

Solvothermal synthesis of sub-200 nm Fe₃O₄ submicrospheres with enhanced catalytic performances by using acicular goethite as solid precursor

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A facile and low-cost chemical method is still in need to make Fe₃O₄ submicrospheres with the size below 200 nm. In this study, Fe₃O₄ submicrospheres of ca. 173 nm with soft-magnetic properties were made by conversion of goethite under solvothermal conditions, and exhibited the good catalytic activity and reusability for selective oxidation of benzyl alcohol to benzaldehyde with H₂O₂ in water (yield: 43.5–46.2% after being recycled seven times).

1. Introduction: The intrinsic peroxidase-like activity of Fe₃O₄ magnetic nanoparticles was first reported in 2007 [1] and has great potential in many oxidative processes that involves catalytic decomposition of H₂O₂ (e.g. heterogeneous Fenton-like oxidative degradation of organic contaminants [2–4] and selective oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) [5, 6]). However, it is well known that nanoparticles with the size of <100 nm are prone to aggregation, which significantly reduces their catalytic activity during the application [7, 8]. Increasing the particle size from nanometers (nm) to micrometers (μm) may alleviate the aggregation; however, microparticles usually exhibit the lower catalytic activity due to the larger size. A reasonable trade-off between activity and aggregation is expected in the Fe₃O₄ particles with the size near the nm/μm border (100–200 nm), which may be promising catalysts with the enhanced catalytic activity and stability.

Solvothermal synthesis of monodisperse Fe₃O₄ microspheres of 200–800 nm was first reported in 2005 by reductive precipitation of soluble Fe³⁺ salts in ethylene glycol (MEG) at 198°C [9]. Since then, it has become a popular method to make Fe₃O₄-based functional nanostructured materials [10–13]. Previous works mainly focused on the effects of process parameters or organic additives on the synthesis of Fe₃O₄ while the effects of iron precursors have been rarely investigated [14, 15]. Without the addition of a capping agent (e.g. surfactant or polymer), the solvothermal synthesis in MEG usually generates Fe₃O₄ microspheres of >200 nm. A facile and low-cost chemical method is still in need to make Fe₃O₄ submicrospheres of sub-200 nm. In this Letter, Fe₃O₄ submicrospheres of ca. 173 nm were made by a precursor-adapted solvothermal synthesis, which comprises thermal treatment of acicular goethite (α-FeOOH) in MEG at 198°C for 14 h, and demonstrated to be a good catalyst with the enhanced catalytic activity and reusability for the selective oxidation of BzOH to BzH with H₂O₂ in water.

2. Experimental

2.1. Synthesis of Fe₃O₄ submicrospheres of ca. 173 nm: All chemicals are of analytical grade from Sinopharm Chemical Reagent and were used as received. Acicular α-FeOOH particles were first prepared according to the literature [16]. Briefly, 10 ml of 4.9 M KOH aqueous solution was slowly dropped to 10 ml of 1.2 M Fe(NO₃)₃·9H₂O aqueous solution in a 60 ml Teflon container under vigorous stirring. After topping up with 20 ml of deionised water, the whole mixture was heated at 100°C for 6 h to get yellow acicular α-FeOOH particles. Then the acicular α-FeOOH particles (0.5 g, 5.6 mmol) were dispersed in 9 ml of

MEG, followed by the addition of 0.461 g (5.6 mmol) of NaOAc. This dispersion was heated in a 60 ml Teflon-lined autoclave at 198°C for 14 h and then quenched to room temperature. Black Fe₃O₄ particles were magnetically separated, washed with ethanol (3 × 10 ml) and 50°C water (3 × 10 ml), and dried overnight.

2.2. Characterisation: X-ray diffraction (XRD) patterns were collected on Bruker D8 Advance Diffractometer with Cu Kα (0.15406 nm) radiation at 30 kV and 20 mA. Scanning electron microscopy (SEM) images were taken on JEOL JSM-5510LV scanning electron microscope. Magnetic properties were investigated by sweeping the external field between ±8 kOe at room temperature on VSM JDAW-2000D vibrating sample magnetometer. The BET specific surface area was measured by N₂ physisorption at 77 K on Micromeritics JW-BK112 surface area and porosity analyser. Before measurement, the sample was pretreated by heating at 50°C under vacuum for 3–4 h. The bulk Fe³⁺/Fe²⁺ ratios in Fe₃O₄ were determined by the 1,10-phenanthroline spectrophotometric method [2, 5, 6].

2.3. Catalytic oxidation of BzOH to BzH with H₂O₂ in water: BzOH (40 mmol, 4.1 ml), deionised water (8.0 ml), Fe₃O₄ catalyst (0.2 g) and H₂O₂ (30 wt% in water, 40 mmol, 4.0 ml) were added to a 50 ml two-neck flask and refluxed at 100°C. After 0.5 h, another 4.0 ml (40 mmol) of H₂O₂ (30 wt% in water) was added and the reaction continued for another 1 h. Then the catalyst was separated from the mixture with a magnet. The product was extracted with ethyl acetate (10 ml), washed with saturated sodium thiosulfate solution (2 × 10 ml), and then analysed by gas chromatography equipped with an AE-FFAP capillary column and a FID.

3. Results and discussion: Fig. 1 shows the XRD pattern of Fe₃O₄ submicrospheres. Six peaks observed at 2θ = 30.1°, 35.5°, 43.1°, 53.5°, 57.0° and 62.6° can be, respectively, indexed to the (220), (311), (400), (422), (511) and (440) diffractions according to the standard pattern of magnetite (PDF no. 65-3107). The bulk Fe³⁺/Fe²⁺ ratio of Fe₃O₄ submicrospheres was measured to be 2.1, which is very close to the theoretical value (2) of magnetite. It confirms that goethite has been successfully converted to Fe₃O₄ with cubic inverse spinel structure after thermal treatment in MEG at 198°C for 14 h. The yield of Fe₃O₄ is 94% (note: Yield of Fe₃O₄ was estimated by $m/m_0 \times 100\%$, where m is the mass of particles recovered after the synthesis and m_0 is the theoretical value of the mass of particles supposing all irons in goethite are converted to Fe₃O₄).

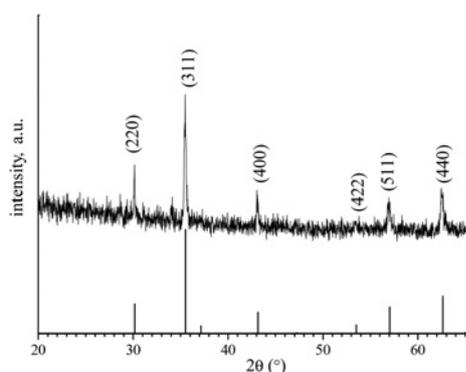


Fig. 1 XRD pattern of Fe_3O_4 submicrospheres. Shown at the bottom is the standard pattern of magnetite (PDF no. 65-3107)

The SEM image of Fe_3O_4 submicrospheres (Fig. 2a) reveals that most particles are discrete spheres of 173 ± 23 nm in size, as shown by the particle size distribution histogram (Fig. 2b) constructed from the sizes of 100 particles in several SEM images. The BET surface area of Fe_3O_4 submicrospheres was measured to be $22.0 \text{ m}^2/\text{g}$ (N_2 adsorption–desorption isotherm shown in Fig. S1).

The magnetisation curve of Fe_3O_4 submicrospheres at room temperature is displayed in Fig. 3. The saturated magnetisation of Fe_3O_4 submicrospheres (96.5 emu/g) is close to the bulk value of magnetite ($85\text{--}100 \text{ emu/g}$) [17, 18]. In close-up view near the origin of the magnetisation curve (Fig. 3 inset), a small hysteresis loop is observed with remanent magnetisation (14.6 emu/g) and coercivity (87.8 Oe), indicative of soft-magnetic properties. The magnetic properties of Fe_3O_4 submicrospheres are suitable for magnetic separation by an external magnet while avoiding aggregation after removal of the applied field.

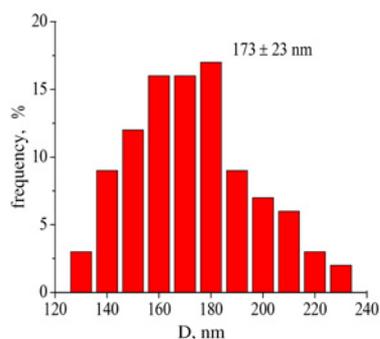
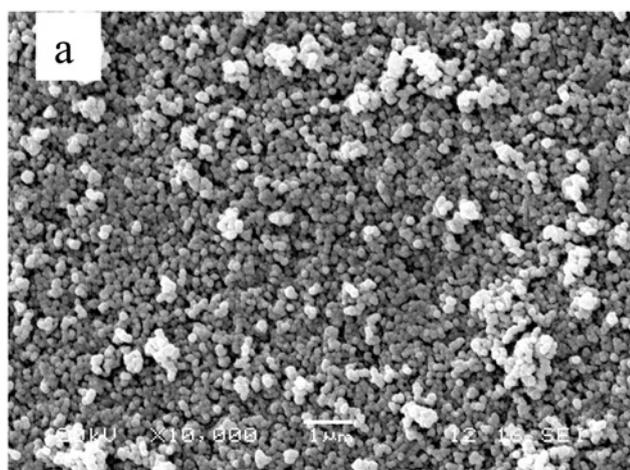


Fig. 2 Fe_3O_4 submicrospheres
a SEM image and
b Particle size distribution histogram

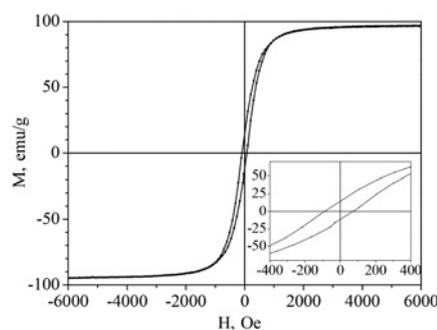


Fig. 3 Room-temperature magnetisation curve of Fe_3O_4 submicrospheres. Inset is close-up view near the origin

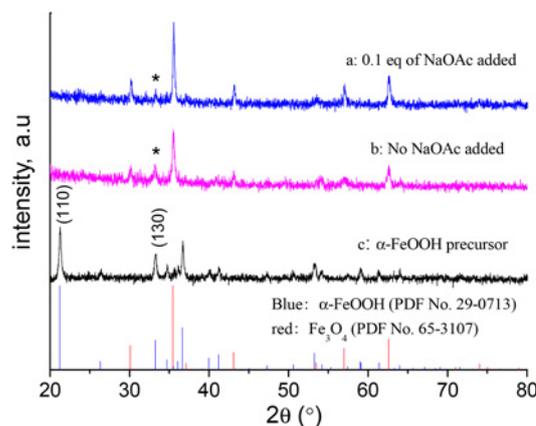


Fig. 4 Effect of the amount of NaOAc on the conversion of goethite to Fe_3O_4 in MEG

The conversion of goethite to Fe_3O_4 in MEG is believed to proceed via dissolution–recrystallisation process. Different morphologies between Fe_3O_4 submicrospheres and acicular $\alpha\text{-FeOOH}$ (Fig. 2 vs. Fig. S2) support the involvement of the dissolution step of acicular $\alpha\text{-FeOOH}$ during the formation of Fe_3O_4 submicrospheres. The acicular $\alpha\text{-FeOOH}$ as a solid precursor was first dissolved to slowly release Fe^{3+} ions into the basic MEG solution, which were then partially reduced to Fe^{2+} by MEG to form Fe_3O_4 particles in a way similar to the solvothermal synthesis of Fe_3O_4 microspheres from soluble Fe^{3+} salts in MEG reported in the literature [9, 12]. The slow release of Fe^{3+} from $\alpha\text{-FeOOH}$ solid precursor is critical to control the particle grow to make the Fe_3O_4 submicrospheres of ca. 173 nm. The addition of NaOAc facilitates the conversion of goethite to Fe_3O_4 . Under the same reaction conditions except reducing the amount of NaOAc in the system, the conversion of $\alpha\text{-FeOOH}$ to Fe_3O_4 was not completed. A peak at $2\theta = 33.2^\circ$ was observed in the XRD patterns of the products synthesised with 0.1 molar equivalent of NaOAc (Fig. 4a) or without NaOAc (Fig. 4b), which corresponds to the (130) diffraction peak of $\alpha\text{-FeOOH}$. It is worth to note that other diffraction peaks of $\alpha\text{-FeOOH}$ (even the strongest (110) peak) were not observed in Figs. 4a and b, implying the (130) crystallographic plane of $\alpha\text{-FeOOH}$ had the slowest dissolution rate under the current solvothermal conditions. The corresponding bulk $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios (4.3 and 7.0, respectively) are obviously higher than the theoretical value (2) of magnetite due to partial conversion of $\alpha\text{-FeOOH}$ to Fe_3O_4 , which is consistent with the observation in the literature that the addition of NaOAc help MEG reduce Fe^{3+} to produce Fe_3O_4 [19].

The catalytic activity of Fe_3O_4 submicrospheres of ca. 173 nm was evaluated by the selective oxidation of BzOH to BzH with H_2O_2 in water. The reaction results were shown in Table 1. No BzOH was converted without a catalyst under the reaction

Table 1 Catalytic performances of various magnetic iron oxide catalysts for BzOH oxidation to BzH with H₂O₂

Entry	Catalyst	BzOH convn, %	BzH yield, %	Sel, %	Refs.
1	Fe ₃ O ₄ (173 nm)	53.5	45.4	84.9	this work
2	Fe ₃ O ₄ (360 nm)	8.3	7.9	94.8	[6]
3	Fe ₃ O ₄ -ECH-D	36.6	34.2	93.5	[6]
4	Fe ₃ O ₄ -L	17–45	13–47	76–88	[20]
5	γ-Fe ₂ O ₃ -L	16–45	13–40	77–88	[20]
6	γ-Fe ₂ O ₃ (50 nm)	33	32	97	[21]
7	γ-Fe ₂ O ₃ (3–5 nm)	85.7	30	35	[21]

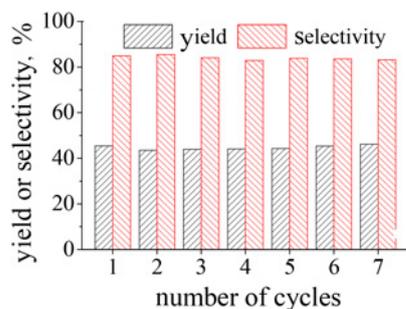


Fig. 5 Recyclability of Fe₃O₄ submicrospheres. The recovered Fe₃O₄ was reactivated by NaBH₄ reduction before reuse

conditions used in this study. The BzOH conversion was measured to be 53.5% on Fe₃O₄ submicrospheres. During the oxidation of BzOH to BzH, the only byproduct detected is benzoic acid. In terms of the BzH yield, the catalytic performance of the Fe₃O₄ submicrospheres is obviously better than those reported in the literature on other magnetic iron oxide particles (including Fe₃O₄ and γ-Fe₂O₃) (BzH yield: 45.4% vs. 13–47% in Table 1).

After the reaction, the Fe₃O₄ submicrospheres were recovered from the reaction mixture with the assistance of a magnet. The recovered Fe₃O₄ had very low activity (BzH yield: 7.0%). The Fe³⁺/Fe²⁺ ratio of Fe₃O₄ increased from 2.1 to 3.1 after the reaction due to the oxidation of Fe²⁺ ions by H₂O₂, which explains the low activity of the recovered Fe₃O₄ [1]. Therefore, the recovered Fe₃O₄ was reactivated by reduction in 10 ml of 0.3 M NaBH₄ aqueous solution at 40°C for 0.5–1 h, which effectively reduced the Fe³⁺/Fe²⁺ ratio to 2.4. The catalytic performance of the recovered Fe₃O₄ submicrospheres after the reactivation is shown in Fig. 5, which confirmed that the catalytic activity of the recovered catalysts could be effectively restored by the NaBH₄ reduction. The reactivated Fe₃O₄ had good recyclability with stable activity and selectivity after seven runs (BzH yields: 43.5–46.2%).

4. Conclusion: Fe₃O₄ submicrospheres of ca. 173 nm were successfully prepared by using acicular goethite as a solid precursor via solvothermal synthesis in ethylene glycol at 198°C for 14 h. They were demonstrated to be good magnetic catalysts with enhanced activity and stability for the selective oxidation of BzOH to BzH with H₂O₂ in water (yield: 43.5–46.2% after seven runs). Considering the wide availability of different iron sources, the precursor-adapted solvothermal synthesis would provide a versatile and promising route to adjust the properties of Fe₃O₄ particles for various purposes.

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