Ultrafast response and recovery trimethylamine sensor based on α-Fe₂O₃ snowflake-like hierarchical architectures

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Tianye Yang [a], Liyong Du [a], Chengbo Zhai [a], Zhifang Li [a], Qi Zhao [a], Yang Luo [a], Dejun Xing [b, **], Mingzhe Zhang [a, *]

[a] State Key Laboratory of Superhard Materials, Jilin University, Changchun, 130012, People's Republic of China
[b] Department of Medical Oncology, Jilin Cancer Hospital, 1018 Huguang Road, Changchun, Jilin, 130012, People's Republic of China

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ABSTRACT

Snowflake-like α-Fe₂O₃ hierarchical architectures have been developed to detect trimethylamine (TMA) gas. The α-Fe₂O₃ has been synthesized by using a facile solvothermal method and a subsequent annealing process. As-fabricated snowflake-like α-Fe₂O₃ based sensor exhibits ultrafast response and recovery time (0.9 s/1.5 s), excellent selectivity, high response, and superior repeatability toward TMA gas. XPS, PL and UV indicates that abundant oxygen vacancies exist in the α-Fe₂O₃ surfaces. Oxygen vacancies provide essential active sites for gas adsorption which enormously improve the ability of electron transfer. The remarkable TMA sensing performance can be attributed to the cooperation of oxygen vacancies providing more active sites, rapid electron exchange between Fe^{3+} and Fe^{2+} cations inducing conductivity greatly change, and unique snowflake-like hierarchical structure possessing large contacting area and monocrystalline feature. Such novel snowflake-like α-Fe₂O₃ hierarchical architectures will be a promising candidate for TMA, fish and sea-food freshness detection.

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1. Introduction

Marine products and fishes are extensively demanded all around the world because they are important biological sources containing valuable proteins, fats, and fat-soluble vitamins for human beings. However, consumption of stale seafood can lead to serious health issues such as gastroenteritis and septicemia [1]. It is important to detect fish freshness in consideration of food safety issue. As for fish freshness detection, the most widely applied method is based on the chemical analysis of decomposition products from adenosine triphosphate (ATP)-related compounds in the tissue of fish. However, it is inevitable to require complicated and time-consuming work [2—4]. Therefore, it is essential and urgent to develop a reliable, fast, continuous, nondestructive and accurate analytical method for evaluating fish freshness.

Trimethylamine (TMA) is a basic tertiary amine compound with the formula $N(CH_3)_3$ and is also a pungent gas secreted from dead fish. The content of TMA gas increases rapidly as the fish begins to deteriorate [5]. Based on this feature, TMA can be used as an effective indicator of seafood quality to evaluate the freshness of fish. In the evaluation of fish freshness, 0—10 ppm TMA is regarded as fresh, 10—50 ppm is preliminary rot, and over 60 ppm is putrid and inedible [6,7]. In addition, exposure to TMA vapor would cause headaches, nausea, and irritation to the eyes as well as to the respiratory system, so the allowable limit set by the National Institute for Occupational Safety and Health in USA is 10 ppm for 10 h [8,9]. Hence, the detection and control of TMA are very important and several detecting methods of TMA gas have been presented, including ion mobility spectrometry, high performance liquid chromatography, gas chromatography, mass spectrometry, and the use of a quartz microbalance [10—14]. Nevertheless, the aforementioned methods usually require complicated equipment, a long sample preparation time, and professional operating skills. It is necessary to develop highly sensitive, fast response and recovery gas sensors for accomplishing rapid, reliable, nondestructive, and real-time detection of trace TMA gas [15].

Among a variety of gas sensitive materials, metal oxide semiconductors (MOS) have been extensively investigated. They are usually recognized as the most economic materials as gas sensors and have many advantages, such as high sensitivity, fast response

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* Corresponding author.
** Corresponding author.
   E-mail addresses: xdejun111162@sohu.com (D. Xing), zhangmz@jlu.edu.cn (M. Zhang).

and recovery, low detection limits, low fabrication cost, simplicity in fabrication, measurement, and function durability compared to other semiconductors [16]. Various metal oxide gas sensors have been used to detect TMA, which include SnO_2, WO_3, MoO_3, $LaFeO_3$, Ru-doped TiO_2 [2,17—22]. However, there are seldom reports done about TMA sensing of Fe_2O_3. Hematite (α-Fe_2O_3) is the most stable iron oxide with n-type semiconducting properties under ambient conditions. It has been extensively applied in various fields as catalysts, pigments, gas sensors, magnetic devices and electrode materials, owing to its low cost, high resistance to corrosion, environmentally friendly and fascinating physicochemical properties [23—29]. Very recently, α-Fe_2O_3 hierarchical architectures have been widely reported such as flute-like porous nanorods, α-Fe_2O_3 with sheaf-like architectures, α-Fe_2O_3 hollow urchin-like spheres and microcubes, etc [30—33]. In gas sensing application, such hierarchical structures usually possess a large surface area which can provide plenty of active sites and more spaces for gases to diffuse into the inner of the sensing film [34—37]. These hierarchical structural characteristics are in favor of adsorption and desorption of target gas, which leads to gas sensing performance enhancement [38]. Therefore, controllable synthesis of desired composition is crucial to achieve high-performance gas sensors.

Herein, we focus on fabricating hierarchical architectures with highly designed structural characteristics which can be potential for gaining high performance TMA sensors. In this paper, snowflake-like α-Fe_2O_3 hierarchical architectures have been successfully synthesized by a facile hydrothermal method and an annealing treatment. The obtained snowflake-like α-Fe_2O_3 presents a hexagonal shape and each snowflake contains six main trunks where plenty of branches grow on. Moreover, such synthesis process leads to abundant oxygen vacancies forming on the α-Fe_2O_3 surface that are confirmed by XPS, PL and UV. And importantly, the as-synthesized α-Fe_2O_3 based sensor exhibits extraordinary sensing characteristic with an ultrafast response time (0.9 s) and recovery time (1.5 s) toward TMA gas.

2. Experimental section

2.1. Synthesis of snowflake-like Fe_2O_3 hierarchical structures

All reagents (analytical-grade purity) were used as purchased without further purification. The synthesis of α-Fe_2O_3 was carried out by a typical solvothermal method with high pressure around 0.901 MPa, high temperature 180 °C for 24 h and then an annealing process. The specific fabrication process of α-Fe_2O_3 precursors is illustrated in detail in the supplementary. Finally, the α-Fe_2O_3 were obtained by calcining the precursors at 450 °C for 3 h in air. The heating rate was controlled at 5 °C min^{-1}.

2.2. Material characterization

The as-prepared products were characterized by Rigaku D/max-2500 X-ray powder diffraction (XRD) with Cu-Ka1 radiation (λ = 1.54056 Å) at a scanning rate of 4° min^{-1}. Field-emission scanning electron microscopy (FESEM) images were obtained by using a Magellan 400 FEI microscope operating at 5 kV. The transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high resolution TEM (HRTEM) images were performed on a JEOL JEM-2200FS microscope. The excitation and emission spectra were performed using a FluoroMax-4 fluorescence spectrophotometer (Horiba Scientific) equipped with a 450 W xenon arc lamp. The room temperature optical absorption spectra were recorded by an UV—visible near-infrared spectrophotometer. The elemental composition and chemical state of the products were investigated by X-ray photoelectron spectroscopy

(XPS) (ESCALAB MK II).

2.3. Fabrication and measurement of gas sensor

The properties of the gas sensor were carried out by a CGS-8 intelligent gas sensing analysis system. The preparation of gas sensor measurement was carried out following our previous reported literature [16]. Typically, the as-synthesized sample was mixed with absolute ethyl alcohol to form a paste. The paste was coated on a ceramic tube on where a pair of gold electrodes was printed beforehand and each electrode was connected with two Pt wires. A Ni-Cr heating wire was inserted into the tube to form an indirect-heated sensing device. The as-prepared gas sensing device was stabilized at a constant temperature for 6 h to fully evaporate ethanol and make ceramic tube and the sample contact closely. After the ethanol was evaporated completely, the α-Fe_2O_3 thin film morphology is maintained on the ceramic tube. A stationary gas distribution method is used for testing gas response in a test bottle under laboratory conditions (40 ± 10% RH, 25 ± 1 °C). The sensor response was defined as S = R_a/R_g. Here, R_a and R_g were the resistances of the sensors in the air and target gas, respectively. The response and recovery time was defined as the time taken by the sensors to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively [39].

3. Results and discussion

3.1. Morphology and composition analysis

The X-ray diffraction patterns of snowflake-like α-Fe_2O_3 hierarchical architectures are displayed in Fig. 1. The patterns are well corresponding to that of JCPDS No. 84-310 and the as-synthesized α-Fe_2O_3 has the rhombohedral structure with lattice constant a = 5.006 Å and c = 13.641 Å, space group no. 167. The strong and sharp peaks indicate that the crystallized samples are well ordered. Furthermore, there are no other peaks of impurities such as ferroferric oxide or ferrous iron oxide, indicating high purity of the final products.

The SEM and TEM measurement are carried out to investigate morphologies and microstructures of the as-synthesized α-Fe_2O_3 samples. Fig. 2 illustrates that the typical SEM images of snowflake-like α-Fe_2O_3 hierarchical architectures. The low magnification SEM images from Fig. 2a and b clearly illustrate that the sample is

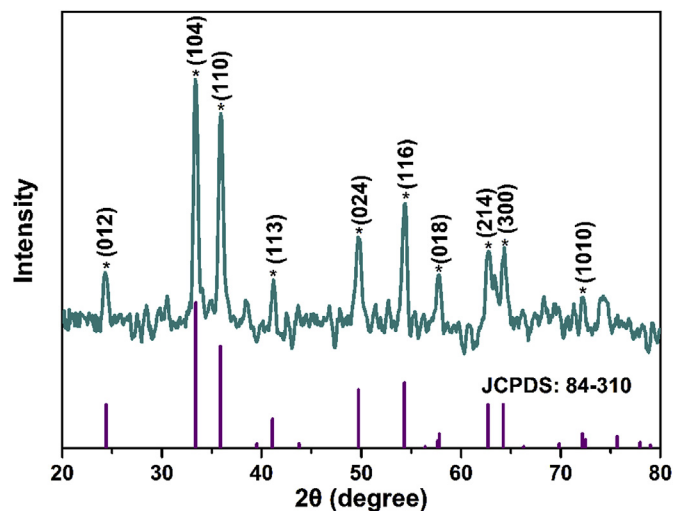**Fig. 1.** XRD patterns of the snowflake-like α-Fe_2O_3 hierarchical architectures.