Glycine-assisted hydrothermal synthesis of peculiar porous $\alpha$-Fe$_2$O$_3$ nanospheres with excellent gas-sensing properties

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Abstract

In this work, peculiar porous $\alpha$-Fe$_2$O$_3$ nanospheres were fabricated by a glycine-assisted hydrothermal method. They have large mesopores (ca. 10 nm) in the core and small mesopores (<4 nm) in the shell. To our best knowledge, there have been so far no reports on the synthesis of such peculiar porous $\alpha$-Fe$_2$O$_3$ nanospheres. X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and transmission electron microscopy were employed to characterize the obtained Fe$_2$O$_3$ nanospheres. Effects of preparation conditions, such as reactants, reaction temperature and reaction duration, were investigated on the morphology and structure of Fe$_2$O$_3$ nanospheres. It was shown that the morphology and structure could be readily controlled by the time and temperature of hydrothermal treatment. The formation mechanism was proposed based on experimental results, which shows that glycine molecules play an important role in the formation of the morphology and porous structure of $\alpha$-Fe$_2$O$_3$. The $\alpha$-Fe$_2$O$_3$ porous nanospheres were used as gas sensing layer, and exhibited excellent gas-sensing properties to ethanol in terms of response and selectivity. The sensors showed good reproducibility and stability as well as short response (9 s) and recovery time (43 s) even at an ethanol concentration as low as 50 ppm. The gas-sensing properties of porous $\alpha$-Fe$_2$O$_3$ nanospheres are also significantly better than those of previously reported Fe$_2$O$_3$ nanoparticles (ca. 30 nm). The sensitivity of the former is over four times higher than that of the latter at varied ethanol concentrations. The gas-sensing mechanism was discussed in details. Both fast response and steady signal make these peculiar nanostructures a promising candidate for ethanol detection.

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1. Introduction

Nanomaterials of well-defined size and morphology have attracted considerable research efforts because of their size- and morphology-dependent properties. Among them are porous metal oxides. A variety of porous metal oxides including those of TiO$_2$ [1,2], SnO$_2$ [3], ZnO [4–9] and Ir$_2$O$_3$ [10] have been synthesized and explored for applications in catalysis, lithium-ion batteries, gas sensing, and so on.

Hematite ($\alpha$-Fe$_2$O$_3$), a stable phase of iron oxide, is an n-type semiconductor ($E_g = 2.1$ eV). It is non-toxic, highly resistant to corrosion, and environment friendly. It has been intensively investigated for applications in catalysts [11–13], lithium-ion batteries [14,15], water treatment [16,17] and gas sensors [18–24]. Hematite of varied morphologies have been fabricated, including nanocrystals [25,26], particles [27–29], cubes [30], rods [31,32], wires [33], tubes [34], flute-like [18], hollow spheres [35] and nanocups [36], and ordered mesoporous Fe$_2$O$_3$ [37].

Glycine-assisted hydrothermal synthesis is frequently used to prepare specific structures [38,39]. For example, Prevot and co-workers prepared flower-like NiAl-layered double hydroxides using Ni (II) glycinate complex as precursor [38]. Zhang and co-workers prepared hollow Ni(OH)$_2$ microspheres using Ni (II) glycinate complex under strong basic conditions. Glycine played an important role in the formation of the specific morphologies and architectures [39].

In the current work, glycine-assisted hydrothermal synthesis was adopted to prepare $\alpha$-Fe$_2$O$_3$ nanomaterials. The obtained nanomaterials were analysed by X-ray powder diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, and selected area electron diffraction. The results showed that the obtained nanomaterials
The annealed \( \alpha\text{-Fe}_2\text{O}_3 \) product was observed by SEM and TEM. Fig. 2a shows its typical low-magnification TEM image. It consists of nearly monodisperse spherical particles of 90 nm in size. Fig. 2b presents a TEM image, showing that the spherical particles in fact contain randomly distributed pores. A close view further reveals that there are two types of pore, one is large mesopores (ca. 10 nm) inside the dashed circle, and the other is small mesopores (<4 nm) at the rim. SEM image (Fig. 2c) also shows that the annealed \( \alpha\text{-Fe}_2\text{O}_3 \) product consists of nearly monodisperse spheres. High-resolution TEM image (Fig. 2d) discloses clear lattice fringes with a spacing of 0.37 nm, which is consistent with the \( d \) value of the (0 1 2) plane [25]. SAED pattern (Fig. 2e) indicates a single-crystal diffraction nature of the annealed \( \alpha\text{-Fe}_2\text{O}_3 \) product. EDS was used to determine the chemical composition of the annealed \( \alpha\text{-Fe}_2\text{O}_3 \) product (Fig. 2f). The results showed that it contains Fe and O, and the atomic ratio of Fe to O is 2:3, in good agreement with the stoichiometry of \( \text{Fe}_2\text{O}_3 \).

Reaction temperature usually plays an important role in hydrothermal synthesis. Fig. 3 shows TEM images of uncalcined \( \alpha\text{-Fe}_2\text{O}_3 \) products obtained at different hydrothermal temperatures. When the hydrothermal temperature is 120 °C, the product consists of nearly monodisperse solid spherical particles of rough surface. Pores are not clearly noticeable inside the spherical particles. The product obtained at 160 °C (Fig. 3c), however, consists of spherical particles with smooth surface. Pores are clearly seen inside the spherical particles (Fig. 3d). Apparently, the porous structure had formed before calcination though calcination might further expand the pore size. Therefore, hydrothermal temperature of 160 °C is appropriate for forming the porous structure.

The addition of urea and glycine may also play an important role in obtaining the porous \( \alpha\text{-Fe}_2\text{O}_3 \) spheres [38,39]. When FeCl\(_3\) and glycine were hydrothermally treated without addition of urea at 160 °C, spherical particles were obtained, which have smooth surface and are uniform in size (Fig. 4a). Mesopores are not clearly noticeable, as shown in magnified TEM image (Fig. 4b) though glycine molecules could form small micelles in solution [38,39]. Without addition of glycine, particles of irregular shapes were obtained (Fig. 4c), and they are nonporous, as revealed in Fig. 4d. The corresponding XRD patterns (Fig. 4e and f) show that both products have a pure rhombohedral phase of \( \alpha\text{-Fe}_2\text{O}_3 \).

### 3.2. Plausible formation mechanism of porous \( \alpha\text{-Fe}_2\text{O}_3 \) nanospheres

Before the hydrothermal treatment, i.e., during the mixing of precursors, several reactions may have occurred, such as precipitation, hydrolysis, dissolution and metal ion complexation. FeCl\(_3\) dissolved in water, and formed a yellow-brown transparent solu-
When glycine was added into the solution, the color of the mixture changed to purple-black, and the solution was opaque. Fe³⁺ ion and glycine might form a coordination compound. At the early stage of the hydrothermal treatment, urea decomposed to NH₃ and CO₂ [41,42]. CO₂ could form stable bubbles due to glycine, and NH₃ dissolved in water and formed a basic solution (after the hydrothermal treatment and the autoclave was opened, NH₃ could smell). Under such basic conditions, glycine (pKₐ₁ = 2.34, pKₐ₂ = 9.60 and pHᵢ = 5.97) was present in the Gly⁻ (H₂N–CH₂–COO⁻) form [39]. Fe³⁺ ions hydrolyzed, and iron oxide nanocrystals formed under the basic conditions. The –COO⁻ terminal of glycine connected with iron oxide nanocrystal. Under the conditions of high temperature and pressure in the autoclave, the nanocrystal and bubble could connect by free glycine molecules in the solution. To understand the formation of the porous α-Fe₂O₃ nanospheres, time-dependent experiments were carried out, and resultant products were analysed by TEM. When the reaction time was ≤30 min, small Fe₂O₃ nanocrystals (shown in Fig. 5a by black arrows) and stable bubbles would form in the mixture [43,44]. By increasing the reaction time to 1 h, nanocrystals assembled together with the assistance of glycine, forming nearly monodisperse raspberry-like porous aggregates (Fig. 5a). With increase of the reaction time, iron oxide nanocrystals further deposited on the surface of raspberry-like aggregates, which continuously transformed to nanospheres having a core with large mesopores (Fig. 5b). Finally, a porous core/shell structure gradually formed (Fig. 5c and d) resulting in the peculiar porous structures. This process is similar to the holing process described in a previous report in which glycine was also used as an additive. Solid spheres formed first, and an interior cavity gradually formed via a core evacuation process [38,39]. XRD patterns of the products (Fig. 6) show that peak intensities gradually increase with the reaction time, indicating

![Fig. 2. Typical TEM (a and b), SEM (c), HRTEM (d) images and SAED (e), EDS (f) patterns of porous α-Fe₂O₃ nanospheres after calcination at 450 °C for 3 h in air.](image)
that the pure α-Fe₂O₃ crystal structure already formed in the early stage of precipitation. The increase in crystallinity confirms that Ostwald ripening (crystallites grow at the expense of smaller ones) is the underlying mechanism in this pore-forming process [38,39,45–47].

3.3. Gas-sensing properties of porous α-Fe₂O₃ nanospheres

Development of gas sensors with improved performance has recently become a hot topic because of increasing concerns over environmental pollution and public safety [48,49]. Porous metal oxides are favorable to the diffusion of target gases due to their large surface-to-volume ratio and well-defined pore structure [49]. As an n-type semiconductor, one of the most important applications of α-Fe₂O₃ is gas sensors. For example, hematite nanostructures containing hierarchical mesopores, such as colloidal crystal clusters and monodisperse porous nanospheres, were used for gas sensors, and showed better sensing performance as compared with commercial α-Fe₂O₃ particles [50,51]. Therefore, a gas sensor was fabricated using porous α-Fe₂O₃ nanospheres, and its sensing properties were investigated.

It is well known that the operation temperature largely affects the sensitivity of a semiconductor sensor [48–55]. In order to determine the optimal operation temperature, the response of the porous α-Fe₂O₃ nanosphere gas sensor to ethanol of varied concentrations in air was evaluated as a function of the operation temperature. As shown in Fig. 7, the sensor response varies with the operation temperature. At three different ethanol concentrations, all the sensitivities increase with increase of the operation temperature from 180 to 260 °C. When the operation temperature is over 260 °C, however, the sensitivity gradually drops with further increase of temperature. The optimal operation temperature of 260 °C was selected for following studies.

Fig. 8 shows a response curve of porous α-Fe₂O₃ nanosphere sensor to ethanol of varied concentrations at 260 °C. Clearly, the voltage response is proportional to the ethanol concentration between 50 and 1000 ppm. The response and recovery times, which are defined as the time to reach 90% of the final resistance, are important parameters for gas sensors. For 50 ppm ethanol, the response and recovery times are 9 and 43 s, respectively. The sensor still has fast response and recovery even exposed to ethanol vapor of high concentration, indicating good response/recovery capabilities.

Practically, the sensor selectivity is extremely important. We thus measured the response of the sensor to several other substances such as CHCl₃, ethyl ether, and CO at identical concentration (50 ppm) and operation temperature (260 °C). As shown in Fig. 9, the porous α-Fe₂O₃ nanosphere sensor has higher sensitivity to ethanol than to the other substances. Therefore, the porous α-Fe₂O₃ nanosphere sensor could selectively detect ethanol in the presence of other potential interfering substances.

The sensing performance of the porous α-Fe₂O₃ nanospheres was compared with that of α-Fe₂O₃ nanoparticles of ca. 30 nm

![Fig. 3. TEM images of porous α-Fe₂O₃ nanospheres obtained at different hydrothermal temperatures: 120 °C (a and b) and 160 °C (c and d) for 10 h.](image-url)
as reported in a previous work [40]. The results are shown in Fig. 10. Clearly, the response profiles are similar in shape, and the sensitivity increases almost linearly with increase of the ethanol concentration in both cases. From Fig. 10, two linear equations could be derived as follows:

Porous \(\alpha\)-Fe\(_2\)O\(_3\) nanospheres : \[ S = 0.062C + 5.59, \quad r = 0.992, \]

(1)

\(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles of ca. 30 nm : \[ S = 0.0072C + 1.61, \quad r = 0.952, \]

(2)

where \(S\) is the sensitivity, \(C\) is the concentration of ethanol. The sensitivity of the porous \(\alpha\)-Fe\(_2\)O\(_3\) nanosphere sensor increases dramatically with increase of ethanol concentration, and is much higher than that of the \(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles, especially at higher ethanol concentrations [40]. The sensitivities of the former are almost several times greater than those of the latter for
all the ethanol vapors of varied concentrations. Thus, the gas-sensing performance of the porous $\alpha$-Fe$_2$O$_3$ nanospheres is much better than that of the previously reported $\alpha$-Fe$_2$O$_3$ nanoparticles.

There are many oxygen vacancies on the surface of the sensing material [9,19,45,49]. When the sensor is in air, oxygen molecules are adsorbed at these oxygen vacancies, forming active oxygen adsorbates, such as $\text{O}^{2-}$, $\text{O}^-$, and $\text{O}_2^-$. The formation of the oxygen adsorbate layer would lead to the transfer of electrons from the sensor surface to the adsorbate layer, and so the electron density would decrease on the sensor surface. The oxygen ions react with ethanol molecules on the surface when the sensor is exposed to ethanol vapor, and thus release the trapped electrons to the sensor. This leads to the change in resistance of the $\alpha$-Fe$_2$O$_3$ sensor. The amount of oxygen and test gas on the surface of materials is strongly dependent on the microstructure of the materials, such as particle size, morphology and porosity. Conventional $\alpha$-Fe$_2$O$_3$ nanoparticle sensors have poor porosity and relatively large particle size, whereas porous $\alpha$-Fe$_2$O$_3$ spheres have abundant pores in their structures, which can facilitate the diffusion of gas molecules and provide more adsorption–desorption sites. Very interestingly, if the as-synthesized Fe$_2$O$_3$ nanospheres were calcined in nitrogen (named as Fe$_2$O$_3$ (N$_2$)) instead of air, the sensor based on Fe$_2$O$_3$ (N$_2$) showed no sensing properties even in ethanol vapor of higher concentration. The mechanism is still under investigation.

**Fig. 5.** TEM images of porous $\alpha$-Fe$_2$O$_3$ nanospheres obtained at 160 °C using varied reaction times: 1 h (a), 2 h (b), 5 h (c) and 8 h (d). Scale bar: 20 nm.

**Fig. 6.** XRD patterns of porous $\alpha$-Fe$_2$O$_3$ nanospheres obtained at 160 °C using varied reaction times.

**Fig. 7.** Response versus operation temperature of porous $\alpha$-Fe$_2$O$_3$ nanosphere sensor to ethanol of varied concentrations.
(ca. 10 nm) in the core and small mesopores (<4 nm) in the shell. To our best knowledge, there have been so far no reports on the synthesis of such peculiar porous $\alpha$-Fe$_2$O$_3$ nanospheres. The time and temperature of hydrothermal treatment influence the structure and morphology of product. The $\alpha$-Fe$_2$O$_3$ crystal phase forms at the early stage, and extended reaction time results in enhanced crystallinity of product. $\alpha$-Fe$_2$O$_3$ nanostructures obtained at different reaction times are shown to follow a nucleation and growth process resembling Ostwald ripening with the assistance of glycine molecules. The porous $\alpha$-Fe$_2$O$_3$ nanospheres were used as a gas sensing layer, and exhibited excellent gas-sensing properties to ethanol in terms of response and selectivity. The gas-sensing properties of porous $\alpha$-Fe$_2$O$_3$ nanospheres are also significantly better than those of previously reported Fe$_2$O$_3$ nanoparticles (ca. 30 nm). Both fast response and steady signal make these peculiar nanostructures a promising candidate for ethanol detection.

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