Humidity-assisted selective reactivity between NO\textsubscript{2} and SO\textsubscript{2} gas on carbon nanotubes

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In spite of the technical importance of detecting environmental SO\textsubscript{2} and NO\textsubscript{2} gases, a selective detection has not been realized because of their similar chemical properties. In this report, adsorption and desorption of SO\textsubscript{2} and NO\textsubscript{2} gas on carbon nanotubes are investigated in terms of different humidity levels at room temperature. A random-network single walled carbon nanotube (SWCNT) resistor is constructed by a dip-pen method using a SWCNT/dichloroethane (DCE) solution. In the case of SO\textsubscript{2} gas adsorption, the resistance increases at high humidity level (92\%) and shows no obvious change at low humidity levels. On the other hand, in the case of NO\textsubscript{2} gas adsorption, the resistance always decreases independent of moisture levels. Our density functional theory (DFT) calculations show that this selective behavior originates from cooperative charge compensation between the SO\textsubscript{2}–H\textsubscript{2}O complex and the p-type CNT resistor. The change of response time and recovery time with different moisture levels is further investigated. This humidity-assisted gas reaction provides a simple route to detect these two gases selectively.

Introduction

Accurate detection of sulfuric oxides and nitric oxides is an important issue since both chemicals adversely affect human health and the environment. Both of them exist as reactive gases that primarily originate from human activities such as coal combustion and petroleum refining, leading to the formation of ground-level smog and acid rain. Detection, particularly of NO\textsubscript{2} gas, with high sensitivity has been realized.\textsuperscript{1–8} Nevertheless, commercialization is still limited due to the poor selectivity from SO\textsubscript{2} gas. To our knowledge, no single device with a simple chemiresistor structure to selectively detect these two gases has been realized yet.

A typical metal oxide for gas sensing with a reasonable sensitivity usually needs to be operated at high temperature. Nanomaterials such as carbon nanotubes (CNTs) which have a large surface area to volume ratio can be a good candidate to operate at room temperature with high sensitivity and also provide less power consumption with size minimization. Recently metal/metal oxide-decorated CNTs have been introduced to modify CNT surfaces and thus control the strength of the interaction with the gases.\textsuperscript{4–6} Polyethyleneimine (PEI) has been suggested to decorate CNT surfaces where amine groups become an electron donor to convert a CNT channel to an n-type, and thus enhance charge donation from CNTs to NO\textsubscript{2}.\textsuperscript{7} The related works are summarized in Table 1. On the other hand, SO\textsubscript{2} gas also behaves as an electron acceptor which is quite similar to NO\textsubscript{2} gas. Therefore, distinguishing these two gases has been a great challenge.

The purpose of this paper is to design a sensor with both high sensitivity and selectivity to NO\textsubscript{2} and SO\textsubscript{2} gas, which can be operated under ambient pressure at room temperature. In this work, the random network single walled (SW) CNTs resistor was constructed by a dip-pen method using dichloroethane (DCE)-dispersed surfactant-free SWCNTs. Selective detection of these two gases was simply achieved by controlling the humidity level. At low humidity levels, NO\textsubscript{2} gas provided high sensitivity, while SO\textsubscript{2} gas showed negligible sensitivity. At a high humidity level (92\%), however, the channel resistance decreased with NO\textsubscript{2} gas but increased with SO\textsubscript{2}. This selective behavior, which was explained by both experiments and density functional theory (DFT) calculations, was attributed to the complicated electron donation process between the SO\textsubscript{2}/H\textsubscript{2}O complex and the p-type CNT resistor.

Experimental

Carbon nanotubes dispersion and device fabrication

The HiPCO SWCNTs (purity: 85 wt\%) were purchased from CNI company. The SWCNTs of 1 mg were dissolved in a 30 mL DCE solution and sonicated for 12 h in a bath type sonicator.
Power Sonic 505. To remove large-size bundles, the SWCNT solution was further centrifuged for 20 min at 21,380 g (15 000 rpm). The supernatant of the SWCNT solution was decanted and used for a dip pen method to fabricate the SWCNT sensor. The next step is to construct electrodes for a sensor. An interdigitated electrode of Pt (3000/23 A) with an area of 200 × 200 mm² was fabricated by using photolithography on a SiO₂ (100 nm)/Si substrate (Fig. 1a). A gap distance of 2.5 mm was maintained between the two electrodes. The SWCNT solution was filled into a home-made dip pen machine with a contact area of 3.14 mm². The number of dip pen contacts and the CNT density were optimized to give the best performance of the sensor. Once the SWCNTs were transferred onto the designed electrode, the sample was heat-treated at 400 °C under Ar ambient for 30 min to stabilize the final microstructure, improve contact, and remove pre-adsorbed molecules.

Measurement setup

NO₂ (SO₂) gas of 20 ppm was diluted to 2 ppm by mixing 450 SCCM of dry air and 50 SCCM target gas through an automatic mass flow controller via a data acquisition card from National Instrument, as shown in Fig. 1d. To control the humidity level, air was flowed into a bubbler, where the humidity level was detected by a humidity detector (Rotronic Hygroflex HF3x), or directly into the chamber. The chamber whose length is 10 cm and the quartz diameter is 2.5 cm, was maintained under ambient pressure at room temperature. A DC bias of 0.1 V (Digital Electronics Co. LTD 1083468) was applied to the electrode through an external resistor to protect the SWCNT channel. Current change was measured using a Keithley 2000 multimeter. All of the data were recorded automatically through a general purpose interface bus by a Labview interface.

Calculational method

Ab initio electronic structure calculations were performed to further understand the experimental findings. The NO₂ (SO₂) with or without H₂O molecules were absorbed on (13, 0) nanotube to examine the adsorption behavior. The density functional theory within the local density approximation (LDA) and generalized gradient approximation (GGA) for the exchange–correlation energy was adopted. Our model structures were relaxed until the atomic forces on the atoms were smaller than 0.05 eV/Å. A double numerical plus polarization basic set was employed within the Dmol³ package with an orbital cut off of 4.0 A in the case of adsorption of NO₂ onto the CNT, since Dmol³ has some weak points for the calculations of the spin system, the plane wave basic set implemented by PWscf with spin.

Table 1 Summary of previous results

<table>
<thead>
<tr>
<th>Analyst</th>
<th>Material</th>
<th>Configuration/Method</th>
<th>Sensing Mechanism</th>
<th>Detect Limit</th>
<th>Response/Recovery</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>NO₂</td>
<td>Bare CNTs</td>
<td>ChemiFET</td>
<td>NO₂ is electron acceptor</td>
<td>2 ppm</td>
<td>&lt;600 s</td>
<td>1</td>
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<td></td>
<td></td>
<td>Chemiresistor</td>
<td>NO₂ is electron acceptor</td>
<td>10 ppb</td>
<td>&lt;120 s</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemiresistor</td>
<td>NO₂ is electron acceptor</td>
<td>20 ppm</td>
<td>/</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemiresistor</td>
<td>NO₂ is electron acceptor</td>
<td>100 ppb</td>
<td>&lt;600 s (150 °C)</td>
<td>4</td>
</tr>
<tr>
<td>Metal-decorated (Au/Pt) CNTs</td>
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<td>Chemiresistor</td>
<td>NO₂ is electron acceptor</td>
<td>25 ppm/500 ppb</td>
<td>4.5 min/3.5 min</td>
<td>5, 6</td>
</tr>
<tr>
<td>Metal oxide decorated CNTs</td>
<td></td>
<td>Chemiresistor</td>
<td>NO₂ is electron acceptor</td>
<td>100 ppb (150 K)</td>
<td>4 s</td>
<td>7</td>
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<tr>
<td>SWCNTs</td>
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<td>Spectroscopic analysis</td>
<td>NO₂ is electron acceptor</td>
<td>/</td>
<td>/</td>
<td>10–13</td>
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<tr>
<td>Theory calculation</td>
<td></td>
<td>/</td>
<td>NO₂ is electron acceptor</td>
<td>/</td>
<td>/</td>
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</tr>
<tr>
<td>SO₂</td>
<td>SWCNTs</td>
<td>Spectroscopic analysis</td>
<td>SO₂ is electron acceptor</td>
<td>10 ppb (150 K)</td>
<td>4 s</td>
<td>8, 9</td>
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<td>/</td>
<td>&lt;60 min</td>
<td>14</td>
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<tr>
<td></td>
<td>MWCNTs</td>
<td>Chemiresistor</td>
<td>SO₂ is electron donor</td>
<td>10 ppb</td>
<td>&lt;1200 s</td>
<td>15</td>
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<td></td>
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<td>0.6 ppm</td>
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<td>16–19</td>
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<tr>
<td>H₂O</td>
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<td>/</td>
<td>H₂O is electron donor;</td>
<td>/</td>
<td>/</td>
<td>10, 11, 20–23</td>
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<td>/</td>
<td>H₂O is electron acceptor (graphene); no charge transfer;</td>
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<td>/</td>
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<td></td>
<td>MWCNTs rope</td>
<td>Chemiresistor</td>
<td>/</td>
<td>/</td>
<td>~200 s</td>
<td>24</td>
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<td></td>
<td>MWCNTs film</td>
<td>Chemiresistor</td>
<td>/</td>
<td>12–75.8%</td>
<td>20 s/10 s</td>
<td>25</td>
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<td>Chemiresistor/Chemiresistor</td>
<td>H₂O is electron donor</td>
<td>35–70%</td>
<td>/</td>
<td>23, 26</td>
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<td></td>
<td>CNT/SiO₂ composite</td>
<td>Chemiresistor</td>
<td>/</td>
<td>0–100%</td>
<td>2–3 min/h</td>
<td>27</td>
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</table>

Fig. 1 (a) Schematic of an SWCNT sensor: CNTs on Pt electrodes on SiO₂/Si substrate, (b) comb-type interdigitated electrode, (c) SWCNTs network between two electrodes, and (d) schematic of experimental setup with measurement system.
polarization functional was used. The kinetic cut-off for wave functions was 35 Ry (475 eV) for all atoms and the convergence threshold for calculation of self-consistent energy was ~10^-5 eV. The structures were relaxed until the forces on the atoms were smaller than 0.025 eV Å^-1.

Results and discussion

Adsorption of SO2 with different humidity levels

Fig. 1 shows a schematic of comb-type interdigitated electrodes which are composed of random-network SWCNTs and the experimental setup. The performance of the device strongly relies on the dispersion and CNT density. Small bundle size and random distribution of SWCNTs in the electrodes are the key factors for having a reasonable range of series resistance that suppresses the dark current and enhances the on-current with gases.\cite{23,24,26} Fig. 1b and 1c are the SEM images of the electrode and typical SWCNTs network used in this study. Individual SWCNTs or small-size bundles of SWCNTs were well distributed between two electrodes with a reasonable density. The optimized series resistance was in a range of a few tens kΩ–MΩ.

Fig. 2a shows a 2 ppm SO2 response to humidity. When the sensor was installed in the chamber, the chamber was purged with dry air (humidity level is about 5%) for 100 s, followed by SO2 uptake. The resistance increased gradually as the humidity level was incremented and the sensitivity was negligible at low humidity levels. The gradual increase of the resistance at a low humidity level originates mainly from humidity (Fig. 2b). The humidity dependence became more obvious at higher humidity levels. With an increasing humidity level, the resistance of the originally p-type CNT channel increased, suggesting charge compensation. In other words, electron donation from H2O compensates hole carriers in the channel, congruent with previous works.\cite{23,24,26} The sensitivity of SO2 gas increased at high humidity levels (92%). The resistance increased more prominently with SO2 uptake and then decreased upon release of SO2 gas. The gas uptake was maintained for about 500 s each time where the resistance approached saturation. This implies that the reaction is still in an equilibrium state, where the adsorption is dominated by energetics. This will be discussed in total energy calculations later. The repeatability was checked in region II with a low humidity level, where dry air was again introduced at the last cycle. Negligible response was again observed, similar to the initial stage in region I. The humidity-assisted reactivity of SO2 gas is intriguing. We emphasize here that no type conversion is involved with/without SO2 even at a high humidity level. As shown in Fig. 2b, the resistance decreased at a moisture concentration of 92%. A high-resistance device was used in this experiment but the response to gases is expected to be similar to the low-resistance device in Fig. 2a. This is in good contrast with previous reports which explained the decrease of resistance at high humidity level by CNTs type conversion from a p-type to an n-type channel.\cite{23,26,29} The similar gas reaction behavior was observed in different devices with initial resistances in a range from ~kΩ to ~MΩ.

Theoretical analysis for cooperative charge transfer between SO2-H2O complex and p-type CNT resistor

The underlying mechanism will be elucidated with DFT calculations. Fig. 3 describes the amount of electrons extracted from intrinsic CNT (without charge doping) as a function of moisture level with/without SO2 (squares) according to theory calculations. With an increasing moisture level, more electrons are extracted from the CNT, i.e., water behaves like a p-type dopant to intrinsic CNT. In the case of SO2 uptake, SO2 extracts electrons from the CNT in the absence of humidity (solid squares). The amount of electrons extracted from CNT is reduced when moisture is introduced but electrons are still extracted from CNT (Fig. 3b). However, this model cannot be applied to explain our experimental observations, since pristine CNTs in experiment are originally p-type due to ambient gas adsorption or substrate effect.\cite{13}

To make our theoretical model similar to the experimental situation, +2 charges (or +0.0167 e/carbon atom) are introduced in the calculation system, i.e., two electrons are extracted from CNT originally to ensure a large Fermi energy shift (3.76 eV) to simulate pristine p-type CNT. Even charges were chosen for calculational convenience. As a consequence, the Fermi level is downshifted below the highest occupied molecular orbital (HOMO) (Fig. 3c). CNT is therefore p-type. It is quite intriguing to observe that in this case electrons are donated to the CNT at
low humidity levels, as shown in Fig. 3a (circles), whereas at high humidity levels, electrons are extracted from H$_2$O–cluster formed by hydrogen bonding again. This theoretical prediction in fact explains experimental observations of pure water adsorption in Fig. 2b. The increase of resistance at low humidity levels is explained by charge compensation from a water molecule to CNT. Thus, when SO$_2$ is introduced at a low humidity level, the effect of SO$_2$ to resistance is minor (Fig. 3a, solid circles) since both H$_2$O and SO$_2$ are electron donors to p-type CNT. However, at a high humidity level, the amount of electrons is slightly donated from SO$_2$-H$_2$O complex to CNT, which is the opposite direction of H$_2$O–cluster adsorption. In other words, the presence of SO$_2$ compensates the effect of H$_2$O-cluster at a high humidity level. This explains why a rather mild resistance change with SO$_2$-H$_2$O was shown in Fig. 2a at high humidity level compared to the rapid decrease of the resistance in the absence of SO$_2$ in Fig. 2b. Thus, all the experimentally observed phenomena can be explained by charge compensation rather than type conversion. This argument still holds true even for the case of a lightly p-doped CNT. Intuitively, electron affinity of positively charged (p-type) CNT increases compared to neutral CNT. In neutral CNT, oxygen in water molecules has a higher electron affinity and thus extracts electrons from CNT independent of the number of molecules, as shown in Fig. 3b. However, in the case of positively charged CNT which has a higher electron affinity than a single water molecule, the single water molecule loses electrons to CNT, while a water cluster still extracts electrons from CNT, as shown in Fig. 3c. The charge transfer direction will be competed by the Fermi level shift of CNTs and humidity level.

Adsorption of NO$_2$ with different humidity levels

Fig. 4 shows the resistance change with 2 ppm NO$_2$ gas exposure at different humidity levels. A similar procedure to SO$_2$ was conducted for NO$_2$ gas. Unlike SO$_2$ gas, the sensitivity was highly independent of humidity level, although there was a slight variation with different humidity levels. With an uptake of NO$_2$ gas the resistance decreased, which is the opposite to that observed for SO$_2$ gas at high humidity levels. This was attributed to the charge transfer from CNTs to NO$_2$ molecules. The repeatability was also confirmed in region II by alternating dry air and 92% moisture. The sensitivity with dry air became lower than that of the initial stage of region I (inset) due to the pre-existing moisture in the previous cycle.

Dynamic response and recovery of NO$_2$ and SO$_2$ gas

Next we investigate the effect of moisture to response time and recovery time of NO$_2$ gas. The response (recovery) to NO$_2$ gas upon gas exposure (release) at different humidity levels was extracted from Fig. 4 and redrawn in Fig. 5a and 5b. The resistance change decreased (increased) exponentially and saturated later. The response curve for adsorption (desorption) can be fitted to $\Delta R = \Delta R_0 - \Delta R_0 \exp(-t/\tau)$. Here $R_0$ is the final resistance change at a long exposure time (recovery), $t$ is time, and $\tau$ is the response (recovery) time constant. At small $t$, the curve can be approximated to $\Delta R = \Delta R_0 t/\tau$. Therefore, $\tau$ can be obtained from the linear slope $S$ ($\tau = \Delta R_0/S$, $S = \Delta R/\tau$). $R_0$ can be extracted from exponential fitting and the slope can be measured from the linear fitting. The linear fitting was plotted in the inset of
Fig. 5a and 5b. Note that the reference resistance during desorption was reset to zero when the gas was released.

The response time constant extracted from the linear slope in Fig. 5c decreased gradually with increasing humidity level. The response time is directly related to the activation barrier height, as shown in the reaction energy curve in the inset of Fig. 5c. The response of NO$_2$ gas on CNTs in the presence/absence of moisture is expected to be endothermic. Thus, the activation barrier height decreases with increasing humidity level. On the other hand, the recovery time constant behaves differently from the response time constant. The recovery time increased gradually with increasing humidity level and decreased at high humidity level (92%). It is also noted that the recovery time is much larger, by about 10 times, than the response time. This implies that the binding energy is much larger than the activation barrier height since gas desorption mainly relies on the binding energy. It has been known that NO$_2$ gas decomposes into NO and NO$_3$ by the metal oxide catalytic reaction. Since transition metals such as Fe and Co are introduced during CNT synthesis, they always remain even after sophisticated multistep purification processes. In this study we used HiPCO SWCNTs with 85 wt% purity and therefore metal catalysts are likely to remain and could be oxidized. Therefore, the dominant species that adsorbs on the CNT surface is not only NO$_2$ but also NO and NO$_3$. The binding energy of NO$_2$, NO, and NO$_3$ are 0.47, 0.44, and 1.08 eV, respectively, as shown in Table 2.

Fig. 4 A similar experiment to SO$_2$ was performed using 2 ppm NO$_2$ gas exposure. The inset shows the enlarged portion of NO$_2$ input at a humidity level < 5% in region I.

(i) At a low humidity level, a possible chemical reaction pathway under the presence of metal oxide (M–O) on the CNT surface is as follows:

\[
\text{NO}_2(g) + \text{O site} \rightarrow \text{NO}_3(\text{ad}) \tag{1}
\]

\[
\text{NO}_2(g) + \text{M site} \rightarrow \text{NO}(g) + \text{M–O} \tag{2}
\]
The sensitivity with SO2 gas was observed at high moisture level only. This also explains why reasonable recovery time constant is expected to decrease; this is indicated in the sketch of Fig. 5d (i).

(ii) At an intermediate humidity level, a possible chemical reaction pathway will be:

\[
\text{NO}_2(g) + \text{H}_2\text{O} \rightarrow \text{NO}_3(g) + \text{H}_2\text{O}
\]

(4)

Following reaction (4), HNO3 is produced, which will form C–O bonds on the CNT surface. This will enhance the reaction (1) and generate more NO3(ad). Another consequence of reaction (4) is further formation of NO3(ad) by following the chemical reaction (5). As a result, NO3 and NO2 coexist at intermediate moisture levels and NO2 becomes dominant with an increasing moisture level. Therefore, the recovery time constant increases due to the dominant NO3 that has a higher binding energy than NO2, this is indicated in the sketch of Fig. 5d (ii).

(iii) At a high humidity level such as 92%, metal oxides and C=O sites are deactivated by the abundant H2O molecules and therefore we expect simply that the CNT surface is covered by H2O molecules. In this case, NO2 is a dominant adsorption species again without further catalytic decomposition. Thus the recovery time constant is expected to decrease; this is indicated in the sketch of Fig. 5d (iii).

However, in the case of SO2, the response/recovery time had no such obvious tendency. This can be explained by the radical nature of NO2 compared to SO2. The highest occupied molecular orbital (HOMO) in NO2 is half-filled and appears to have bonding interactions with the valence and conduction bands of metal oxides.31 This induces the catalytic decomposition, SO2 which has fully occupied HOMO is stable by itself, making the decomposition difficult to realize. Our calculation shows that the binding energy of a SO2 molecule on the CNT surface is 0.05 eV from GGA, which is less than the 0.09 eV observed for a NO2 molecule. The binding energy of SO2 on H2O-covered CNT is 0.235 eV (GGA) and 0.439 eV (LDA), stronger than that on intrinsic CNT (Table 2). This also explains why reasonable sensitivity with SO2 gas was observed at high moisture level only.

### Conclusion

This study developed a new route to selectively detect NO2 and SO2 gas by simply introducing humidity. In the case of NO2, the device resistance decreased regardless of the humidity level, since it behaves like a p-type dopant. However, the device resistance increased upon SO2 exposure only at a high humidity level (92%), while SO2 was rather insensitive at a low humidity level. This different behavior is a consequence of different charge transfer direction between a SO2–H2O complex and a H2O–cluster upon a p-type CNT. Our density functional theory calculations by introducing p-type CNT provided consistent data with experimental results. To date, this simple method of introducing moisture provides a possibility to selectively detect NO2 and SO2 under ambient conditions for the first time.

### Acknowledgements

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### Notes and references

29 At a high humidity level, an additional conduction channel of a water layer might be formed on the surface of the CNT. However, the conductivity through the liquid channel is still much smaller than that of CNTs. Therefore, conduction through a liquid channel should be negligible. See paper *J. Am. Chem. Phys.*, 2002, 124, 9058–9059.