Reduced graphene oxide–polyaniline hybrid: Preparation, characterization and its applications for ammonia gas sensing†

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Here we present a useful ammonia (NH3) gas sensor based on reduced graphene oxide (RGO)–polyaniline (PANI) hybrids. PANI nanoparticles were successfully anchored on the surface of RGO sheets by using RGO–MnO2 hybrids as both of the templates and oxidants for aniline monomer during the process of polymerization. The resultant RGO–PANI hybrids were characterized by transmittance electron microscopy, infrared spectroscopy, Raman spectroscopy, UV-Vis spectroscopy, and scanning electron microscopy. The NH3 gas sensing performance of the hybrids was also investigated and compared with those of the sensors based on bare PANI nanofibers and bare RGO sheets. It was revealed that the synergetic behavior between both of the candidates allowed excellent sensitivity and selectivity to NH3 gas. The RGO–PANI hybrid device exhibited much better (3.4 and 10.4 times, respectively, with the concentration of NH3 gas at 50 ppm) response to NH3 gas than those of the bare PANI nanofiber sensor and bare graphene device. The combination of the RGO sheets and PANI nanoparticles facilitated the enhancement of the sensing properties of the final hybrids, and pave a new avenue for the application of RGO–PANI hybrids in the gas sensing field.

1. Introduction

Graphene, as a two-dimensional honeycomb carbon sheet, has aroused much interest1–6 due to its unique properties, including high Young’s modulus7 and specific surface area,8 excellent thermal conductivity,9 as well as interesting quantum Hall effect,10 etc. Many potential applications, such as chemical sensors,11 field-effect transistors (FETs),12 and transparent conductive electrodes,13 etc., have been reported based on the nanostructures of this novel carbon material. Graphene has been considered as an excellent candidate for gas sensing applications mainly due to the following merits:14 (i) its two-dimensional honeycomb structure, which means that all its carbon atoms are exposed to the environment, and can easily provide a high surface area, leading to high sensitivity to the various gas molecules; (ii) its inherently low electric noise due to the high quality of its crystal lattice as well as its two-dimensional nature, which tends to screen charge fluctuations of more than one-dimensional systems such as carbon nanotubes.

Based on the above advantages, the graphene sheets obtained by different preparation methods, including mechanical exfoliation of graphite,11 chemical vapor deposition method,15 chemical and thermal reduction of graphene oxide,16–19 etc., have been widely studied and exhibit excellent sensing properties. In order to improve the sensing performance of these graphene-based sensors, many sensing materials, such as conducting polymers,20 metals,21–23 and metal oxides,24 have been anchored on the surface of graphene sheets, and play important roles in the improvement of the sensitivity and selectivity of the resultant gas sensors.

Polyaniline (PANI), as an excellent sensing material, has been extensively studied based on its high sensitivities, excellent reliability, and low cost properties.25,26 Hybridization of PANI with carbon nanotubes (CNTs) has been widely studied and demonstrates attractive sensing properties.27–29 It is revealed that PANI plays important roles in enhancement of the sensing performance of CNTs-based devices. However, few reports have been focused on the graphene–PANI hybrids, especially for ammonia (NH3) gas sensing applications. It is expected that the decoration of PANI on the surface of graphene can greatly improve the sensitivity and selectivity of the sensor, through combination of both excellent sensing materials.

Therefore, we demonstrate, for the first time here, a useful NH3 gas sensor based on graphene–polyaniline (PANI) hybrids. PANI nanoparticles have been successfully anchored on the surface of reduced graphene oxide (RGO) sheets by using...
RGO–MnO$_2$ hybrids as both of the templates and oxidants for aniline monomer during the process of polymerization. The resultant RGO–PANI hybrids have been studied as excellent sensing materials for the detection of NH$_3$ gas.

2. Experimental

2.1. Materials

Aniline was obtained from Shanghai Chemical Reagents Co. Ltd (China) and purified by distillation. Concentrated ammonia solution (25 wt%) and all other chemicals (analytical reagent grade) were purchased from Shanghai Chemical Reagents Co. Ltd (China) and were used without further purification. All organic solvents were purified by distillation.

2.2. Preparation of reduced graphene oxide (RGO)–MnO$_2$ hybrids

GO used here was prepared by the modified Hummers method, which has been mentioned in our previous reports. The GO–MnO$_2$ hybrids were prepared by a similar method to that demonstrated by Zeng et al. Typically, 0.4 g of GO was dispersed in distilled water by sonication (45 KHz) for 1 h in order to form the suspension with the concentration at 1 mg mL$^{-1}$, and then 0.7859 g of MnCl$_2$·4H$_2$O was added. After vigorous stirring for 5 h, KMnO$_4$ aqueous solution (0.6285 g of KMnO$_4$ dissolved in 10 mL of distilled water) was added into the solution for 15 min. The mixture was stirred for another 12 h. The resultant suspension was filtered through G5 sintered glass, and washed with water until the filtrate became colorless. After washing with ethanol several more times, the resultant GO–MnO$_2$ hybrid powder was dried at 60 °C overnight in the vacuum oven.

In order to obtain thermally reduced graphene oxide (RGO)–MnO$_2$ hybrids, 50 mg of GO–MnO$_2$ hybrid powder was heated in the oven at 350 °C for 3 h.

2.3. Preparation of RGO–PANI hybrids

The resultant RGO–MnO$_2$ powder was dispersed in 50 mL of distilled water by sonication for 1 h, and a RGO–MnO$_2$ suspension (noted as A) with the concentration of 1 mg mL$^{-1}$ was formed. To another beaker, 100 µL of aniline and 5 mL of concentrated sulfuric acid were added. The mixture was diluted by adding 45 mL of water and sonicated for several minutes in order to form a transparent solution (noted as B). Both solution A and B were cooled below 15 °C, and then solution B was poured into suspension A with vigorous stirring. The mixture was allowed to be stirred for another 12 h in order to make sure the reaction took place completely. The resultant black powder was filtered through G5 sintered glass, and washed with sulfuric acid solution (with the concentration of 3 wt%) to remove Mn$^{2+}$ and free monomers, followed by washing with distilled water twice to remove the free acid. Finally, the RGO–PANI hybrid powder was dried at 80 °C overnight in the vacuum oven.

2.4. Fabrication of sensing devices based on RGO–PANI hybrids

The electrodes for the sensors array were fabricated by the standard microfabrication procedures, which have been illustrated by us before. In order to fabricate the sensing devices based on RGO–PANI, the typical protocols were designed as follows: 0.1 µL of RGO–PANI ethanol suspension (0.25 mg mL$^{-1}$) 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 RGO–PANI bridging each electrode gap could be formed. For the purpose of comparison, the sensing devices based on bare graphene were also fabricated according to our previous work.

As far as the sensing device based on PANI nanofibers is concerned, the sensing materials were synthesized according to the methodology demonstrated by Hyder et al. The acid-doped PANI nanofibers were dispersed in distilled water in order to form an aqueous suspension with the concentration of ~0.1 mg mL$^{-1}$. 0.1 µL of PANI nanofibers aqueous suspension was extracted and deposited onto the electrode gap. After evaporation of the solution through putting the devices in the vacuum oven at 80 °C for 1 h, networks of PANI nanofiber bridging each electrode gap could be formed.

2.5. Characterization

Transmission electron microscopy (TEM) was obtained on JEM-2100 (Japan), and the accelerating voltage was 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker 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. All the UV-Vis absorption spectra were conducted on a Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer. The morphologies of the samples were observed by field emission scanning electron microscope (FE-SEM, Carl Zeiss Ultra 55). Qualitative analysis of particle composition was carried out using energy dispersive X-ray analysis (EDX) equipped with FE-SEM. The surface area studies were performed on a Micromeritics Tristar 3020 automated gas adsorption system.

Gas sensing measurements were carried out on a homemade gas handling system, which was illustrated in our previous work. A homemade Teflon gas flow chamber was used to control the gas–vapor environment for the devices during the test. Dry air was purged into ammonia aqueous solution and bubbled through a dry tube filled with NaOH flakes, in order to obtain dry ammonia gas. The analyte gases with different concentrations were generated by mixing saturated vapors with dry air controlled by mass flow controllers. All gas sensing tests were carried out at room temperature (25 °C). The gases were passed through the gas chamber containing the device during the sensing measurements. 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 Agilent 4156C. The sensor response was evaluated by the resistance change at a sampling voltage of 500 mV.
3. Results and discussion

3.1. Synthesis and characterization of RGO–PANI hybrids

The schematic illustration for the preparation of RGO–PANI hybrids is shown in Fig. 1. The single GO sheets could be formed by vigorous sonication of GO paper in distilled water, which was benefit for the further combination of Mn$^{2+}$, due to myriads of –COOH groups on the GO sheets. While dipping with KMnO$_4$ aqueous solution, the reaction took place immediately, and GO–MnO$_2$ hybrids were formed. The reduction of GO–MnO$_2$ could happen during the process of thermal annealing. As a result, RGO–MnO$_2$ hybrids were synthesized. As we know, MnO$_2$ can be used as both of the template and oxidant for the polymerization of aniline monomer.\[38,39\] Thus RGO–MnO$_2$ hybrids could be exploited as both of the templates and oxidants for aniline monomer during the process of polymerization, in order to obtain RGO–PANI hybrids.

The morphology of hybrid materials has been analyzed by TEM, as shown in Fig. 2. It was obvious that the GO sheets stacked together and formed a very flat thin layer. Furthermore, the edges of many sheets slightly curved (Fig. 2a). The morphology of RGO–MnO$_2$ hybrids can be observed in Fig. 2b. MnO$_2$ exhibited a needle-like structure on the surface of RGO sheets. The selected area electron diffraction patterns (SAED) image (inset of Fig. 2b) verified amorphous structures of the resultant RGO–MnO$_2$ hybrid bulks, which suggested that uniform decoration of amorphous MnO$_2$ on the surface of carbon sheets had been achieved during the process of the reaction between Mn$^{2+}$, MnO$_4$/$\text{C}_0$ and H$_2$O. After polymerization process, PANI could be decorated on the surface of RGO sheets instead of MnO$_2$. The complete removal of MnO$_2$ in RGO–PANI hybrids could be verified by EDX (Fig. S1†), the disappearance of the characteristic peaks of Mn suggested that MnO$_2$ and Mn ions had been removed. From Fig. 2c and d, we can observe that PANI nanoparticles have been formed on the surface of carbon sheets. This was different from the phenomena observed in the work reported by Pan et al.\[39\] in which PANI nanotubes could be formed via using MnO$_2$ nanowires as both the oxidants and templates. It might be ascribed to the following reasons: (i) in the work of Pan et al.,\[39\] β-MnO$_2$ nanowires were used and the polymerization was inclined to take place anisotropically along the axis of the wire, while in our work, the MnO$_2$ layers were amorphous, and they could be dissolved in acid solution immediately, resulting in isotropic homogeneous formation of PANI nanoparticles; (ii) RGO sheets played important roles in preventing the particles from aggregating, and consequently formed the uniform nanoparticles decorating the surface of carbon sheets.

The FT-IR spectroscopy was utilized to confirm the process for the preparation of RGO–PANI hybrids. Fig. 3a illustrates the typical spectra of GO. As shown in Fig. 3a, the peaks located at 3453 cm$^{-1}$ and 1412 cm$^{-1}$, which correspond to the O–H stretching and vibration mode of intercalated water, could be observed; the characteristic peaks of oxygen moieties located at 1230 cm$^{-1}$, 1628 cm$^{-1}$ and 1737 cm$^{-1}$, correspondence to C–O (n(epoxy or alkoxy)), C=O in carboxylic acid, and carbonyl moieties (ν(carbonyl), respectively, suggest that the oxidation of graphite by modified Hummers method took place and the formation of GO was achieved successfully. As for the RGO–MnO$_2$ hybrids, the band appearing at 3453 cm$^{-1}$ shifted to 3387 cm$^{-1}$, which could be assigned to the O–H stretching mode of adsorbed water on the surface of MnO$_2$ (Fig. 2c). Furthermore, the C=O vibration band located at 1737 cm$^{-1}$ was disappeared, and a weak shoulder peak located at 1722 cm$^{-1}$ appeared, suggesting that the GO had undergone partial reduction during the thermal annealing process.\[40\] In addition, the appearance of sharp peaks located at 600 cm$^{-1}$ might be assigned to the Mn–O stretching and bending vibrations.\[41\] After the polymerization

Fig. 1 The schematic illustration for the preparation of RGO–PANI hybrids.

Fig. 2 TEM images of (a) GO, (b) RGO–MnO$_2$ hybrids (inset: SAED image), (c) and (d) RGO–PANI hybrids.

Fig. 3 FTIR spectra of (a) GO, (b) RGO–MnO$_2$, and (c) RGO–PANI hybrids.
process, the resultant RGO–PANI hybrids showed typical absorption peaks at 1498, 1578, and 3236 cm$^{-1}$, as shown in Fig. 3c. These bands were associated with stretching mode of benzenoid and quinoid rings as well as N–H stretching mode of benzenoid amine groups of PANI, respectively, which suggests that the PANI had been successfully decorated on the surface of the RGO sheets.

The Raman spectra for the hybrids were also characterized as shown in Fig. 4. For all of the samples, especially for GO (Fig. 3a), distinctive peaks for the D bands and G bands could be observed. The D band located at 1345 cm$^{-1}$ (disorder mode), which was a breathing mode of $\kappa$-point phonons of $A1_g$ symmetry; and G band centered at 1588 cm$^{-1}$ (tangential mode), assigned to the $E2g$ phonon of C sp$^2$ atoms, can be found in Fig. 4. As to RGO–MnO$_2$ hybrids, we could observe from Fig. 4b that the characteristic peaks of D band and G band weakened, and a new characteristic peak of MnO$_2$ located at 643 cm$^{-1}$ appeared, which was in accordance with the anti-symmetry stretching mode located at 600 cm$^{-1}$ in the FTIR spectrum (as shown in Fig. 3b), suggesting the successful addition of MnO$_2$ on the surface of carbon sheets. Fig. 4c presents the spectrum of RGO–PANI hybrids. Besides the characteristic peaks of carbon (D band and G band), a new shoulder peak located at 1160 cm$^{-1}$ could be observed, which might be attributed to the C–H bending of the quinoid ring. Furthermore, the peak of D band widened, this might be due to the existence of characteristic peak of PANI located at 1373 cm$^{-1}$, which was assigned to the C–N stretching vibration of the cation radical species.

The process for the preparation of RGO–PANI hybrids was also monitored by UV-Vis spectroscopy. As shown in Fig. 5a, the absorption peak of the GO dispersion could be observed at 250 nm. After thermal annealing process, the absorption peak red-shifted to 266 nm for the resultant RGO–MnO$_2$ hybrids (Fig. 5b), suggesting that the recovery of electronic conjugation within the graphene sheets occurred. Furthermore, the absorption exhibited in the visible region (600–800 nm) might be in relation with the MnO$_2$ on the surface of RGO sheets. The spectrum for RGO–PANI hybrids was shown in Fig. 5c. Besides the characteristic peak of RGO located at 266 nm, there was a new peak centered at 371 nm, corresponding to the polaron transition bands after doping as well as the localization of electrons ($\pi$–$\pi^*$ transition). The weak shoulder peak located at 464 nm could be correlated with the polaron–$\pi^*$ transition of PANI, suggesting that PANI had been successfully anchored onto the surface of RGO sheets.

3.2. Evaluation of sensing device based on RGO–PANI hybrids

In order to fabricate the sensing devices based on RGO–PANI hybrids, the sensing materials dispersion in ethanol were dipped on the electrode according to our previous reports. The UV–Vis spectra of (a) GO, (b) RGO–MnO$_2$ hybrids, and (c) RGO–PANI hybrids dispersed in ethanol. The concentration of the dispersion is 0.02 mg mL$^{-1}$. NH$_3$, as a toxic gas, was used here as the analyte, with the purpose of demonstrating the potential utility as well as probing the sensing properties of the resultant hybrid sensors. As we know, a trace amount of ammonia gas, which could be released from ammonium nitrate exists in explosives, and is necessary to be detected. Furthermore, the ammonia gas, which was widely used in various fields, including the production of fertilisers, plastics, synthetic fibres, dyes and pharmaceuticals, etc., is harmful to human health. Therefore, it is important to develop ammonia gas sensors and monitor for NH$_3$ leaks. The dry air was used here to bubble 4 wt% of NH$_3$ aqueous solution through the dry tube filled with NaOH flakes, in order to remove the...
humidity and obtain the dry mixture of NH₃ gas and air. The concentration of NH₃ gas could be determined by the following equation:  

\[ F_{NH_3} = \frac{P_{NH_3}}{F_0 - P_{NH_3}} F_c \]  

where \( F_c \) (sccm) is the carrier flow rate, \( P_0 \) is the outlet pressure in the bubbler headspace, and \( P_{NH_3} \) is the vapor pressure of NH₃, which can be determined by ammonia/water vapor–liquid equilibrium data available in Perry’s Handbook.

During the test process, the sensors were placed in the chamber and the dry air was purged to establish an environmental dynamic equilibrium. NH₃ gases with different concentration were switched into the chamber, and the variations of the resistance of the devices were monitored by the Agilent. The sensor response (\( R \)) toward NH₃ gas was calculated according to the following equation:

\[ R(\%) = 100 \times \frac{\Delta R}{R_0} = 100 \times \left( \frac{R_{gas} - R_0}{R_0} \right) \]  

where \( R_0 \) is the resistance of RGO–PANI hybrids network before exposure to NH₃ gas, and \( R_{gas} \) is the resistance of RGO–PANI hybrid network in the NH₃–air mixed gases.

Fig. 7 displays the comparison of the dynamic response of the resultant sensor based on RGO–PANI hybrids with the sensing devices based on bare PANI nanofibers and bare RGO toward NH₃ gas under the concentration of 50 ppm. In order to compare the response of the sensor based on the hybrids with those of the devices based on the bare PANI nanofibers and bare RGO, the exposure time of about 18 min was defined here as the effective response time. As the NH₃ gas was released to the chamber, the resistances of all devices increase significantly. About 5.2% change of the resistance can be achieved for the bare RGO based sensor, which is consistent with the order of the response for the graphene foam reported by Yavari et al. (as shown in Table 1). As far as the sensing device based on PANI nanofibers is concerned, about 13.4% change of the resistance can be achieved. Meanwhile, the exposure of the device based on the hybrids to NH₃ gas (50 ppm) can result in a 59.2% change of the resistance, which suggests that the gas sensor based on RGO–PANI hybrids exhibits much better response than those of the gas sensors based on bare PANI nanofibers and bare RGO. About 3.4 and 10.4 times larger response to NH₃ with 50 ppm concentration for the sensor based on RGO–PANI hybrids can be achieved compared with the sensors based on bare PANI nanofibers and bare RGO, respectively.

Furthermore, we can observe from Fig. 7 that the resistance of the device based on RGO–PANI hybrids increases more rapidly than that of the device based on bare RGO, when the NH₃ gas was introduced into the chamber. The resistance changes become smaller and smaller with the exposure time. Similarly with the device based on the bare RGO, the sensor based on the hybrids is very difficult to saturate.

The recovery behaviors of the devices have also been studied in Fig. 7. In order to stimulate the desorption process in the sensing materials, an IR lamp was been used. During the irradiation with IR lamp, we can observe that the recovery of the resistance to its initial value during the period of ~2.4 min has been achieved for the bare RGO device. Physically-absorbed NH₃ gas can be easily desorbed from the surface of RGO sheets during the illumination process. As for the sensing device based on PANI nanoparticles, a longer period (3.2 min) is needed to remove the absorbed NH₃ gas and reach the steady state. The resistance cannot recover to its initial state due to the acid–base reaction. About 87.3% of the resistance can be achieved for the sensing device based on PANI nanofibers during the desorption process. Similarly with the device based on PANI nanoparticles, the resistance of the RGO–PANI hybrids cannot recover to its initial state either. About 81.5% of the resistance can be achieved, which suggests that the acid-doped PANI nanoparticles on the surface of RGO sheets are more reactive to NH₃ gases during the sensing process. Due to the high surface ratio of RGO sheets and PANI nanoparticles, a recovery period of ~4 min is needed for the sensing device based on the hybrids.

The sensory responses of the sensing device based on RGO–PANI hybrids to different concentrations of NH₃ gases (5–50 ppm) over a period of 18 min at room temperature have been further studied (as shown in Fig. 8). The results show that the sensing devices exhibit an excellent response to different concentrations of NH₃ gases. During the exposure of the device to different concentrations of NH₃ gas, the resistance of the sensing device increased significantly over a period of 18 min. ~25.1% of the resistance change can be achieved for the case of 5 ppm of NH₃ gas. With the increase of the concentration of NH₃ gas, the resistance of the device increases accordingly. The device undergoes ~32.5% and ~48.5% of resistance changes when exposed to 10 ppm and 20 ppm of NH₃ gases, respectively.
Especially for the concentration at 50 ppm, the resistance variations increase rapidly when the devices expose to the NH$_3$ gases. It is suggested that the synergetic effects have occurred between PANI nanoparticles and RGO sheets, resulting in a great enhancement of the sensing performance. When the concentration of NH$_3$ gas is close to the surface of the hybrids, NH$_3$ gases can probably penetrate into the PANI layer and interact with the surface of RGO sheets, leading to a rapid increase of the sensing performance.

Based on the response results mentioned above, the source of the excellent resistance responses of the hybrid sensors may be ascribed to the following items:

(i) The acid–base doping/de-doping process of PANI on the surface of RGO sheets. As we know, PANI has been reported to be an excellent acid–base sensor accounting for its reversible acid–base doping process. This can be also observed from the repeatability of the response of the sensor based on RGO–PANI hybrids to 5 ppm NH$_3$ gas as shown in Fig. 9a. During the desorption process, the illumination causes the recovery of the resistance during the period of ~4 min. However, the resistance value can not reach its initial state, due to the acid–base reaction as shown in Fig. 9b. As the exposure of the device to NH$_3$, the de-doping process occurs, and the acid doped PANI nanoparticles can switch from the Emeraldine salt state (conductive state) to Emeraldine base state (insulating state) gradually, resulting in an increase of the resistance. Since the PANI nanoparticles are anchored on the surface of RGO sheets, the large surface area can also make sure of the better NH$_3$ sensing performance of hybrids than that of PANI nanofibers. This can be verified by testing the surface areas of hybrids and PANI nanofibers. The surface area values of 32 m$^2$ g$^{-1}$ and 22 m$^2$ g$^{-1}$, for RGO–PANI hybrids and PANI nanofibers, respectively, suggest that a larger surface area of PANI on the surface of RGO sheets can be achieved, which is of benefit for the adsorption of NH$_3$ gas, and results in a much better sensing performance.

(ii) The intrinsic sensing properties of RGO sheets enhanced by PANI. Generally, RGO under ambient conditions exhibits p-type behavior, due to the electron withdrawing nature of absorbed water or oxygen containing moieties which induce a hole-like carrier concentration. NH$_3$ is an electron donor. The exposure of RGO sheets to NH$_3$ gas can cause a decrease in the number of charge carriers, resulting in an increase in resistance. In order to illustrate the effect of PANI on the NH$_3$ sensing properties of RGO sheets, the sensing device based on de-doped PANI molecules attached RGO sheets is designed (see ESI†). Since the PANI molecules have been de-doped, the PANI molecules (Emeraldine base state) are insulated, i.e., the circuit networks of sheets are totally dependent on the RGO sheets. This is beneficial for the study of the effect of PANI on the sensing properties of RGO sheets. The dynamic response of the resultant sensor toward NH$_3$ gas under the concentration of 50 ppm have been tested and displayed in Fig. S2.† Similar with the devices based on bare RGO, PANI nanofibers and the hybrids, the

![Fig. 8](image-url) 

Fig. 8 The response curves of the hybrid sensor to NH$_3$ gases under the concentrations of 5–50 ppm.

![Fig. 9](image-url) 

Fig. 9 (a) The repeatability of the response of RGO–PANI hybrid sensor to 50 ppm NH$_3$ gas. (b) The schematic illustration for the variation of chemical structures of PANI during the de-doping process.

<table>
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<th>NH$_3$ sensing materials</th>
<th>Response to 50 ppm NH$_3$ (%)</th>
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<tr>
<td>RGO–PANI hybrids</td>
<td>59.2</td>
<td>—</td>
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<td>Bare PANI nanofibers</td>
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<td>—</td>
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<td>Bare RGO</td>
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<td>—</td>
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<td>Graphene foam</td>
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</tr>
<tr>
<td>TiO$_2$–PANI hybrids</td>
<td>~35%</td>
<td>49</td>
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responses to NH$_3$ gas have been executed through exposure of repeatable characteristic, as shown in Fig. 9a, four cycles of for the rapid increase of the resistance observed in Fig. 7. Of the analytes except NH$_3$ (as shown in Fig. 10), the gas sensor based on the hybrids exhibits higher responses than those of the device based on bare RGO. Since the acid–base de-doping process has been excluded in this situation, it is suggested that the intrinsic properties of RGO sheets enhanced by PANI play an important role in the increase of sensing performance. PANI, as a conducting polymer, can interact with RGO sheets through $\pi$–$\pi$ interaction. During the sensing process, the electron transfer may occur between the conjugated polymer and RGO sheets, and consequently increase the sensing performance of the resultant hybrids. This hypothesis can also explain the reason for the rapid increase of the resistance observed in Fig. 7.

Furthermore, the sensor response exhibits an excellent repeatable characteristic, as shown in Fig. 9a, four cycles of responses to NH$_3$ gas have been executed through exposure of the hybrid based sensor to 50 ppm NH$_3$ gas repeatedly. It is found that the response levels of the sensor can be maintained after repeated cycles of exposure to NH$_3$ and recovery. Actually, the performance of the gas sensor based on the hybrids is very stable for a long period of time under normal operating conditions. Even after several months, the sensing device still shows excellent sensing performance. Therefore, it is suggested that RGO–PANI hybrid can be considered as excellent sensing materials and have potential applications in the sensing areas.

The selectivity, as one of the key factors for the evaluation of a gas sensor, has also been studied as shown in Fig. 10. 20 ppm of NH$_3$ gas has been used for the evaluation of the hybrid sensor through the comparison with other different analytes, e.g., DMMP, methanol, dichloromethane, cyclohexane, and chloroform. The saturated concentration of other vapors have been produced at room temperature and diluted with dry air to 1% concentration. As shown in Fig. 10, more than 2 times magnitude of response to NH$_3$ for the hybrid sensor can be observed in comparison with other analytes. Especially noticing that the concentration of methanol vapor is 1670 ppm, which is more than 80 times higher than the concentration of NH$_3$ gas, more than 2.8 times magnitude of response to NH$_3$ can be achieved compared with methanol, suggesting that the hybrid sensors exhibit a high selectivity and can be considered as an excellent candidate for the detection of NH$_3$ gas.

The sensing performance of the sensor based on RGO–PANI hybrids has been also compared to that of gas sensor based on bare RGO, through exposure of the sensors to different analytes as shown in Fig. 10. The gas sensor based on the hybrids exhibits much better response than that of the gas sensor based on bare RGO. Through the decoration of PANI nanoparticles, about 5.7 times larger response to 20 ppm NH$_3$ for the resultant hybrid sensor can be achieved compared with the sensor based on bare RGO. The acid–base de-doping process of PANI nanoparticles plays an important role in the enhancement of the sensing performance after exposure of the sensor to NH$_3$, resulting in the selective response to NH$_3$ gas. Actually, as for all of the analytes, the hybrid sensor exhibits much better response than that of the bare RGO device. This suggests that not only do PANI nanoparticles play important roles in the response, but also the RGO sheets contributes to the final sensing performance of the sensors. The synergetic effects of the combination of RGO and PANI result in the enhancement of the resultant hybrid sensing device.

Since the sensing device based on the hybrids is very stable, and shows better response than the sensors based on bare PANI nanofibers and bare RGO, it is suggested that RGO–PANI hybrids can be used as excellent sensing materials for the detection of NH$_3$ gas and hold great potential for the real environmental monitoring.

4. Conclusions

In this work, novel ammonia (NH$_3$) gas sensing devices based on reduced graphene oxide (RGO)–polyaniline (PANI) hybrids have been successfully fabricated and studied for the first time. PANI nanoparticles were successfully anchored on the surface of RGO sheets by using RGO–MnO$_2$ hybrids as both of the templates and oxidants for aniline monomer during the process of polymerization. The resultant RGO–PANI hybrids exhibited excellent sensing performance to NH$_3$ gas. The RGO–PANI hybrid device exhibited much better (3.4 and 10.4 times respectively with the concentration of NH$_3$ gas at 50 ppm) response to NH$_3$ gas than those of the sensors based on bare PANI nanofibers and bare RGO. It reveals that the combination of graphene and PANI exhibit positive synergetic effects on ammonia gas detection, which is expected to hold great promise for real-world applications.

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