃O₄ was checked by XPS spectra, in which the photoelectron peaks at 711.1 and 724.5 eV are the characteristic doublet of Fe 2p₃/₂ and 2p₃/₂ core-level spectra of iron oxide, respectively, which is consistent with the oxidation state of Fe in Fe₃O₄ (Fig. 2b) (Teng et al. 2003). SEM images (Fig. 3) show that the Fe₃O₄ particles are monodisperse and have a spherical shape with the average diameter of about 100 nm.

Mesoporous structure of the nanospheres was substantiated by the measurement of nitrogen adsorption–desorption isotherms and the Barrett–Joyner–Halenda pore size distributions (Fig. 4). The type of isotherm in Fig. 4a is presented in a boundary between

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**Fig. 1 a TEM image, b enlarged TEM image, and c high-resolution TEM image of the Fe₃O₄ mesoporous nanospheres synthesized with 0.1 mol of NH₄Ac. The parallel lattice fringes across the whole particle can be observed clearly.**
type IV and type V with an apparent hysteresis loop in the range 0.6–1.0 \( P/P_0 \). Combining with the TEM data, the presence of mesopores could be reconfirmed.

In Fig. 4b, the peak at around 7.6 nm could be assigned to the textural mesopores of the \( \text{Fe}_3\text{O}_4 \) nanospheres, which is in good agreement with the TEM observation.

To investigate the formation process of the mesoporous structure, evolution experiments were carried out and the intermediate products at different stages (3–12 h) were studied by TEM and SEM techniques (Fig. 5). With reaction time for 2 h, no precipitation from the orange solution (iron acetate) was observed. When reaction time was increased to 3 h, small primary particles aggregated into loosely nanoclusters (Fig. 5a, d). Further prolonging the time to 4.5 h, mesopore can be seen in the nanospheres (Fig. 5b, e). Finally, at the time of 12 h, the well-formed mesoporous structure and the spherical morphology are observed in Fig. 5c, f. The crystallinity of the particle becomes higher with increasing the reaction time, which can be demonstrated by XRD patterns (Fig. 6).

Based on the above results, we offered a plausible mechanism involving the nanocrystals aggregation and recrystallization process. At room temperature, acetate groups can coordinate with iron to form iron acetate, which is confirmed by the color change to deep brown with the addition of ammonium acetate. With increasing temperature, iron ions were released and reduced to form the primary \( \text{Fe}_3\text{O}_4 \) nanocrystals (Liu et al. 2009b). These nanocrystals have a tendency to aggregate together, and at the same time, lots of nanobubbles of \( \text{NH}_3 \) are produced from the ammonium acetate hydrolysis, then the loose nanoclusters are formed as shown in Fig. 5a. Because of the high ammonia concentration and the high viscosity EG medium, the gas bubbles could coexist with nanocrystals in the clusters. These nanoscale ammonia gas...
Fig. 4  a N\textsubscript{2} adsorption–desorption isotherm and b the corresponding pore size distribution of the Fe\textsubscript{3}O\textsubscript{4} mesoporous nanospheres synthesized with 0.1 mol of NH\textsubscript{4}Ac

Fig. 5  SEM (a–c) and TEM (d–e) images of the Fe\textsubscript{3}O\textsubscript{4} products collected at different reaction time: a, d 3 h; b, e 4.5 h, and c, f 12 h synthesized with 0.05 mol of NH\textsubscript{4}Ac at 200 °C. All scale bars are 50 nm. Using FeCl\textsubscript{3}-6H\textsubscript{2}O and NH\textsubscript{4}Ac as starting materials and EG as reaction medium, the magnetite materials were prepared at 200 °C by undergoing two steps: nucleation (nanocrystal formation) and crystals growth (aggregation and mesopores completion process)
bubbles entrapped in the cluster and remained in the new-formed particles through the recrystallization process and finally became the interior pores of the particles (Fig. 5f). As SEM images shown in Fig. 5a–c, the surfaces clearly become smoother with increasing reaction time, further confirming the nanocluster recrystallization process. This bubble-assisted oriented attachment process can be depicted by the cartoon in Fig. 5, which represents that the magnetite materials undergo two steps: nucleation (nanocrystal formation) and crystals growth (aggregation and mesopores completion process).

It was found that enough high concentration of ammonium acetate is necessary to generate mesoporous structure. Abundant ammonia gas bubbles is the key point to form the mesopores and enough high alkalinity is crucial for the oriented attachment process. In a control experiment, when the ammonium acetate quantity decreased to 0.02 mol, only simple hollow spheres were obtained (Fig. 7a). Generally, it was thought that the gas bubble worked as the center, on which the nanocrystals grew to form the big hollow spheres (Peng et al. 2003; Hu et al. 2009). This gas-centered process can be supported by the HRSEM image (Fig. 7b), from which the wormlike particles in the interior were thought to be coming from the dissolution of the gas (Han et al. 2009). Further decreasing the concentration of ammonium acetate (0.01 mol) just leads to the aggregated magnetite nanoparticles, as shown in the TEM and SEM images (Fig. 7c, d).

**Fig. 6** XRD patterns of the Fe$_3$O$_4$ products collected at different reaction time. a 3 h, b 4.5 h, and c 12 h

**Fig. 7** a, b SEM and enlarged SEM images of the Fe$_3$O$_4$ product prepared with 0.02 mol of NH$_4$Ac. c, d SEM and TEM image of the Fe$_3$O$_4$ product prepared with 0.01 mol of NH$_4$Ac.
To investigate the magnetic properties of the products, magnetization curves were obtained by measuring with a superconducting quantum interference device. As shown in Fig. 8, all samples exhibit superparamagnetic behavior without obvious hysteresis loop. The magnetite nanospheres dispersed in ethanol were homogeneously suspended before applying the magnetic field. However, the nanoparticles were attracted and moved to the side near the magnet within 15 s, indicating the rapid magnetic response. In fact, the saturation magnetization (Ms) values of the Fe$_3$O$_4$ nanoparticles are 105.8, 98.1, and 89.1 emu/g for products prepared with the ammonium acetate amount of 0.1 mol (1.67 mM), 0.05 mol (0.83 mM), and 0.02 mol (0.33 mM), respectively. The Ms values are high, which would attribute to the high purity and good crystallinity of our products (Pinna et al. 2005). Also, the material synthesized with higher ammonium acetate content has much higher Ms value as 105.8 emu/g than the conventional one prepared using sodium acetate (i.e., 89.1 emu/g) (Deng et al. 2005), which should attribute to the fact that higher alkalinity facilitated the crystallization (Zhao et al. 2009).

**Conclusion**

In summary, we have proposed a gas bubble induced formation mechanism for fabrication of mesoporous Fe$_3$O$_4$ nanoparticles. The evolution experiment demonstrated a nanocrystal aggregation and bubble-assisted recrystallization process. It is found that enough high concentration of ammonium acetate is necessary for producing ammonium bubbles to form the mesopores in magnetite nanospheres. Interestingly, by decreasing the amount of ammonium acetate, the simple hollow spheres and tiny aggregated particles could be also prepared facilely. Both mesoporous and simple hollow spheres show superparamagnetic behavior and strong magnetic response with higher saturation magnetization value compared with the materials without using ammonium acetate. Other metal oxide materials with mesoporous or hollow structure will be fabricated via this new approach involving the gas bubble induced mesopores process. The high Ms value combined with the unique interior structure would make the magnetite as ideal candidates for targeted drug delivery system, where the particles can be directed by an external magnetic field.
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References


