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Surfactant-free fabrication of Fe_3O_4 nanospheres with selective shape

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ABSTRACT

Three different magnetite nanospheres including glossy nanospheres, cluster nanospheres and hollow nanospheres were prepared in the similar solvothermal procedure. Such a process is very simple and controllable without any template or surfactants involved; only the necessary alkali source for the magnetite synthesis was employed as shape-controlled reagent. X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), N_2 adsorption–desorption analysis and a superconducting quantum interference device magnetometer (SQUID) were used to characterize the composition, morphologies, and properties of these nanospheres. Furthermore, the effects of different types of basic reagents on the morphologies were discussed; the pH value and local Ostwald ripening were presumed to be key factors to determine the three different shapes of Fe_3O_4 nanospheres.

1. Introduction

Iron oxide-based magnetic materials have been extensively pursued for multidisciplinary researches, not only for fundamental size-dependent magnetism and optoelectronics but also for biomedical applications due to their low toxicity [1–5]. Various strategies, such as hydrothermal/solvothermal procedure, mechanochemical reaction, ultrasonic chemical co-precipitation and microwave method, have been developed for synthesizing different magnetite nanostructures [6–13]. In particular, shape-selective synthesis of Fe_3O_4 nanostructures has been regarded as a longstanding challenge but a vital work because the intrinsic properties of nanocrystals are mainly determined by their shape, crystallinity and structure. Tremendous attempts have been made to prepare various kinds of magnetite with the involvement of different additives/surfactants, which were proven to effectively control the crystallinity, shape and structure of magnetite [14–18]. However, the additives/surfactants involved often passivated, to varying degrees, the surface of the crystals, which would play a negative role in subsequent application, especially, for catalysis. In addition, the formation mechanism became more complex due to the involvement of additives/surfactants, which has proven unfavorable to the fundamental experimental studies [19]. Therefore, to develop a facile and reliable procedure for the synthesis of Fe_3O_4 nanostructures with controlled morphologies is needed, especially, in a similar reaction system, which would be helpful to the systematic investigation and profound understanding of the formation mechanism.

In this work, we develop a facile and reliable solvothermal approach for the synthesis of three different magnetite nanospheres, such as glossy nanospheres, cluster nanospheres and hollow nanospheres. The three different nanospheres could be regulated by the addition of different alkali sources in the similar solvothermal procedure without any additional additives/surfactants involved. A plausible mechanism based on chelation and local Ostwald ripening is proposed. To the best of our knowledge, this is the first promising method for tuning the shapes of magnetite by only adding different basic reagents, which might be further used to direct the synthesis of other materials with selective shape in similar system.

2. Experimental section

Materials: CH_3COONa (sodium acetate), $CH_2(COONa)_2$ (sodium malonate), $(CH_2COONa)_2 \cdot 6H_2O$ (disodium succinate hexahydrate), Na_2CO_3 (sodium carbonate), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ethylene glycol (EG) and other chemical reagents were of analytical grade and used as received without further purification. Millipore water (18.2 MΩ cm at 25 °C) was used throughout all experiments.

Preparation of three different Fe_3O_4 nanospheres: The three magnetite nanospheres were fabricated by a simple sovolthermal treatment of $FeCl_3 \cdot 6H_2O$ and different alkali sources in EG. In a typical procedure, as for glossy nanospheres, 5 mmol of $FeCl_3$ was dissolved in 40 mL of EG to form a clear solution, followed by the

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addition of 22 mmol of disodium succinate hexahyrate. The mixture was vigorously mixed via ultrasonication to give a homogeneous solution. Then the solution was transferred into a Teflon-lined stainless steel autoclave (50 mL of capacity), sealed, kept at 200 °C for 10 h. After the autoclave was allowed to cool down to room temperature, the precipitates were collected by magnetic separation, and washed at least three times with water and ethanol under sonication, then dried under vacuum at room temperature before characterization.

As for cluster nanospheres, the only change is the amount of disodium succinate, which was reduced to 5.5 mmol. As for hollow nanospheres, there are two changes. One is the alkali reactants, which was adjusted to 5.5 mmol of disodium succinate hexahyrate mixing with 33 mmol of anhydrous NaAc; the other is the amount of $FeCl_3$, which was increased to 20 mmol. The rest of the synthesis conditions were kept the same as those mentioned above for the fabrication of glossy nanospheres.

Characterization: FE-SEM images were obtained using a Hitachi S-4800 field emission electron microscope at an accelerating voltage of 5 kV. XRD measurements were performed on a Japan Shimadzu XRD-6000 diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm); a scanning rate of $0.05^\circ\,s^{-1}$ was applied to record the patterns in the 2θ range of 20–70°. N_2 adsorption–desorption isotherms were obtained at 77 K on an ASAP 2020 volumetric adsorption equipment made by Micromeritics Instrument Corporation. Magnetic properties were measured on a superconducting quantum interference device magnetometer at 300 K.

3. Results and discussion

The crystal structures and crystallinity of the three Fe_3O_4 nanostructures were determined by an XRD technique. As shown in Fig. 1, all of the obtained products exhibited high crystalline quality; they were indexed to face-centered-cubic (fcc) magnetite (JCPDS no. 75-0033) and no impurity peaks were observed. More specifically, compared with glossy nanospheres, cluster nanospheres and hollow nanospheres exhibited broader diffraction peaks, indicating the smaller size of the crystal unit. Calculations using the Debye–Scherrer formula for the strongest peak (311) showed the grain size of 10 nm and 53 nm for cluster nanospheres and hollow nanospheres, respectively.

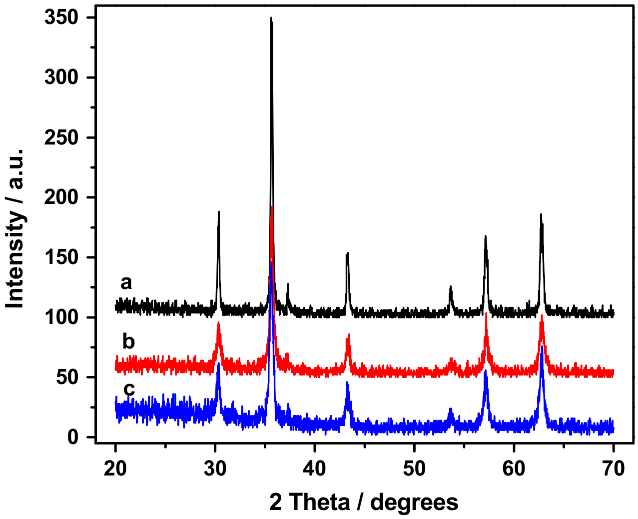

Fig. 1. XRD patterns of three different magnetite nanospheres: (a) glossy nanospheres, (b) cluster nanospheres and (c) hollow nanospheres.

The morphologies of the products were found to depend strongly on the types and amount of alkali in the reaction system. When the alkali was disodium succinate with the amount of 22 mmol, the product was dominated by glossy nanospheres as shown in Fig. 2a and b, which shows an excellent monodispersity and a well-defined uniform spherical shape with the average diameter of about 500 nm. When the amount of disodium succinate was decreased to 5.5 mmol, the transformation from glossy nanospheres to cluster nanospheres with average diameter of about 300 nm was observed as shown in Fig. 2c and d. Also the cluster nanospheres became a hierarchical structrure, which was made up of many primary nanoparticles (ca. 13 nm). When the alkali were a mixture of 5.5 mmol of disodium succinate and 33 mmol of sodium acetate, hollow nanospheres with the diameters of 500 nm were obtained as shown in Fig. 2e and f. The hollow nanospheres consisted of smaller building blocks (ca. 60 nm) assembled together to form the shell wall. Partly bowl-shaped broken spheres with open pores proved their hollow interior structure. Therefore, the SEM results indicated that cluster nanospheres and hollow nanospheres were composed of many primary particles, in accordance with the results of XRD analysis.

N_2 absorption and desorption analysis and variable-field magnetization were carried out to further investigate the details of three nanospheres and the data are shown in Table 1. The specific surface area of glossy nanospheres, cluster nanospheres and hollow nanospheres were determined to be about 7.2, 19.1 and 28.6 $m^2\,g^{-1}$, respectively, and the corresponding saturation magnetization values were 86.9, 74.5 and 81.1 emu g^{-1}, respectively. Furthermore, in contrast with the ferromagnetism behavior of glossy nanospheres and hollow nanospheres exhibited, the cluster nanospheres displayed superparamagnetic properties without remanence and coercivity detectable, suggesting that the primary crystals of cluster nanospheres were less than the threshold size of the ferrites (about 15 nm) [13,20]. These data were consistent with the XRD and SEM results that cluster and hollow nanospheres were made up of smaller primary nanoparticles.

In the process of hydrothermal synthesis, it is usually supposed that EG acts both as a high-boiling-point solvent and a reducing agent. Fe(III) could partly be reduced to Fe(II) by EG. Their respective ions are then hydrolyzed to form $Fe(OH)_3$ and $Fe(OH)_2$ in the basic medium, followed by the generation of Fe_3O_4 primary nanoparticles via dehydration of these hydroxides [21,22]. Afterward, the formation of Fe_3O_4 glossy nanospheres seemed to be reasonable through the oriented attachment of these primary particles to achieve minimization of their surface energy as well as their magnetic dipole alignment [5].

It should be noted that none of the magnetite nanomaterials was formed without the addition of basic reagents or using only weak basic reagents (such as sodium lactate, alginic acid sodium, and sodium bicarbonate). Even disodium succinate was employed as basic reagent, when its amount was less than 2.5 mmol or the reaction time was less than 4 h, instead of a black product, a thick yellow mixture without magnetic performance was obtained, suggesting the absence of magnetite.

When the amount of disodium succinate was 5.5 mmol, the formation of $Fe(OH)_3$ and $Fe(OH)_2$ could be affected by the decrease of pH. According to the precipitation theory, at the lower pH value, the dimension of $Fe(OH)_n$ primary nanoparticles could be smaller than that in the higher pH value; these smaller nanoparticles were more inclined to be attached together by the chelated molecules to minimize the surface energy of the total system. As a result, these molecule-chelated nanocrystals would nucleate in the supersaturated solution and finally aggregate into larger secondary particles, i.e. cluster nanospheres.

As for hollow nanospheres, anhydrous NaAc is critical for the synthesis of the hollow structures in this system. In control

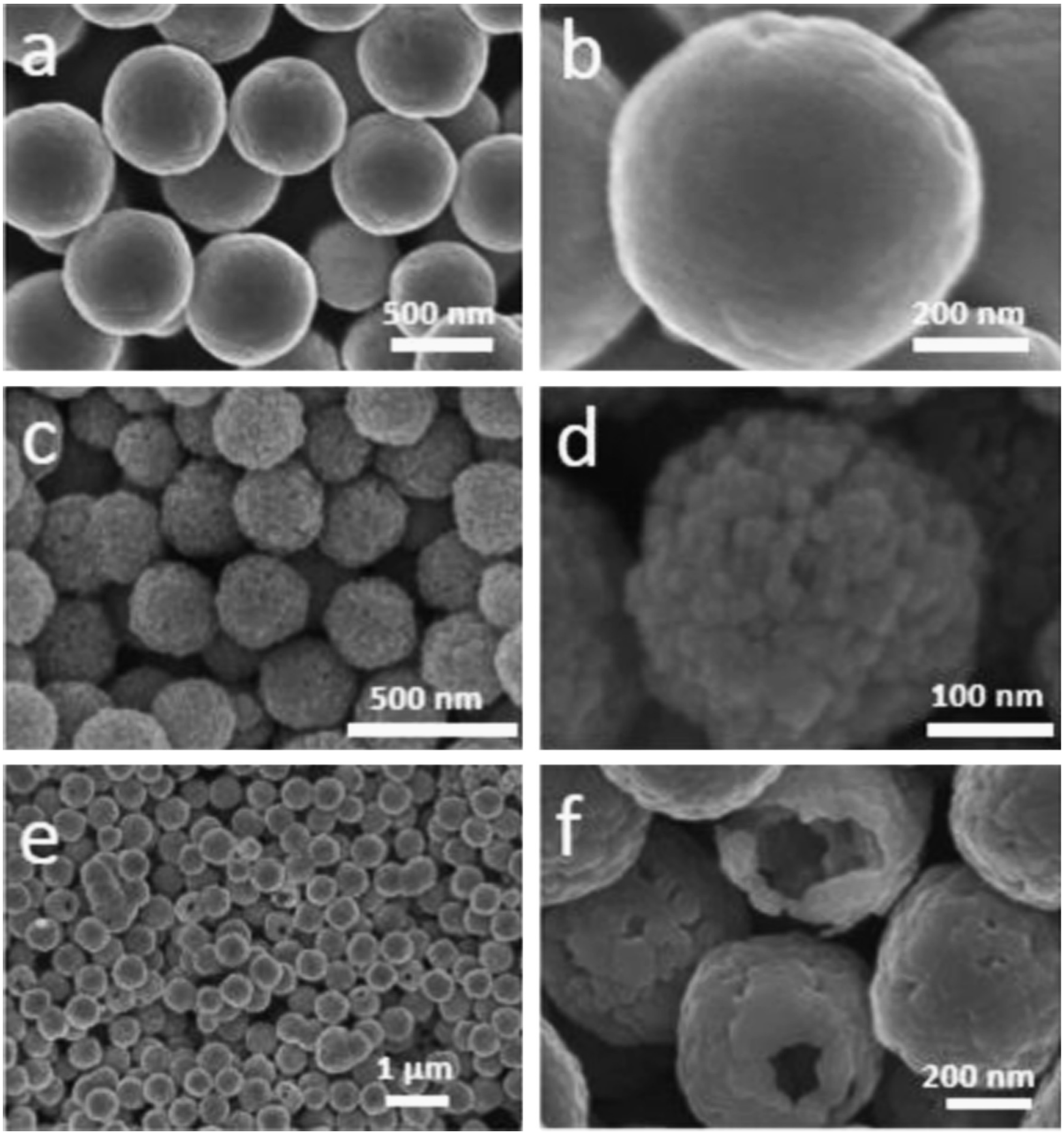

Fig. 2. Typical SEM images of three different magnetite nanospheres. (a and b) glossy nanospheres, (c and d) cluster nanospheres, and (e and f) hollow nanospheres.

Table 1
The specific surface area and magnetic properties of three different magnetite nanospheres.

Sample	Glossy	Cluster	Hollow
Specific surface area ($m^2\ g^{-1}$)	7.2	19.1	28.6
Saturation magnetization value ($emu\ g^{-1}$)	86.9	74.5	81.1

experiments, hollow nanostructures could not be obtained in the presence of other sodium salts, such as $NaCO_3$, NaOH, disodium succinate and $NaOCH_3$, instead of NaAc. As the reaction proceeded, hydrolysis and alcoholysis of $Fe(AC)_n$ were regarded as two possible pathways to get Fe_3O_4 primary nanoparticles. The primary particles formed through hydrolysis were believed to be thermodynamically unstable [23]. The metastable particles could be subjected to Ostwald ripening, which gradually dissolved and transformed into these stable species. At a certain ratio of iron to acetate ligands, the different chelation modes between the exterior and interior particles of the nanospheres might provide different opportunities for local ripening. As a result, the hollow structures with larger building blocks were formed.

4. Conclusion

In summary, we demonstrate a simple and novel approach for the synthesis of shape-selective magnetite nanospheres. Three different nanospheres, including glossy nanospheres, cluster nanospheres and hollow nanospheres, could be regulated by the addition of different alkali sources in the similar solvothermal procedure without any additional additives/surfactants involved. The pH value and local Ostwald ripening were presumed to be key factors to determine the shape of Fe_3O_4 nanospheres. Such investigation is of particular significance for understanding of the formation mechanism in sovlothermal/hydrothermal process, and provides an effective solution for the surfactants-free synthesis of magnetite nanostructures with selective shape.

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