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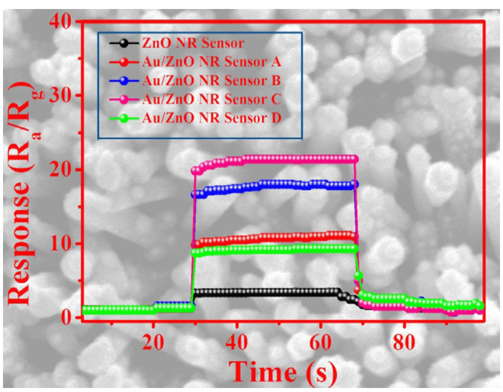
Highly sensitive gold-decorated zinc oxide nanorods sensor for triethylamine working at near room temperature

Xiaopan Song, Qi Xu, Hongyan Xu, Bingqiang Cao *

Materials Research Center for Energy and Photoelectrochemical Conversion, School of Materials Science and Engineering, University of Jinan, Jinan 250022, Shandong, China

GRAPHICAL ABSTRACT



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ABSTRACT

There is an increasing worldwide demand for chemiresistive sensors for specific gas working at low temperature, in particular for standalone and mobile systems, which call for small and low power devices. In this paper, we successfully assemble highly sensitive triethylamine (TEA) gas sensors working at near-room temperature with gold (Au)-decorated ZnO nanorods. ZnO nanorods grow directly on flat Al_2O_3 ceramic electrodes by a cost-effective hydrothermal method and Au nanoparticles are deposited onto ZnO nanorods by DC-sputtering. Au-loaded ZnO (Au/ZnO) nanorods sensor at working temperature of 40 °C and relative humidity of 30% exhibits high response (22–50 ppm TEA), low detection concentration (~1 ppm), and short response/recovery time (11 s/15 s), which are all much better than the pristine ZnO nanorods sensor. When the relative humidity increases, the sensor response decreases due to the water molecules adsorption. Moreover, the enhanced sensing properties of the Au/ZnO sensors are discussed in detail with the semiconductor depletion layer model introduced by the Au/ZnO Schottky contact and the catalytic effect of noble gold nanoparticles.

1. Introduction

Triethylamine (TEA), as a kind of important organic amine, has widespread applications including catalyst, organic solvent, high energy fuel, preservative, and bactericide [1–4]. It is also one of the toxic gases released from harvested fishes and sea creatures during their deterioration process [5,6]. TEA is harmful to human body and can cause irritations to the dermal, ocular, and respiratory systems. In addition, long-term exposure to TEA may eventually result in abnormal embryos [7–9]. Several methods have been adopted to detect TEA, such as gas chromatography, ion mobility

* Corresponding author.
E-mail address: mse_caobq@ujn.edu.cn (B. Cao).

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spectrometry, and liquid chromatography [10–12]. But, these traditional detecting methods are usually time-consuming due to complex operating process [10,13]. Therefore, it is still a strong demand to develop convenient, fast, and on-line TEA detecting method with high selectivity and sensitivity.

Semiconducting metal oxide nanostructures offer a promising platform for gas sensors with several advantages in terms of low cost, simple fabrication, and good compatibility with microelectronic processes [1]. Zinc oxide (ZnO) is a typical n-type semiconductor with a direct wide band gap of 3.37 eV at room temperature [14–18]. ZnO nanostructures such as nanowires [19], nanorods [20,21], and nanotubes [22] have been demonstrated for sensor applications with high sensitivity due to their large specific surface area, less agglomerated configuration, and high crystallinity [23]. Particularly, they have exhibited good sensing property to C_2H_5OH [18], CO [21], NH_3 [24], H_2S [25], and so on. For TEA gas sensor applications, Zhang et al. [26] fabricated ZnO nanorods sensor to detect TEA at 270 °C. Then, our group prepared ZnO nanosheets to detect TEA and obtained high response (78.4 for 50 ppm) and fast response time (6 s) at 320 °C [27].

Moreover, noble metal nanoparticles have been adopted to decorate semiconductors to improve their gas sensing properties such as sensitivity, selectivity, and response time. Au nanoparticles are typical noble metal with advanced optical, electrical, and catalytic properties [28,29]. Au nanoparticles modified ZnO nanostructures have been used to enhance the sensing performance of semiconductor chemiresistive gas sensor. For instance, Li et al. [30] reported Au@ZnO yolk-shell nanospheres to detect 100 ppm acetone and the response was about 2–3 times higher than that of ZnO hollow nanospheres at 300 °C. Majhi et al. [31] prepared Au@ZnO core-shell nanoparticles, which exhibited better selectivity to H_2 than pure ZnO nanoparticles. Zou et al. [32] developed a solution combustion method for the synthesis of Au/ZnO nanostructure, which also exhibited good sensitivity and fast response time (3 s) toward acetone at 300 °C. Generally, the ZnO TEA gas sensor usually works at temperature as high as 250–400 °C [33]. This leads to high power consumption and fast device failure. Moreover, high temperature may result in the ignition of flammable and explosive target gases. Therefore, the fabrication of gas sensors with low working temperature is still highly desirable.

In this paper, a high-performance TEA sensor working at near room temperature (40 °C) is fabricated with Au/ZnO nanorods grown directly on flat Al_2O_3 substrates, which also simplified the traditional slurry-coating process for gas sensor fabrication. Au nanoparticles are decorated onto the ZnO nanorods by DC-sputtering under different deposition time of 5–20 s. The TEA sensor results indicate that the Au/ZnO composite nanorod sensor working 40 °C exhibits an ultrafast response (11 s), good stability, and a dramatic response enhancement in comparison with ZnO TEA sensor. The sensing performances and their gas sensing mechanism are discussed in detail in the following sections.

2. Experimental

2.1. Direct growth of ZnO and Au/ZnO nanorods on flat Al_2O_3 electrodes

All reagents were purchased from Sinopharm Chemical Reagent (Shanghai, China). The flat Al_2O_3 substrates were cleaned with acetone, ethanol, and deionized (DI) water by ultrasonication. The substrate is consisted with a pair of Au electrodes, Pt lead wires, and a heater (Fig. S1(a)). Fig. 1(a) schematically illustrates the fabrication process of ZnO nanorods sensor as well as Au/ZnO nanorods sensor. ZnO nanorods were synthesized via a low-temperature hydrothermal method as described below. 4.407 g zinc acetate dehydrate ($Zn(Ac)_2{\cdot}2H_2O$) was dissolved in 25 ml of ethylene glycol methyl ether with continuous stirring to get a clear solution. After that, cleaned flat Al_2O_3 substrates were immersed into the solution at room temperature for 2 h and then annealed at

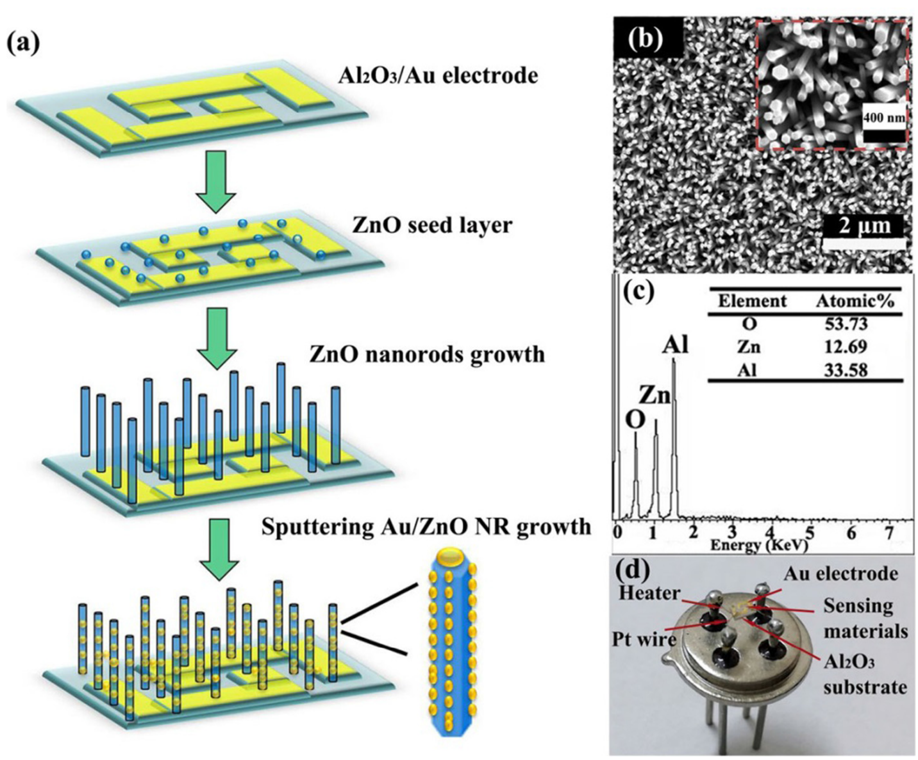

Fig. 1. (a) Schematic for the growth process of Au/ZnO nanorods; (b) SEM image of ZnO nanorods, inset is a local enlarged SEM image; (c) EDS spectrum of ZnO nanorods; (d) Optical image of gas sensor of ZnO nanorods fixed on an electronic bracket.