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Controlled synthesis of hollow magnetic Fe_3O_4 nanospheres: Effect of the cooling rate

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ABSTRACT

The controlled synthesis of hollow magnetite (Fe_3O_4) nanospheres of varying sizes and structures was successfully obtained via a facile solvothermal process and varying cooling processes. The Fe_3O_4 nanospheres were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and superconducting quantum interference device magnetometry. The diameters of the as-synthesized nanospheres were controlled at around 500–700 nm by simply changing the cooling rate, which had an obvious influence on the morphology and magnetic properties of these Fe_3O_4 nanospheres. While a low cooling rate triggered the formation and extension of the cracks present in the Fe_3O_4 nanospheres, a sudden drop of temperature tended to favor multi-site nucleation of the crystals as well as the formation of compact and smooth hollow nanospheres with superior crystallinity and high saturation magnetization. The growth mechanism of hollow magnetite oxide nanospheres was proposed and the correlation between the structure and the magnetic properties of the hollow nanospheres was discussed, which promises the potential of the hollow nanospheres in various applications such as drug delivery and cell separation.

Introduction

Over the past decades, nanoscale magnetite (Fe_3O_4) has attracted extensive attention because of its good hydrophilic, biocompatible, nontoxic properties, and its relative chemical stability (Lin et al., 2012), which renders it an ideal candidate for applications in cell separation (Arshady, 1993), drug delivery (Liu et al., 2005), and hyperthermia therapy (Kawashita et al., 2005). To date, nanoscale Fe_3O_4 materials with different morphologies have been prepared, such as nanospheres (Lu, Salabas, & Schüth, 2007), nanowires (Zhang et al., 2004), and nanosheets (Chin et al., 2007). Among these structures, much attention has been focused on nanospheres, owing to their distinctive performance in constructing core–shell mutifunctional nanostructures comprising magnetite (core) and other nonmagnetic materials (shell) (Liu, Hu, Zhang, Fang, & Wang, 2008; Zhang et al., 2013). Traditionally, the crystallinity and magnetic properties of Fe_3O_4 nanospheres are important in the application of these core–shell multifunctional materials. Therefore, it is crucial to find a feasible method to improve the magnetic properties and crystallinity of Fe_3O_4 magnetic nanospheres. Recently, some research has been carried out concerning Fe_3O_4 nanosphere growth by the hydrothermal method, and the effect of the experimental conditions on the nanosphere growth has also been addressed (Deng et al., 2005; Xu, Zhang, Ou, Zhang, & Han, 2013). However, to the best of our knowledge, there have no reports studying the effect of the cooling method on the structure and the magnetic properties of Fe_3O_4 nanospheres. In this study, we report the effects of the cooling method on the morphology and crystallinity of Fe_3O_4 nanospheres as well as the correlation between the structure and the magnetic properties of the samples with varying cooling methods. Finally, a growth mechanism was also proposed.

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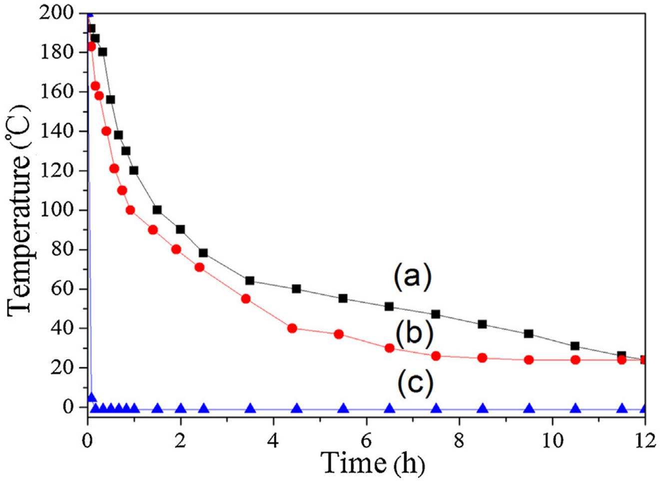

Fig 1. Temperature–time plots for the different cooling methods of (a) furnace cooling (sample (1)), (b) air cooling (sample (2)), and (c) ice-water cooling (sample (3)).

Experimental

Synthesis of Fe_3O_4 nanospheres

All chemicals were of analytical grade without further purification. The Fe_3O_4 nanospheres were synthesized by a modified solvothermal method similar to that in Stefan et al.'s report (Stefan et al., 2014). Typically, 3.6 g of $FeCl_3{\cdot}6H_2O$ was dissolved in 90 mL of ethylene glycol (EG), followed by the addition of 12 g of $NaAc{\cdot}3H_2O$. After vigorous magnetic stirring for 30 min at room temperature, the as-formed solution was transferred to a Teflon^{TM}-lined stainless-steel autoclave with a 150 mL capacity and sealed to heat at 200 °C in an oven for 12 h. The solution was then cooled down using the varying cooling conditions, including furnace cooling (sample (1)), air cooling (sample (2)), and ice-water cooling (sample (3)). The cooling rate of the system is shown in Fig. 1, where it can be seen that the temperature of samples (1) and (2) decrease quickly for the first 4 h, with the cooling rate of sample (2) being greater. After that, for 12 h the temperature of the samples (1) and (2) was made to decrease slowly to room temperature (25 °C). For sample (3), the temperature was decreased to 4.5 °C in 5 min, after which the temperature was decreased within 10 min to be in the range 0 to −1 °C and the sample was kept at that temperature for 12 h.

The final products were all washed with ultra-high-purity water (18 MΩ cm) and ethanol several times and then dried in air at 55 °C for 12 h.

Characterization

X-ray diffraction (XRD) patterns of nanospheres were obtained by a X'Pert PRO diffractometer (PANalytical, Netherlands) with Cu Kα radiation over an angular range of $10^\circ \leq 2\theta \leq 90^\circ$. The morphology of the samples was observed using field emission scanning electron microscopy (FE-SEM; SU8020, Hitachi, Japan) and using transmission electron microscopy (TEM; JEM-2010, JEOL, Japan) equipped with an energy dispersive X-ray (EDX) system. The temperature change of the system was monitored using an infrared thermometer (568EX, Fluke, USA). The magnetic properties of the nanospheres were measured using a superconducting quantum interference device magnetometer (SQUID-VSM; Quantum Design, USA), where the magnetic hysteresis (M–H) loops were obtained at room temperature in a magnetic field ranging from −20,000 to 20,000 Oe.

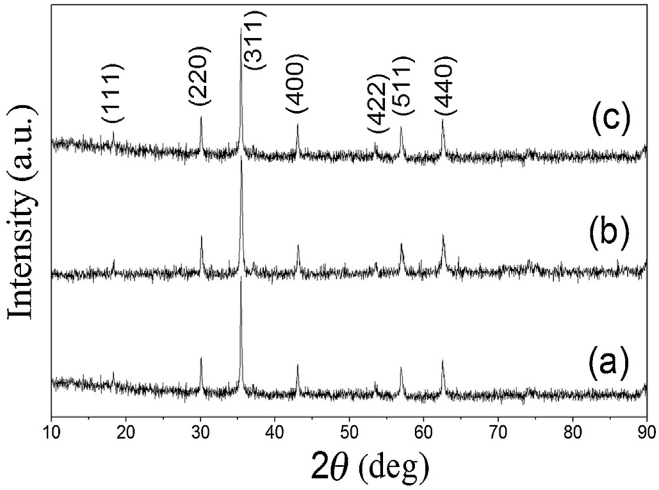

Fig. 2. XRD patterns of the Fe_3O_4 nanospheres samples prepared by (a) furnace cooling (sample (1)), (b) air cooling (sample (2)), and (c) ice-water cooling (sample (3)).

Results and discussion

To analyze the phase structure of the nanospheres, samples (1)–(3) were evaluated using XRD measurements, where Fig. 2 shows typical XRD patterns of the Fe_3O_4 nanospheres. As can be seen in Fig. 2, all of the diffraction peaks can be indexed as cubic structure Fe_3O_4 (JCPDS card no. 85-1436), which is consistent with previous reports (Mathur et al., 2006; Wang, Chen, Zeng, & Hou, 2004). No peaks from impurities were detected, suggesting the formation of single-phase Fe_3O_4. The strong and sharp diffraction peaks signify that the Fe_3O_4 nanospheres were well crystallized (Zhang, Tong, Li, Zhang, & Ying, 2008). To further analyze the effect of the cooling method on the crystallinity of the Fe_3O_4 nanospheres, we fit the diffraction peaks of the three samples in Fig. 2. The area under the three strongest diffraction peaks centered at 30.08°, 35.43°, and 62.53°, which were present in all of the diffraction curves for samples (1)–(3), were calculated and normalized. While the crystallinity of sample (3) was set as 100%, the crystallinity of samples (1) and (2) was calculated to be 92.1% and 87.1%, respectively. This suggests that the high crystallinity present in sample (3) is likely because the high cooling rate accelerates the crystallization rate. The low cooling rate, however, cannot provide enough driving force for continuous crystallization (e.g., sample (1)), which is similar to a previous report (Shi, Ma, Wang, & Ma, 2012).

Deng et al. (2005) have reported the effect of precursor concentration and growth time on the morphology and size of the Fe_3O_4 spheres. Besides the precursor concentration and reaction time, our experimental evidence indicates that the cooling approach also plays a crucial role in the dominating morphology, the size and the magnetic properties of Fe_3O_4 nanospheres. Fig. 3 shows SEM and TEM images of the three samples obtained under different cooling conditions, where all of the samples are basically spherical in shape and have a narrow diameter distribution. Excluding nanospheres that had agglomerated, we selected and measured the size of ~200 representative nanospheres during the TEM observation, where the measured sizes were then used to calculate an average nanosphere size for samples (1)–(3) of about 700, 600, and 500 nm, respectively. The effect of the cooling approach upon the growth of the spheres may then addressed as follows: Figs. 1 and 3 demonstrate that a higher cooling rate results in the growth of smaller-sized nanospheres. At a lower cooling rate, the comparative temperature and pressure of the autoclave was maintained for an extended time which allowed for continuous growth of the Fe_3O_4 crystals