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An integrated micro-chip with $Ru/Al_2O_3/ZnO$ as sensing material for SO_2 detection

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ABSTRACT

SO_2 sensor is highly demanded in the application fields such as environmental protection and food manufactory. Herein, an integrated microsensor is developed for SO_2 gas detection. For the fabrication of microsensor, ZnO nanosheets sensing material is firstly loaded onto the sensing area of the microsensor by using inkjet printing technology. Then, Al_2O_3 loaded with Ru nanoparticles (Ru/Al_2O_3) as catalyst are locally deposited onto the surface of ZnO nanosheets layer. Gas sensing performance measurements indicate that the fabricated microsensor exhibits a selective response to SO_2, and a good linear relationship in the range of 5–115 ppm SO_2 gases. Besides, this integrated microsensor has short response and recovery time. On-line mass spectrometry (on-line MS) experiment further reveals the formation of sulfur monoxide ($SO^•$) radical as an intermediate product for SO_2 sensing. During the sensing process, Ru/Al_2O_3 as catalyst layer brings SO_2 molecules to be broken down into easily detectable species (i.e. $SO^•$), and then ZnO nanosheets with abundant gas transport channels capture the produced SO generating output signals. Therefore, this kind of sensing material configuration exploits the advantage of each element, and makes it possible for trace and selective detection of SO_2 gas.

1. Introduction

As a kind of air pollutant, sulfur oxides (SO_x) cause serious acid rain, soil acidification and climate change [1]. Moreover, when molecules of SO_x react with basic compounds in atmosphere, they would turn into $PM_{2.5}$ (i.e. particulate matter less than 2.5 μm wide) [2]. SO_x mainly discharge from industrial and anthropogenic activities, although it can come from volcano eruption [3]. Emissions are growing worldwide and about one hundred megatons of SO_x are being discharged into atmosphere every year [4]. Sulfur dioxide (SO_2) is a major component of the family of SO_x, and can be used as the indicator for SO_x monitoring [5]. Apart from polluting the environment, SO_2 is also harmful to human health. Frequently exposure to low concentrations of SO_2 [down to ppm (parts per million) level] can cause bronchial diseases [6]. Additionally, SO_2 is widely applied in the winemaking and dried fruits industries due to its ability to kill microbes and bacteria [7,8]. Hence, it is meaningful to measure SO_2 in atmosphere and residue in wine/dried fruits accurately for air-quality monitoring and human health protection.

Over last few decades, various attempts have been made for the detection of SO_2 [9–13]. For example, fluorescence analysis is a frequently used method in which fluorescent probes with aldehyde or levulinate group have specific reactions with SO_2 or its derivatives. However, the aldehyde-based probes can only be operated in acidic solutions, and may suffer from the interference from sulfur containing molecules, and the labile ester linkage in levulinate-type probes may induce a high background signal [14]. Chemiresistive sensors based on metal oxide semiconductors are another kind of methods to detect toxic or flammable gases such as H_2S, NO_2, H_2 and NH_3 due to their merits of low-cost, long lasting and easy fabrication [15–18]. According to the working principle of chemiresistive gas sensors as proposed in literatures [19], target molecules should react/interact with the adsorbing oxygen species (such as O_2^-) at the surface of metal oxide sensing material to release or capture electrons. The process of electrons releasing/capturing can lead a resistance change (ΔR) and brings a detectable sensing signal. However, SO_2 molecule possesses indistinctive redox characteris-

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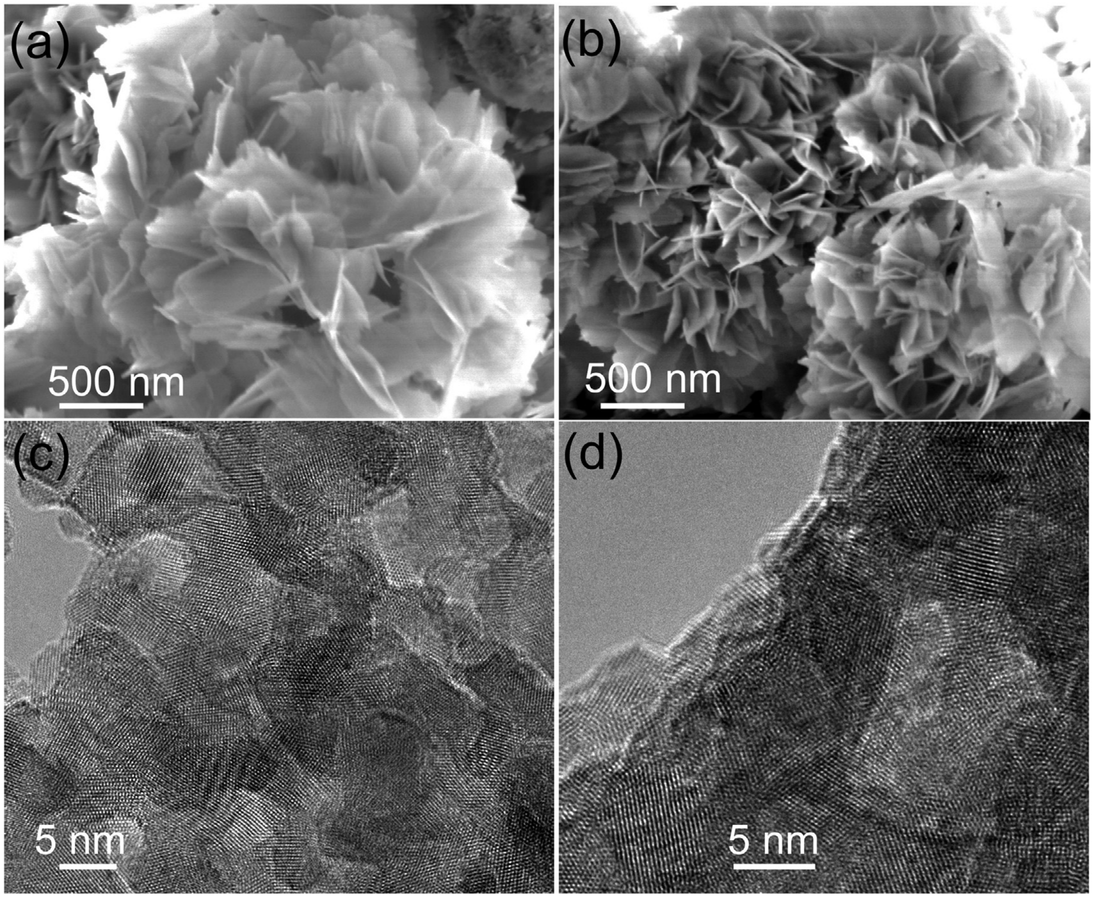

Fig. 1. Morphology characterization of prepared ZnO nanosheets: (a and b) SEM images and (c and d) TEM images.

tics compared with other typical sulfur compounds such as H_2S or SO_3, resulting in a poor reactivity with the adsorbing oxygen species. In fact, SO_2 is a reaction product which is normally produced during H_2S detection by using metal oxide sensor [20]. So, it is still difficult to detect trace SO_2 by using semiconductor sensors and only a few chemiresistive sensors have been reported for SO_2 detection [21–24].

In order to detect SO_2 by using chemiresistive sensors, it is necessary to transform SO_2 molecules into some detectable species. Inspired from the strategy of CO_2 reduction [25–28], some effective catalysts can be introduced for SO_2 transformation before chemiresistive response. Herein, one of the widely researched catalysts of Ru/Al_2O_3 is firstly used for SO_2 sensor construction. ZnO nanosheets with abundant gas adsorption sites as well as wide resistance change characteristics are employed as chemiresistive sensing material. A kind of lab-made integrated micro-chip [29], which can be batch fabricated with MEMS (Micro-Electro-Mechanical System) technology, is used as the chemiresistive sensing platform. With the assistance of Ru/Al_2O_3 catalyst and ZnO nanosheets, the detection of SO_2 gas at ppm-level can be successfully realized on the integrated MEMS micro-chip chemiresistive platform.

2. Experimental section

2.1. Chemicals

Amphiphilic triblock copolymer Pluronic P123 (M_{av} = 5800, $EO_{20}PO_{70}EO_{20}$), $Zn(COO)_2{\cdot}2H_2O$, hexamethylenetetramine (HMTA) ruthenium(III) nitrosyl nitrate solution [$Ru(NO)(NO_3)_x(OH)_y$, x + y = 3 in dilute nitric acid, 1.5% Ru] are purchased from Sigma-Aldrich. Ethanol, urea, $KAl(SO_4)_2{\cdot}12H_2O$ and ethylene glycol (EG) are of analytical grade and purchased from Shanghai Chemical Reagent Corp.

2.2. Synthesis of ZnO nanosheets

The ZnO nanosheets are synthesized by using a modified method as reported in literature [30]. The synthesis process of ZnO nanosheets is detailed as follows. 0.2 g of P123 is dissolved into a mixture of 4 mL of ethanol and 0.45 mL of deionized water under stirring. Then, 0.1 g of zinc acetate and 0.045 g of HMTA are sequentially added. After stirring for 15 min, 46 mL EG is added into the abovementioned solution. The solution is allowed to stir for half an hour. Thereafter, the obtained solution is aged for 7 days. After that, the solution is sealed in a 100 mL Teflon-lined autoclave and aged at 110 °C. After heating for 15 h, the light-yellow solid is collected sequentially by filtering, washing for 3 times and then drying at room temperature.

2.3. Synthesis of Al_2O_3 microspheres

Al_2O_3 microsphere substrate is prepared by using a hydrothermal method [31]. 1.7 g of $KAl(SO_4)_2{\cdot}12H_2O$ is dissolved in 60 mL of water. Then, 0.42 g of urea is added into the abovementioned solution. After the chemicals are dissolved completely, the clear solution is transferred into a 100 mL Teflon-lined autoclave and aged at 170 °C for 3 h. After heating for 15 h, the product is col-