Highly responsive chemical sensing on NO_2 at room temperature based on reduced porous graphene

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ABSTRACT

We report on a high-performance room-temperature NO_2 sensor based on porous and multi-defective reduced porous graphene (rPG). The rPG sebsor exhibits much higher responsivity than that of sensor made from reduced graphene oxide (rGO) without artificial nanopores, especially under lower NO_2 concentration. The limit of detection of rPG sensor is as much as 28% towards 500 ppb NO_2. The remarkable surface reactivity stemmed from abundant defective sites, especially edge-defective sites of nanopores, is highly responsible for the excellent responsivity and sensitivity of rPG sensor. Moreover, the unique porous structure of rPG also contributes to the outstanding gas-sensing performance by providing open gas diffusion path, and thus significantly improving the utilization of surface active sites.

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1. Introduction

Room-temperature (RT) gas sensors are attracting dramatically increasing interests due to energy efficiency and security requirements of consumer gas sensors [1]. Graphene, graphene oxide (GO) and reduced graphene oxide (rGO) are promising materials for room-temperature (RT) gas sensing [2]. Their unique atom-thick two-dimensional structure and excellent physical properties, such as large specific surface area, low electrical noise and high electron mobility at RT, make them meet the basic demand of adequate RT conductivity and high surface reactivity for room-temperature gas detection [3]. Recently, a new category of graphene materials – porous graphene (PG) [4] stands out as a better candidate for RT chemical gas sensors [5–7]. PG is a porous graphene network with plentiful in-plane nanopores on the conjugated carbon surface, possessing fascinating integrated features of high specific surface area, abundant porous channel, and numerous active defective sites including edge defects and oxygen functional groups. Considerable theoretical [8–10] and experimental [11–14] studies have revealed that defective sites are helpful to improve gas-sensing performance. On the one hand, binding energies could be highly improved due to the formation of hydrogen bond OH⋯O (N) between oxygen functional groups and NO_2, as well as weak covalent bond C⋯O (N) benefited from the wrinkle and warping of graphene gauze [8,10]. The calculation by Tang et al. demonstrated that the binding energy could be increased

from only 0.19 eV between NO_2 and pristine graphene to 0.37–1.14 eV for defective sites [8]. Therefore, a larger number of NO_2 molecules would be adsorbed on the surface of defective graphene. On the other hand, charge transfer was also increased through the stronger hydrogen bond [8,10]. The sensing mechanism of graphene-based NO_2 sensor is molecular doping, *i.e.*, NO_2 molecules act as electron acceptors to withdraw electrons from graphene-based materials [15]. Therefore, charge transfer plays an important role in determining sensitivity and responsivity of sensors.

In this work, rPG was prepared though modest reduction of the PG prepared via a ferrioxalate-mediated photo-Fenton method in our previous work [16]. Then, the resultant rPG was characterized and room-temperature NO_2-sensing performance was tested in comparison with that of common rGO without artificial nanopores.

2. Experimental

The detailed materials preparation, characterization and gas sensing testing are available in ESI. Responsivity and sensitivity are the important evaluation parameters for gas-sensing performance. The detailed definitions of responsivity and sensitivity are also presented in ESI.

3. Results and discussion

The TEM images (Fig. 1a and b) showed that the surface of rPG sheets was rough and a great number of nanopores were broadly
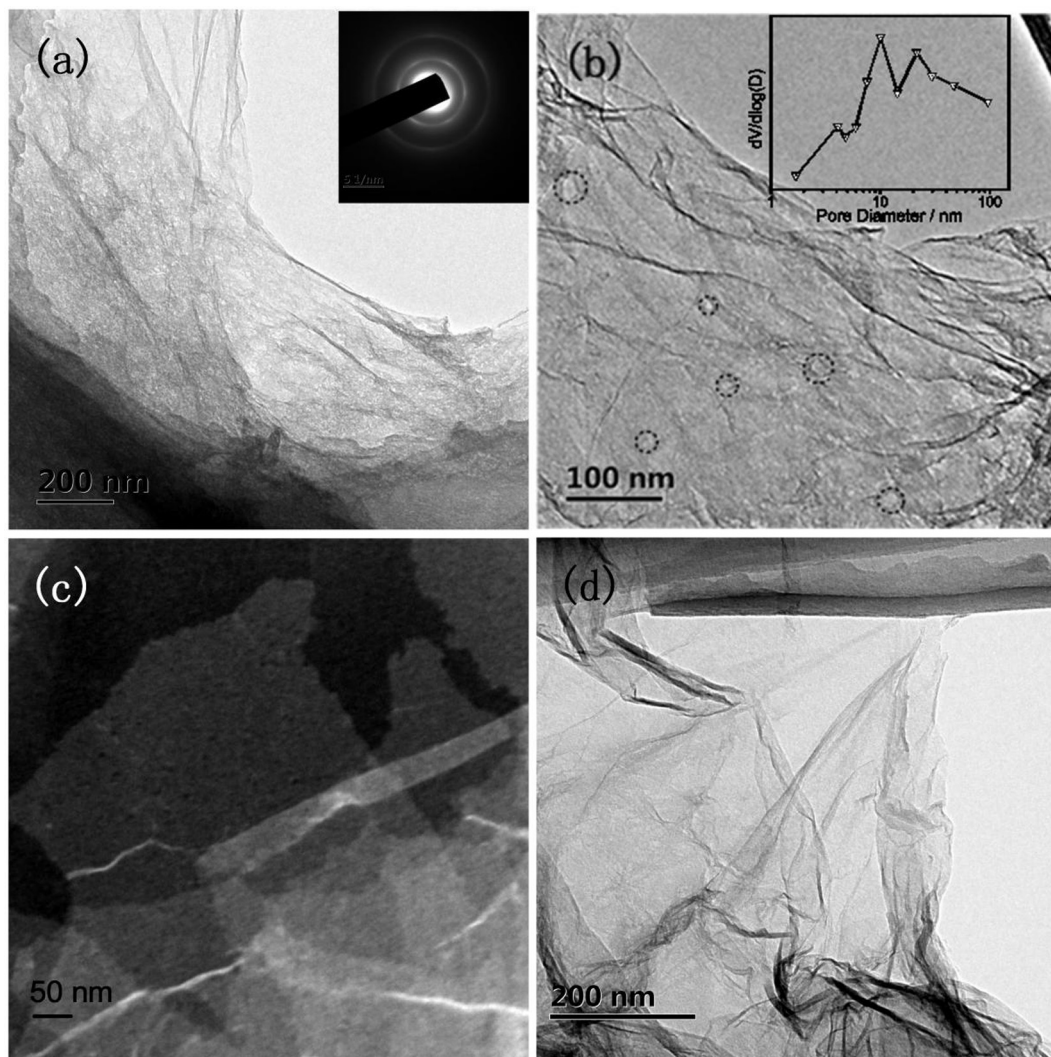
Fig. 1. TEM images of rPG sheets (a and b), the larger nanopores in (b) are marked with broken black line. Inset in (a) is SAED pattern. Inset in (b) is the pore size distribution detected by N$_2$ adsorption measurement. Dark field STEM images of rPG sheets (c). TEM image of rGO sheet without nanopore (d).

distributed in the rPG sheets. The pore diameters ranging from approximately 4 to 20 nm were detected by N$_2$ adsorption measurement (inset in Fig. 1b). The corresponding selected area electron diffraction (SAED) pattern (inset in Fig. 1a) showed legible hexagonal patterns, indicating rPG has been reduced moderately. In order to observe the nanopores more clearly, a high angle annular dark field (HAADF) scanning TEM (STEM) image was displayed in Fig. 1c. As a contrast, the smooth and clean surface of rGO sheets was presented in Fig. 1d.

Both Raman spectra (Fig. 2a) of rPG and rGO had the characteristic peaks of carbonaceous materials, that is, D band at 1350 cm^{-1} for local defects and disorders, and G band at 1580 cm^{-1} for sp^2-hybridized carbon atoms. The intensity ratio I$_D$/I$_G$ increased from 0.987 for rGO to 1.018 for rPG, indicating more defects and disorders on rPG. This result was confirmed by the C (1s) XPS results (Fig. 2b and c). The deconvoluted C (1s) peaks of rPG and rGO were composed of six sub-peaks, including sp^2 C=C (284.6 eV), C—H (285.1 eV), sp^3 C—C (285.6 eV), C—OH/C—O—C (286.6 eV), C=O (287.3 eV) and O=C—O (288.8 eV). Of which, both C—H and sp^3 C—C were assigned to "defect peak" [17], whose intensities depended on the destruction level of crystalline order. For convenience, the relative amount of each bond to the C (1s) spectra was calculated and presented in Fig. 2d. Apparently, the defect content of rPG was much more than that of rGO, while rGO has more oxygen functional groups than rPG.

Fig. 3a showed the gas-sensing performances of rPG and rGO sensors under different NO$_2$ concentration. It can be clearly observed that the output signal conductivity increased upon the injection of NO$_2$ and decreased after NO$_2$ was released, indicating the same p-type nature of rPG and rGO. The response of rPG sensor was significantly increased compared to that of rGO sensor, especially at lower concentration. For 1 and 20 ppm NO$_2$, the responsivity of rPG sensor respectively was 10.6 and 2 times that of rGO sensor. When concentration as low as 0.5 ppm, rGO sensor had no response, while rPG sensor still had a 11.7% conductance increment. We summarized some room-temperature NO$_2$ gas sensors reported in the literatures [5,11,18,19], and compared their performances with our rPG gas sensor (Table 1 in ESI). The rPG sensor we reported here exhibited attractive responsivity and competitive sensitivity.

It has been known that both defects and oxygen functional groups were effective adsorption sites for NO$_2$ molecules. Therefore, in the case of higher content of oxygen functional groups in rGO, the abundant edge defects of rPG made great contribution to its higher responsivity and sensitivity. Besides, the unique porous structure of rPG was beneficial for gas molecules access and