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Gas sensor based on p-phenylenediamine reduced graphene oxide

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ABSTRACT

We present a useful gas sensor based on chemically reduced graphene oxide (CRG) by drop drying method to create conductive networks between interdigitated electrode arrays. CRG, which is formed from the reduction of graphene oxide by p-phenylenediamine (PPD), can be used as an excellent sensing material. Its efficient dispersion in organic solvents (i.e., ethanol) benefits the formation of conductive circuits between electrode arrays through drop drying method. Preliminary results, which have been presented on the detection of dimethyl methylphosphonate (DMMP) using this simple and scalable fabrication method for practical devices, suggest that PPD reduced CRG exhibits much better (5.7 times with the concentration of DMMP at 30 ppm) response to DMMP than that of CRG reduced from hydrazine. Furthermore, this novel gas sensor based on CRG reduced from PPD shows excellent responsive repeatability to DMMP. Overall, the efficient dispersibility of CRG reduced from PPD in organic solvents facilitates the device fabrication through drop drying method, the resultant CRG-based sensing devices, with miniature, low cost, portable characteristics, as well as outstanding sensing performances, can ensure its potential application in gas sensing fields.

1. Introduction

With the development of sensing technology in many fields, including environment monitoring, industry and agriculture production, medical diagnosis, military and public safety, etc., chemiresistive sensors play more and more important roles, due to their low power consumption and the ease of high precision resistance measurements [1–5]. Many sensing materials, including semi-conducting metal oxide [6], organic semiconductors [7], carbon nanotubes (CNTs) [8], etc., have been used for chemiresistive sensors and exhibit great potential for gas sensing applications.

As a nanometer-thick two-dimensional analog of CNTs, graphene has emerged as another promising candidate for sensing, owing to its exceptional electronic, mechanical, chemical, and thermal properties [9–15]. Similar with CNTs, the high fraction of surface atoms in graphene makes this carbon nanosheet an ideal candidate for sensing applications. Since Novoselov et al. [16] firstly demonstrated the gas sensing potential of graphene through exposure of the devices to water, ethanol vapors, or ammonia gas, many research papers focused on this topic emerged [17–20]. It has been demonstrated that excellent sensing performance of graphene toward NO_2, NH_3, H_2O, CO, trimethylamine, I_2, ethanol, HCN, dimethyl methylphosphonate (DMMP), DNT, etc., could be achieved [17–22]. Several methods, including micromechanical exfoliation of graphite [16], chemical vapor deposition [23], and solution-based chemical reduction of graphene oxide (GO) [24], have been developed to prepare graphene nanosheets and hold great potential for gas sensing applications. Among, chemically reduced graphene oxide (CRG), which is synthesized by the chemical reduction of GO, has been aroused much attention for using as chemiresistors [25–29], due to its scalable production, solution processibility, large available surface area, etc. Chemical reduction of GO by hydrazine has been successfully achieved through elimination of oxygen-containing groups, and the resultant CRG exhibits a substantially rapid electrical response to many gases or vapors [18,25]. Ruoff group [30] has reported an all-organic vapor sensor based on CRG, which is synthesized by the reduction of GO using ascorbic acid as a mild and green reducing agent. The resultant rugged and flexible sensor using inkjet-printed films of CRG on poly(ethylene terephthalate) can reversibly detect NO_2 and Cl_2 vapors in air at ppb level. Although many reports have been reported on the sensing properties of CRG, it is still a great challenge to develop the sensing devices based on CRG with miniature, low cost and portable characteristics.

Herein, we have reported for the first time that CRG reduced from p-phenylenediamine (PPD) could be used as an excellent sensing material. Sensing devices can be easily fabricated through using drop drying method to create conductive CRG networks between interdigitated electrode arrays. The DMMP gas sensing

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performance of the resultant sensing device is much better than that of the devices based on CRG reduced from hydrazine fabricated via drop drying method. We expect the easy, green and scalable fabrication of the sensors based on CRG reduced by PPD, with excellent performance, miniature, low cost and portable characteristics, can pave a new avenue for the application of CRG in gas sensing field.

2. Experimental

2.1. Materials

The natural graphite (500 meshes) used in this study was obtained from Shandong Tianyuan Co. Ltd in China. DMMP (97%) was purchased from Sigma–Aldrich and used as received. All of other chemicals (analytical reagent grade) were purchased from Shanghai Chemical Reagents Co. Ltd. (China) and were used without further purification. All of organic solvents were purified by distillation.

2.2. Preparation of graphene oxide (GO)

Modified Hummers method was exploited here to prepare GO. The typical procedure was as follows, graphite (1 g, 500 meshes) and concentrated sulfuric acid (25 mL) were added into a 250 mL of flask, and vigorous stirring was executed. Then 1.25 g of $NaNO_3$ was added. After keeping stirring for 1 h, the mixture was cooled to 0 °C using an ice-water bath. 3.7 g of $KMnO_4$ was added in small portions during 2 h. Followed by increasing the temperature to 35 °C, the reaction was allowed to take place for another 2 h. Subsequently, the reaction was quenched by adding 0.1 L of ice water and 3.5 mL of H_2O_2 (30%). The resultant GO was filtered, and washed with plenty of aqueous HCl (3%) until no precipitation of $BaSO_4$ occurred in the presence of aqueous $BaCl_2$ solution. Further washing with water was carried out until the chloride test with $AgNO_3$ was negative, and the resultant products were dried at 40 °C for 24 h in the vacuum oven.

2.3. Preparation of chemically reduced graphene oxide (CRG)

The CRG reduced from PPD was obtained by the method reported by Chen et al. [31]. Typically, 75 mg of GO was dispersed in 75 mL of water through ultrasonication for 1 h at room temperature, and PPD (680 mg) dissolved in ethanol (75 mL) was added. The mixture was allowed to be sonicated for another 10 min, and the reaction took place by refluxing the mixture in a water bath at 90 °C for 24 h. After cooling down the temperature, the black suspensions were filtered, washed with water and acetone several times. The resultant black powder, noted as CRG, was transferred into ethanol, followed by mild ultrasonication, and consequently, stable graphene colloids in ethanol with different concentrations (1 mg/mL and 0.025 mg/mL) were formed. The CRG powder was also obtained by drying the purified CRG in the vacuum oven at 80 °C overnight.

For the purpose of the comparison, the CRG reduced by hydrazine, noted as CRG-2, was also prepared according to the Refs. [32,33]. A typical process was as follows, 90 μL of ammonium hydroxide (32%) and 7.2 μL hydrazine hydrate were added to 10 mL of the suspension of the GO (1 mg/mL). Reduction was carried out by stirring the mixture at 100 °C for 1 h. The resulting stable black suspension was diluted 40 times with water for further use.

2.4. Fabrication of sensing devices based on CRG

The standard microfabrication procedures, which have been illustrated by us before [34–37], were exploited here in order to obtain the electrodes for the sensors array. The interdigitated electrode fingers were formed by sputtering 10 nm Cr and 180 nm Au onto a patterned photoresist mold. A lift-off process was further carried out to remove the photoresist. The resultant electrodes were sonicated in ethanol, washed with deionized water thoroughly and finally dried by nitrogen flow.

In order to fabricate the sensing devices based on CRG, the typical protocols have been designed as follows: 0.1 μL of CRG ethanol suspension (0.025 mg/mL) was extracted and deposited onto the electrode gap using a microsyringe. After evaporation of the solution through putting the devices in the vacuum oven at 80 °C for 1 h, networks of CRG bridged each electrode gap could be formed. The sensing devices based on CRG-2 could be also fabricated according to the method mentioned above.

2.5. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker (Germany) VERTEX 70 spectrometer (KBr pellets) over a range from 400 to 4000 cm^{-1} with DTGS or MCT as detector. Raman scattering was performed on a Renishaw inVia Reflex Raman spectrometer using a 514-nm laser source. The thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere using a heating rate of 10 °C/min started from 50 °C up to 600 °C. To avoid the thermal expansion of the GO due to rapid heating, GO samples were also heated from 50 °C to 600 °C at 1 °C/min. The morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra 55). Transmission electron microscopy (TEM) was obtained on JEM-2100 (Japan), and the accelerating voltage was 200 kV.

A homemade gas handling system, which can generate and deliver DMMP vapor as illustrated in our previous reports [34–37], is used to evaluate the sensing properties of the sensors. Dry air, as both of the carrier and of the diluting gas, was used to bubble DMMP liquid through a porous glass-disc bubbler, in order to obtain DMMP vapor. The concentration of DMMP vapor can be easily controlled by dilution with dry air using mass flow controllers. The humidity inside the test chamber was monitored by a Honeywell HIH-4000 humidity sensor (Honeywell Inc.) and is less than 20%. All gas sensing tests were carried out at room temperature (25 °C). The flow rate of the balance gas (dry air) was controlled to be at 1 L min^{-1}. The resistance variation during testing was monitored using a precision semiconductor parameter analyzer (Agilent 4156C). The sensor response was evaluated by the resistance change at a sampling voltage of 50 mV.

3. Results and discussion

3.1. Synthesis and characterization of CRG

Modified Hummers method was executed to oxidize graphite, and consequently, a stable yellow-brown aqueous solution of GO (as shown in Fig. 1(a)) was formed. During the reduction process of GO, PPD was used as a green reducing agent as well as an excellent stabilizer, the resultant CRG (without drying) can be efficiently dispersed in ethanol. As shown in Fig. 1(b), the homogenous colloid suspension of CRG in ethanol with the concentration at 1 mg/mL can be formed. After diluting with ethanol, the colloid with a brown color was formed (as shown in Fig. 1(c)), no precipitates can be observed, even after several weeks. This is fascinating, since the process is very easy and green, which can also benefit further fabrication of sensing devices through solution operations.

The FT-IR spectroscopy was utilized to confirm the process for the preparation of CRG. Fig. 2(a) illustrates the typical spectra of the natural graphite. As shown in Fig. 2(a), a broad peak located