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Highly sensitive and selective room-temperature nitrogen dioxide sensors based on porous graphene



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Keywords: Porous graphene Gas sensor Nitrogen dioxide High-Performance	Development of high-performance nitrogen dioxide sensors is extremely important not only for industrial applications but also for environmental monitoring and health protection. For practical applications, gas sensors with high sensitivity for low concentrations of nitrogen dioxide are desired. Here, a simple process to fabricate high-performance gas sensors based on porous reduced graphene oxide (PRGO) through a simple drop-casting technique is presented. The PRGO used as active sensing material is prepared through a scalable solution etching approach. This sensor exhibited a high sensitivity in the sub-0.5 ppm range with good selectivity and reversibility, as well as a low experimental detection limit of 20 ppb, which is much lower than the threshold exposure limit proposed by the National Ambient Air Quality Standard (53 ppb). Furthermore, it can be performed at room temperature without UV/IR light illumination or thermal assistance. This superior performance could be attributed to the high adsorption site density due to the edge sites of porous graphene. The relationship between the sensing performance and the microstructure or chemical composition of porous graphene were systematically investigated. This work paves the way for a facile tailoring of the sensor behavior as a function of graphene micromorphology.

1. Introduction

Detection of toxic gas is extremely important for monitoring of environmental pollution and air quality [1-10]. Nitrogen dioxide is a common hazardous gas in the environment mainly caused by fossil fuel combustion. It acts as a source of acid rain and contributes to the formation of ozone. Meanwhile, it is also particularly dangerous to human respiratory system at a concentration greater than 1 ppm [11,12]. National Ambient Air Quality Standard (NAAQS) sets a limit exposure of 53 ppb (annual average) for NO₂ [13]. Thus, it is extremely necessary to detect trace amounts of NO₂ and to precisely monitor its concentration in-situ before developing solutions to prevent the public from being harmed by this airborne contaminant. For pursuing high performance NO2 sensors with both high sensitivity and low detection limit, various sensing materials have been employed including semiconducting metal oxides [14-17], conducting polymers [18,19] and carbon nanomaterials [20-25]. Among these, graphene, a carbon allotrope of two-dimensional material class, has attracted most attention due to its excellent electronic conductivity, large surface area, versatile surface chemistry and capability of detection at room temperature [26-34].

The two-dimensional nature of graphene gives rise to extreme sensitivity to its surroundings, thus promising high performance for gas detection [35-37].

However, there are still several challenges to be addressed before achieving a NO₂ sensor with practical importance. For example, previously reported graphene-based NO2 sensors usually exhibit excellent sensitivities at high gas concentrations, whereas they can seldom detect this gas at concentrations lower than 0.5 ppm without additional assistance [1,2,38,39]. In fact, the reversibility of most graphene-based sensors is unsatisfactory [39]. After exposure to NO₂, the sensing signal can hardly return to its pristine value in pure N₂ or air atmosphere without the treatment of IR/UV irradiation or high operation temperature. In order to enhance the sensing performance of graphenebased NO2 sensors, defects have been induced to serve as adsorption sites [40]. Chemically reduced graphene oxide (RGO) has been considered as a promising sensing materials for low-cost preparation, largescale manufacturing and abundant oxygen-containing defects introduced during the oxidation-reduction process [41,42]. However, the sensitivity of RGO-based NO2 sensors still cannot fully satisfy the environment monitoring demands (with limit of detection lower than

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53 ppb at room temperature and ambient pressure). Extra defects, e.g. edge defects, have been further introduced into graphene by electron beam lithography [43], block-copolymer lithography [44], nanosphere lithography [45] and self-organized growth of porous graphene [46]. Independent of the technique, the resultant graphene nanostructures yield highly active graphene edges, with a number of possible chemical terminations, which is beneficial for gas adsorption. In fact, it has been shown that gas sensing sensitivity can be enhanced considerably for porous graphene [47]. For example, Bøggild and coworkers reported the fabrication of nanoporous graphene through patterning by spherical block copolymer, and the obtained porous graphene showed 6 times higher response to NO₂ compared with that of its non-patterned counterpart [44]. Mulchandani et al. reported a method of nanosphere lithography combined with reactive ion etching for patterning graphene (prepared by ethanol-CVD), and the resulting sensor showed a higher response and faster sensing speed compared with the nonetching one [45]. Huang and coworkers demonstrated a hydrothermal steaming of a single GO sheet on Si wafer, and displayed significant enhanced response towards NO2 [47]. However, the aforementioned etching methods all suffer from low productivity, where only one or just a few porous graphene sheets can be acquired, critically limiting their practical applications. Moreover, most of them employed complicated lithography process, which is costly and time-consuming.

Here, we develop high-performance chemiresistor NO_2 sensors based on PRGO with various edge defects and oxygen-containing functional groups. The PRGO was prepared by a low-cost and largescale capable solution-etching approach. Compared with the aforementioned lithography technique, this method is far more facile and cost-effective. The resulting NO_2 sensor showed a high sensitivity in the sub-500 ppb range and a low experimental limit of detection (LOD) of 20 ppb at room temperature. Furthermore, it has a good repeatability and excellent cross-selectivity. The relationship between the sensing performance and the microstructure or chemical composition of porous graphene were systematically investigated. This work paves the way for a facile tailoring of the sensor behavior as a function of graphene micromorphology.

2. Experiment

2.1. Preparation of PRGO

Graphene oxide (GO) was prepared by a modified Hummers' method from graphite and the details were reported in the literature [48,49]. Porous graphene oxide (PGO) was synthesized using the method developed by Xu and co-workers [48]. Briefly, 50 mL 2 mg mL^{-1} GO aqueous dispersion was mixed with 5 mL 30% H₂O₂ aqueous solution and then heated at 100 °C for different times (1-8 h) under stirring. The solution underwent a color change from light brown to dark brown. The as-prepared PGO was purified by dialysis to remove the residual H₂O₂ (denoted as PGO-1, PGO-2, PGO-4, PGO-8 based on etching time). The obtained PGO solution was then diluted to 0.25 mg mL⁻¹. Successively, 190 µL of ammonium hydroxide (30%) and different amount of hydrazine (2.8 $\mu L,$ 5.6 $\mu L,$ 8.4 $\mu L,$ 11.2 $\mu L,$ 14 $\mu L)$ were added to 50 mL PGO dispersion. Mild sonication was applied for uniform dispersion. Then the mixture was heated at 92 °C for 1 h under stirring for reduction. The solution underwent a color change from dark brown to black. Finally, a small amount of aggregation was removed by filtration to yield a stable PRGO suspension, denoted as PRGO-20%, PRGO-40%, PRGO-60%, PRGO-80%, PRGO-100% based on degree of reduction.

2.2. Fabrication of sensors

Sensors were fabricated through a drop-casting method on interdigitated electrodes (IEs). The IEs adopted here were prepared by photolithography and lift-off method via successive evaporation deposition of 5 nm-thick Cr and 50 nm-thick Au on SiO₂/Si wafers. The width of the Au finger and the gap between adjacent fingers were both 50 μ m. Before use, IEs were cleaned in acetone and water under sonication alternatively, followed by a UV-ozone treatment for 5 min. 5 μ L of PRGO suspension (0.006 mg mL⁻¹) was drop-casted on the IE. Then, the IE was dried in air for 2 h forming a thin PRGO membrane on its surface. Finally, the IE was connected to silver wire by silver paste for sensing tests.

2.3. Sensing tests

All of the sensing tests were performed using an electrochemical analyzer (CHI 760D potentiostat-galvanostat, CHInstruments Inc.). A two-electrode configuration was employed for all of the measurements. The sensitivity of the sensor was monitored by applying a constant bias of 1 V on the sensor and recording the conductance change. A mass-flow controller was used to control the flow rate and concentration of N₂ or NO₂/N₂ mixture. In a flow-through gas exposure system, all sensors were initially exposed to 1000 sccm N₂ (99.9%) flow. After a constant current was observed, the sensor was exposed alternately to NO₂ or N₂. For each type of sensor at least 3 devices were tested and average values were reported. The standard deviations of the responses were measured to be less than 10%, indicating good repeatability of the devices.

2.4. Characterizations

High-resolution transmission electron microscope (HRTEM) image was taken by Tecnai G2 F20 HRTEM. Raman spectra were recorded using a spectrometer (inVia Reflex, Renishaw, UK) with a laser excitation wavelength of 532 nm in the range of 800-3000 cm⁻¹. X-ray photoelectron spectra (XPS) were taken by ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific, USA). The BET surface area of samples was recorded on a Micromeritics ASAP2020 M + C instrument based on the nitrogen adsorption/desorption isotherm at 77 K. The sheet conductivities of RGO or PRGO were carried out on a Jandel fourpoint conductivity probe by using a linear array four-point head.

3. Results and discussion

The preparation of PRGO and subsequent fabrication of the PRGObased sensing device is illustrated in Fig. 1. GO sheets were etched by mild oxidation to produce porous microstructures which were subsequently reduced through a wet chemical approach to obtain the final PRGO with in-plane nanopores. The simplicity of the solution etching reaction makes the process readily scalable for large-scale production of PRGO. HPRGO sensing layers were deposited onto the surface of gold interdigitated electrodes by a facile drop-casting method. TEM studies and BJH pore size distribution revealed abundant in-plane pores with sizes of a few nanometers across the whole basal plane of PGO (Fig. 2a and b), suggesting an efficient etching of carbon atoms by H₂O₂. And the specific surface area of PRGO was more than 3 times that of RGO, due to the formation of nanopores. The edge of nanopores are terminated by oxygen-containing groups, since the etching of GO was conducted by oxidizing agent. Therefore, we named them edge defects. The PGO shows significant deoxygenation (Fig. 2c), indicating that the PGO has fewer oxygen functionalities than the GO, which is ascribed to the etching of the highly oxygenated defect regions. However, the decrease of I_D/I_G in Raman spectra demonstrated that, although the oxygen functionalities were removed, the newly generated edge microstructures make PGO more defective (Fig. 2d). After the reduction process, further deoxygenation and restoration of sp² conjugation structure occur, leading to an increase of I_D/I_G (Fig. 2c and d).

Current versus voltage (I–V) curves of the PRGO coated IE exhibit linear relationships indicating ohmic contact between the sensing material and IE, reflecting that the electrical contact plays a negligible role Download English Version:

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