Hydrothermal synthesis of 3D hollow porous Fe$_3$O$_4$ microspheres towards catalytic removal of organic pollutants

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Abstract

Three-dimensional hollow porous superparamagnetic Fe$_3$O$_4$ microspheres were synthesized via a facile hydrothermal process. A series of characterizations done with X-ray diffraction, Brunauer-Emmett-Teller method, Fourier transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy indicated that the production of Fe$_3$O$_4$ microspheres possessed good monodispersity, uniform size distribution, hollow and porous structural characters, and strong superparamagnetic behavior. The obtained Fe$_3$O$_4$ microspheres have a diameter of ca. 300 nm, which is composed of many interconnected nanoparticles with a size of ca. 20 nm. The saturation magnetization is 80.6 emu·g$^{-1}$. The as-prepared products had promising applications as novel catalysts to remove organic pollutants (methylene blue) from wastewater in the presence of H$_2$O$_2$ and ultrasound irradiation.

Keywords: Hydrothermal synthesis; Fe$_3$O$_4$ microspheres; Porous; Enzyme mimetics; Organic pollutants

Background

In recent years, porous metal oxides have attracted considerable attention due to their potential applications in the field of lithium-ion batteries [1], drug delivery carrier [2], catalysis (including enzyme mimetics) [3], sensors [4], separation [5], and magnetic resonance imaging [6]. Among the porous metal oxides, iron oxide (Fe$_3$O$_4$) has become a particularly intriguing research target due to its low cost, good biocompatibility, as well as outstanding stability in physiological conditions [7-10]. Despite the great effort that has been made towards the synthesis of porous Fe$_3$O$_4$ with various sizes and morphologies, it still remains a big challenge to develop controlled and efficient ways for the synthesis of porous Fe$_3$O$_4$ microspheres with uniform size and strong magnetic performances in a large scale [11-13]. The hydrothermal method is one of the widely used methods for preparing functional inorganic nanomaterials [14-16]. It has a series of advantages for the resulting products, such as good crystallinity, uniform sizes, and special morphology, followed by excellent properties. Up to now, the Fe$_3$O$_4$ nanomaterials with different sizes and morphologies have been extensively reported by using this method. However, few reports are associated with the synthesis of 3D hollow porous Fe$_3$O$_4$ microsphere structures with uniform sizes on a large scale. Herein, we report a facile hydrothermal method for the construction of 3D hollow porous Fe$_3$O$_4$ microspheres from nanoparticle building blocks. Synthesis systems based on ethylene glycol (EG) and cetyl-methyl-ammonium bromide (CTAB) have been extensively adopted for the preparation of inorganic nanomaterials. In the whole reaction, EG was used as a solvent and CTAB as a dispersant. The as-prepared Fe$_3$O$_4$ microspheres exhibited porous structure, large surface area, strong superparamagnetic characters, as well as peroxidase-like activity, which are used as efficient enzyme mimetics to degrade organic pollutants (methylene blue).

Methods

Synthesis and characterization of 3D hollow porous Fe$_3$O$_4$ microspheres

All chemicals were of analytical grade and used as received without further purification (purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Typically,
FeCl₃ (0.8 g) was added into a beaker containing 40 mL ethylene glycol to become a clean yellow-brown solution at room temperature. Then, NaAc (3.6 g) and CTAB were subsequently added. The mixture solution was stirred vigorously for 10 min and was transferred into a Teflon-lined autoclave and heated to 200°C for 24 h. After cooling down to room temperature, the resulting products were collected and washed with deionized water and ethanol three times. The washed products were dried at 60°C for 1 day.

X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker AXS micro-diffractometer (D8 ADVANCE; Bruker AXS GmbH, Karlsruhe, Germany) with Cu-Kα radiation (λ = 1.5406 Å) from 10° to 80° at a scanning speed of 0.33° min⁻¹. The surface chemical groups of Fe₃O₄ microspheres were recorded by Fourier transform infrared spectroscopy (FTIR; Bruker Vector-22 FTIR spectrometer). The pore sizes and distribution curves were derived from the adsorption isotherm by employing the Barrett-Joyner-Halenda (BJH) method, and the surface areas were calculated through the Brunauer-Emmett-Teller (BET) equation. The magnetization versus magnetic field curves were measured at 300 K by a vibrating sample magnetometer (VSM; PPMS-9 T (EC-II), Quantum Design, San Diego, CA, USA). The surface morphology and structure were observed using a field emission scanning electron microscope (FESEM; Carl Zeiss AG, Oberkochen, Germany) operated at an accelerating voltage of 5.0 kV and a transmission electron microscope (TEM; JEM-2010, JEOL, Tokyo, Japan).

Catalytic degradation of methylene blue
Methylene blue was employed as a model dye pollutant to evaluate the catalytic activity of 3D porous Fe₃O₄ microspheres for the activation of H₂O₂ under ultrasonic irradiation. Briefly, 0.5 mL of Fe₃O₄ microsphere stock solution (with different concentrations) was added into 10 mL aqueous solution of methylene blue (2 μg/mL) at pH 5.0. The mixed solution was put for 10 min to achieve adsorption-desorption equilibrium. Then, the degradation was done by rapidly adding H₂O₂ (with different concentrations) and was carried out with ultrasonic irradiation for 3 min. The solution was reacted for 20 min. Lastly, the Fe₃O₄ microspheres were collected using a magnet. The concentration of methylene blue in the clear solution was determined by measuring the absorbance of the solution at 662 nm on a UV-vis spectrophotometer (UV-2450, Shimadzu Co., Kyoto, Japan).

Results and discussion
The chemical composition and phase purity of the resulting product was determined by XRD. As shown in Figure 1a, all the diffraction peaks can be assigned to the Fe₃O₄ phase (JCPDS card no. 65-3107). No other impurities are observed. The strongest diffraction peak (311) was used to estimate the crystalline size. According to the Debye-Scherrer formula, the calculated crystalline size is about 23 nm, which is consistent with the average grain sizes as observed in the following SEM images. The BET method of nitrogen adsorption/desorption was further employed to reveal the surface area and pore distribution of the as-obtained Fe₃O₄ products. The N₂ adsorption-desorption isotherm and pore size distribution curve of the sample are shown in Figure 1b. The sample is a typical IV isotherm with a type-H3 hysteresis; there are two-level broad pore size distributions in the range of 3 to 5 nm and 40 to 100 nm (inset). In addition, the specific surface area of the Fe₃O₄ sample calculated by BET method is 148 m² g⁻¹. Such high surface area might be due to the existence of a hollow internal structure, which is confirmed by subsequent TEM observation.

The morphology of the sample was subsequently examined using both SEM and TEM. From Figure 2a, one can see that the as-obtained products were spherical in morphology, and the particles are highly dispersed. The average size of these particles is ca. 300 nm. From the SEM image with the higher magnification in Figure 2b, the surface morphology was clearly revealed. The individual Fe₃O₄ microsphere is composed of lots of interconnected...
nanoparticles with a size of ca. 20 nm. Many void spaces could be observed between nanoparticles, making the whole microsphere a porous structure. From a broken microsphere, it could also be clearly seen that the microsphere is hollow and composed of densely packed subunits. The hollow interior is further confirmed by TEM images. Figure 2c is the TEM image of Fe$_3$O$_4$ microspheres. The clear variation in contrast shows that the as-prepared F$_3$O$_4$ microsphere is hollow and has a porous structure. Meanwhile, the higher magnification of an individual microsphere (Figure 2d) indicated that a great number of particles connected to each other to form a 3D hollow porous structure, which is consistent with the SEM observation.

Figure 2c shows the TEM image of Fe$_3$O$_4$ microspheres. The clear variation in contrast shows that the as-prepared F$_3$O$_4$ microsphere is hollow and has a porous structure. Meanwhile, the higher magnification of an individual microsphere (Figure 2d) indicated that a great number of particles connected to each other to form a 3D hollow porous structure, which is consistent with the SEM observation.

Figure 3a shows the magnetic curves of the prepared 3D hollow porous Fe$_3$O$_4$ microspheres. It does not show any hysteresis, revealing that the 3D hollow porous Fe$_3$O$_4$ microsphere has a typical superparamagnetic behavior. The saturation magnetization reaches up to 80.6 emu·g$^{-1}$, which is higher than the PEG additive-synthesized Fe$_3$O$_4$ microspheres. The strong magnetic performances would be helpful to the removal of heavy metal ions or organic pollutant in waste water. To determine the surface chemical compositions, FTIR measurement was performed in the range of 400 to 4,000 cm$^{-1}$. As shown in Figure 3b, the peak at 3,453 cm$^{-1}$ was assigned to the -OH stretch. The peaks at 605 and 448 cm$^{-1}$ can be assigned to the
vibrations of Fe-O. Other characteristic peaks at 1,638, 1,402, and 1,045 cm\(^{-1}\) were due to the CTAB molecules. The results showed that the 3D hollow porous microspheres were coated by a layer of CTAB molecules.

Based on the above results, a possible formation mechanism of the 3D hollow porous microspheres was put forward as follows: The ethylene glycol acts as both a solvent and a reducer during the solvothermal process. On one hand, it can afford -OH groups to coordinate with Fe\(^{3+}\). With the changes of pH (the addition of NaAc), high temperature, as well as high pressure, the Fe\(_3\)O\(_4\) nuclei are generated; they quickly grow up to become small nanoparticles and aggregate to form the microspheres, owing to the high surface energy. With a longer reaction time, the microspheres continue to grow up and finally form the hollow porous structure, probably owing to the Ostwald ripening. The addition of CTAB is used to control and disperse the resulting products. In fact, the detailed mechanism is rather complex and remains a further discussion to materials chemists.

The treatment of organic dyes in wastewater is a challenging task in industries. Considering the unique structure and large surface area of Fe\(_3\)O\(_4\) microspheres, it is expected that a strong affinity to organic molecules can be achieved by using these Fe\(_3\)O\(_4\) microspheres as sorbent material [17-21]. Furthermore, a recent research has shown that Fe\(_3\)O\(_4\) magnetic nanoparticles have a peroxidase-like activity [3,17]. In the presence of H\(_2\)O\(_2\), Fe\(_3\)O\(_4\) nanoparticles could efficiently do catalytic oxidation of organic dyes via the well-known Fenton reaction [22]. To assess the catalytic ability of the 3D hollow porous Fe\(_3\)O\(_4\) microspheres to the activation of H\(_2\)O\(_2\) herein, methylene blue is chosen as the model compound of organic pollutants, which is a widely used staining agent. Figure 4a shows the influence of 3D hollow porous Fe\(_3\)O\(_4\) concentrations on the degradation rates of methylene blue in the presence of H\(_2\)O\(_2\) (certain concentration). One can see that the removal efficiency of methylene blue increases followed by the increase of Fe\(_3\)O\(_4\) concentrations (reaction time is 30 min). When the concentration of Fe\(_3\)O\(_4\) reaches up to 600 mg/L, the removal efficiency of organic dyes approaches 90%. With the continuous rise of the concentration of Fe\(_3\)O\(_4\) microspheres, the removal efficiency has no obvious changes, indicating that a saturation state is completed. Therefore, 600 mg/mL is applied as the optimal concentration for methylene blue clearance. On the other hand, the concentration of H\(_2\)O\(_2\) has also influenced the removal efficiency of methylene blue. In the absence of H\(_2\)O\(_2\), methylene blue is partly removed (about 10%), indicating that 3D hollow porous Fe\(_3\)O\(_4\) microspheres can adsorb organic pollutants. In the presence of H\(_2\)O\(_2\) with different concentrations, the removal efficiency was obviously enhanced, as shown in Figure 4b. When the concentration of H\(_2\)O\(_2\) is 0.6 mol/L, the removal efficiency of methylene blue reaches the maximum (near 90%). Accordingly, an optimal concentration of H\(_2\)O\(_2\) at 0.6 mol/L was recommended for practical use.

Based on the above results, a possible catalytic mechanism of 3D hollow porous Fe\(_3\)O\(_4\) as the peroxidase mimetic is proposed as follows: due to the large surface and unique structures, H\(_2\)O\(_2\) and methylene blue molecules can be adsorbed onto the surface of 3D hollow porous Fe\(_3\)O\(_4\) microspheres. Under the influence of ultrasound irradiation, H\(_2\)O\(_2\) molecules are activated by the bound Fe\(^{2+}\) and Fe\(^{3+}\) of Fe\(_3\)O\(_4\) microspheres to generate reactive oxygen species (including \(\cdot\)OH, \(\cdot\)O\(_2\), \(\cdot\)HO\(_2\)). These radicals can further attack organic pollutants to degrade them.

**Conclusions**

In summary, we have developed a simple one-pot hydrothermal procedure for the synthesis of 3D hollow porous Fe\(_3\)O\(_4\) microspheres composed of lots of nanoparticles assembled on a large scale. The as-prepared microspheres have good dispersibility, large BET surface, strong superparamagnetic performance, as well as peroxidase-like
activity, which can be used as a kind of adsorbent and catalytic materials for the removal of organic pollutants. We believe that the easy preparation method, the large-scale output, the unique structure, as well as the outstanding performances endow these 3D microspheres many promising applications ranging from biomedicine to energy materials as well as environmental remediation.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
XW and JH conceived the study and designed the experiments. XW and YL performed the experiments. XW, YL, GL, and HH analyzed the data. JH and XW and JH conceived the study and designed the experiments. XW and YL.

Acknowledgements
This work was supported by the National Natural Science Foundation of China (NSFC Project Nos. 81472001, 31400851, 21106117, and 21036004).

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Received: 11 November 2014 Accepted: 20 November 2014

Published: 30 November 2014

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