Nanocasting synthesis and gas-sensing behavior of hematite nanowires

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HIGHLIGHTS

- Uniform α-Fe_2O_3 NWs with the diameter of 4, 6 and 8 nm were synthesized by nanocasting method.
- Bandgap decreased with the increasing diameter for quantum size effect.
- The α-Fe_2O_3 NWs based gas-sensors exhibited high sensitivity and fast response-recovery.
- Bandgap and crystallinity would influence the gas-sensing behavior except for surface area.

GRAPHICAL ABSTRACT
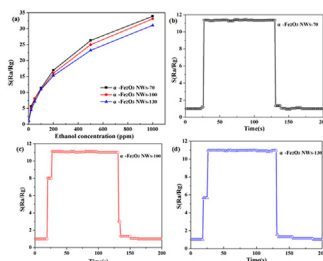
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ABSTRACT

The dispersed and uniform hematite nanowires (α-Fe_2O_3 NWs) with the different diameter were synthesized using SBA-15 as hard templates by the nanocasting method, and the diameter of α-Fe_2O_3 NWs was about 4, 6 and 8 nm, respectively. The BET surface area of α-Fe_2O_3 NWs changed a little, while the bandgap decreased from 2.07, 2.03 to 1.91 eV with the increasing diameter according to quantum size effect. Compared all samples, the sensitivity of α-Fe_2O_3 NWs based gas-sensors increased from 10.64 to 11.43 with the bandgap and BET surface area α-Fe_2O_3 NWs in 100 ppm ethanol at 300 °C, and the response–recovery time was also improved for the good crystallinity. It's concluded that the surface area greatly affected the gas-sensing performance of α-Fe_2O_3 NWs based sensors, while the bandgap and crystallinity also influenced the gas-sensing behavior to some extent. The α-Fe_2O_3 NWs based gas-sensors exhibited the high sensitivity, fast response–recovery and good selectivity to ethanol.

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1. Introduction

Hematite (α-Fe_2O_3) was an important multifunctional material with applications such as catalysts, gas sensors, optical devices, lithium-ion batteries and electromagnetic devices [1–4]. Owing to its high thermal stability under ambient conditions, environmentally friendly features and low production cost, α-Fe_2O_3 have been widely studied and used as a gas-sensing material [5,6]. Due to surface reactions of oxidation or reduction, the working mechanism of α-Fe_2O_3 gas sensor was based on the change of the electrical conductivity. The above surface reactions were directly depended on the oxygen vacancies at the surface, which required the higher specific surface area with more active centers and defects at the surface of nanoparticles [7,8]. Therefore, α-Fe_2O_3 nanostructures were particularly investigated to improve the gas-sensing properties [9,10], which included hollow nanostructure [11], nanowires [12], nanoparticles [13], nanospheres [14,15] and other structures [16,17].

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Owing to the unique microstructure, huge surface area and excellent physical performance, one-dimensional (1D) nanostructures have attracted the interest of the researchers. And 1D α-Fe_2O_3 nanostructures based gas sensors had presented their high sensitivity, good selectivity, rapid response and recovery time. Patil et al. had synthesized α-Fe_2O_3 nanorods by calcining the α-FeOOH precursor in air, and α-Fe_2O_3 nanorods based gas sensors exhibited the outstanding gas-sensing performance to 5 ppm liquid petroleum gas with the reasonable response and good selectivity [18]. Wang et al. had prepared α-Fe_2O_3 nanoshuttles by hydrothermal method, which presented a rapid response and recovery times of 3–5 s and 2 s to 10–100 ppm toluene [19]. Sarkar et al. had prepared α-Fe_2O_3 nanoribbons by the solvothermal method, indicating the high sensitivity to liquid petroleum gas for α-Fe_2O_3 nanoribbons based gas sensors [20]. However, few studies focused on the influence of the diameter on the gas-sensing properties of α-Fe_2O_3 nanowires (NWs) based sensors. This should be attributed to the difficulty of the synthesis for the dispersed uniform α-Fe_2O_3 NWs.

Only when the controllable nanostructures with the uniform grain size were synthesized, the influence of the grain size of the α-Fe_2O_3 NWs on the gas-sensing properties could be deduced. Owing to the good uniformity and high controllability for target products, the nanocasting method was the first choice for the synthesis of the controllable nanostructures in many preparation methods [21]. Silica SBA-15 with the well-ordered hexagonal straight mesoporous structures was the good candidates as the hard template for nanowires [22,23]. In our previous works, Co_3O_4 and α-Fe_2O_3 nanowires had been synthesized using SBA-15 as hard template with the nanocasting method, the magnetic properties and gas-sensing performance were investigated in detail [23,24].

By adjusting the mesopores size of SBA-15 with the chemical conditions, the uniform and well-dispersed nanowires with different diameters could be obtained with nanocasting method. In this way, the influence of the diameter of nanowires on the gas-sensing performance was discussed in detail. In this paper, α-Fe_2O_3 NWs were synthesized with the nanocasting method using the above SBA-15 (with the different pore-size) as templates. The microstructure of SBA-15 and α-Fe_2O_3 NWs was characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption/desorption isotherm and UV–vis spectrum. Furthermore, the gas-sensing properties of α-Fe_2O_3 NWs based sensors were discussed in detail, and the relationship of the gas sensitivity of α-Fe_2O_3 NWs based gas sensors with the surface area, crystallinity and bandgap was concluded.

2. Experimental section

All chemicals were of analytical grade and used as purchased. Mesoporous silica SBA-15 templates were prepared by the method described previously [25]. The hydrothermal temperature for the synthesis of SBA-15 was 70, 100 and 130 °C, and the samples were marked as SBA-15-70, SBA-15-100 and SBA-15-130, respectively. For the synthesis of α-Fe_2O_3 NWs, ferric nitrate and SBA-15 powders (the atomic ratio of Si:Fe$=$2:1) were dissolved in ethanol and then added hexane until a fine powder was formed. After the powder was heated at 550 °C for 6 h, 2 M NaOH aqueous solution was added to the above powder to remove SBA-15. The well-dispersed α-Fe_2O_3 NWs were separated from the bundled α-Fe_2O_3 NWs with the 12,000 rps, which were marked as α-Fe_2O_3 NWs-70, NWs-100 and NWs-130, respectively. All above samples were filtered and washed with the deionized water and ethanol, and then were dried at 80 °C for 4 h.

The morphology of all samples was examined by TEM (JME-1200EX). The structure character of samples was analysed by the small-angle XRD and XRD (XD-5A, Cu target, wavelength 0.154 nm). UV–vis spectrum was obtained by a UV3600 spectrophotometer. Nitrogen physisorption experiments were measured at 77 K on a Micrometrics ASAP 2020 surface area and porosity analyzer. The BET (Brunauer–Emmett–Teller) surface areas were estimated from the relative pressure range 0.06 to 0.2.

To measure the sensing properties of the α-Fe_2O_3 NWs-70, NWs-100 and NWs-130, the sensors were prepared as follows: A proper amount of each sample was mixed with several drops of deionized water in an agate mortar to form a homogeneous paste, which was deposited on the alumina ceramic tube assembled with platinum wire electrodes for electrical contacts. The prepared gas sensing device was aged at 300 °C for 5 days to improve the stability of the sensor. Then a Ni–Cr alloy wire was passed through the alumina ceramic tube and used as a heater by tuning the heating voltage (V_h). Then the gas sensing tests were performed on a WS-60A gas sensing measurement system, which was a static system using atmospheric air as the interference gas. The relative humidity (RH) was about 55%. The sensitivity ($S=Ra/Rg$) of a sensor was defined as the ratio of sensor resistance in air (Ra) to that in a target gas (Rg). 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 was injected and removed, respectively [26].

3. Results and discussion

The small-angle XRD (SXRD) was introduced in Fig. 1 to characterize the detail microstructure of mesoporous silica SBA-15, which was treated hydrothermally at the different temperature of 70, 100 and 130 °C, respectively. The three peaks for (100), (110) and (200) could be detected evidently, indicating the well-ordered hexagonal mesoporous structure of all samples. The three peaks of all SBA-15 samples shifted to the low angle direction with the increasing hydrothermal temperature. It could be concluded that the mesopores of SBA-15 become bigger with the increasing hydrothermal temperature. The cell parameter was calculated from and the cell parameter increased from 9.8 nm for SBA-15-70 to 11.3 nm for SBA-15-130, which proved the change trend of mesopores. And the above as-prepared SBA-15 could be used as hard templates to synthesize the α-Fe_2O_3 NWs in the following.
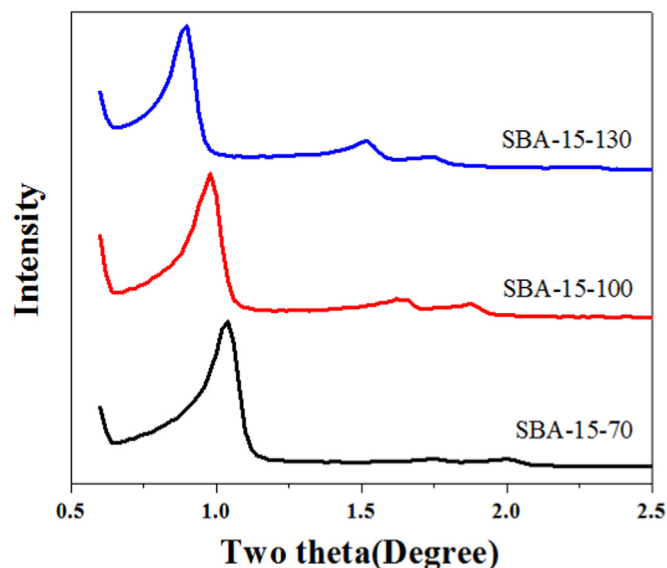

Fig. 1. SXRD spectrum of the SBA-15-70, SBA-15-100 and SBA-15-130.