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Ag/SnO_2/graphene ternary nanocomposites and their sensing properties to volatile organic compounds

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ABSTRACT

Combined with the π-conjugate system of graphene, the SnO_2/graphene nanocomposites exhibited highly sensitive to benzene as reported previously. However, the SnO_2/graphene nanocomposites presented lower sensitive to other volatile organic compounds (VOCs) than benzene. For further improving the sensitivity to VOCs, noble metal was added to those nanocomposites. Here, Ag/SnO_2/graphene ternary nanocomposites have been synthesized by a wet-chemical method. The synthesized ternary nanocomposites exhibit high sensitive to VOCs, especially acetone. The lowest detection concentration to acetone is 0.005 ppm. The sensing mechanism is speculated and the role of Ag nanoparticle, SnO_2 nanoparticle, and graphene are clearly discussed.

1. Introduction

Volatile organic compounds (VOCs) refer to those organic chemicals having high vapor pressure at room temperature [1]. Some VOCs are common indoor air pollutions (*e.g.* formaldehyde) and some are important products in industry (*e.g.* acetone and furan). In particular, acetone is one of the most important volatile organic compounds which may be used as industrial solvent [2] and easily-made drug chemicals [3]. However, it is not only highly volatile and flammable but also harmful to human body because of its anesthetic effects on the central nervous system [4]. Besides, it is also one of the generally accepted biomarkers for noninvasive diagnosis of human type-I diabetes [5]. Therefore, to develop efficient and convenient sensing technology for VOC detection becomes necessary for human health in residential buildings and process control in industries.

Metal oxide gas sensors have been extensively exploited to detect VOCs because of their advantages including compact size, easy production, low cost and simple measuring electronics [6–9]. However, the morphology and structure of the sensing materials significantly influence their sensing performances. Nanomaterials have many unique performances, such as large area, small size effect and so on [10–14]. Therefore, various nanostructured metal oxides have been prepared to improve gas sensing properties [15–18]. Many methods have been developed to synthesize metal oxide nanostructures [19–22]. Xu and co-workers found that the particle size heavily affected the sensitivity of sensor [23]. When the particle size of SnO_2 is less than 6 nm, which is double of the width of its depletion layer, the crystalline SnO_2 becomes highly sensitive to ambient gas molecules. Although many methods have been reported to synthesize SnO_2 nanoparticles with the size of sub-6 nm [24,25], it is difficult for single-component SnO_2 to reach a high sensitivity. This is due to that the SnO_2 nanoparticles with small size could easily congregate together and grow larger by Ostwald ripening to form a compact film under heating conditions [26]. Graphene has been used to synthesize nanocomposite with SnO_2, in which the SnO_2 nanoparticles are uniform, small size and well dispersed [27] because the oxygen-contained functional groups on graphene may anchor stannic ions and grow into SnO_2

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colloids as seeds during the formation process of SnO_2 nanoparticles. Combined with the π-conjugate system of graphene, the SnO_2/graphene nanocomposites exhibited highly sensitive to benzene. However, the SnO_2/graphene nanocomposites presented lower sensitive to other VOCs than benzene. For further improving the sensitivity to VOCs, noble metal was added to that nanocomposite. Here, Ag/SnO_2/graphene ternary nanocomposites have been synthesized by a wet-chemical method. The synthesized ternary nanocomposites exhibit high sensitive to acetone.

2. Experimental

2.1. Materials

Graphite powder, $NaNO_3$, H_2SO_4, $KMnO_4$, H_2O_2, HCl, $AgNO_3$, ammonia, acetone, furan, formaldehyde, chlorebenzene and $SnCl_4 \cdot 5H_2O$ were all analytically pure grade and purchased from China National Pharmaceutical Group Corporation Company.

2.2. Instrumentation

The morphology of the Ag/SnO_2/graphene nanocomposite was characterized by transmission electron microscopy (TEM; JEOL JEM-2010) operated at an accelerating voltage of 200 kV. Energy dispersive spectroscopy (EDS) was measured by Oxford INCA X-Max 50.

2.3. Preparation of graphene oxide

Graphene oxide was firstly prepared by a modified Hummers' method [28]. 1 g of graphite, 1 g of $NaNO_3$, and 46 mL of concentrated H_2SO_4 were stirred together in an ice bath for 30 min, followed by the slow addition of 6 g of $KMnO_4$. After 1 h, the flask was shifted to oil bath and reaction mixture was allowed to stir at 35 °C for 2 h, and then temperature is slowly allowed to increase to 60 °C and allowed to stir for 2 h. Finally, the reaction mixture was added to 200 mL of water allowed to stir at 90 °C for 5 h and the reaction was ended by the addition of 10 mL of 30% H_2O_2 which results in change of color from yellow to brown. The warm solution was filtered and washed with 5% HCl and then with deionize water. The filter cake was dissolved in water, and sonicated to exfoliate oxidized graphene. The obtained mixture was centrifuged firstly at 2000 rpm for 5 min to remove all visible particles, and then centrifuged at 8000 rpm for 10 min. After it was washed and dried in vacuum at 60 °C overnight, the dried graphene oxide was prepared.

2.4. Preparation of Ag/SnO_2/graphene nanocomposite

The Ag/SnO_2/graphene nanocomposite was synthesized as following procedure by one-step wet chemical method. 0.1 g of the dried graphene oxide was added to 500 mL of DI water. The mixture was sonicated for 90 min. 2.4 g of $SnCl_4 \cdot 5H_2O$ was dissolved to 20 mL of DI water and then 8 mL of the graphene oxide solution was added and stirred for 5 h for the formation of SnO_2 colloids. Then, different concentrations of $AgNO_3$ solutions (600, 60, 6, 0.6 mmol/L) were added, respectively. The mixture was stirred for 5 min under sunlight. Ag nanoparticles formed by the reduction of $AgNO_3$ under the radiation of sunlight [29]. Then, the mixture was centrifugated for 5 min at 8000 rpm. In order to improve the crystallinity of the SnO_2 and remove the residual water molecules and functional groups from the graphene, the product was heated at 350 °C for 2 h under an argon atmosphere.

2.5. Gas-sensing measurement system

Gas-sensing measurements were performed by using a computer controlled gas-detecting system as reported previously [30]. A Keithley 6487 picoameter/voltage sourcemeter was used as both current recorder and power source. Typically, a certain volume of saturated organic vapor of the sample under standard atmospheric pressure was introduced by an injecting needle into the testing chamber. After a while, another certain volume of the sample vapor was injected into the testing chamber in succession to form a step of response. The detected concentration of the gases inside the testing chamber was determined by the concentration (known at the specific temperature) and injected volume of its saturated vapor. Once the gas-sensing measurement was over, the gases in the testing chamber were finally released by inputting fresh air.

3. Results and discussion

3.1. Characterization of the Ag/SnO_2/graphene nanocomposites

The Ag/SnO_2/graphene nanocomposites were synthesized as the following three steps. Firstly, graphene oxides were prepared by a modified Hummers' method. Secondly, the SnO_2 colloids grew by adsorbing stannic ions onto the oxygen-contained functional groups of the graphene oxides. Thirdly, Ag nanoparticles formed on the surfaces of SnO_2 colloids by the reduction of $AgNO_3$ under the radiation of sunlight. The formation of Ag particles was adjusted by the concentration of $AgNO_3$ solutions. Fig. 1 shows the TEM images of the samples synthesized by different concentrations (600, 60 and 6 mmol/L) of $AgNO_3$ solutions. From Fig 1a, many large particles can be seen. Those are the aggregates of Ag particles, which are formed because the concentration of $AgNO_3$ solutions is so high that Ag particles aggregate each other. Fig 1b shows the nanocomposite of Ag, SnO_2 and graphene, in which the large particles are Ag nanoparticles and the small particles are SnO_2 nanoparticles as shown in our previous report [27]. When the concentration of $AgNO_3$ solutions becomes further lower, there are few Ag particles formed as show in Fig. 1c. Therefore, the optimized concentration of $AgNO_3$ solutions is around 60 mmol/L. EDS spectrum proves the existence of Ag element in Fig. 2. The peaks of Cu element are caused by the TEM grid.

3.2. Operating temperature of the Ag/SnO_2/graphene nanocomposites

Sensing performance of metal oxide gas sensors is usually highly dependent on the operating temperatures [31,32]. Therefore, it was systematically investigated that the responses of the Ag/SnO_2/graphene nanocomposite to 150 ppm of acetone at different operating temperatures as shown in Fig. 3. During a typical sensing process, oxygen gases are adsorbed on the surface of the SnO_2 sensing material in air. The adsorbed oxygen species can capture electrons from the inner of the SnO_2 film. The negative charge trapped in these oxygen species causes a depletion layer and thus a reduced conductivity. When the sensor is exposed to reducing gases, the electrons trapped by the oxygen adsorbate will return to the SnO_2 film, leading to a decrease in the potential barrier height and thus an increase in conductivity. There are different oxygen species including molecular (O_2^-) and atomic (O^-, O^{2-}) ions on the surface depending on working temperature. Generally, the molecular form dominates below 150 °C, while the atomic species play an important role at higher temperature [33]. The temperature dependence studies show that the responses reach a maximum at the operating temperature of 300 °C suggesting that the sensor worked mostly depending on atomic species. Therefore, 300 °C is