

## Highly enhanced gas-sensing properties of indium-doped mesoporous hematite nanowires



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### ABSTRACT

Mesoporous indium (In)-doped hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) nanowires were synthesized with mesoporous SBA-15 silica as a hard template, and then the influence of In dopant on the microstructure and gas-sensing performance was investigated in detail. With characterization by transmission electron microscopy, X-ray diffraction, UV–vis spectroscopy, and nitrogen physisorption experiments, it was shown that the average grain size increased for up to 1 mol% In dopant and then decreased with increasing In dopant content, while the surface area changed in the inverse manner. Because of the low melting point of In, In acted as a fluxing agent and entered the  $\alpha\text{-Fe}_2\text{O}_3$  lattice when the In content was low, and the average grain size increased. With higher In content, In precipitated out the lattice and existed at the grain boundary, and the grain size decreased. It is concluded that In in the lattice increased lattice distortion and In at the boundary increased the surface area and oxygen vacancies, which were both beneficial for improving the gas-sensing performance. The response of In-doped  $\alpha\text{-Fe}_2\text{O}_3$  nanowires increased by about 30%–50% as compared with that of pure  $\alpha\text{-Fe}_2\text{O}_3$  nanowires. The gas sensor based on 3 mol% In-doped  $\alpha\text{-Fe}_2\text{O}_3$  nanowires exhibited the best gas response and a rapid response-recovery time toward ethanol at the optimum temperature. Owing to the same valence, In dopant affected only the microstructure and components of the  $\alpha\text{-Fe}_2\text{O}_3$  lattice, which was necessary to improve the gas-sensing behavior.

### 1. Introduction

Owing to their high sensor response, low fabrication cost, simple manufacturing process, and good process compatibility, gas sensors based on semiconducting metal oxides have been widely used in many fields, such as monitoring of dangerous gases and alarm in firefight [1–5]. Various wide-bandgap semiconductors, such as ZnO, SnO<sub>2</sub>, NiO, WO<sub>3</sub>,  $\alpha\text{-Fe}_2\text{O}_3$ , and In<sub>2</sub>O<sub>3</sub>, have been used as gas sensors [6–13]. Because of its high electron mobility and excellent response for reaction with both oxidizing and reducing gases, the n-type semiconductor  $\alpha\text{-Fe}_2\text{O}_3$ , with an energy gap of 2.1 eV, has been widely used to develop gas sensors. Gas sensors based  $\alpha\text{-Fe}_2\text{O}_3$  have been fabricated to detect many reducing gases (ethanol, acetone, H<sub>2</sub>, CO, CH<sub>2</sub>O, CH<sub>3</sub>OH, and NO<sub>x</sub>) [14–18]. However, for the high requirement of detection precision of pollution and dangerous gases, the shortcomings of  $\alpha\text{-Fe}_2\text{O}_3$ -based sensors, such as the high operating temperature, low gas response, and low stability, gradually became evident.

The gas-sensing mechanism of semiconductors can be explained by the resistance change caused by the adsorption of oxygen and reaction with the target gas molecules on the surface. For n-type  $\alpha\text{-Fe}_2\text{O}_3$

nanostructures, the adsorbed oxygen ions extract electrons from the conduction band of the metal oxide to form an electron-depletion layer at the surface, which has a high-resistance state in air. When reducing gases are introduced, the adsorbed oxygen ions at the surface prefer to react with the reducing gas and reinject the electron into the conduction band. As a result, the electron-depletion layer disappears, and the resistance decreases in the target gas [19–21]. Therefore, these surface reactions depend directly on the oxygen vacancies on the surface and the reaction activation energy, which requires a larger specific surface area with more active centers at the surface and a lower activation energy [5,19].

Recently, research to improve the performance of gas sensors has been conducted in two directions: one involves fabricating sensors by use of nanostructures as a gas-sensing medium, and the other involves doping with metallic elements or heavy metals [20]. Compared with traditional nanostructures, one-dimensional metal oxide nanostructures exhibit excellent performance as gas sensors because of the huge specific surface area, high stability owing to good crystallinity, dimensions comparable to the extension of the depletion layer, possibility of surface functionalization, and so on. Various forms of metal oxide

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nanostructures, such as nanowires, nanorods, nanofibers, and nanotubes [5–8], have been developed as gas-sensing materials.

In addition, the applications of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures as gas sensors have been intensively studied [21–24]. For example, Ce-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanotube sensors were reported to exhibit a high response to acetone at a low operating temperature [21]. La-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanotube sensors exhibited a much higher response, better selectivity, and shorter response-recovery time toward 50 ppm acetone than pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sensors [22]. Cu-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hierarchical microcube sensors exhibited a good response to 19–100 ppm ethanol, which was about three times higher than that of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures [20]. Besides, significant efforts have been made to improve the gas-sensing performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures by the doping of Ag, Zn, and Nd [23–25].

Indium (In), a transition metal, has proved to be an effective dopant element to improve the gas-sensing properties of semiconductor oxides [26–28]. However, the gas-sensing properties of In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> have rarely been reported. Previously, we studied the gas-sensing properties of mesoporous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowire bundles and dispersed  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires, showing the better gas-sensing performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowire bundles because of the larger surface area [10]. To further improve the gas-sensing properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowire bundles, element doping was considered one of the best choices. With the same valence as Fe<sup>3+</sup>, In was selected as the doping transition metal to investigate its influence on the gas-sensing performance. In this work, In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires were synthesized by the nanocasting method using mesoporous SBA-15 silica as a hard template, and the influence of In dopant on the microstructure and morphology of the as-prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires was investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD), UV–vis spectroscopy, and nitrogen physisorption experiments. Furthermore, the gas-sensing properties of the pure and In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires toward ethanol were investigated in detail.

## 2. Material and methods

All chemicals were of analytical grade and were used as purchased without any further purification. Ordered mesoporous SBA-15 silica templates were prepared by the method described previously [10]. In a typical nanowire preparation process, 8 mmol of In(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with different In/(Fe + In) molar percentages (0 mol%, 1 mol%, 3 mol%, and 5 mol%) and 1 g SBA-15 in sequence were dissolved and dispersed in ethanol, and then hexane was added. After fine powders had formed, the powders were calcined at 550 °C for 6 h. Then 2 M NaOH aqueous solution was added to remove the silica template, and all samples were filtered and washed with deionized water and ethanol, and then dried at 80 °C for 4 h.

The crystal structure of the as-prepared products was determined by XRD (XD-5A, Cu target, wavelength 0.154 nm, step 0.02°). The morphology of all samples was examined by means of TEM (JME-1200EX) and energy-dispersive spectroscopy (EDAX TEAM Apollo XL). BaSO<sub>4</sub> powder was used as the substrate material to obtain the UV–vis spectrum with a UV3600 spectrophotometer to deduce the bandgap of both samples. Nitrogen physisorption experiments were conducted at 77 K with a Micrometrics ASAP 2020 surface area and porosity analyzer. The Brunauer-Emmett-Teller (BET) surface areas were calculated for the relative pressure range from 0.06 to 0.2.

To measure the gas-sensing properties of mesoporous pure and In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires, the sensors were prepared in the following way: The same amount of each sample was mixed with several drops of deionized water in an agate mortar to form a homogeneous paste, which was then deposited on an alumina ceramic tube assembled with platinum wire electrodes for electrical contacts. The thus prepared gas-sensing device was aged at 300 °C for 5 days to increase the stability of the sensor. Then a Ni-Cr alloy wire was passed through the alumina ceramic tube and used as a heater by the tuning of the heating voltage.

Gas-sensing tests were then performed with a WS-60 A gas-sensing measurement system, which is a static system that uses atmospheric air as the interference gas. The relative humidity was about 60%. The sensor response ( $S = R_a/R_g$ ) was defined as the ratio of the sensor resistance in air ( $R_a$ ) to that in the target gas ( $R_g$ ). The response and recovery times were defined as the times required for a change in the resistance to reach 90% of the equilibrium value after the detected gas had been injected and removed, respectively [10].

## 3. Results and discussion

The XRD patterns of pure and In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires with different In dopant content (1 mol%, 3 mol%, and 5 mol%) are illustrated in Fig. 1. All the diffraction patterns showed the characteristic peaks corresponding to the phase structure  $R\bar{3}c$  (167) according to JCPDS card no. 33–0664. No other phases containing In dopant were detected, indicating the lower In dopant or In dopant into the crystal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> lattice. The curve of 1 mol% In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires was smoother than the curves of 3 mol% In-doped and 5 mol% In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires, which suggests a higher crystallization degree of 1 mol% In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The average grain size and lattice constant were calculated with the Scherrer formula and the cubic crystal cell parameter formula from XRD data (Table 1) [32]. The grain size of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires decreased from 23.7 nm for 1 mol% In dopant to 23.35 nm for 3 mol% In dopant and to 22.40 nm for 5 mol% In dopant. The lattice constant also decreased with increasing In<sup>3+</sup> concentration. The variations of the average grain size and lattice constant depending on the doping concentration powerfully indicated that In replaced Fe ions in the lattice, as the ionic radius of In<sup>3+</sup> (0.84 Å) is larger than that of Fe<sup>3+</sup> (0.64 Å). Because of the low melting point of In, In acted as a

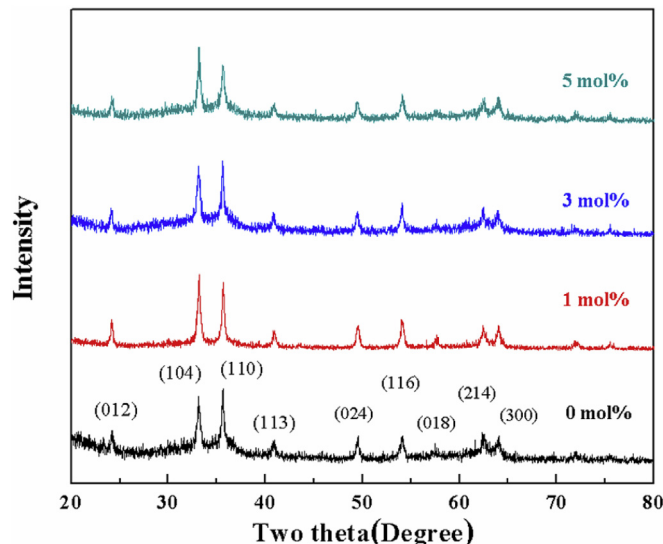


Fig. 1. X-ray diffraction patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires.

Table 1

The crystallite size and lattice constants of pure and In-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires.

Sample	Crystallite size (nm)	<i>a</i> (Å)	<i>c</i> (Å)
Pure $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	22.95	5.0341	13.7221
1 mol% In-doped $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	23.70	5.0354	13.8268
3 mol% In-doped $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	23.35	5.0475	13.7352
5 mol% In-doped $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	22.40	5.0367	13.7345

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