Improved photocatalytic and gas sensing properties of α-Fe₂O₃ nanoparticles derived from β-FeOOH nanospindles

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Abstract

α-Fe₂O₃ nanoparticles were synthesized through calcining the as-synthesized spindle-like β-FeOOH precursors at 600 °C. X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) results showed that β-FeOOH nanospindles with a diameter of ~50 nm and lengths up to 100–150 nm were readily changed to α-Fe₂O₃ nanoparticles with a size of 30–150 nm after heat-treatment for 2 h. The photocatalytic performances of the as-prepared samples were evaluated by photocatalytic decolorization of methylene blue (MB) in the presence of H₂O₂ at ambient temperature. The results indicated that the α-Fe₂O₃ nanoparticles exhibited the highest photocatalytic activity compared with the β-FeOOH nanospindles and the commercial α-Fe₂O₃ powders. The gas-sensing measurement results demonstrated that the products showed an excellent gas response to ethanol and acetone. The results showed that these α-Fe₂O₃ nanoparticles may have potential applications in gas sensor and photocatalysts.

Keywords: E. Sensors; β-FeOOH; α-Fe₂O₃; Nanoparticles; Photocatalysts

1. Introduction

Hematite (α-Fe₂O₃) is the most thermodynamically stable iron oxide with n-type semiconducting properties (E₉ = 2.1 eV) under ambient conditions. It has been extensively used in many fields, such as magnetism [1,2], catalysts [3,4], gas-sensing [5,6], pigments [7] and water treatment [8,9], as well as in other biological and medical fields due to its low cost, environmental friendliness, and fascinating physicochemical properties. Nanostructured materials are expected to have improved physicochemical properties compared with bulk materials due to their size effects, large surface area to volume ratios and possible quantum confinement effects [10].

Many efforts have been directed to fabricate α-Fe₂O₃ nanostructures with specific size and morphology [11–13] because of their unique electrical, optical and magnetic properties for the potential applications in a lot of fields. Stimulated by these intriguing properties and extensive applications, a variety of methods have been reported for the synthesis of α-Fe₂O₃ nanostructures, including the vapor–solid growth method, sol–gel approach, hydrothermal technique and the chemical precipitation process. Zhonglin Wang groups have synthesized uniform α-Fe₂O₃ nanowire arrays by a vapor–solid method, and systematically studied the growth mechanism of the α-Fe₂O₃ aligned arrays [14]. Wael Hamd et al. fabricated α-Fe₂O₃ mesoporous films by a template-directed sol–gel method combined with a dip-coating approach and followed by annealing at various temperatures in air [15]. Guohong Qiu et al. have synthesized nanosized α-Fe₂O₃ powder by a microwave-assisted hydrothermal reaction of Fe(NO₃)₃ in the presence of urea at 120 °C [16]. Although there are a lot of successes in the synthesis of α-Fe₂O₃ nanostructures, a facile method is still required.

Herein, α-Fe₂O₃ nanoparticles are prepared by a combined method of hydrolysis and calcination. The hydrolysis of FeCl₃ solution gives uniformly sized β-FeOOH nanospindles that serve as the precursor for α-Fe₂O₃ nanoparticles. Despite the size and shape changes, the calcination-derived α-Fe₂O₃ nanoparticles show phase pure hematite and high crystallinity. Moreover, the well-defined β-FeOOH precursor may provide a natural defense from the heavy agglomeration of α-Fe₂O₃.
nanoparticles, resulting in network-like nanoparticle aggregates. These networks should have an effective contact surface area and accessible diffuse pathway for the molecule adsorption and desorption. It is thus expected that the as-synthesized α-Fe2O3 nanoparticles show high photo-catalytic activity and gas-sensing performance. The visible light photo-degradation of MB on the synthesized α-Fe2O3 nanoparticles shows their obviously higher ability than that of the β-FeOOH precursor. Furthermore, the gas-sensing measurements of the synthesized α-Fe2O3 nanoparticles exhibit an excellent ethanol- and acetone-sensing performance.

2. Experimental

2.1. Sample preparation

All the reagents used in the experiment were analytical grade without further purification. The precursor β-FeOOH was obtained from hydrolysis of diluted aqueous iron chloride (FeCl3·6H2O) solution. In a typical process, 0.02 mol L−1 aqueous solution of FeCl3 was heated at 80 °C for 24 h under magnetic stirring. After cooling to room temperature, the product was washed with deionized water and ethanol for several times, and then dried at 40 °C in air for 8 h. After that, the as-obtained β-FeOOH was heated in air at 600 °C for 2 h to obtain the α-Fe2O3.

2.2. Characterization

The phase and crystallinity of the obtained samples were characterized by XRD using a Bruker D8 advanced X-ray diffractometer with Cu Kα radiation (λ=1.54056 Å). The 2θ range used was from 10° to 80°. TEM images were obtained on a Hitachi H-600 with an accelerating voltage of 100 kV.

2.3. Photocatalytic experiment

The photocatalytic experiment was carried out in an equipment of XPA-7 (G8) photochemical action instrument (Xujiang Electromechanical plant, Nanjing, China). A 350 W Xe lamp was used as a light source with cutoff filter (< 420 nm). In a typical process, aqueous suspensions of MB (50 mL, 10 mg L−1) and 10 mg of samples were mixed into a quartz tube. Prior to irradiation, the solution was continuously stirred for 30 min in the dark to ensure the establishment of an adsorption–desorption equilibrium. Then 100 μL H2O2 (30% aqueous solution) was added into the solution. The UV–vis spectrophotometer (Shimadzu UV-2450 PC) was used to monitor the concentration of MB during the photodegradation. The percentage of photodegradation is reported as C/C0, where C is the concentration of MB for each irradiated time, and C0 is the starting concentration.

2.4. Sensor fabrication

The method and instrument of the gas sensing test were similar to that of our previous work [17]. The as-synthesized sensor was fixed into the gas sensing apparatus and aged at 300 °C for 48 h. Gas sensing measurements were carried out on a computer-controlled WS-30A system (Zhengzhou, China). Here, the gas response is defined as Rg/Ra, where Rg and Ra are the resistance of the sensor in clean air and in detected gas, respectively.

3. Results and discussion

3.1. Structure characterization

Fig. 1 shows the XRD patterns of the precursor and the as-synthesized sample. Fig. 1a exhibits the precursor fabricated by the hydrolysis of iron chloride solution. It is obvious that almost all the reflections can be readily indexed to a tetragonal β-FeOOH phase (JCPDS no. 34-1266). A complete conversion from β-FeOOH to α-Fe2O3 is achieved by the calcination of the spindle-shaped β-FeOOH, which can be proved by the XRD pattern in Fig. 1b. The product shows a hexagonal structure of α-Fe2O3 (JCPDS no. 33-0664, (a) 5.035 Å, (b) 5.535 Å and (c) 13.74 Å).

The morphologies of the obtained precursor and product were characterized by TEM. Fig. 2a shows the TEM image of the β-FeOOH precursor that exhibits a regular spindle shape with a diameter of about 50 nm and length of about 100–150 nm. Furthermore, the spindle-shaped β-FeOOH completely transformed to α-Fe2O3 nanoparticles after heated at 600 °C for 2 h, as shown in Fig. 2b. Interestingly, the morphology of the α-Fe2O3 nanoparticles is irregular particle with a size of about 30–150 nm.

3.2. Photocatalytic experiment

The visible-light photocatalytic activity of the β-FeOOH, the commercial α-Fe2O3 and the as-prepared α-Fe2O3 nanoparticles was evaluated by the degradation of MB solution. Fig. 3a gives the evolution of the MB absorption spectra in the

Fig. 1. Powder XRD patterns of β-FeOOH precursor (a) and α-Fe2O3 nanoparticles (b).
The presence of α-Fe₂O₃ nanoparticles as a function of time under visible light irradiation (λ > 420 nm). The intensity of the characteristic peak of MB at λ = 663.5 nm was found to decrease gradually with prolong irradiation time, showing its effective photodegradation of MB. Fig. 3b shows a plot of the photodegradation extent of the MB molecules with the increase of the irradiation time for the β-FeOOH, the commercial α-Fe₂O₃ and the α-Fe₂O₃ nanoparticles in the presence of H₂O₂ at ambient temperature. It can be seen that the degradation of MB molecules by the α-Fe₂O₃ nanoparticles is fast and approaches to 80% within 120 min. As comparison, a negligible degradation of MB is found in the absence of the α-Fe₂O₃ nanoparticles or in the presence of the β-FeOOH precursor (Fig. 3b). The commercial α-Fe₂O₃ shows a certain adsorption performance. However, the photocatalytic property is much lower than that of the α-Fe₂O₃ nanoparticles.

### 3.3. Gas-sensing performance

As is well-known, the response of a semiconductor gas sensor is highly affected by its operating temperature. In order to determine the optimum operating temperature, the response of the α-Fe₂O₃ sensor to 100 ppm ethanol at different operating temperatures was tested, as shown in Fig. 4. It is obvious that the response increased with temperature, reached the maximum value at 340 °C, and decreased further with prolong temperature. The phenomenon can be explained by the following. With the increase of operating temperature, the amount of gas adsorbed becomes high and the adsorption attains a balance at a suitable temperature (namely optimum temperature). However, the amount of gas adsorbed will reduce when the operating temperature keeps on increasing, and the balance will change to desorption, leading to a decreased gas response.
sensitivity when the operating temperature exceeds the optimum values [18]. The maximum response reached 10 toward 100 ppm ethanol at 340 °C. Therefore, the optimal operating temperature was fixed at 340 °C for the subsequent gas detections.

The response and recovery behavior were further investigated with the α-Fe₂O₃-based sensor exposed to ethanol, acetone and methanol at different concentrations at 340 °C, respectively, as shown in Fig. 5(a–c). It can be seen that the output voltage increases suddenly on the injection of the tested gas, and then decreases rapidly to the initial value after exposure to air, which indicates that the α-Fe₂O₃-based sensor has good reversibility. Fig. 5(d) illustrates the response defined as \( R/R_0 \) to ethanol, acetone and methanol, respectively. With the increase in the gas concentration, the response greatly increased. The response values of the α-Fe₂O₃-based sensor to ethanol and acetone were 2.94 and 2.58, respectively, even at low concentration of 10 ppm, indicating that the sensor has good gas-sensing properties.

4. Conclusions

In conclusion, α-Fe₂O₃ nanoparticles were prepared through annealing the β-FeOOH precursor obtained from hydrolysis of FeCl₃ · 6H₂O. Moreover, the gas sensing property and the photocatalytic activity of the synthesized products were evaluated. The results showed that the α-Fe₂O₃ nanoparticles exhibited excellent photocatalytic properties towards MB and high gas response to ethanol and acetone, suggesting that these products may have potential applications in the field of photocatalysis and gas sensors.

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