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Introduction

Control of morphologies and microstructures of functional semiconductor oxides continues to be a fundamental issue in modern materials science and technology.1-3 Growth of oxides with hierarchical nanostructures has attracted tremendous attention in recent years because diverse properties can be integrated by tailoring the morphology, size, and assembling organization of the primary nanobuilding blocks.⁴⁻⁶ As stimulated by both the unique properties and promising applications of such hierarchical architectures, great efforts have been focused on the design of rational methods to organize the nanoscaled building blocks into complicated 3-dimension (3 D) structures. Generally, the efficient route to the preparation of hierarchical nanostructures is probably selfassembly through a spontaneous process.⁷⁻¹⁰ However, it remains a significant challenge to develop simple, green and inexpensive synthesis strategies for hierarchically selfassembled architectures with designed chemical components and morphologies.

Hematite (α -Fe₂O₃), the most stable iron oxide with n-type semiconducting properties under ambient conditions, has been recognized as a promising semiconductor material. Due to its nontoxicity, stability, and low cost, many applications of

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Controlled synthesis of hierarchical Sn-doped α -Fe₂O₃ with novel sheaf-like architectures and their gas sensing properties

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Monodisperse Sn-doped α -Fe₂O₃ with novel wheat sheaf-like hierarchical architectures were synthesized by a facile one-step hydrothermal method. Field emission scanning electron microscopy and transmission electron microscopy images revealed that these sheaf-like microstructures were built from filamentary crystals-stacked nanoparticles. The high resolution transmission electron microscopy image from a single "filament" showed that all the nanoparticles were highly oriented. The morphology and size of products could be controlled by simply adjusting the concentration of Sn⁴⁺. A possible formation mechanism involving oriented aggregation and Ostwald ripening was proposed on the basis of the results of timedependent experiments. To demonstrate the usage of such α -Fe₂O₃ hierarchical architectures, the obtained sample was applied to fabricate a gas sensor which was then tested for response to three kinds of gases (ethanol, methanol, and formaldehyde). Results of that test showed that the sensor had high response, and rapid response kinetics to ethanol at the operating temperature of 250 °C.

> α-Fe₂O₃, such as gas sensors and Li-ion batteries,¹¹⁻¹⁴ have been widely investigated. Over the past few years, in order to highlight some special properties demanded by particular technological applications, various well-defined simple shapes of iron oxides nanostructures, including particles (0 D),¹⁵ rods, wires, and tubes (1 D),^{16–18} disks, sheets, and rings (2 D)^{19–21} have already been synthesized via a variety of methods. Recently, many efforts have been focused on the synthesis of complex 3 D hierarchical architectures using these lowdimensional nanostructures as building blocks due to their more outstanding properties and promising applications in various fields.²²⁻²⁴ Despite these advances, the novel morphologies of α-Fe₂O₃ nanocrystals spur researchers to explore their yet unknown properties and potential applications. For this purpose, the synthesis of hierarchical α-Fe₂O₃ nanomaterials should be given more attention. However, to the best of our knowledge, studies of wheat sheaf-like iron oxide nanostructures have been rarely reported.

> In this paper, we report the synthesis of monodisperse Sndoped α -Fe₂O₃ "wheat sheaf" by a facile one-step hydrothermal method. The hydrothermal reaction was performed in an ethanol-water mixed solvent using ferric trichloride and sodium stannate as the precursors. The effect of the amount of Sn⁴⁺ ions on both morphology and size of products was investigated. Moreover, the formation process had been studied through the morphology evolution with different reaction time, and a possible formation mechanism was speculated. The gas sensing properties of the sensors based on

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the synthesized novel Sn-doped $\alpha\text{-}Fe_2O_3$ hierarchical architectures exhibited high response to ethanol.

Experimental

Synthesis of Sn-doped a-Fe₂O₃ "wheat sheaf"

All the reagents in the experiment were analytical grade (Beijing Chemicals Co. Ltd.) and used as received without further purification. In a typical experiment, 4.054 g FeCl₃·6H₂O was dissolved in 30 mL water-ethanol mixture (1:1, v/v) under magnetic stirring. Then 1.2 g $(CH_2)_6N_4$ (HMT) was added to the above solution. After several minutes of ultrasonic dispersing, an appropriate amount of Na₂SnO₃·6H₂O was added to the solution with stirring. The mixture was transferred into a Teflon-lined stainless steel autoclave, which was heated and maintained at 160 °C for 12 h. After the reaction, the autoclave was allowed to cool to room temperature naturally. The resulting precipitates were collected by centrifugation, washed several times with deionized water and ethanol, and finally dried in vacuum at 80 $^\circ C$ for 12 h. A series of Sn-doped α -Fe₂O₃ hierarchical architectures with different tin amounts were synthesized, named as sample 1 (0.0 wt% Sn), sample 2 (1.0 wt% Sn), sample 3 (2.0 wt% Sn), and sample 4 (4.0 wt% Sn).

Characterization

The X-ray diffraction (XRD) patterns of the as-prepared products were recorded by a Rigaku TTRIII diffractometer using Cu-K α radiation ($\lambda = 1.5406$ Å). Data were collected over the 2θ range 20–70°. Field-emission scanning electron microscopy (FESEM) observations were carried out using a JEOL JSM-7500F microscope with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were conducted using a JEOL JEM-3010 microscope with an accelerating voltage of 200 kV. The energy dispersive X-ray spectrometry (EDX) result was measured by the SEM attachment.

Fabrication and measurement of gas sensors

The details of the sensor fabrication are similar to those of sensor fabrication reported in other literature.^{25,26} The synthesized Sn-doped α -Fe₂O₃ "wheat sheaves" were mixed with deionized water to form a slurry, and then coated onto an alumina tube (4 mm in length, 1.2 mm in external diameter, and 0.8 mm in internal diameter), on which a pair of gold electrodes was installed at each end, and each electrode was connected with a Pt wire. After drying in air at room temperature, the devices were sintered at 400 °C for 2 h in air using a muffle furnace. A Ni-Cr alloy coil, as a heater to control the operating temperature of sensor, was inserted into the alumina tube.

The measurement was processed by a static process in a test chamber under laboratory conditions (30-40 RH%, 23 $^{\circ}$ C): a given amount of the tested gas was injected into a closed glass chamber by a microsyringe and mixed with air. Then the sensor was put into the chamber for the measurement of the



Fig. 1 Morphological characterization of the 4 wt% Sn-doped α -Fe₂O₃ products: (a) panoramic, (b) enlarged, and (c–d) high-magnification FESEM images.

sensing performance. The gas response behavior was investigated at operating temperature between 175 to 325 °C in 25 °C increments. The gas response was defined as the ratio between R_a (the resistance when exposed to air) and R_g (the resistance when exposed to test gas). The response time and recovery time were defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively.

Results and discussion

The morphologies and microstructures of the 4.0 wt% Sndoped α -Fe₂O₃ hierarchical architectures obtained with 1.2 g HMT at 160 °C for 12 h were illustrated by FESEM and TEM observations. A panoramic FESEM image of the as-prepared product without any dispersion treatment is shown in Fig. 1a. It can be seen that the sample had good monodispersity and uniformity. Fig. 1b and c show the enlarged FESEM images of such Sn-doped α -Fe₂O₃ hierarchical architectures. They look like a wheat sheaf-as if a bundle of filamentary crystals had been bandaged in its middle, with the top and bottom fanning out while the middle remaining relatively thin-hence the name "sheaf structures". The individual sheaf had an average length of \sim 3 µm, and the diameter of middle section was about 1 µm (Fig. 1c). The high-magnification FESEM image (Fig. 1d) shows the detailed morphology of the Sn-doped α -Fe₂O₃ sheaf structures. Apparently, the rough surfaces of the nanofilaments were exhibited, and the single nanofilament had an average diameter of ~ 20 nm. Moreover, it is obvious that the nanofilaments were built from a large number of nanoparticles

In addition, in order to get deeper insight into the structure of such novel Sn-doped α -Fe₂O₃ hierarchical architecture, the detailed TEM observations were further carried out. A typical TEM image of an individual "wheat sheaf" is presented in Fig. 2a. It is found that the size and shape were similar to



Fig. 2 (a) TEM image of an individual Sn-doped α -Fe₂O₃ "wheat sheaf" with its corresponding SAED pattern shown in the inset. (b) The HRTEM image of the nanofilament of the sheaf structures. (c–e) Higher magnification HRTEM images recorded in different areas of the nanofilament crystal in (b). (f–i) FESEM image of a single sheaf structure and corresponding elemental mapping images.

those of FESEM observations. The SAED pattern taken from the top/bottom of the "wheat sheaf" is shown in the inset of Fig. 2a. The pattern was characterized as a transitional state from a single crystalline spot array to poly-crystalline rings, which indicates the single crystalline nature of the building blocks and the presence of some ordered arrangement of such crystallites in the architectures. In order to obtain more detailed structural information for the well-aligned filamentary crystals, a HRTEM image (Fig. 2b) was recorded on the top of filamentary crystal. Fig. 2c-e show the magnification HRTEM images obtained from the marked fringe of the filamentary crystals in Fig. 2b, from which the lattice fringes could be observed clearly and the lattice spacing was 0.251 nm, corresponding to the (110) plane of α -Fe₂O₃. The result confirms that the filamentary crystal consisted of the single crystalline nanoparticles and all the primary nanoparticles were perfectly oriented. The SEM elemental mapping was conducted to clearly identify the spatial distributions of Fe, O, and Sn in the sheaf structure (Fig. 2f-i). The signals of Fe and O were obviously detected. The Sn signals were uniformly distributed over the entire "wheat sheaf" as expected.

The influences of experimental parameters on the microstructures of final as-prepared products were investigated. The results show that the amount of Sn ion played an important role in controlling the morphologies and sizes of the α -Fe₂O₃ hierarchical architectures. Keeping other conditions unchanged, in the absence of Sn ions, the resultant product was composed of uniform and dispersed particles, which had a round-edged hexahedral morphology with an average size of about 1.2 μ m, as shown in Fig. 3a. Apparently, the rough



Fig. 3 FESEM images of products obtained with different Sn amounts at 160 $^\circ C$ for 12 h: (a) 0.0 wt%, (b) 1.0 wt%, (c) 2.0 wt%, and (d) 4.0 wt%.

surface of the hexahedral microstructures was exhibited. No other morphologies could be detected, which indicates that the high yield and uniformity were achieved in this way. These hexahedral particles transformed into the uniform rice-like particles (Fig. 3b) with the introduction of Sn ions (1.0 wt%) into the solution. As the amount of Sn was increased to 2.0 wt%, the high symmetric peanut-like particles were formed with coarse surfaces (Fig. 3c). The length of such microstructure was about 2 µm, and the average diameters of the center section was about 800 nm. Moreover, it can be seen that the ends of the peanut-like microstructure were composed of nanoparticles, which were perfectly oriented. Further increase of Sn ions (4.0 wt%), the peanut-like structure of Sn-doped α -Fe₂O₃ evolved into sheaf structure (Fig. 3d). The detailed morphology characteristics of them were described previously. With the increase in concentration of tin ion, the size of the assynthesized products got larger gradually. Therefore, on the basis of the morphological study, it can be concluded that tin ion plays an important role in forming hierarchical "wheat sheaf" microstructures.

Fig. 4(a) shows the typical XRD patterns of the assynthesized pure α -Fe₂O₃ and Sn-doped α -Fe₂O₃ hierarchical architectures. It can be seen that all of the diffraction peaks could be indexed to the phase-pure rhombohedral α -Fe₂O₃. This was in good agreement with the JCPDS file of α -Fe₂O₃ (JCPDS 33-0664). For the as-prepared Sn-doped α -Fe₂O₃ hierarchical architectures, no other crystalline phase corresponding to tin oxide and its related secondary or impurity phase were detected in the Fig. 4(a). The results indicated that the substitution of Sn did not affect the rhombohedral structure of iron oxide. To investigate the effect of doping on the crystallinity of α -Fe₂O₃ hierarchical microstructures, the (104) and (110) diffraction peaks were monitored. Typically, it is obvious that there was 0.12 degree right shift (towards larger angle) in both the (104) and (110) diffraction peaks of 4.0 wt% Sn-doped α -Fe₂O₃ compared with those of pure α -Fe₂O₃ (Fig. 4(b)). This proved that Sn ion incorporation led to lattice



Fig. 4 (a) XRD patterns of samples with different Sn contents. (b) Comparison of (104) and (110) peaks from XRD patterns.

deformation in the doped α -Fe₂O₃, which was ascribed to the difference of ionic radius between Sn⁴⁺ (0.071 nm) and Fe³⁺ (0.064 nm). The unusual shift might result from the lattice distortion caused by the stress during the preparation.²⁷ A similar observation has been found in Cu-doped ZnO nanowire arrays²⁸ and Co-doped ZnO bulk materials.²⁹ However, no characteristic peaks of SnO or SnO₂ were observed for Sn-doped α -Fe₂O₃. All of results indicated that Sn ions systematically entered into the crystal lattice of α -Fe₂O₃ without deteriorating the original crystal structure.

To reveal the growth process of novel Sn-doped α -Fe₂O₃ "wheat sheaf" and possible growth mechanism, the study of the morphology evolution of Sn-doped α -Fe₂O₃ sheaf structures with different reaction time had been conducted. The corresponding results are shown in Fig. 5. When the hydrothermal time was 1 h, it can be seen that the product was entirely comprised of relatively uniform rod-like nanoparticles (Fig. 5a). With the reaction time increasing to 3 h,



Fig. 5 FESEM images of morphology evolution of 4.0 wt% Sn-doped α -Fe₂O₃ hierarchical architectures prepared with different reaction time: (a) 1 h, (b) 3 h, (c) 6 h, (d) 12 h. The insets show the enlarged images. (e) Schematic illustration of the possible formation process of the Sn-doped α -Fe₂O₃ sheaf structures.

these rod-like nanoparticles transformed into uniform elliptic particles with smooth surfaces (Fig. 5b). The diameters of the obtained Sn-doped α -Fe₂O₃ ellipsoid along long and short axis directions were about 2 µm and 1.5 µm respectively. Moreover, the ellipsoids were composed of nanoparticles (the inset in Fig. 5b). As the hydrothermal process was prolonged to 6 h, FESEM image (Fig. 5c) shows that cantaloupe-like particles with 1.5 µm in center diameter and 2.5 µm in length were obtained. Different from the elliptic microstructures mentioned above, the cantaloupe-like microstructures had almost the same diameter in both the center and end sections. The building blocks of the cantaloupe-like architectures exhibited ordered arrangement (the inset in Fig. 5c). When reaction time was 12 h, monodisperse and uniform sheaf-like structures could be produced (Fig. 5d and the inset). The detailed characteristics of them had been described previously.

On the basis of above results, the possible formation mechanism of novel Sn-doped α -Fe₂O₃ sheaf structures has been proposed, as shown in Fig. 5e. It included the production of rod-like nanoparticles through hydrolysis, the aggregation of the nanoparticles to form elliptic structures, the anisotropic growth of the elliptic structures and finally the formation of sheaf structures *via* Ostwald ripening. Initially, small hematite nanocrystals were generated through conventional nucleation and subsequent crystal growth. These small nanocrystals tended to diffuse and aggregate to form larger ones, which resulted in the formation of elliptic Sn-doped α -Fe₂O₃ structures. During this process, due to the elimination of the interface, there was a thermodynamic driving force for the aggregated growth of nanocrystals, which led to the reduction

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of the surface energy. Because the interfacial energy between the nanocrystal and the solution was larger than that between the nanocrystal and the elliptic microstructures, the nucleation and growth of hematite nanocrystals would preferably occur on the initially formed elliptic structures. Together with the ripening process, cantaloupe-like hematite microstructures were formed. With the further increased reaction time, the ripening process kept on and finally well defined Sn-doped α -Fe₂O₃ sheaf structures were obtained. The formation process was similar to that of hierarchically peanut-like α -Fe₂O₃ and dumbbell-like LiFePO4 microstructures, which was also involved in the oriented aggregation and Ostwald ripening.^{30,31} The detailed mechanism for the formation of the novel Sn-doped α -Fe₂O₃ sheaf structures is still under investigation by our group. Here is a working hypothesis that agreed well with the observations of electron microscopy.

Gas sensors have attracted a remarkable interest due to the growing concern on environmental monitoring and domestic/ public safety. Therefore, to demonstrate the potential application, gas sensors based on novel α -Fe₂O₃ hierarchical architectures were fabricated and their gas sensing performances were investigated. It is well known that the response of a gas sensor is highly influenced by its operating temperature.^{32,33} Firstly, the optimal operating temperature of sensors based on pure α -Fe₂O₃ (sample 1) and Sn-doped α -Fe₂O₃ (sample 4) nanostructures to ethanol gas was investigated. Fig. 6a shows the response of the gas sensors towards 100 ppm ethanol at different operating temperature. It is obvious that the responses of the tested sensors varied with operating temperature. The response to C₂H₅OH rapidly increased and reached its maximum at the operating temperature of 250 °C, and then decreased with a further rise of the operating temperature. Therefore, the optimal operating temperature of 250 °C was chosen for ethanol, to further examine the characteristics of the gas sensors. Moreover, the response of Sn-doped α -Fe₂O₃ was higher than that of pure α -Fe₂O₃. It is well known that the gas response depends directly on the number of chemisorbed oxygen species.^{34,35} In the presence of Sn-doped α-Fe₂O₃, Sn acts as electron donator, which increases the amount of free electrons. More chemisorbed oxygen species will be formed due to many free electrons. In other words, the Sn⁴⁺ doping can facilitate the formation of chemisorbed oxygen species. Therefore, the Sn-doped α-Fe₂O₃ displays higher response. Then, the dynamic response characteristics of the sensor based on 4.0 wt% Sn-doped α -Fe₂O₃ to different gases were investigated. Fig. 6b displays the response of the sensor to 100 ppm C₂H₅OH, CH₃OH, and HCHO at 250 $^{\circ}$ C, respectively. It is obvious that the sensor showed sensitive and reversible response to these gases. Moreover, the sensor presented the rapid response and recovery to CH₃OH and HCHO. However, the response of the sensor to either CH₃OH or HCHO was lower than that to C₂H₅OH.

Response time and recovery time are also important parameters of a gas sensor. Fig. 7a shows the response transient of sensor based on 4.0 wt% Sn-doped α -Fe₂O₃

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Fig. 6 (a) Response of sensors using as-prepared Sn-doped α -Fe₂O₃ sheaf structures and pure α -Fe₂O₃ structures to 100 ppm C₂H₅OH as a function of the operating temperature. (b) Response of the sensor towards 100 ppm C₂H₅OH, HCHO, and CH₃OH, respectively.

nanostructures to 40 ppm ethanol at 250 °C, and the results indicate that the hierarchical Sn-doped α -Fe₂O₃ sensor had a fast response-recovery process. The response time and recovery time of the sensor were about within 1 and 15 s, respectively. The four reversible cycles of the response curve indicated a stable and repeatable characteristic, as shown in the inset of Fig. 7a. The response characteristics and recovery characteristics were further investigated with the sensor being orderly exposed to different concentrations of ethanol at 250 °C. It can be seen that the characteristics of response and recovery were almost reproducible with the quick time of response and recovery. This almost square response shape observed indicated that the sensor responded rapidly to test gas, quickly achieving a near steady state.³⁶ Then the resistance of sensor changed slowly due to test gas diffusing through the material and occupying the remaining surface reaction sites. When the sensor was exposed to air, the resistance returned to near baseline level. The response was about 1.7, 3.2, 3.8, 4.3, and 6.1 to 20, 40, 50, 60, and 80 ppm ethanol, respectively, as shown in Fig. 7b.



Fig. 7 (a) Response transient of the sensor to 40 ppm ethanol at 250 $^{\circ}$ C. The inset displays four periods of response curve. (b) Response transients of the sensor to different concentrations of ethanol.

The sensing mechanism of metal oxides gas sensors has been clarified in previous works.37-39 The most widely accepted theory is based on the change in resistance of the sensor upon exposure to different gas atmospheres. When the sensor is exposed to air, oxygen molecules adsorb onto the surfaces of α -Fe₂O₃, and form chemisorbed oxygen species by capturing electrons from the conductance band of α -Fe₂O₃. The decrease of the electron concentration in the conduction band leads to high resistance. When the sensor is exposed to ethanol, methanol, or other reductive gas atmospheres at a moderate temperature, these gas molecules will react with the adsorbed oxygen species on the surface of α -Fe₂O₃. This process releases the trapped electrons back to the conductance band of α -Fe₂O₃ and results in an increase the electron concentration. This effect eventually increases the conductivity of the α -Fe₂O₃ sheaf structures.

The concepts of sensor design are determined by three key factors: receptor function, transducer function and utility factor of the sensing body.⁴⁰ The good performance observed here is likely to be unique architecture. In the wheat sheaf-like hierarchical structure, the size of nanofilament reaches a scale comparable with the electron depletion layer thickness, and thus complete depletion (transducer function) will be

achieved. Moreover, these novel architectures were randomly oriented to provide a large number of pores. This network of pores can facilitate the diffusion of the test gas (utility factor) and improve the kinetics of the reaction of the test gas with surface-adsorbed oxygen species. Therefore, the sensor based on Sn-doped α -Fe₂O₃ with wheat sheaf-like structure show high response, short response time and recovery time to ethanol.

Conclusions

In summary, novel Sn-doped α -Fe₂O₃ hierarchical sheaf structures are synthesized by a simple one-step method. This method is based on hydrothermal treatment of ferric trichloride in a mixed solvent of ethanol-water. The current method is suitable for inexpensive, large scale synthesis Sn-doped α -Fe₂O₃ hierarchical "wheat sheaves". The oriented aggregation and Ostwald ripening mechanism are proposed to account for the formation of these hierarchical sheaf structures. The as-prepared Sn-doped α -Fe₂O₃ microstructures exhibit good gas sensing performance when used as sensing materials in a gas sensing sensor.

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