NO$_2$ and humidity sensing characteristics of few-layer graphenes

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Sensing characteristics of few-layer graphenes for NO_2 and humidity have been investigated with graphene samples prepared by the thermal exfoliation of graphitic oxide, conversion of nanodiamond (DG) and arc-discharge of graphite in hydrogen (HG). The sensitivity for NO_2 is found to be highest with DG. Nitrogen-doped HG (n-type) shows increased sensitivity for NO_2 compared with pure HG. The highest sensitivity for humidity is observed with HG. Sensing characteristics of graphene have been examined for different aliphatic alcohols and the sensitivity is found to vary with the chain length and branching.

Keywords: gas sensor; NO_2 sensor; humidity sensor; graphene

1. Introduction

Gas sensor characteristics of various nanostructures have been investigated in the past few years [1–3]. Thus, many metal oxide nanostructures show good sensing characteristics for gases, such as NO_2, NH_3, hydrocarbons and ethanol [1–10]. Carbon nanotubes (CNTs) are known to exhibit fast response and high sensitivity for detection of small concentrations of toxic gases at room temperature. Semiconducting CNTs can be used for detecting a very small concentration of NH_3, NO_2 and other gases [11–15]. Graphene is a new nanocarbon with a two-dimensional structure containing sp^2 carbon network. Single layer graphene comprising a sheet of the sp^2 carbon network is of primary interest; however graphenes with more than one layer have also been investigated in recent months. If the number of layers is more than 10, the properties become similar to those of bulk graphite. Single layer graphene is a gapless semiconductor, but with the increase in the number of layers the gap opens up, affecting the electronic properties. Recent studies on the interaction of graphene with gas molecules have indicated that it can act as a good sensor [16–24].

Schedin et al. [22] have shown that the increase in the charge carrier concentration induced by gas molecules adsorbed on the surface of graphene can be used to fabricate

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sensitive gas sensors. On the basis of theoretical investigations on the adsorption of gas molecules on single layer graphene as well as on graphene nanoribbons, it has been predicted that the doping in carbon nanostructures may improve the sensitivity [25–28]. Ao et al. have applied density functional theory to show that aluminium doped graphene can be used as a good detector for carbon monoxide [29]. Functionalised graphite nanostructures are able to sense traces of pollutant gases such as NO_2 [30]. Water vapour sensing characteristics of reduced graphene oxides have been reported [31]. Reduced graphene oxide is also shown to be a good sensor for toxic vapours [32]. Spin-coated hydrazine-functionalised graphene dispersions are able to detect NO_2, NH_3 and 2,4-dinitrotoluene [33].

We considered it important to examine the gas sensing characteristics of few-layer graphenes prepared by different methods. For this purpose, we have prepared graphene by the thermal exfoliation of graphitic oxide (EG), conversion of nanodiamond (DG) and by arcing graphite rods in a hydrogen atmosphere (HG) [34–37]. We have also prepared nitrogen- and boron-doped graphene samples (N–HG and B–HG) to study the effect of doping on the gas sensing characteristics. We have studied sensing of NO_2 and humidity by all the above graphene samples. We have also examined the sensing characteristics of EG for different aliphatic alcohols.

2. Experimental technique

Graphene was prepared by four different methods, namely the EG, DG and arc-discharge of graphite in HG. To prepare EG, graphitic oxide was prepared by reacting graphite powder with a mixture of concentrated nitric acid and sulphuric acid with potassium chlorate at room temperature for 5 days and the thermal EG was carried out in a long quartz tube at $1050°C$ under an argon atmosphere [34]. Thermal DG to graphene was carried out at $1650°C$ in a helium atmosphere to obtain DG [35]. To prepare HG, direct current arc-discharge of graphite evaporation was carried out in a water cooled stainless steel chamber filled with a mixture of hydrogen and helium with the proportion H_2 (200 Torr)–He (500 Torr) with the discharge current in the 100–150 A range and maximum open circuit voltage of 60 V [37]. Boron doped graphene (B-doped HG) was prepared by carrying out arc-discharge using a boron-stuffed graphite electrode (3 at% boron) in the presence of H_2 (200 Torr) and He (500 Torr). Nitrogen doped graphene (N-doped HG) was prepared by carrying out arc-discharge of graphite electrodes in the presence of H_2 (200 Torr), He (200 Torr) and NH_3 (300 Torr).

The as-synthesised graphene samples were characterised by X-ray diffraction (Cu-Kα radiation), transmission electron microscopy (TEM) (JEOL JEM 3010), field emission scanning electron microscopy (FESEM) (Nova Nanosem 600), atomic force microscopy (AFM) (CP 2 atomic force microscope) and Raman spectroscopy (Labraman-HR) using an He–Ne laser (632.81 nm). Brunauer–Emmett–Teller surface areas were measured using a Quantachrome Autosorb-1 instrument. The surface areas were measured at 77 K using N_2 as the adsorbate.

The sensing devices were prepared as follows: 300 nm thick gold film was deposited on a glass substrate by thermal evaporation to make source and drain with a 15 μm separation between the electrodes. Graphene samples were dispersed in methanol using ultrasonica-tion and 5 μL of the dispersion was dropped onto the electrodes by dielectrophoresis.

Gas sensing properties were measured using a home-built computer-controlled characterisation system consisting of a test chamber, sensor holder, a Keithley multimeter-2700, a Keithley electrometer-6517A, mass flow controllers and a data acquisition system. The test gas was mixed with N_2 to achieve the desired concentration and the flow rate was maintained using mass flow controllers. By monitoring the output voltage across the sensor, the resistance of the sensor in dry air or in the test gas can be measured. The resistance of the graphene samples increased in contact with NO_2, while the resistance decreased in contact with water and alcohol vapours. The sensitivity (response magnitude) S was determined as the ratio $\Delta R/R_{air}$, where ΔR is the difference of resistance of the graphene sample in the presence of the test gas and in dry air, R_{air} is the resistance of the samples in dry air. The resistance of the sensors prepared by us based on graphene was in the range 0.1–15 kΩ. The response time is defined as the time required for the resistance to reach 90% of the equilibrium value after the test gas is injected and recovery time is taken as the time necessary for the sensor to attain a resistance 10% above the original value in air. The controlled humidity environments were achieved using saturated aqueous solutions of LiCl, $MgCl_2$, K_2CO_3, NaBr, KI, NaCl, KCl and K_2SO_4 in a closed glass vessel at an ambient temperature of 25°C which yielded approximately 11.3%, 32.8%, 43.1%, 57.5%, 68.8%, 75.3%, 84.3% and 97.3% relative humidity (RH), respectively. These RH levels were independently monitored by using a hygrometer (Keithley 6517A). Then a Keithley multimeter was used to measure the change in the sensor resistance in the testing circuit. To measure alcohol sensing characteristics of EG sample, N_2 gas was bubbled at a constant flow rate (100 sccm) through a gas bubbler containing different alcohols to get alcohol vapours with alcohol concentration around 200 ppm in the test chamber.

3. Results and discussion

We have characterised the graphene samples by a variety of techniques. Figure 1(a) and (b) show typical transmission electron micrographs (TEM) and Raman spectra of thermally exfoliated graphene (EG) and arc-discharge graphene (HG) samples. The TEM image of EG shows existence for 4–5 layers of graphene while bi- and tri-layer graphenes are mostly present in HG. The Raman spectra show the presence of the D, G and 2D bands in all the samples [36]. The intensity of 2D band is greater in HG than in EG. Analysis of the (002) reflections in the X-ray diffraction patterns of the grapheme samples shows that EG and DG samples possess between 3 and 6 graphene layers, while HG, N-doped HG and B-doped HG samples possess between 2 and 3 layers only and that was further verified by AFM cross-section height profile analysis. The BET surface areas of EG and DG were high (1260 m^2/g and 930 m^2/g, respectively) but that of HG and doped HG samples were rather low (~400 m^2/g). Typical low-magnification FESEM images of dielectrophoretically deposited graphene samples (EG and DG), taken at magnifications of 1000× and 1500×, respectively, between two gold electrodes are shown in Figure 2(a) and (b), respectively. In the inset of Figure 2(a), we show a higher magnification image (20,000×) of EG, revealing the sheet-like morphology of graphene.

We have measured the current–voltage (I–V) characteristics for all the graphene samples at 1000 ppm NO_2 and different RH. Figure 3(a) shows the typical Ohmic behaviour of N-doped HG in air and in NO_2. Figure 3(b) shows I–V characteristics of DG
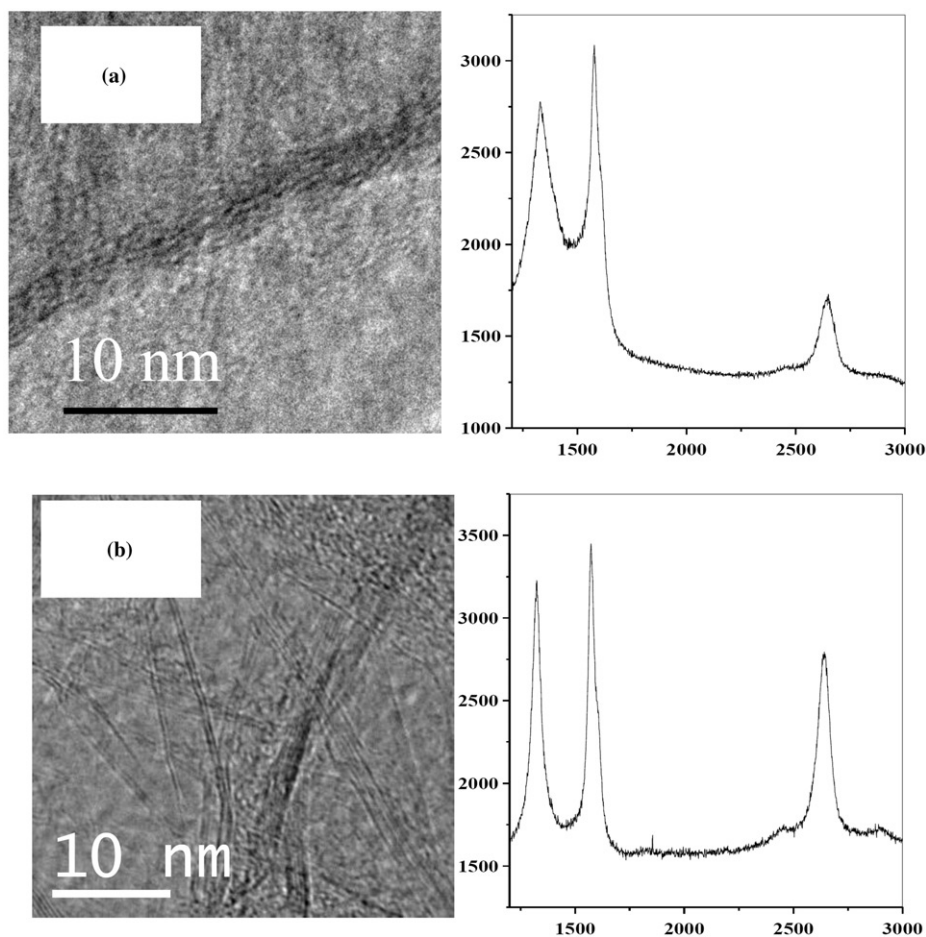
Figure 1. TEM images and Raman spectra of (a) EG and (b) HG samples.

at 4% and 84% RH. These I–V characteristics demonstrate that the graphene samples can be used for sensing these vapours.

Figure 4(a) and (b) show typical gas sensing characteristics of the graphene samples for different concentrations of NO_2. We find the highest sensitivity with DG, the value reaching 65%. The response time is quite reasonable with both HG and DG, the values being around 15 min, but it is high with EG ($\sim$50 min). Rapid response and recovery times are found when the molecular adsorption occurs on low-energy binding sites. The sensing characteristics of graphene for NO_2 are fully reversible on heating the samples to 150°C to remove the adsorbed gases.

We have examined the effect of doping graphene on the NO_2 sensing characteristics of HG prepared by arc-discharge in hydrogen. The sensitivity of HG decreases on boron doping and increases significantly on nitrogen doping. Figure 4(c) shows the sensing characteristics of the N-doped HG sample for different concentrations of NO_2. It appears that n-type graphene is a better sensor for NO_2 as it is an electron withdrawing molecule.
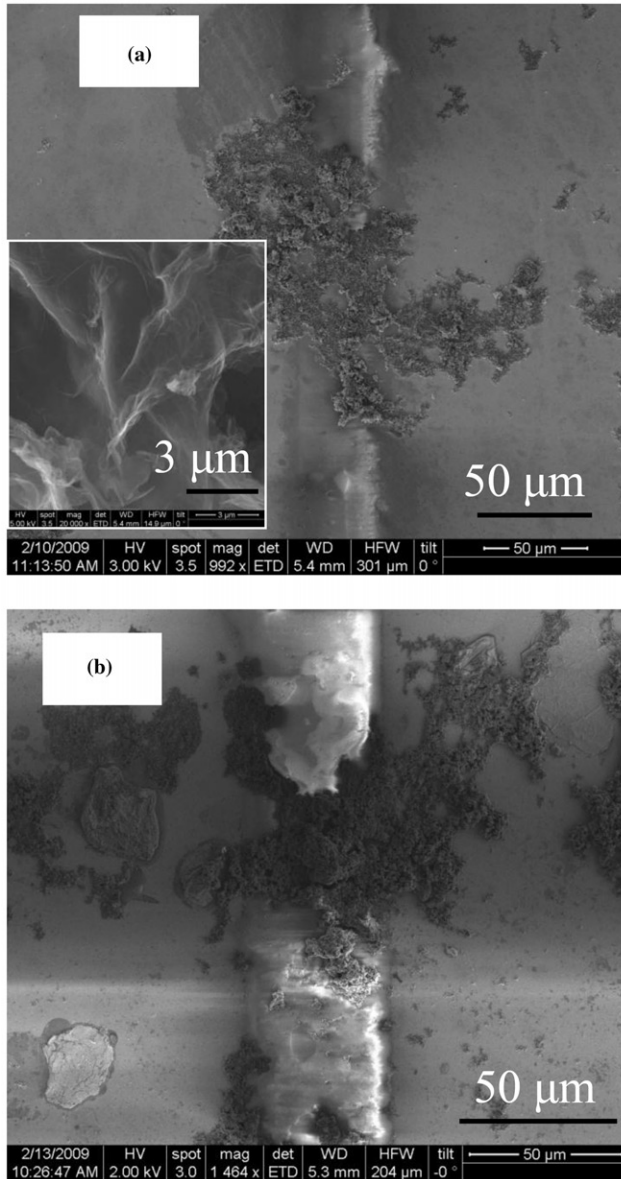
Figure 2. FESEM images of dielectrophoretically deposited (a) EG and (b) DG between two gold electrodes.

The response times with the B- and N-doped HG samples are 15 and 50 min, respectively. In Figure 5(a), we show the variation of sensitivity for the graphene samples exhibiting the highest sensitivity. We see that the value of the sensitivity increases with NO_2 concentration and is satisfactory beyond 100 ppm. We have carried out sensitivity measurements for NO_2 over repeated cycles and obtained reproducible results.
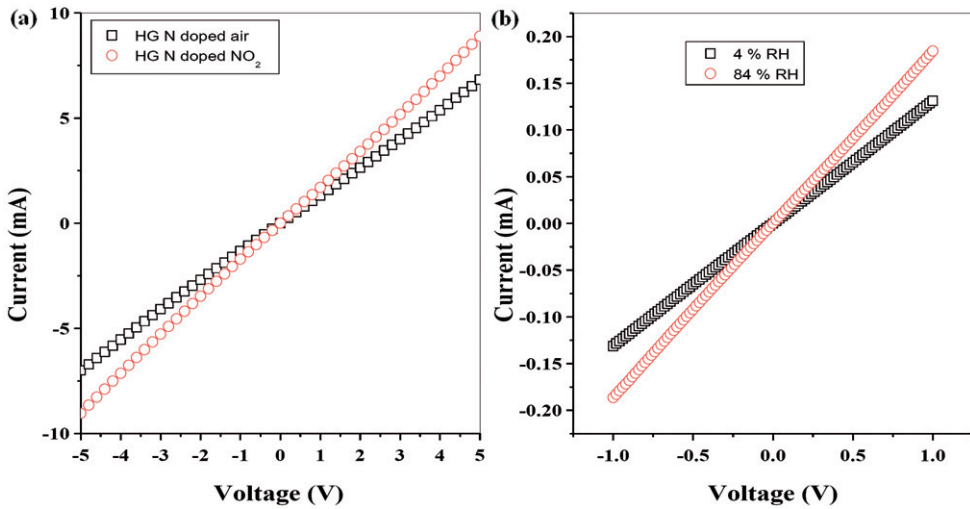
Figure 3. I–V characteristics of (a) N-doped HG (at 25°C) in air and in 1000 ppm of NO_2 and (b) DG (at 25°C) in 4% and 84% RH.
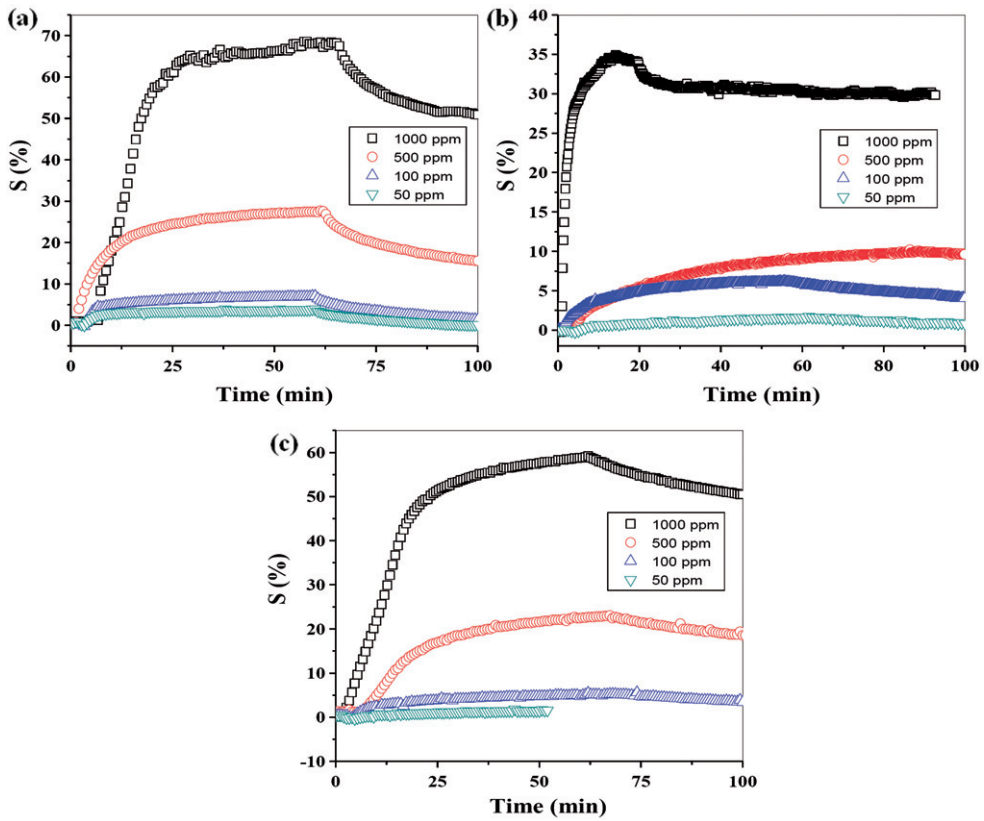

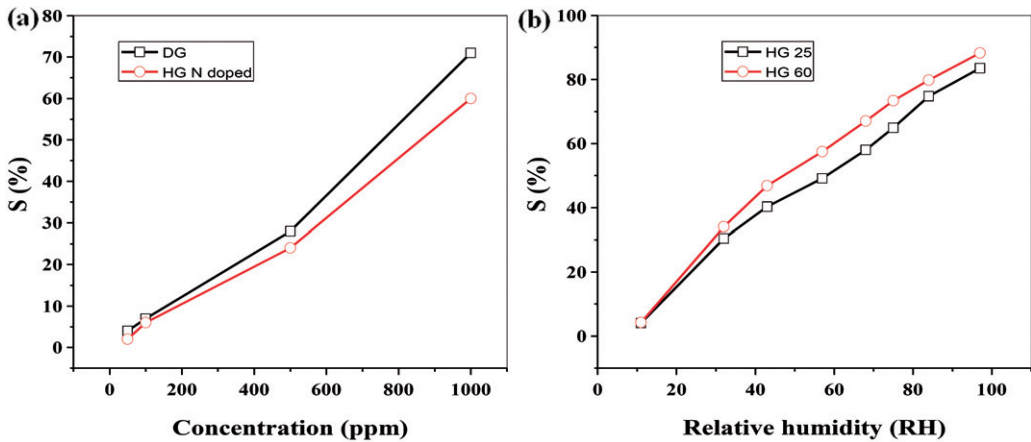Figure 4. Gas sensing characteristics of (a) DG (b) HG, and (c) N-doped HG for 1000, 500, 100 and 50 ppm of NO_2.

Figure 5. (a) Variation of sensitivity of DG and N-doped HG for NO_2 with the concentration of NO_2. (b) Variation of sensitivity of HG with RH at 25°C and 60°C.
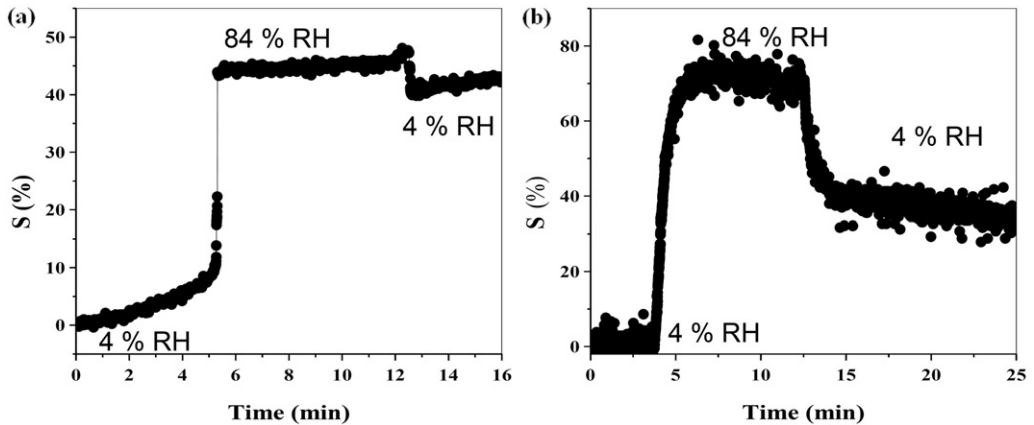

Figure 6. The change in sensitivity of (a) EG and (b) HG accompanying the dynamic switch between dry air (4% RH) and 84% RH.

For practical applications, however, it may be necessary to anneal the sensor-device and remove the absorbed NO_2 after each cycle.

The sensitivity of the three graphene samples for humidity was measured at 25°C and 60°C. Typical sensing characteristics are shown in Figure 6(a) and (b). High sensitivity for humidity is found with HG, the value reaching 80%. The response time varies between 3 and 5 min for the three graphene samples. The first step change in sensitivity is due to the RH change from 4% to 84% and the second step change is due to the RH change from 84 to 4%. The recovery time is too high (a few hours) to show the results in the time scale. In Figure 5(b), we show the typical variation of sensitivity with RH in the case of HG at 25°C and 60°C. The sensitivity increases with % RH as expected and is satisfactory above 20% RH.
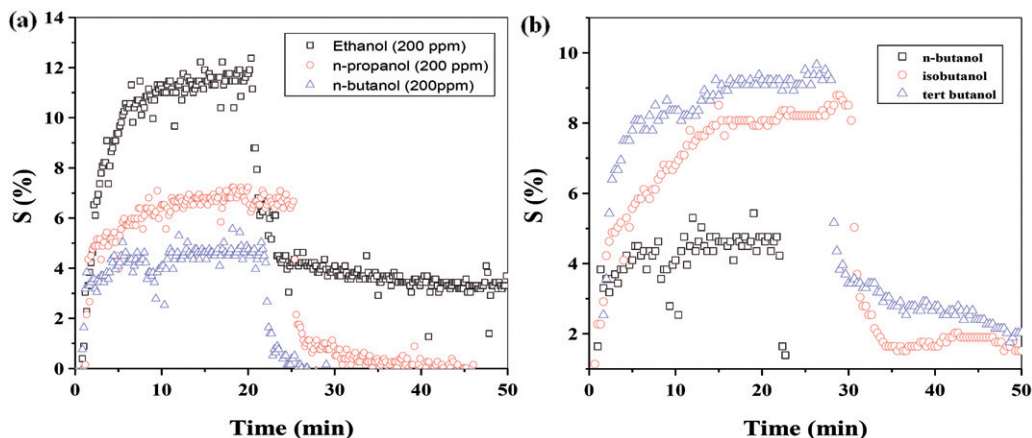
Figure 7. Alcohol sensing characteristics of EG (all alcohols at 200 ppm) at 25°C: (a) methanol, ethanol, n-propanol and n-butanol, (b) n-butanol, iso-butanol and t-butanol.

We have also examined the sensing characteristics of EG for different aliphatic alcohols. In the case of normal aliphatic alcohols, the sensitivity varies with the chain length in the order ethanol > n-propanol > n-butanol, as shown in Figure 7(a). The sensitivity depends on branching in the case of isomeric butyl alcohols with t-butanol > iso-butanol > n-butanol, as shown in Figure 7(b).

4. Conclusions

In conclusion, thick film sensors prepared with few-layer graphene samples show satisfactory sensing characteristics for NO_2 and H_2O. Graphene prepared by nanodiamond conversion shows the best sensitivity for NO_2 although it does not have the highest surface area. It may be because the surface of nanodiamond-converted graphene (DG) is less functionalised compared with EG and HG. N-doped graphene shows enhanced sensitivity for NO_2 since the latter is an electron-withdrawing molecule. HG prepared by arc-discharge in a H_2 atmosphere shows the best sensitivity for humidity. Since water is an electron donor molecule, it appears that HG which has no oxygen functional groups shows the best sensing characteristics. It is interesting that the sensing characteristics of EG for aliphatic alcohols depend on the chain length and branching.

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