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Featured Letter

High-performance ethanol sensors based on hematite fluffy microtubes assembled with interconnected ultrafine nanorods

Limao Cairang [a,b,1], Jing Long Bai [b,1], Chang Hui Zhao [c,1], Bao Yu Huang [b], Geng Zhi Sun [d], Zhen Xing Zhang [b], Xiao Jun Pan [b], Jin Yuan Zhou [b,*], Guo Heng Zhang [a,*], Er Qing Xie [b]

[a] College of Electrical Engineering, Northwest Minzu University, Lanzhou 730030, China
[b] School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China
[c] Department of Electrical and Electronic Engineering, Southern University of Science and Technology, Shenzhen 518055, China
[d] Institute of Advanced Materials, Nanjing Tech University, Nanjing 211816, China

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ABSTRACT

It is reported that the response is dependent on its specific surface area, and the response/recovery rates are on the electron transfer channels. In this work, the authors have designed a type of fluffy hematite (α-Fe_2O_3) microtubes. Results indicate that these fluffy α-Fe_2O_3 microtubes are highly porous and composed of interconnected ultrafine nanorods. And the assembled gas sensors show a response of 16.8 to 100-ppm ethanol gas at 260 °C, the response time is of 2 s and the recovery time is of 25 s. Moreover, the sensors also show good gas selectivity and long-term stability.

1. Introduction

Metal oxide semiconductors show great interest in the field of various sensors [1–4]. Taken hematite (α-Fe_2O_3) for instance, it has been extensively investigated as gas sensing materials because of its low-cost, environmentally friendly, and good stability [5]. However, the α-Fe_2O_3 based sensors often suffer from low response and long response/recovery time [6,7]. To improve their gas-sensing performances, one of the most common approaches is to design various micro/nano-structures of α-Fe_2O_3, such as nanoflowers [8], nanospheres [9], microspheres [10], microrods [11], and etc. Generally, the main fundamental principle in the above approach is to construct a type of nanostructures with high specific surface area, ultrafine crystalline size, and facilitated electron channels [12]. Recently, Tan et al. [13] prepared a type of porous α-Fe_2O_3 microrods, obtained high response, ultra-fast response/recovery characteristics and superior stability to ethanol. To further increase the surface area, the authors have designed a type of α-Fe_2O_3 fluffy microtubes in this work. The resultantα-Fe_2O_3 fluffy microtubes are highly porous and assembled with interconnected ultrafine nanorods. Interestingly, the assembled gas sensors using these α-Fe_2O_3 microtubes show high response, fast response/recovery rates, and good stability towards ethanol.

2. Experimental section

First, a type of $FeSO_4$ solution was prepared by dissolving 5 mmol $FeSO_4{\cdot}7H_2O$ powder into 20 mL ethylene glycol; and another type of $H_2C_2O_4$ aqueous solution was prepared by dissolving 5 mmol $H_2C_2O_4$ powder in 10 mL deionized (DI) water. Second, the obtained $FeSO_4$ solution was quickly added into $H_2C_2O_4$ aqueous solution under vigorous stirring at 40 °C to form a type of yellow homogeneous mixture solution. Subsequently, this mixture solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, which was heated to 150 °C and kept for 12 h. After cooling down naturally, a type of yellow $FeC_2O_4{\cdot}2H_2O$ precipitate was collected via centrifugation, washing using DI water, and drying at 60 °C in a vacuum oven. Third, 0.15 g $FeC_2O_4{\cdot}2H_2O$ powder was dispersed in 20 mL of 5 M NaOH aqueous solution, following by vigorous stirring for 1 h. Then a type of dark green $Fe(OH)_2$ powder product was collected via centrifugation, washing using DI water, and drying at 60 °C in a vacuum oven. Finally, a type of rufous

* Corresponding authors.
E-mail addresses: zhoujy@lzu.edu.cn (J.Y. Zhou), zhgh0325@qq.com (G.H. Zhang).
[1] These authors contributed equally to this work.

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Fe_2O_3 powder was obtained via annealing $Fe(OH)_2$ powder at 400 °C in air for 30 min.

The samples were studied by X-ray diffraction (XRD, Philips X'Pert Pro), field emission scanning electron microscope (FESEM, Hitachi, S4800), high-resolution transmission electron microscope (HRTEM, FEI, Tecnai G2 F30, equipped with energy dispersive X-ray spectroscopy (EDX) system), X-ray photoelectron spectroscopy (XPS, PHI-5702), and Brunauere- Emmette-Teller system (Micrometrics, ASAP 2010).

3. Results and discussion

It is reported that α-Fe_2O_3 nanosheets can be synthesized via interfacial-reaction between FeC_2O_4 nanorods and NaOH [14]. Thus, a type of α-Fe_2O_3 fluffy microtubes constructed with ultrafine nanorods was designed as shown in Fig. 1. First, a type of yellowy $FeC_2O_4{\cdot}2H_2O$ nanorods was prepared by mixing solutions of Fe^{2+} and $C_2O_4^{2-}$ ions. Then the OH^- was employed to etch and react with Fe^{2-} ions, achieving dark green $Fe(OH)_2$ fluffy microtube intermediates. Finally, the collected $Fe(OH)_2$ fluffy microtubes can be oxidized/decomposed into a type of rufous α-Fe_2O_3 via annealing at 400 °C in air.

The morphology changes from the obtained $FeC_2O_4{\cdot}2H_2O$ precursors to α-Fe_2O_3 products can be observed by FESEM and HRTEM. After the hydrothermal reaction, the formed yellowy FeC_2O_4 precursors are comprised of uniform and smooth nanorods with a prism shape (Fig. 2(a)). These nanorods are 10–15 μm in length and ~500 nm in diameter (inset of Fig. 2(a)). After etched and reacted with NaOH and annealed in air, the smooth FeC_2O_4 nanorods were converted into a type of fluffy microtubes of α-Fe_2O_3 (Fig. 2(b)). These fluffy microtubes possess a diameter of ~1 μm

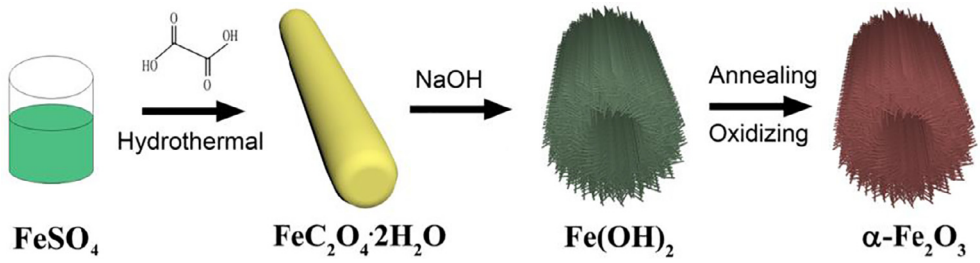

Fig. 1. Formation process of α-Fe_2O_3 fluffy microtubes.

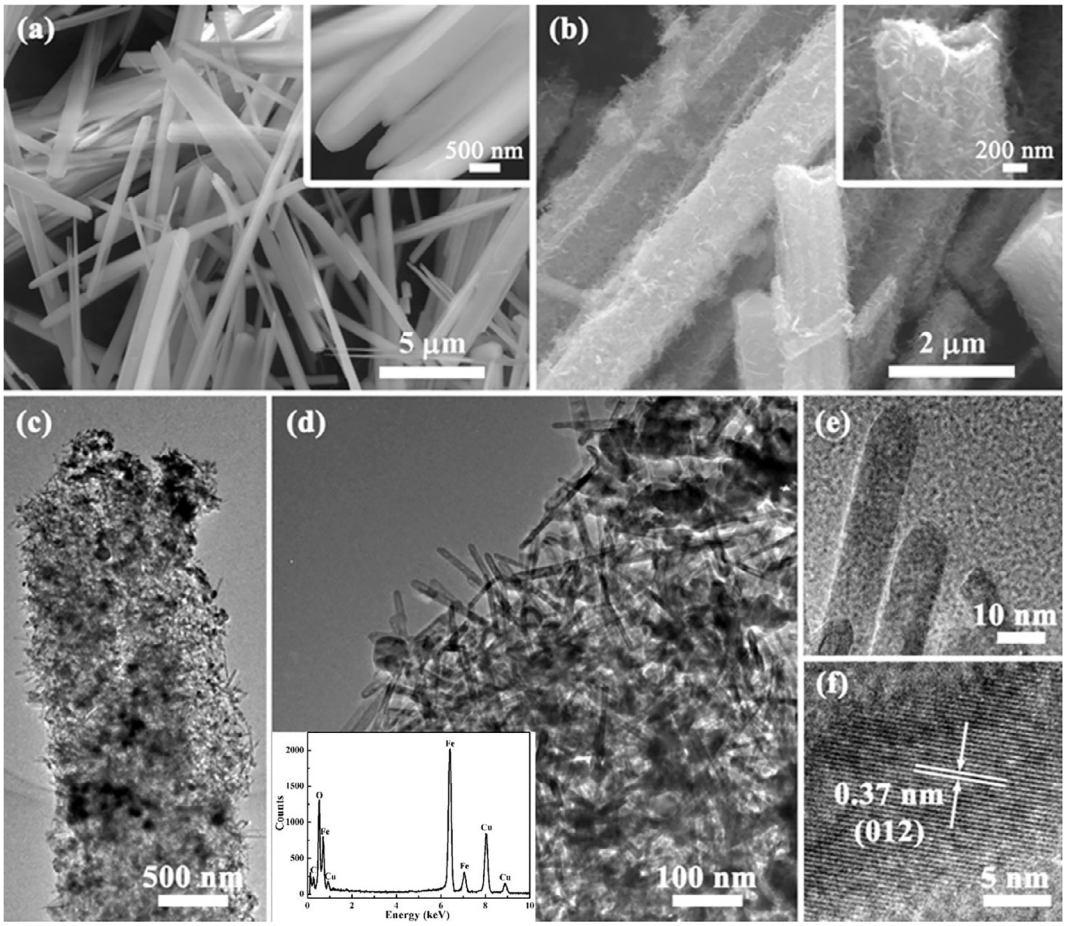

Fig. 2. (a and b) SEM images of FeC_2O_4 precursors and α-Fe_2O_3 product, respectively, the insets shows the corresponding magnified images. (c and d) TEM images of α-Fe_2O_3 fluffy microtubes, (e) TEM and (f) HRTEM images of α-Fe_2O_3 nanorods.