



A facile hydrothermal synthesis of porous magnetite microspheres

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ABSTRACT

Porous magnetite (Fe_3O_4) microspheres can be direct acquired by hydrothermal reaction of Fe-citrate complex ($\text{Fe}(\text{NH}_4)_2\text{H}(\text{C}_6\text{H}_5\text{O}_7)_2$) in neutral solution. Results show that the obtained Fe_3O_4 particles are nearly spherical in shape and about $2\ \mu\text{m}$ to $3\ \mu\text{m}$ in mean diameter. Every magnetite microsphere is made of many ultrafine Fe_3O_4 nanoparticles and porous in structure. The as-prepared porous magnetite microspheres have higher surface area ($\sim 83\ \text{m}^2/\text{g}$) and excellent magnetic properties ($M_s = 81\ \text{emu/g}$, $H_c = 145\ \text{Oe}$) at room temperature.

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1. Introduction

Magnetite FCC- Fe_3O_4 (space group: $Fd-3m$) has become the focus of renewed technological interest in magnetic and electronic applications, such as spintronic devices [1,2]. In past decades, magnetite (Fe_3O_4) nanoparticles have been produced via coprecipitation of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions by a base, usually NaOH, or $\text{NH}_3\cdot\text{H}_2\text{O}$, in an aqueous solution [1–4]. It is a simple method for obtaining Fe_3O_4 materials. However, the value of $\text{Fe}^{2+}/\text{Fe}^{3+}$ cannot be accurately controlled due to the reduction of Fe^{2+} in reaction system. In addition, using some reducing agents such as ethylene glycol (EG)[5–8], diethylene glycol (DEG) [9], aspartic acid (AA) [10], carbon monoxide (CO) [11], diamine hydrate ($\text{H}_4\text{N}_2\cdot\text{H}_2\text{O}$) [12,13], oleylamine (OAm) [14] and electron [15], Fe^{3+} ions can be partially reduced into Fe^{2+} ions and subsequently coprecipitated to obtain magnetites. However, the authors [5] have emphasized that Fe^{3+} could not be reduced to Fe^{2+} by EG alone and sodium acetate (NaOAc) is indispensable to mediate reduction progress. This partial reducing and coprecipitating method has also limitation due to difficulty to insure the right ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ which influences the purity of the final product. Most importantly, the magnetites obtained by the above method are usually single-crystal magnetite microspheres [5] or large single-crystal clusters [8,9] or single crystalline octahedron-shaped magnetite nanoparticles [16] which are all not porous ones.

Recently, sonochemical method has been successfully used to fabricate ZnO hollow microspheres [17] and CuO hollow architectures [18] in our previous work. In the present work, we show that Fe_3O_4

porous microspheres can be prepared by a simple hydrothermal method using iron (III) citrate complex ($\text{Fe}(\text{NH}_4)_2\text{H}(\text{C}_6\text{H}_5\text{O}_7)_2$) as a precursor. The main advantages of this method are (1) the preparation procedure of Fe_3O_4 micropowder is simple, (2) the precursor, $\text{Fe}(\text{NH}_4)_2\text{H}(\text{C}_6\text{H}_5\text{O}_7)_2$, a nontoxic material, can be easily synthesized from readily available $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ or $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and trisodium citrate (Na_3Cit), (3) trisodium citrate (Na_3Cit) can completely reduce Fe^{3+} to Fe^{2+} , and (4) the solvent, H_2O , is an environment-friendly and most commonly used solvent.

2. Material and methods

The porous magnetite microsphere was prepared as follows. In a typical preparation, firstly, 0.01 mol $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and 0.02 mol trisodium citrate (Na_3Cit) were added to 100 ml beaker with 60 ml deionized water and continuously stirred for 10 min to form a homogeneous fawn solution. Then, the pH value of the above solution was adjusted to 7 by adding proper ammonia ($\text{NH}_4\cdot\text{H}_2\text{O}$). Finally, the colloidal solution was transferred into to a 100 ml Teflon-lined autoclave and maintained at $200\ ^\circ\text{C}$ for 24 h. After cooling to ambient temperature naturally, the solid black products or magnetic powders in the autoclave were collected by a magnet, ultrasonically rinsed for several times in deionized water and ethanol, respectively, and finally dried in a vacuum oven at $80\ ^\circ\text{C}$ for 4 h.

X-ray diffraction (XRD) patterns were measured on a Philips X'pert diffractometer using $\text{CuK}\alpha$ radiation (0.15419 nm). Morphology of the products was observed on a Sirion 200 FEG field emission scanning electron microscope (FESEM). High resolution transmission electron microscopic (HRTEM) examination was conducted on a JEOL-2010 microscope attached with an energy-dispersive x-ray spectrometer

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(Oxford, Link ISIS). Nitrogen adsorption isotherms were measured at 77 K on Micrometrics ASAP 2020 equipment. Magnetization measurements were carried out on a superconducting quantum interference device (SQUID) at room temperature.

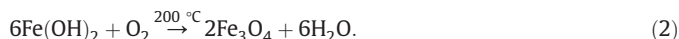
3. Results and discussion

After the precursor solution was heated at 200 °C for 24 h, the black powders were collected by a magnet. The corresponding x-ray diffraction (XRD) is illustrated in Fig. 1. The diffraction peaks match well with the standard values of Fe₃O₄ (JCPDS NO. 89-4319), indicating that the as-prepared products are Fe₃O₄ phase.

Field emission scanning electron microscopic (FESEM) observations have shown that the obtained Fe₃O₄ is of collective-like morphology with nearly spherical shape, as illustrated in Fig. 2A and its inset. These microspheres are 2–3 μm in mean diameter (see Fig. 2A inset).

The microstructural examination was conducted for such Fe₃O₄ microspheres. Fig. 2B presents the typical TEM image. Under the transmission electron microscopic (TEM) fields, some micropores on the microspheres are found clearly. The surface of the spheres is thus rough. The diffraction pattern shows that a single sphere possesses multicrystal structure as shown in the inset of Fig. 2B. It means that the whole single microsphere is packed by many ultrafine Fe₃O₄ nanoparticles from different crystal orientations.

The formation of the magnetite could be described in the following reactions.



During heating at 200 °C, the complexes Fe (NH₄)₂H (C₆H₅O₇)₂ will decompose and form Fe(OH)₂, which is finally oxidized to Fe₃O₄ molecules [reactions (1) and (2)]. When the concentration of Fe₃O₄ molecules was supersaturated, ultrafine Fe₃O₄ nanoparticles would be formed in the solution by nucleation and growth. Finally, these ultrafine Fe₃O₄ nanoparticles will be assembled into Fe₃O₄ microspheres by CO₂ gas bubble templates due to reduce the energy of the reaction system.

Further, the nitrogen sorption measurement was conducted to evaluate the porous structure and specific surface area for such magnetite nanoparticles. Fig. 3 shows the nitrogen adsorption–desorption isotherm. The specific surface area was thus estimated, by Brunauer–Emmett–Teller (BET) equation [19], to be 83 m²/g. In addition, the sorption exhibits type IV isotherm and the pore analysis has revealed

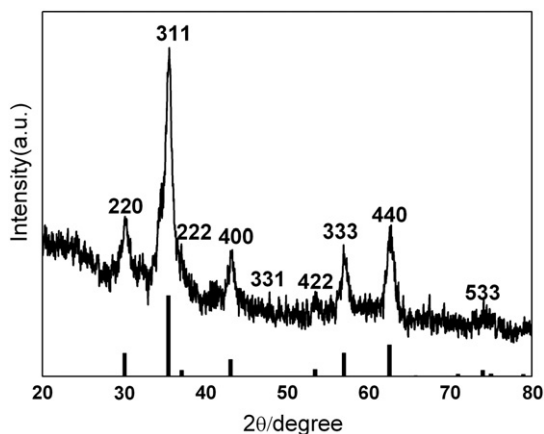


Fig. 1. XRD patterns of the as-synthesized products and standard Fe₃O₄ powders (the line spectrum).

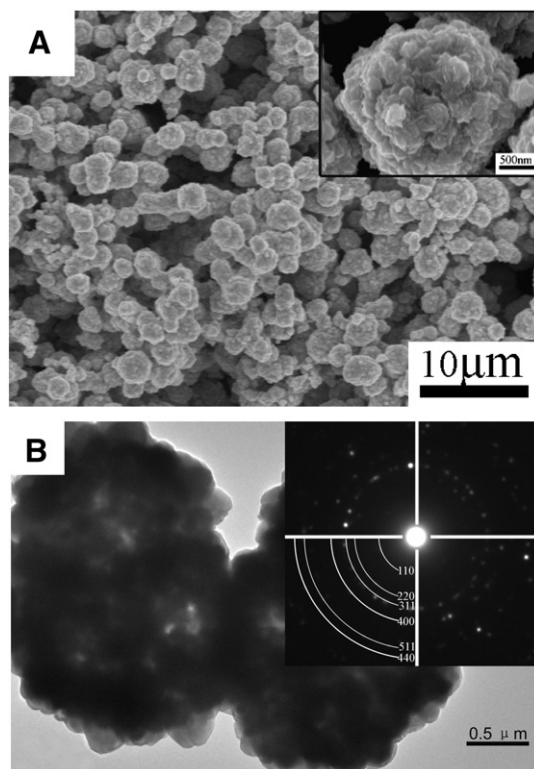


Fig. 2. Microstructural examination of Fe₃O₄ microspheres. (A): low-magnification SEM image of Fe₃O₄ microspheres. (B): low-magnification TEM image of Fe₃O₄ microspheres. Inset: diffraction pattern and spot indexing with different planes of Fe₃O₄.

that the pore sizes in the porous microspheres mainly fall into 3–8 nm, as seen in the inset of Fig. 3. As for the abroad pore size distribution around 40 nm should be mainly contributed from the pileup of the microspheres during N₂ sorption measurement.

Such porous oriented Fe₃O₄ microspheres have exhibited good magnetic property. Fig. 4 presents the corresponding magnetization as a function of magnetic field, or the M versus H curve. The saturation magnetization (M_s) and the coercivity (H_c) of the magnetite microspheres are about 81 emu/g and 145 Oe, which are close to the values of bulk Fe₃O₄ (85–100 emu/g and 115–150 Oe, respectively [20]), as shown in the down-right inset of Fig. 4, corresponding to an expanded low-field hysteresis curve. Obviously, in addition to the normal applications in, such as constructing nanoscale magnetic devices and high-density storage media [20–23], our porous

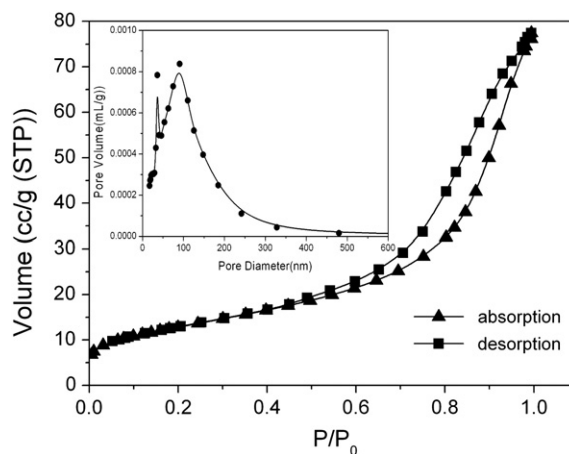


Fig. 3. N₂ sorption isotherm of the porous magnetite microspheres. Inset: pore diameter distribution.

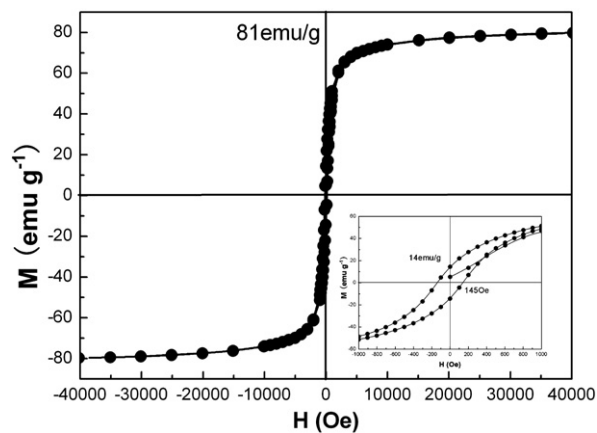


Fig. 4. Magnetization hysteresis loop of the porous magnetite microspheres. The down-right inset is an expanded low-field curve.

magnetite microspheres, due to both the high specific surface areas and strong magnetic properties, could be used as an effective adsorbent for removal of some toxic chemicals, which are usually difficult to remove and particularly important in environment remediation.

4. Conclusions

In conclusion, this work demonstrates that the Fe_3O_4 porous microspheres with 2–3 μm in mean diameter can be formed by one-pot hydrothermal reaction of $\text{Fe}(\text{NH}_4)_2\text{H}(\text{C}_6\text{H}_5\text{O}_7)_2$ in neutral solution. These Fe_3O_4 porous microspheres have excellent magnetic properties and higher surface area. The proposed method is easy, non-toxic, and reproducible. Owing to these advantages, this method is quite promising for the mass production of Fe_3O_4 micropowders.

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References

- [1] Tao Ke, Dou Hongjing, Sun Kang. Facile interfacial coprecipitation to fabricate hydrophilic amine-capped magnetite nanoparticles. *Chem Mater* 2006;18:5273–8.
- [2] Jean-Philippe De'ry, Borra Ermanno F, Ritcey Anna M. Ethylene glycol based ferrofluid for the fabrication of magnetically deformable liquid mirrors. *Chem Mater* 2008;20:6420–6.

- [3] Daou TJ, Pourroy G, Be'gin-Colin S, Grene'che JM, Ulhaq-Bouillet C, Legare' P, et al. Hydrothermal synthesis of monodisperse magnetite nanoparticles. *Chem Mater* 2006;18:4399–404.
- [4] Atul Bharde, Aijaz Wani, Yogesh Shouche, Joy Pattayil A, Prasad Bhagavatula LV, Murali Sastry. Bacterial aerobic synthesis of nanocrystalline magnetite. *J Am Chem Soc* 2005;127:9326–7.
- [5] Deng Hong, Li Xiaolin, Peng Qing, Wang Xun, Chen Jinping, Li Yadong. Monodisperse magnetic single-crystal ferrite microspheres. *Angew Chem Int Ed* 2005;44:2782–5.
- [6] Ningning Guan, Yaotao Wang, Dejun Sun, Jian Xu. A simple one-pot synthesis of single-crystalline magnetite hollow spheres from a single iron precursor. *Nanotechnology* 2009;20:1–8.
- [7] Cui Zhi-Min, Jiang Ling-Yan, Song Wei-Guo, Guo Yu-Guo. High-yield gas-liquid interfacial synthesis of highly dispersed Fe_3O_4 nanocrystals and their application in lithium-ion batteries. *Chem Mater* 2009;21:1162–6.
- [8] Liu Jia, Sun Zhenkun, Deng Yonghui, Zou Ying, Li Chunyuan, Guo Xiaohui, et al. Highly water-dispersible biocompatible magnetite particles with low cytotoxicity stabilized by citrate groups. *Angew Chem Int Ed* 2009;48:5875–9.
- [9] Ge Jianping, Yongxing Hu, Biasini Maurizio, Beyermann Ward P, Yin Yadong. Superparamagnetic magnetite colloidal nanocrystal clusters. *Angew Chem Int Ed* 2007;46:4342–5.
- [10] Xiao-Fei Qu, Qi-Zhi Yao, Gen-Tao Zhou, Sheng-Quan Fu, Jian-Liu Huang. Formation of hollow magnetite microspheres and their evolution into durian-like architectures. *J Phys Chem C* 2010;114:8734–40.
- [11] Li Zhen, Sun Qiao, Gao Mingyuan. Preparation of water-soluble magnetite nanocrystals from hydrated ferric salts in 2-pyrrolidone: mechanism leading to Fe_3O_4 . *Angew Chem Int Ed* 2005;44:123–6.
- [12] Zhang DongEn, Zhang XiaoJun, Ni XiaoMin, Song JiMei, Zheng HuaGui. Fabrication and characterization of Fe_3O_4 octahedrons via an EDTA-assisted route. *Cryst Growth Des* 2007;7:2117–9.
- [13] Ming Hu, Ji-Sen Jiang, Xiaodong Li. Surfactant-assisted hydrothermal synthesis of dendritic magnetite microcrystals. *Cryst Growth Des* 2009;9:820–4.
- [14] Zeng Yao, Hao Rui, Xing Bengang, Hou Yanglong, Zhichuan Xu. One-pot synthesis of Fe_3O_4 nanoprisms with controlled electrochemical properties. *Chem Commun* 2010;46:3920–2.
- [15] Switzer Jay A, Gudavarthy Rakesh V, Kulp Elizabeth A, Guojun Mu, He Zhen, Wessel Andrew J. Resistance switching in electrodeposited magnetite superlattices. *J Am Chem Soc* 2010;132:1258–60.
- [16] Li Ling, Yang Yang, Ding Jun, Xue Junmin. Synthesis of magnetite nanooctahedra and their magnetic field-induced two-/three-dimensional superstructure. *Chem Mater* 2010;22:3183–91.
- [17] Deng Chonghai, Hanmei Hu, Shao Guoquan, Han Chengliang. Facile template-free sonochemical fabrication of hollow ZnO spherical structures. *Mater Lett* 2010;64:852–5.
- [18] Deng Chonghai, Hanmei Hu, Zhu Wenli, Han Chengliang, Shao Guoquan. Green and facile synthesis of hierarchical cocoon shaped CuO hollow architectures. *Mater Lett* 2011;65:575–8.
- [19] Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. *J Am Chem Soc* 1938;60:309–19.
- [20] Liu Fei, Cao Peijiang, Zhang Huairuo, Tian Jifa, Xiao Congwen, Shen Chengmin, et al. Novel nanopyramid arrays of magnetite. *Adv Mater* 2005;17:1893–7.
- [21] Mathur Sanjay, Barth Sven, Werner Ulf, Hernandez-Ramirez Francisco, Romano-Rodriguez Albert. Chemical vapor growth of one-dimensional magnetite nanostructures. *Adv Mater* 2008;20:1550–4.
- [22] Mu-Tung Chang, Li-Jen Chou, Chin-Hua Hsieh, Yu-Lun Chueh, Zhong Lin Wang, Yasukazu Murakami, et al. Magnetic and electrical characterizations of half-metallic Fe_3O_4 nanofibers. *Adv Mater* 2007;19:2290–4.
- [23] Chun-Jiang Jia, Ling-Dong Sun, Feng Luo, Xiao-Dong Han, et al. Large-scale synthesis of single-crystalline iron oxide magnetic nanorings. *J Am Chem Soc* 2008;130:16968–77.