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Dipole-modified graphene with ultrahigh gas sensibility

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ABSTRACT

This study reports the supramolecular assembly of functional graphene-based materials with ultrahigh gas sensing performances which are induced by charge transfer enhancement. Two typical Donor-π-Accepter (D-π-A) structure molecules 4-aminoquinoline (4AQ, μ = 3.17 Debye) and 4-hydroxyquinoline (4HQ, μ = 1.98 Debye), with different charge transfer enhancing effects, were selected to modify reduce oxide graphene (rGO) via supramolecular assembly. Notably, compared to the 4HQ-rGO, the 4AQ-rGO exhibits more significant increase of gas response (R_a/R_g = 3.79) toward 10 ppm NO_2, which is ascribed to the larger dipole moment (μ) of 4AQ and hence the more intensive enhancing effect of charge transfer on the interface of rGO. Meanwhile, 4AQ-rGO sensors also reveal superior comprehensive gas sensing performances, including excellent gas sensing selectivity, linearity, repeatability and stability. It is believed that the present work demonstrates an effective supramolecular approach of modifying rGO with strong dipoles to significantly improve gas sensing properties of graphene-based materials.

1. Introduction

The two-dimensional honeycomb crystal lattice of graphene provides various possibilities for assembling with functional conjugated molecules [1–8]. Thus, the graphene-based materials are considered as one of the most promising functional hybrid materials with wide application in many high-technological realms, such as electronics, sensors, photovoltaics, and catalysts [9–17]. In 2007, Novoselov's group reported a high-performance graphene-based sensor for detecting individual gas molecule [5], proving that the ultrahigh sensitivity is actually attributed to the charge transfer between the graphene and target gas molecule. Inspired by this mechanism, great efforts have been devoted to enhance the charge transfer capability of graphene-based gas sensing materials by decorating method [1,18,19], covalent bonding [20–23] or non-covalent bonding modification [24–26]. At this point, selecting the appropriate approach to modify graphene without turning on new issues is always expected and balanced during preparation process. For example, a composite with high charge transfer capability could be obtained when the graphene was modified with metal oxide WO_3 nanoparticles; however, the high operating temperature for metal oxide-modified graphene limited its practical application [27]. Therefore, modifying graphene with organic molecules could be another option. As expected, covalent-modifying graphene with organic functional molecules has been reported as an effective approach to enhance charge transfer [21], although the severe reactions required during the material preparation would damage the intrinsic electrical properties of graphene. Therefore, herein based on our previous works, supramolecular modifying graphene with functional organic molecules has been adopted to prepare graphene-based gas sensing materials with high charge transfer capability, avoiding any loss of intrinsic electrical properties of graphene [28,29]. Thus, functional organic molecules which could enhance charge transfer between the graphene and target gas molecule, will facilely be assembled on the graphene. What molecule does better job, in this case, will be the only question since supramolecular assembly works for various "guests". With respect to charge transfer, it is well known that a dipole generated with presence of intermolecular charge transfer in a Donor-π-Acceptor (D-π-A) molecule will facilitate the electron migration from donor to the acceptor [30,31]. Thus, dipolar molecules could be promising candidates to enhance the charge transfer capability of materials.

In this paper, we present a supramolecular approach of modifying reduce graphene oxide (rGO) with two dipolar molecules

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of 4-aminoquinoline (4AQ, μ = 3.17 Debye) and 4-hydroxyquinoline (4HQ, μ = 1.98 Debye) to enhance the charge transfer capability of material for achieving superior comprehensive gas sensibility. Comparing with 4HQ-rGO sensor which possesses relatively smaller dipole 4HQ, the as-prepared 4AQ-rGO sensor exhibits much higher gas response (R_a/R_g = 3.79 toward 10 ppm NO_2), excellent selectivity and repeatability. The density functional theory (DFT) calculation indicates that the final gas sensitivity of the composite is directly related to the dipole moment of the stacked molecules on the graphene which essentially enhance charge transfer between the graphene and target gas molecule.

2. Experimental

2.1. Materials

Graphene Oxide (GO) was purchased from XianFeng NANO Co., Ltd. 4-Aminoquinoine (4AQ, 98%), 4-Hydroxyquinoline (4HQ, 98%) and hydrazine hydrate were obtained from Alfa Aesar. All the chemicals used in the work were of analytical grade and not further purified.

2.2. Synthesis of 4AQ-rGO and 4HQ-rGO materials

Firstly, the GO was dissolved in deionized (DI) water by vigorous ultrasonication to form a homogeneous brown aqueous solution (1 mg mL^{-1}). Next, 4 mL of GO aqueous solution and 92 mg of 4AQ (or 4HQ) were added in 10 mL of DI water. Then, 5 mL NaOH solution (4 mg mL^{-1}) and 10 mL hydrazine hydrate (1.12 μL mL^{-1}) were added to the solution for reduction of GO. The mixture was kept at 80 °C for 1 h under stirring. Finally, the mixture was purified by washing several times with DI water and was re-dispersed in 20 mL DI water to obtain the stable 4AQ-rGO (or 4HQ-rGO) solution.

2.3. Material characterizations

The surface morphologies of prepared materials were examined by Scanning Electron Microscopy (SEM; HITACHI S-4800). The surface properties were investigated through X-ray Photoelectron Spectroscopy (XPS; ESCALAB250). The structural properties of samples were characterized by Raman Scanning spectroscopy (LabRAM HR8000). The chemical structures and functional groups of the samples were examined by Fourier Transform Infrared Spectroscopy (FT-IR; Nicolet iN10MX). The components of the 4AQ-rGO and 4HQ-rGO were examined by UV–vis Spectrum (UV-1750).

2.4. Gas sensing measurement

The gas sensing measurements were carried out by a CGS-1TP intelligent gas sensing analysis system. The detail of gas sensor preparation and measurement were described in the literatures [32,33]. The sensor response is defined as R_a/R_g, where R_a and R_g are the resistance of the seneor in the air and the tested gas atmosphere, respectively. The I-V characteristic curve was tested on a SA6101 electrical analysis system (Sinoagg Co., Ltd, China) and the voltage applied on samples varied from DC −6 to 6 V with a step of 0.1 V.

2.5. Computational details

The density functional theory (DFT) calculations were carried out based on B3LYP and performed by the DMol3 code. The atomic orbital was specified by double numerical plus polarization (DNP).

3. Results and discussion

3.1. Preparation of 4AQ-rGO sensor

In this work, dipolar molecules were selected to modify the graphene via supramolecular assembly. It has been reported that a dipole will be generated due to the presence of intermolecular charge transfer in a D-π-A molecule [34–37]. Hence, it is hypothesized that the charge transfer capability of the composite could be regulated by modifying rGO with different dipolar molecules. Herein, 4AQ and 4HQ those have similar D-π-A structure (Fig. S1, Supporting Information) but different dipole, have been selected to modify rGO via π-π stacking interaction to obtain 4AQ-rGO and 4HQ-rGO. 4AQ and 4HQ are two typical dipolar molecules with a π conjugated structure by which they will be able to be assembled on graphene surface through strong π–π stacking interaction. After the reduction process in hydrazine hydrate, the excellent black dispersion of 4AQ-rGO and 4HQ-rGO are obtained. The preparing process of 4AQ-rGO via supramolecular assembly for NO_2 gas sensing is described in a schematic, as shown in Fig. 1.

3.2. Characterizations of graphene-based materials

The morphologies of the prepared materials rGO, 4AQ-rGO and 4HQ-rGO sheets deposited on the interdigitated electrode (IE) were investigated and shown in Fig. 2. Fig. 2a shows that the surface of rGO layers are wrinkled because the rGO sheet is easily aggregated and stacked. The stacked structure is causing loss of efficient interlaminar surface area of the material, weakening the gas response. On the contrary, the 4AQ-rGO (Fig. 2b) and 4HQ-rGO (Fig. 2c) nanosheets are uniformly coated on the IEs and the planar sheets are quite thin. There is no severe aggregation happened to the graphene-based material after supramolecularly assembled with dipolar molecules.

As shown in the Raman-scattering spectroscopy (Fig. 3a), the four materials exhibit two obvious Raman peaks at 1334 cm^{-1} and 1594 cm^{-1}, which are assigned to the D- and G-band, indicating the formation of rGO-based materials. The I_D/I_G value represents the defect content and edge area of grapheme [38,39]. It is obvious that the I_D/I_G value of rGO (1.35), 4AQ-rGO (1.33) and 4HQ-rGO (1.34) are higher than that of GO (1.15), revealing the formation of new sp^2 clusters after reduction, which indirectly confirms the successful chemical reduction by hydrazine hydrate. It is also concluded from their I_D/I_G values that the reduction degrees of the three prepared materials are identical.

The graphene-based materials were characterized by Fourier transform infrared (FT-IR) spectroscopy, as shown in Fig. 3b. Two characterized peaks attributed to the hydroxyl (—OH) and carboxyl (C=O) groups of GO are evidently observed at 3407 cm^{-1} and 1722 cm^{-1} respectively. Meanwhile, the characteristic peaks in the pristine GO are significantly reduced in the rGO, 4AQ-rGO and 4HQ-rGO spectra, indicating the successful reduction of GO to rGO. In the FT-IR spectrum of 4AQ-rGO, two peaks appear at 3067 cm^{-1} and 2919 cm^{-1}, which are assigned to the stretching frequencies of the amino group (—NH$_2$). Moreover, the characteristic peaks of the in-plane bending δ(—NH$_2$), ν(C=N) and ν(C—NH$_2$) are recorded at 1634 cm^{-1}, 1512 cm^{-1} and 1480 cm^{-1}, respectively. Meanwhile, the FT-IR spectrum of 4HQ-rGO exhibits a wide characteristic peak at 2919 cm^{-1}, which is attributed to the —OH stretching vibration. Three peaks at 1595 cm^{-1}, 1473 cm^{-1}, 1061 cm^{-1} are attributed to the ν(C=C), ν(C$_5$H$_5$N) and ν(C—OH), respectively. Further, the as-prepared rGO, 4AQ-rGO and 4HQ-rGO materials were characterized by X-ray photoelectron spectroscopy (XPS) (Fig. 3c). The appearance of characteristic peaks of N1s at 400 eV in the XPS