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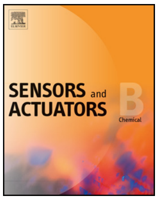

# Room-temperature, high selectivity and low-ppm-level triethylamine sensor assembled with Au decahedrons-decorated porous α-$Fe_2O_3$ nanorods directly grown on flat substrate

Xiaopan Song[a], Qi Xu[a], Tao Zhang[b], Bao Song[c], Cuncheng Li[b], Bingqiang Cao[a,d,*]

[a] Materials Research Center for Energy and Photoelectrochemical Conversion, School of Materials Science and Engineering, University of Jinan, Jinan 250022, Shandong, China
[b] School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, Shandong, China
[c] School of Mechanical Engineering, University of Jinan, Jinan 250022, Shandong, China
[d] School of Physics and Physical Engineering, Qufu Normal University, Qufu 273165, Shandong, China

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## ABSTRACT

Chemiresistive based gas sensors with low operating temperature (e.g. room-temperature), high selectivity, and fast response for specific target gas are highly desired. Herein, we successfully construct triethylamine (TEA) gas sensors with gold (Au) decahedrons (DHs)-decorated porous α-$Fe_2O_3$ nanorods, which can work at 40 °C and exhibit high selectivity and low-ppm-level response. Porous α-$Fe_2O_3$ nanorods with high specific surface area are directly grown on seeded flat substrate with electrodes by a cost-effective hydrothermal method. Au DHs synthesized by one-pot polyol reaction method are deposited onto such α-$Fe_2O_3$ nanorods by spin-coating. Such Au DHs/α-$Fe_2O_3$ nanorods sensor working at temperature as low as 40 °C and relative humidity (RH) of 30% exhibits high response (17–50 ppm TEA), low detection concentration (~1 ppm), and short response/recovery time (12/8 s), which are all much better than the control α-$Fe_2O_3$ nanorods sensor. When the RH increases, the sensor response decreases due to the water molecules adsorption. Furthermore, the enhanced sensing properties toward TEA are discussed in terms of the formation of Au/$Fe_2O_3$ metal/semiconductor Schottky contact and the catalytic activity of Au DHs.

## 1. Introduction

Triethylamine (TEA) gas sensors have drawn much attention for wide application in chemical industry. TEA is explosive and can cause irritations to the dermal, ocular, and respiratory systems if the concentration is higher than 10 ppm in air [1,2]. In addition, long-term exposure to TEA may eventually result in abnormal embryos [3–5]. Traditional methods such as gas/liquid/film chromatography and electrochemistry analysis have been adopted to detect TEA gas [6,7]. However, their further applications are limited because of the complex operation, expensive apparatus cost, and strict testing environment. Therefore, it is still a strong demand to develop convenient, fast, and portable instrument with high selectivity and sensitivity to detect TEA gas in daily life or industrial production process [8].

Metal oxide semiconductor (MOS) nanostructures such as ZnO [9], $SnO_2$ [10], $In_2O_3$ [11], and α-$Fe_2O_3$ [12–15] have been widely adopted as gas sensing materials with some advantages like simple growth and fast response. Among them, hematite (α-$Fe_2O_3$), as a typical *n*-type transition MOS with a band gap of 2.1 eV [16] has exhibited impressive sensing property to acetone [17], toluene [18], ethanol [19], formaldehyde [20], and so on. Nevertheless, gas sensors for TEA detection based on α-$Fe_2O_3$ have been reported very little. Sun et al. [21] fabricated mesoporous α-$Fe_2O_3$ microrods for TEA gas sensors, which showed a response of 11.8–100 ppm TEA at 275 °C. However, their sensing response needs further improvement. Recently, our group prepared porous α-$Fe_2O_3$ nanorods to detect TEA and obtained high response (8.2 for 50 ppm) and fast response time (7 s) at 40 °C [22].

Noble metals like gold and silver decorated on oxide semiconductors can further enhance the sensor sensitivity and selectivity, and also result in higher response as well as lower operating temperature. For instance, Cao et al. [23] synthesized Ag/$Cr_2O_3$ porous

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[*] Corresponding author at: Materials Research Center for Energy and Photoelectrochemical Conversion, School of Materials Science and Engineering, University of Jinan, Jinan, 250022, Shandong, China.
*E-mail address:* mse_caobq@ujn.edu.cn (B. Cao).

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microspheres, and their response to 50 ppm of TEA was about 3 times higher than that of pristine $Cr_2O_3$. Guanwan et al. [24] reported that the response of Au/$\alpha$-$Fe_2O_3$ nanorods, which exhibited ultrahigh sensitivity (46.4–100 ppm acetone) at 270 °C. Peeters et al. [25] prepared Au/$\varepsilon$-$Fe_2O_3$ nanocomposites, which exhibited better selectivity to $NO_2$ than pure $\varepsilon$-$Fe_2O_3$ nanocomposites. Zhang et al. [26] developed an efficient, green, and general strategy for the synthesis of Au/$\alpha$-$Fe_2O_3$ nanospindles, which also exhibited good sensitivity toward ethanol at 140 °C. Despite the high response obtained, it is inconvenient to fabricate these sensors by the traditional slurry-coating process. Sometimes it may destroy the intrinsic nanostructure physical properties. Thus, the *in-situ* growth of sensing materials on $Al_2O_3$ electrodes is a promising strategy to simplify the traditional fabrication process.

In this Paper, we report a high-performance Au decahedrons/$\alpha$-$Fe_2O_3$ nanorods TEA sensor on flat $Al_2O_3$ substrate with pre-designed electrodes, which can work at near room-temperature. Hematite seed layer are grown on electrodes by a simple sol-gel method. Porous $\alpha$-$Fe_2O_3$ NRs directly grow via hydrothermal method and Au DHs are synthesized by one-pot polyol reaction method. Then, Au DHs are decorated onto the porous $\alpha$-$Fe_2O_3$ NRs by controlling the spin-coating speed (1000–3000 rpm). Due to the formation of Schottky contact between Au/$Fe_2O_3$ and the catalytic activity of Au decahedrons, the Au/$\alpha$-$Fe_2O_3$ NRs sensor working at 40 °C exhibits higher response and better selectivity to TEA than that of pristine $\alpha$-$Fe_2O_3$ NRs sensor. The TEA gas sensing mechanism of Au/$\alpha$-$Fe_2O_3$ NRs is discussed in detail.

## 2. Experimental

### 2.1. Direct growth of porous $\alpha$-$Fe_2O_3$ NRs on flat $Al_2O_3$ electrodes

The flat $Al_2O_3$ electrodes (1 mm × 1.5 mm), which consist of a pair of Au electrodes, Pt lead wires, and a heater, were cleaned with ethanol, acetone, and deionized (DI) water by ultrasonication. Hematite seed layer and $\alpha$-$Fe_2O_3$ NRs array were *in-situ* grown on flat $Al_2O_3$ electrodes by sol-gel method and hydrothermal method, respectively. First, 4.054 g ferric chloride ($FeCl_3{\cdot}6H_2O$), 0.211 g polyvinyl alcohol (PVA), and 150 μL hydrochloric acid (HCl 36.5–38%) were dissolved in 50 mL of DI water with continuous stirring to get a clear solution. Hematite seed layers were formed on the cleaned flat $Al_2O_3$ substrates by spin coating (4000 rpm for 30 s) the above solution, then annealed at 500 °C in air for 2 h. A 30 mL of aqueous solution consisting of 0.810 g $FeCl_3{\cdot}6H_2O$, 2.548 g sodium nitrate ($NaNO_3$), 90 μL HCl, and 160 μL acetontrile was transferred into 50 mL Teflon-lined stainless steel autoclave. At the same time, the flat $Al_2O_3$ electrodes with seed layer were immersed into the aqueous solution. After the reaction at 100 °C for 4 h, we got the FeOOH NRs. Finally, the precursors were annealed at 650 °C for 20 min in air to obtain the porous $\alpha$-$Fe_2O_3$ NRs.

### 2.2. Growth of Au decahedrons onto porous $\alpha$-$Fe_2O_3$ nanorods

On the basis of our experimental design, the growth process of Au DHs/$\alpha$-$Fe_2O_3$ NRs arrays is schematically illustrated in Fig. 1. The Au decahedrons were synthesized according to our earlier work [27–29]. Then, the Au DHs-decorated porous $\alpha$-$Fe_2O_3$ NRs arrays were grow by spin coating (30 s) a 0.25 mM solution of Au DHs onto the porous $\alpha$-$Fe_2O_3$ NRs arrays to form Au/$\alpha$-$Fe_2O_3$ heterostructure. By controlling the spin-coating speed (1000, 2000, and 3000 rpm), Au/$\alpha$-$Fe_2O_3$ NRs arrays with different loading content of Au DHs were fabricated, and the corresponding gas sensors were named as Au/$\alpha$-$Fe_2O_3$ NRs sensor A, B and C, respectively.

### 2.3. Material characterization and sensor properties testing

The morphology, structure, and crystalline phase of the samples were characterized by field emission scanning electron microscope (FESEM, Quanta FEG250), transmission electron microscope (TEM, JEM-2100F, JEOL), X-ray diffraction (XRD, D8-Advance, Bruker), and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI), respectively. The Brunauer-Emmett-Teller (BET) specific surface area of the sample was investigated by measuring nitrogen adsorption–desorption isotherm with a Physisorption Analyzer (Micromeritics Instrument Corporation TriStar II 3020). The corresponding intensity change of the gaseous products including $N_2$, $CO_2$, and $H_2O$ was measured by an on line mass spectrometer (MS) (Pfeiffer, MS GSD 320). The gas sensor properties were measured with a static gas-sensing characterization system (WS-60A, Weisheng Electronics, China). The electronic circuit of sensor measurement system is exhibited (Fig. S1), where $R_S$ is the sensor resistance, $V_H$ is the heating voltage, $R_L$ is a loading resistance and the applied voltage ($V_c$) is 5 V. The desired concentrations of the testing gases is calculated by the following formula:

$$Q = \frac{V \times \varphi \times M}{22.4 \times d \times p} \times 10^{-9} \times \frac{273 + T_R}{273 + T_B} \qquad (1)$$

where $Q$ (mL) is the liquid volume of the volatile compound, $V$ (mL) is the volume of the testing chamber, $\varphi$ is the required gas volume fraction, $M$ (g mol$^{-1}$) is the molecular weight, $d$ (g cm$^{-3}$) is the specific gravity, and $\rho$ is the purity of the volatile testing liquid, $T_R$ and $T_B$ (°C) are the temperature at ambient and test chamber, respectively. Firstly, the devices are put into an airproof test box. Test gas such as TEA with calculated concentration is injected into the testing chamber by a microsyringe. Secondly, when the load voltage is not changing, the TEA gas is exposed to the air until the load voltage to the stable again. Finally, the measuring procedure is stopped. The detailed measuring procedures were reported in our earlier work [2,30]. The sensor response ($S$) was defined as the ratio of $R_a/R_g$, where $R_a$ and $R_g$ are the resistances of the sensor in air and in target gas, respectively.

## 3. Results and discussion

### 3.1. Structural and morphological characteristics

The structure and crystalline phase of the obtained samples were characterized by XRD. Fig. 2 displays the typical XRD spectra of FeOOH, $\alpha$-$Fe_2O_3$, and Au/$\alpha$-$Fe_2O_3$ NRs samples. All the diffraction peaks of spectrum I can be indexed to FeOOH (JCPDS No. 75–1594) together with XRD peaks from flat $Al_2O_3$ electrode. After calcination at 650 °C, the sample is identified as hematite ($\alpha$-$Fe_2O_3$, JCPDS No. 89-0597). Owing to removal of the OH groups during the calcination process, porous $\alpha$-$Fe_2O_3$ NRs are grown [24], as shown in the inset of Fig. 3(a). When the Au DHs are deposited on the $\alpha$-$Fe_2O_3$ NRs, the peaks of Au are not detected in spectrum III due to the low loading content.

The morphology of $\alpha$-$Fe_2O_3$ and Au/$\alpha$-$Fe_2O_3$ NRs was investigated with SEM. As shown in Fig. 3(a), $\alpha$-$Fe_2O_3$ NRs grow nearly perpendicular on the substrate and their diameters are about 100 ~ 150 nm with numerous micropores. Fig. 3(b) is the corresponding EDS spectrum of $\alpha$-$Fe_2O_3$ NRs. The peaks of O, Fe, and Al can be clearly observed in this spectrum. No other peaks exist for impurities, demonstrating the growth of pure $\alpha$-$Fe_2O_3$ NRs on flat $Al_2O_3$ substrates. Fig. 3(c–h) are the SEM images and the corresponding EDS spectra of $\alpha$-$Fe_2O_3$ NRs after Au decorating, indicating that the NRs array morphology can be well maintained. Moreover, the Au content can be well controlled and decreases from 0.25% (Au/$\alpha$-$Fe_2O_3$ NRs A) to 0.04% (Au/$\alpha$-$Fe_2O_3$ NRs C) as the spin-coating speed increases from 1000 to 3000 rpm.