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Doping composite of polyaniline and reduced graphene oxide with palladium nanoparticles for room-temperature hydrogen-gas sensing

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ABSTRACT

A composite consisting of polyaniline (PANI) and reduced graphene oxide (rGO) was synthesized by in situ polymerization of the monomer aniline in the presence of rGO under acidic conditions. The PANI–rGO composite substrate was doped with Pd nanoparticles via chemical reduction. The resulting Pd–PANI–rGO nanocomposite was characterized by transmission electron microscopy, scanning electron microscopy, X-ray diffraction, and Fourier-transform infrared spectroscopy before it was utilized to fabricate a hydrogen sensor. Compared with the sensor based on PANI–rGO or PANI, the Pd–PANI–rGO sensor was highly sensitive and selective to hydrogen gas, with fast response time in air at room temperature. The significantly enhanced sensitivity resulted from the faster spill-over effect, dissociation of hydrogen molecules on Pd, and the high surface area of the PANI–GO composite. Based on its improved sensing properties, ease of fabrication, and stable operation, the Pd–PANI–rGO nanocomposite shows promise for high-performance hydrogen-sensing applications.

Introduction

Graphene, a very attractive two-dimensional carbon nanomaterial with superior electrical conductivity, excellent mechanical flexibility, and high thermal and chemical stability, has been widely used in many fields such as integrated electronics and optoelectronics [1–3]. Through wet-chemical methods, graphene can be simply made into either graphene oxide (GO) or reduced graphene oxide (rGO). Compared with raw graphene, oxidized graphene is hydrophilic and has good

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dispersion in water, both of which are important criteria for solution processing and further modification [4]. Meanwhile, these oxygen-containing groups enable graphene sheets to strongly interact with small polar molecules or polymers to form graphene-intercalated or exfoliated composites [5]. However, pristine GO is not suitable for gas-sensing applications because of the low adsorption energies of gas molecules on the GO surface [6]. In addition, the selectivity of a graphene-based gas sensor must be improved for each target gas. To overcome this drawback, functionalization of GO with metal particles, a polymer, or a metal oxide is considered to be an effective way to improve the gas-sensing capability of GO because of the synergistic effects of GO and the additive [7–10].

In recent years, the synthesis and application of conducting polymers have attracted great interest in the scientific community [11–13]. Among various polymers that have been developed, polyaniline (PANI) is one of the promising candidates for gas sensing [14–17]. PANI has good thermal and electrochemical stability, a unique conducting mechanism, unusual doping and dedoping chemistry, and low cost, which lead to potential application in many fields such as battery electrodes, supercapacitor, gas sensors, and electrocatalytic devices [18–20]. Moreover, PANI has the highest environmental stability and is recognized as the only conducting polymer that is stable in air. PANI has been utilized as a sensor material because it is sensitive at room temperature, and the application of PANI-based sensors has been expanded to the detection of a range of gases by combining PANI with other nanomaterials [21–25]. The incorporation of rGO in a polymer is a good way to exploit the advantages of both materials while greatly improving the thermal stability and electrical properties of the polymer [26–28]. In addition, a large number of polymer–rGO nanocomposites have become accessible in the form of end-functionalized derivatives because of their small particle size and intercalation properties [29]. Therefore, the gas-sensing potential of polymer–GO nanocomposites has attracted much recent research attention [23,30,31]. In particular, PANI-based sensors have been shown to exhibit ultrahigh sensitivity, fast response, satisfying reversibility, etc., and they are suitable for practical applications [32,33].

To the best of our knowledge, no attempt has been made until our current study to examine the performance of a conducting-polymer–graphene composite decorated with metal nanoparticles. Therefore, it is a significant body of work that explores the fabrication of a H_2 gas sensor based on graphene–PANI nanocomposites and investigates the properties of the nanocomposites and performance of the sensor. In this study, different mass concentrations of rGO were optimized to improve the detection performances. Infrared, morphological, and electrical characterizations of the graphene–PANI thin films were also carried out.

Experimental

Materials

Aniline, ammonium persulfate (APS), cetyltrimethylammonium bromide (CTAB), K_2PdCl_6, and indium–tin oxide (ITO; surface resistivity: 70–100 Ω/sq) glass were obtained from Sigma–Aldrich, USA. Reduced graphene oxide (>99.5%), with a thickness of 4–20 nm and a diameter of 0.5–10 μm, was supplied by Chengdu Organic Chemicals Co. Ltd, China. All chemicals and reagents were used as received, except for aniline, which was distilled under reduced pressure before use.

Preparation of Pd–PANI–rGO

The PANI–rGO composites were prepared according to established procedures. In brief, 0.15 g of rGO was dispersed in 100 mL of a 0.01 M HCl solution and ultrasonicated for 2 h to form a uniform suspension; 0.5 mL of aniline was then added to the suspension and ultrasonicated for 1 h before polymerization. Next, 0.5 g of APS was dissolved in 20 mL of deionized water and slowly added drop by drop to the prepared suspension from a burette. After stirring for 4 h, the solution was filtered and washed thoroughly with deionized water and methanol, and then dried in an oven at 60 °C under vacuum. Different concentrations of rGO were employed in our research. For comparison, PANI was also prepared under the same conditions.

The PANI–rGO composite was doped with Pd nanoparticles as follows: First, 1 mg of K_2PdCl_6 was added to 5 mL of deionized water (density: 0.2 g/L); 0.1 g of the PANI–rGO powder was then dispersed in the solution under sonication for 2 h. Next, 1 mL of a $NaBH_4$ solution (density: 1 g/L) was added drop-wise to the mixture with vigorous stirring for 20 min. The mixed solution was then dried at 60 °C under vacuum for 10 h. Fig. 1 shows a schematic diagram of the preparation of Pd–PANI–rGO.

Sensor fabrication and sensing tests

The H_2 sensor was fabricated on an ITO layer deposited on a glass substrate. Before the fabrication, the sheets of ITO/glass were sonicated in ethanol, washed with deionized water, and then dried in a nitrogen flow. Copper foil tape with conductive adhesive on one side was purchased from Shanghai Mingyu Metal Materials Company Inc., China. The electrical contacts were made by attaching two copper foils (with a 5-mm separation) onto the ITO surface. The effective sensing area was 0.5 × 3 cm^2. Next, 0.1 g of the Pd–PANI–rGO powder was suspended in 5 mL of an ethanol solution under sonication for

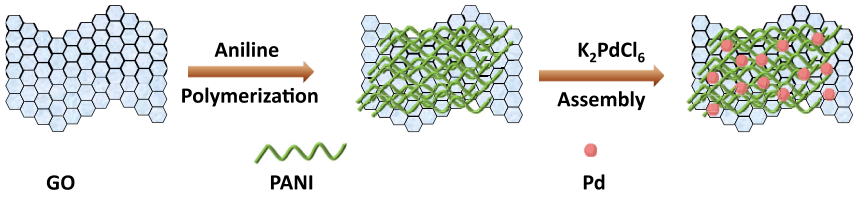

Fig. 1 – Schematic diagram of the preparation of the Pd–PANI–rGO nanocomposite.