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Hydrothermally synthesized Pd-loaded SnO_2/partially reduced graphene oxide nanocomposite for effective detection of carbon monoxide at room temperature

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ABSTRACT

In this paper, palladium (Pd)-loaded tin dioxide (SnO_2)/partially reduced graphene oxide (PRGO) nanocomposites with different proportions of Pd loading and PRGO nanosheets were synthesized by the facile hydrothermal method for carbon monoxide (CO) sensing applications. The crystal structure, morphology and composition of sensitive materials were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectrometer (EDX), respectively. Characterization data show that PRGO nanosheets act as a template for growth of small-sized SnO_2 nanoparticles. The gas sensing properties of all sensors were investigated by exposing them to various concentrations of CO gas ranging from 50 to 1600 ppm at 26 °C. The synthesized 5%Pd-loaded SnO_2/PRGO-1.5% sensor exhibited a very reproducible performance with fast response and recovery time (~2 min) at 26 °C. The ability of detecting CO gas at room temperature could be attributed to the high specific surface area of PRGO nanosheets, good conductivity of PRGO and special interactions between PRGO nanosheets and Pd-loaded SnO_2 nanoparticles.

1. Introduction

Carbon monoxide (CO) is one of the most harmful gases present in the environment. It is produced by the incomplete combustion of carbon-based fuels used in car engines, gas fires, domestic appliances, etc. [1]. CO is notorious as the invisible silent killer because it is a colorless, odorless and tasteless gas [2]. When CO is inhaled, it combines with the oxygen-carrying hemoglobin of the blood and hemoglobin is no longer available for delivering oxygen to bodily tissues [1]. Exposure to a low concentration of CO can cause a headache and dizziness, whereas exposure to a higher concentration can result in convulsion, respiratory arrest and even death [2]. It is, therefore, imperative to develop low-cost sensors that can reliably detect CO at maximum permissible exposure level at room temperature.

Recent advances demonstrated that graphene, a two-dimensional sheet of sp^2 bonded carbon atoms on honey comb lattice, has attracted considerable attention in gas sensing field due to its large specific surface area and remarkable electronic properties [3]. Up to now, different methods have been applied for production of graphene. These methods consist of the mechanical cleavage of graphite [3], epitaxial growth [4–6], chemical vapor deposition [7,8], liquid phase exfoliation of graphite [9] and thermal/chemical reduction of graphene oxide (GO) [10,11]. Among these methods, reduction of GO is recognized as a versatile and inexpensive route for large-scale production of graphene [12–17]. Graphene-derived by this method could contain a significant amount of oxygen functional groups especially epoxy and hydroxyl groups. These functional groups can act as active sites for interaction with gas molecules [18]. However, reduced graphene oxide (rGO)-based gas sensors suffer from the limited response, poor selectivity, long response and recovery time [13,19–21]. Of late, Panda et al. synthesized functionalized rGO layers by the wet chemical method and measured the sensitivity of the sensor in 10–30 ppm of CO. Though a quick response was observed, the sensor suffered from long recovery time to a significant extent. The sensor may recover almost abundantly and come to their initial baseline value if exposed to UV light, after removal of the target gas [22]. To improve their gas sensing performance, semiconductor metal oxide nanoparticles can incorporate with rGO [23–27]. By incorporation of semiconductor metal oxide nanoparticles into graphene, the outstanding properties of them combine and might

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result in some particular properties because of the synergetic effect between them. Tin dioxide (SnO_2), a wide band gap n-type semiconductor, is one of the most widely used materials for gas sensing application [28–33]. However, the pure SnO_2 is sensitive to a broad spectrum of gases. To modify the selectivity, noble metals such as palladium (Pd), platinum (Pt) are incorporated in the semiconductor metal oxide matrix [34–41]. Li et al. showed that the Pd nanoparticles attached on the surface of semiconducting materials (ZnO, In_2O_3) improve the response and selectivity of chemical sensors [42–44]. Moreover, more recently Hooriabad Saboor et al. [45] applied Pd nanoparticles to modify the SnO_2 thick film for sensing NO_2. For CO detection, Pd is also the most commonly used dopant which promotes selectivity and sensitivity of the SnO_2-based gas sensor [34–38]. Thus far, several Pd-doped SnO_2-based CO gas sensors, prepared with different methods, have been reported. For example, Wang et al. [38] reported a one-step microwave assisted hydrothermal route for the synthesis of Pd-doped SnO_2 nanoparticles as a CO gas sensor. They demonstrated that the amount of Pd doping has a strong effect on sensor response. However, the relatively high operating temperature (100 °C) is required. Recently, many researchers have proved that modification of rGO nanosheets with SnO_2 nanoparticles is an effective method to overcome the high operating temperature problem of metal oxide sensors [46–49]. For instance, Ge et al. [50] fabricated a more rapidly responding room temperature NO_2 sensor based on Ag nanoparticles-SnO_2-rGO hybrids. Lin et al. [46] have prepared SnO_2/graphene composite by a hydrothermal method for detection of NH_3 at room temperature. Although these sensors exhibit better sensing performance than that of rGO, some special problems such as the tendency of graphene layers to be re-stacked by removing the functional groups, construct obstacle to achieve high surface area for gas molecule interaction. More recently, a new class of graphene derivative known as partially reduced graphene oxide (PRGO) has emerged, in which, π conjugations are restored only partially [51,52]. The partial restoration of the sp^2 hybridized network by mild reduction of GO result in retaining some functional groups crucial for gas sensing application while simultaneously attaining conductivity. Esfandiar et al. [53] showed that partially reduced graphene oxide has a great potential for improving the H_2 sensing properties of Pd-doped WO_3 sensor owing to the presence of its functional groups.

In the present work, we evaluate the CO sensing performance of Pd-loaded SnO_2/PRGO thin film sensors containing various amounts of Pd loading and PRGO nanosheets. For this purpose, the sensitive nanocomposites were synthesized by a simple two-step hydrothermal procedure. The hydrothermal procedure is an efficient method for preparation of nanostructure material without post-synthetic annealing or calcination [54]. During the hydrothermal reaction process, single crystalline SnO_2 nanoparticles were formed on the graphene nanosheets. Hence, the PRGO nanosheets act as a template for growth of metal oxide nanoparticles. The surface morphology and crystalline structure of prepared samples were characterized by field emission scanning electron microscope (FESEM), transmission electron microscope (TEM) and X-ray diffraction (XRD). The responses of synthesized nanocomposites toward CO were measured at 26 °C. At last, the possible sensing mechanism of the proposed sensor is also discussed.

2. Experimental details

2.1. Materials

All the reagents were of analytical grade and used as received without further purifications. Natural graphite flakes (99/8%, 325 mesh) and tin (IV) chloride pentahydrate ($SnCl_4{\cdot}5H_2O$, 98%) were purchased from Alfa Aesar and Sigma-Aldrich, respectively. All other reagents including sulfuric acid (H_2SO_4, 97%), sodium nitrate ($NaNO_3$, 99%), hydrochloric acid (HCl, 37%), silver nitrate ($AgNO_3$, 99.8%), hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$, 99%), sodium sulfate (Na_2SO_4, 99%), sodium hydroxide (NaOH, 98%), palladium (II) chloride ($PdCl_2$, 59% Pd) and absolute ethanol were commercially available from Merck. Doubly distilled water was used throughout the experiment.

2.2. Preparation of graphite oxide

Graphite oxide was synthesized by the modified hummers' method [55]. In brief, 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 4 h. Next, 6 g of $KMnO_4$ was added slowly for about 20 min to the above mixture. Once mixed, the ice bath was removed and the suspension was stirred for another 2 h. After that, 92 ml of distilled water was added dropwise, and the suspension was heated in a water bath at 98 °C for 15 min. Again, the reaction mixture was diluted with 200 ml of warm water followed by adding 20 ml of H_2O_2 (30%) drop by drop. The obtained mixture was repeatedly centrifuged at 4000 rpm and washed with HCl aqueous solution (10%) followed by distilled water. Then, it was subjected to dialysis for 3 days to completely remove metal ions and acids and pH gets neutral. Finally, the product was dried in air at room temperature.

2.3. Preparation of Pd-loaded SnO_2/PRGO nanocomposites

The Pd-loaded SnO_2/PRGO nanocomposites were synthesized by a facile hydrothermal method. In the first step, the PRGO has been synthesized according to the methodology demonstrated by Esfandiar et al. [53]. Briefly, 2 mg of graphite oxide was dispersed in distilled water by sonication for 1 h in order to form the clear brown dispersion of graphene oxide. Then, the aqueous solution partially reduced through the hydrothermal method at 120 °C for 2 h [11]. In the second step, 1.26 g of $SnCl_4{\cdot}5H_2O$, 0.9 g of NaOH and 0.3 g of Na_2SO_4 were dissolved into 20 ml of water by vigorous magnetic stirring for 5 min. Afterward, 30 ml of ethanol was injected into the above solution and stirred to form a white transparent suspension. Next, $PdCl_2$ (with Pd/Sn ratio of 5 wt%) was added gradually to the mixed solution. Then, the synthesized Pd-loaded SnO_2 suspension was added dropwise to the 0.5 wt% (relative to Sn) PRGO suspension under vigorous stirring. The resulting mixture was transferred into 100 ml Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h. After cooling down to room temperature, the final product was collected by centrifugation and washed with distilled water and absolute ethanol several times and dried in air. Furthermore, we prepared samples by adding the various amount of $PdCl_2$ powder to the solution of 2 mg PRGO and labeled as 5 wt% Pd, 7 wt% Pd and 10 wt% Pd. In addition, the content of GO increased from 2 mg to 7 mg. These fabricated sensors would have additional post label of PRGO-0.5 wt%, PRGO-1 wt%, PRGO-1.5 wt%. Hereafter, "wt%" will be expressed simply by "%" throughout the text, including all figures. The synthesis of sensitive nanocomposites is schematically shown in Fig. 1.

2.4. Fabrication of gas sensor and measurement

To study the gas sensing behavior of samples, the fine powder of Pd-loaded SnO_2/PRGO was dispersed in distilled water through ultrasonication. Then, 10 μl of dispersion was deposited onto the Au interdigitated electrodes (Drop sense, Spanish) and allowed to be dried. The photograph of the sensor coated with the sensing material is shown in Fig. 2. The active area of the Au interdigitated electrodes with a SiO_2 substrate was 5 mm × 7 mm and both finger width and interfinger spacing of gold track were 5 μm.