Freeze drying-assisted synthesis of Pt@reduced graphene oxide nanocomposites as excellent hydrogen sensor

Xiaojing Lu [a,1], Xinjie Song [b,1], Cuiping Gu [a,*], Haibo Ren [a], Yufeng Sun [c], Jiarui Huang [a,*]

[a] College of Chemistry and Materials Science, Center for Nano Science and Technology, Anhui Normal University, Wuhu, Anhui, 241000, People's Republic of China
[b] Department of Food Science and Technology, Yeungnam University, Gyeongsan, Gyeongbuk 712749, Republic of Korea
[c] School of Mechanical and Automotive Engineering, Anhui Polytechnic University, Wuhu, 241000, People's Republic of China

ARTICLE INFO

ABSTRACT

Quick and efficient detection of low concentrations of hydrogen remains a challenge because of the stability of hydrogen. A sensor based on reduced oxide graphene functionalized with Pt nanoparticles is successfully fabricated using a freeze-drying method followed by heat treatment. The structure and morphology of the Pt@rGO nanocomposites are well analyzed by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The as-prepared Pt@rGO nanocomposites show excellent hydrogen gas sensing properties at a low working temperature of 50 °C. The sensitivity toward 0.5% hydrogen is 8%. The response and recovery times of the sensor exposed to 0.5% hydrogen are 63 and 104 s, respectively. The gas-sensing mechanism of Pt@rGO sensor is also discussed.

1. Introduction

With the increasingly severe shortages of energy and global environmental pollution, the quest for alternative energy sources that are renewable and environment-friendly has been attracting widespread concern in the past few years, particularly under the realization that the combustion of fossil fuels has been causing serious harm to human health and environment [1,2]. It is generally acknowledged that hydrogen is a major component of the universe (75% wt) and the final product of combustion is the environmentally benign water [3]. Moreover, with the excellent physical characteristics of a fast rate of burn, abundant burning heat, and relatively low point of ignition [3,4], hydrogen is considered to be one of the most attractive energy sources in contrast to the traditional fossil fuel, which has extensive applications in many fields [5–7]. On the contrary, the low-temperature flammability of hydrogen poses risks since it can easily explode when the volume concentration reaches only 4% in air [8]. Because of the odorless, colorless, and tasteless nature of hydrogen, it cannot be easily detected when its concentration reaches a dangerous level. Therefore, a gas sensor with high sensitivity and unique selectivity for hydrogen needs to be urgently developed in the near future.

Since 2004, graphene, known as a single carbon molecule with a two-dimensional nanosheet structure, has attracted immense attention owing to its excellent physical and chemical properties, including a large specific surface area [9], high conductivity [10,11], and excellent mechanical strength [12]. Among graphene-related materials, reduced graphene oxide (rGO) possesses some outstanding and exceptional characteristics compared to graphene and graphene oxide (GO). First, a vast number of defects and functional groups existing on the surface of rGO can afford a large number of chemically active sites, which is conducive for coupling with other metal particles and metal oxides to form functionalized composites [13,14]. In addition, after the reduction of GO, the quantity of large oxygen-containing groups on the surface of rGO, such as the carboxyl, epoxy, and carbonyl, decreases sharply. This partly restores the amount of sp^2-carbon conjugation in rGO, resulting in the improvement of its conductivity [15]. Undoubtedly, the introduction of rGO in a hydrogen gas sensor could enhance its sensing performance.

Recently, a great deal of attention has been paid to metal nanoparticles (NPs), owing to their outstanding properties such as their strong catalytic activity [16], good charge mobility [17,18], and excellent sensing ability [19]. Among various metal nanoparticles, noble metal Pt and Pd have been gaining increasing attention owing to their excellent stability and strong catalytic activity [20,21], with high sensitivity and unique selectivity to hydrogen gas. However, some disadvantages render it difficult to apply them widely for the detection of hydrogen; these are their high costs and relatively low conductivities attributed to their

---

discontinuous particles. Therefore, gas sensors based on rGO functionalized with Pt or Pd NPs are likely to be promising candidates for practical application in the upcoming years. This is because the nanocomposites possess a large specific surface area [22], high conductivity [23], and good selectivity of Pd or Pt toward hydrogen [24]. In recent years, sustained and tremendous efforts have been devoted to fabricate hydrogen sensors based on rGO modified with Pd or Pt NPs via different methods. For example, Peng et al. reported successful fabrication of a hydrogen sensor based on Pt-Pd@rGO via a chemical reduction method and the sensor was shown to be highly responsive to hydrogen [25]. Ghosh et al. prepared Pt-modified rGO sensor, with high sensitivity and selectivity to 200–5000 ppm of hydrogen, via a simple hydrothermal method [26]. Wang et al. reported the synthesis of a hydrogen sensor based on rGO incorporated with Pt particles through an alternating current dielectrophoresis technique and demonstrated an excellent response and selectivity [27]. However, to date, there are only few reports on hydrogen sensors based on Pt NPs anchored on the surface of rGO fabricated via a freeze-drying route followed by heat treatment.

In this study, composites of rGO functionalized with Pt NPs were successfully prepared via a freeze-drying route followed by heat treatment. The hydrogen sensors based on Pt@rGO composites exhibited excellent sensing performances toward hydrogen at a low working temperature. The sensing mechanism of the Pt@rGO composites toward hydrogen is also discussed.

2. Experimental details

2.1. Preparation of graphene oxide

All chemicals were of analytic grade and used without further purification. Graphene oxide (GO) was prepared from natural graphite flakes via a modified Hummers method [28]. A typical synthesis procedure is as follows: 20 mL of concentrated H_3PO_4 and 180 mL of concentrated H_2SO_4 were slowly added to a mixture of 6.0 g of $KMnO_4$ and 1.0 g of graphite under stirring in an ice bath. Then, the mixture was maintained at 50 °C for 12 h with continuous stirring. The solution was cooled to room temperature and 400 mL deionized water and 3 mL 30% hydrogen peroxide were added. The product was collected by centrifugation and washed several times with deionized water, 30% HCl, and ethanol. After drying under vacuum for 12 h, graphite oxide was obtained. Finally, 5 mg of the prepared graphite oxide was dispersed in 20 mL of deionized water and ultrasonicated for 12 h to obtain a homogeneous solution.

2.2. Preparation of Pt NPs

4 mL of a H_2PtCl_6 solution (0.2 M) was mixed with deionized water (14 mL), ethanol (21 mL), and polyvinyl pyrrolidone (103 mg) in a round bottom flask for 4 h at 100 °C. The final product was centrifuged and washed five times with distilled water.

2.3. Preparation of Pt@rGO nanocomposites

4.0 mg of the Pt NPs was mixed with 5 mL of the as-synthesized GO suspension (0.4 mg/mL). The mixture was ultrasonicated for 15 min to obtain a uniform solution and then freeze-dried at −50 °C for 2 days, and yellow precursor (Pt@GO nanocomposites) was obtained. Finally, the yellow precursor was annealed at 200 °C for 2 h and black product (Pt@GO nanocomposites) was obtained. During this annealing process, GO will be reduced to rGO via thermal reduction [29]. Furthermore, the annealing process will make the Pt NPs and the rGO combine firmly.

2.4. Characterization

The products were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000, with high-intensity Cu $K\alpha$ radiation with a wavelength of 1.54178 Å), field emission scanning electron microscopy (FESEM,

Hitachi S-4800, operated at 5 kV), transmission electron microscopy (TEM, Hitachi H-800 operated at an accelerating voltage of 200 kV), and Raman spectroscopy (Bruker -Senterra, laser wavelength = 532 nm). X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250 system using an Al-$K\alpha$ 150 W non-monochromatized X-ray source and a hemispherical energy analyzer at a pass energy of 30 eV.

2.5. Gas-sensor fabrication and response test

The structure of the sensor is nearly the same as the one reported in a previous work [30]. First, the Pt@rGO sensing material was dispersed in ethanol to obtain a homogeneous suspension. Next, the outer surface of a tube-like aluminum-based substrate was uniformly coated by the suspension where Au electrodes were deposited on the aluminum substrate. The treated-substrate was dried for 2 h at room temperature and then annealed for another 2 h at 200 °C. This annealing process will make the structure of sensing film stable. After that, in order to regulate the working temperature of the sensor, a small Ni-Cr alloy coil was inserted into the aluminum tube. A sensor fabricated with the Pt@rGO sensing material is exhibited in Fig. 1a. Moreover, the sensor was maintained at the working temperature for 2 days to enhance the long-term stability. In this study, the sensing response of the sensor to hydrogen was measured by adopting the method of stationary-state gas distribution. Fig. 1b illustrates the test principle of the gas sensing system. The measurement was performed on an electrochemical work station (CHI-660E, Shanghai Chenhua Instruments Limited). The electrical resistance of the gas sensor was determined by measuring the electric current that flowed when a potential difference of 0.6 V was applied between the Au electrodes. The target gas, hydrogen, was injected into the test chamber and mixed with air. In this study, the sensor response is defined as $\Delta R/R_a$, in which $\Delta R = R_g - R_a$, where, R_a is the resistance in air and R_g represents the resistance in air mixed with the gas to be detected. The response or recovery time is expressed as the time required for the sensor output to reach 90% of its saturation value after applying or switching off the gas in a step function.

3. Results and discussion

3.1. Structure and morphology

The structure of Pt@rGO nanocomposites was investigated by XRD (Fig. 2). The XRD pattern shows a characteristic diffraction peak at 29.22° that can be attributed to the (002) plane of rGO [31]. In addition, there is no diffraction peak at 10°, indicating a complete transformation of GO to rGO. The diffraction peaks at 39.76°, 46.27°, and 67.47° can be assigned to the (111), (200), and (220) planes of Pt, respectively, confirming the existence of crystalline Pt with a face-centered cubic structure [32]. Thus, the composites consist of crystalline Pt NPs and rGO.

The morphology and nanostructure of the as-synthesized Pt@rGO were characterized by FESEM and TEM. The SEM images in Fig. 3a and b shows that a vast number of Pt NPs are uniformly dispersed on the surfaces of rGO. As shown in Fig. 3c, the TEM images further reveal that a large number of Pt NPs with an average diameter of 4 nm are anchored on the surface of the rGO, in good agreement with the SEM results. Moreover, close inspection of the cross-sectional high-resolution TEM image (Fig. 3d) revealed that the distance between the parallel lattice planes is 0.22 nm, which is associated with the (111) crystal planes of face-centered cubic Pt [33].

Raman spectroscopy has been widely used to characterize carbon materials, especially for analyzing the structure and ratio of the sp^2/sp^3 carbon atoms. As shown in Fig. 4, Pt@rGO composites exhibit two distinct bands appearing at ~1335 and 1598 cm^{-1} that can be attributed to the in-plane A_{1g} zone-edge mode (D band) and the doubly degenerate zone center E_{2g} mode (G band) [34]. Fig. 4a and b displays the Raman spectra of GO (dark line) and Pt@rGO (red line), respectively. The G peak is the characteristic peak corresponding to sp^2 hybridized C-C bonds in