



# Enhanced gas sensing in pristine carbon nanotubes under continuous ultraviolet light illumination

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The advance of nanomaterials has opened new opportunities to develop ever more sensitive sensors owing to their high surface-to-volume ratio. However, it is challenging to achieve intrinsic sensitivities of nanomaterials for ultra-low level detections due to their vulnerability against contaminations. Here we show that despite considerable achievements in the last decade, continuous *in situ* cleaning of carbon nanotubes with ultraviolet light during gas sensing can still dramatically enhance their performance. For instance in nitric oxide detection, while sensitivity in air is improved two orders of magnitude, under controlled environment it reaches a detection limit of 590 parts-per-quadrillion (ppq) at room temperature. Furthermore, aiming for practical applications we illustrate how to address gas selectivity by introducing a gate bias. The concept of continuous *in situ* cleaning not only reveals the tremendous sensing potential of pristine carbon nanotubes but also more importantly it can be applied to other nanostructures.

Nanomaterials are known to be extremely sensitive to their surrounding environment<sup>1-3</sup>. Accordingly intense research is underway to develop new sensing materials and devices for a wide range of areas including environmental pollution, space exploration, homeland security, biology and medicine. Single-walled carbon nanotubes (SWNTs) have been regarded as one of the most exciting materials due to their high surface-to-volume ratio and unique electronic structure<sup>4-6</sup>. Ironically the ultrahigh sensitivity of SWNTs is easily compromised by various unintentional contaminants from the device fabrication process as well as the ambient environment. Indeed, here we show that despite the significant progress that has been made in the last decade, we are still far from what a pristine SWNT based sensor can truly offer for detection of gases such as NO, NO<sub>2</sub> and NH<sub>3</sub>. It is well known that nitrogen oxides including NO and NO<sub>2</sub> play an important role in the chemistry of our atmosphere. NH<sub>3</sub> is another toxic gas for proper safety monitoring. Since gases of interest even at very low concentrations can have significant impact on the environment, therefore, the capability to detect extremely low levels of these species becomes important. Among various explored nanotube sensors<sup>1-3,7,8</sup>, response based on conductance change is one of the easiest to implement. Because pristine SWNTs are speculated to be relatively limited in sensor performance, much effort has been focused on functionalized nanotubes<sup>9-14</sup>. The detection limit (DL) reported for each of these gases using carbon nanotubes as the electrical sensing material spreads over several orders of magnitude. Multiple factors have been discussed in the literature that includes the quality of tubes, multi-walled versus single-walled, the sensor catchment area, metal contacts, method of device fabrication as well as the detection environment. There is another commonly overlooked factor that we will examine in the present study, which is the surface condition of the sensing material, although the performance volatility of SWNT based devices due to interactions with ambient species is well recognized. The extreme sensitivity of the electronic properties of SWNTs to oxygen was reported in the literature<sup>15</sup>. Our previous study showed that the variation of oxygen in the ambient could lead to reversible continuous transformations of a SWNT from p-type to n-type, accompanied with significant changes of conductance<sup>16</sup>. Furthermore, water vapor could also interact with carbon nanotubes<sup>17</sup>. Fortunately, these contaminants can be removed by methods such as Ultraviolet (UV) light illumination. UV light induced molecular desorption from SWNTs had been reported previously where the desorption mechanism was attributed to plasmon excitation of nanotubes<sup>18</sup>. Plasmon induced photodesorption had also been observed before on metal surfaces<sup>19</sup>. In this study we will unveil the ultrasensitivity of pristine carbon nanotubes and show that applying continuous *in situ* UV light illumination during gas detection can enhance a SWNT-sensor's performance by orders of magnitude under otherwise identical sensing conditions.

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## Results

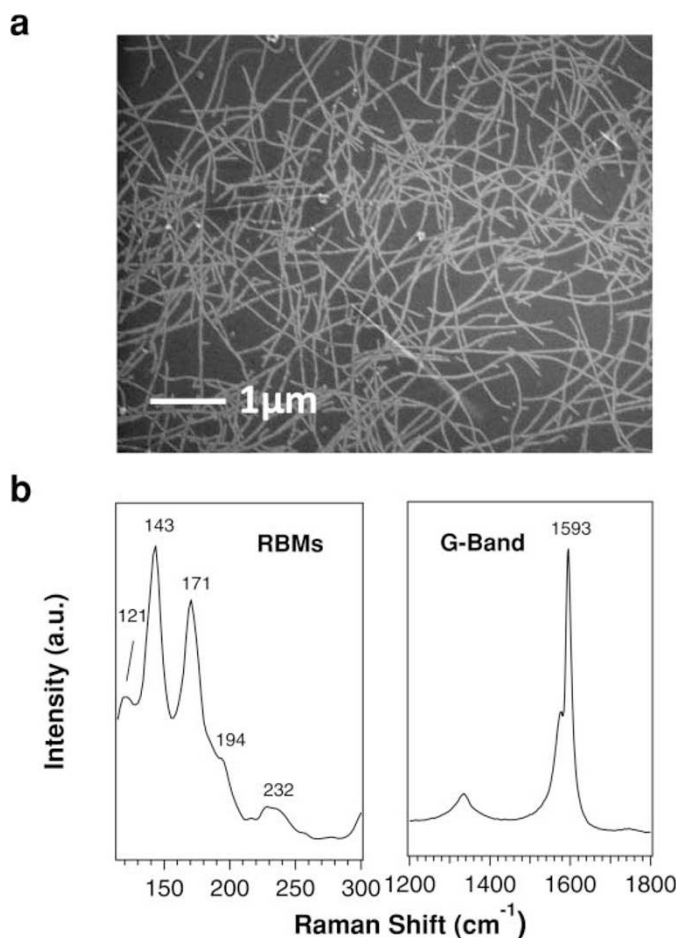
All SWNTs used in this study were obtained from direct growth by chemical vapor deposition (CVD) using iron nanocatalysts supported on a SiO<sub>2</sub>/Si substrate. Scanning electron microscopy (SEM) image shows that the nanotube film has a uniformly distributed thin layer of tubes of a few microns in length (Fig. 1). Typical Raman spectrum of our SWNT films taken with 532 nm laser excitation and averaged from 50 micron-size spots through an automatic mapping stage is shown in Fig. 1b. The radial breathing mode (RBM) peak frequencies ( $\omega_{\text{RBM}}$ ) indicate that the tubes are single-walled with diameters ( $D$ ) mostly in the range of 1–2 nm ( $D \sim 234 \text{ cm}^{-1}\text{nm}/\omega_{\text{RBM}}$ )<sup>20</sup>. More details of sample synthesis and characterization were published previously<sup>21</sup> (see Methods section for device fabrication details).

First we investigated the effect of UV light illumination on a SWNT sensor's performance in dry air (Fig. 2). The sensor's response was recorded as the change of conductance normalized by the initial conductance commonly defined as the sensitivity. After the electrical conductance of the sample had been stabilized, we exposed the device to 200 parts-per-million (ppm) of NO. Without UV light, the sensor had very big ( $\sim 0.6$  or 60%) and fast response ( $\sim 10$  seconds) to the first NO exposure, while subsequent exposures had much smaller ( $\sim 7\%$ ) but quite reproducible response. We attribute the smaller response at later cycles to partial device recovery which appears to have many active sites still occupied by pre-adsorbed NO molecules. The assumption has been justified in Fig. 2b where the application of UV light illumination during air flushing not only dramatically reduced the recovery time down to a few seconds but also enhanced the signal 5 times, i.e., from  $\sim 7\%$  to  $\sim 36\%$ . This observation prompted us to

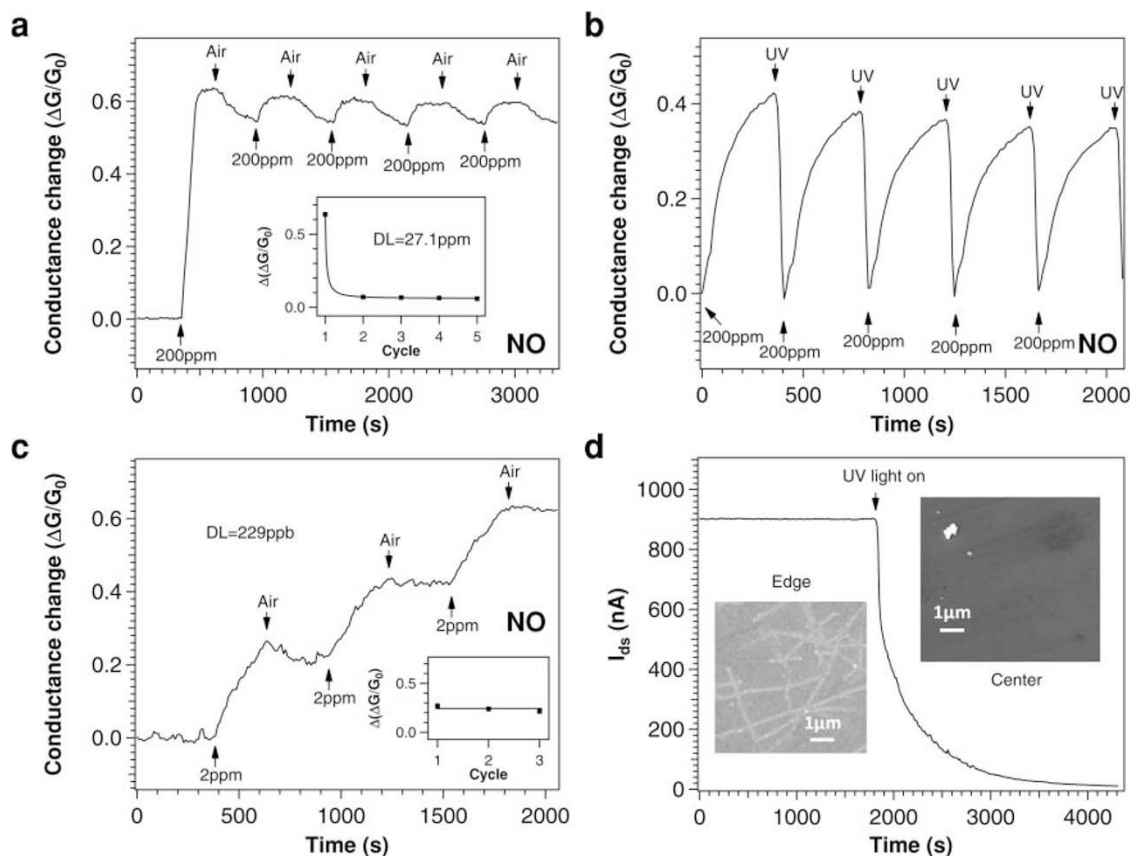
investigate the idea of *in situ* device cleaning during the process of gas detection. As expected, NO sensing with continuous *in situ* UV light illumination shows much improved sensitivity, where estimated DL improves about 2 orders of magnitude from 27.1 ppm down to 229 ppb (Fig. 2c). Although this sensitivity enhancement is astonishing considering that the experiment was carried out in a practical setting suitable for many sensor applications, unfortunately we found that the sensor would eventually lose its performance. The life time of the sensor was observed to depend on the thickness of the SWNT film, e.g., thicker SWNT films appeared to last longer. Electrical study shows that the SWNT sensor continuously loses conductance under UV light illumination. SEM images taken after  $\sim 1$  hour of illumination indicates that the center of the film has no SWNTs left while the edge of the sample which is further away from the light has much lowered density of SWNTs than before the UV light was applied (Fig. 2d). Since the center of the film receives the strongest intensity because of its closer distance to the light source, this observation suggests that SWNTs are probably gradually removed by the UV light irradiation. This result is not very surprising considering UV light induced ozone formation in an oxygen rich environment and a potential ozone-SWNT chemical reaction<sup>22</sup>, yet the detailed mechanism of nanotube removal under UV light requires further investigation and is outside the scope of the current study.

In order to prevent damage to the active sensing material, i.e., SWNTs, next we studied the effect of UV light illumination in an inert environment. The effect is clearly illustrated by a drastic 10 fold current change on a pre-cleaned SWNT film with UV light placed in flowing N<sub>2</sub>, while it is  $\sim 200$  fold compared to when the sample was initially in air (Fig. 3). The linear I-V relationship points to good ohmic contact between nanotubes and their metal contacts. Independent of the presence of gas analytes, no hysteresis had been observed on the device throughout the current study. In addition, the SWNT sensor was found to have very stable baseline conductance even after multiple cycles of UV light illumination, which suggests that there is no noticeable damage done to nanotubes by the UV light in a controlled inert environment. Because the decrease of conductance clearly excludes the possibility of UV light induced photoelectrical effect, the apparent explanation is that SWNTs are so sensitive to their environment that any minor imperfection of the sample sealing system or very low level of interactive impurities present in a 99.9999% pure inert carrier gas (N<sub>2</sub> or Ar) will be enough to dope nanotubes and make their conductance increase after the UV light is turned off. These results further point to the intrinsic ultrasensitivity of pristine SWNTs and the crucial role of surface cleanliness prior to molecular sensing. The effect of continuous *in situ* UV light illumination on a SWNT sensor's performance is further demonstrated below for the detections of NO, NO<sub>2</sub> and NH<sub>3</sub> in an inert carrier gas of atmospheric pressure at room temperature. Due to ultra-low level gas detections in the present work, extra caution had been paid regarding all aspects of experiments (see Methods).

The electrical response of a SWNT film to NO molecules in flowing N<sub>2</sub> is shown in Fig. 4. Before gas sensing, the sensor was continuously pumped for 1 day with a mechanical pump (the vacuum level was in the millitorr range), then annealed at 100°C while pumping for another day, and finally the device was put under continuous UV light illumination in flowing N<sub>2</sub> until the sensor had reached a flat baseline conductance of less than 1% drift over a 5-minute period. This step was found to be critical in order to obtain the best gas sensitivity. The NO detection was then done with *in situ* UV light kept on throughout the experiment. We have observed a  $\sim 30\%$  conductance increase at 10 parts-per-trillion (ppt) of NO exposure. A linear response is observed with concentrations up to 50 ppt. Further increase of NO level leads to a non-linear behavior, presumably indicating that a different mechanism of gas adsorption has occurred<sup>23</sup>. DL can be derived from the noise of the baseline and



**Figure 1** | Sample characterizations. Typical (a) SEM image and (b) Raman spectrum of the SWNT films used for gas sensing studies.

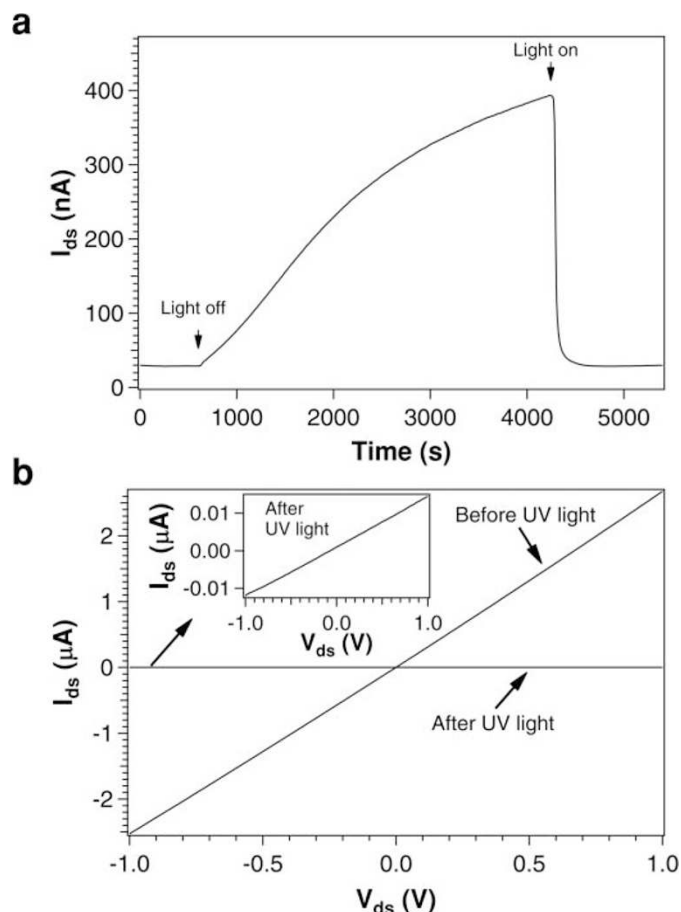


**Figure 2 | Comparison of NO gas sensing in air.** (a) Relative change of conductance ( $\Delta G/G_0$ ) versus time recorded with repeated 200 ppm of NO exposures. The inset shows the amplitude of signal at each cycle. DL is estimated to be 27.1 ppm. (b) Same experiment but with UV light illumination added during air flushing. (c) Same experiment but at 2 ppm of NO exposures under continuous *in situ* UV light illumination. The experiment was done after the conductance had been stabilized under UV light. The inset shows the sensor response at each cycle. DL is estimated to be 229 ppb. (d) Current versus time recorded before and after UV light was shed on the SWNT film. The device gradually loses conductance after  $\sim 1$  hour of UV light illumination, where SEM images taken from the edge and center regions of the film are shown in the lower left and upper right panels, respectively.

the slope of  $\Delta(\Delta G/G_0)$  versus concentration<sup>24</sup>. A noise value of  $3.54 \times 10^{-3}$  and a slope of 0.018 thus render DL = 590 ppq (see Methods). For comparison, tin oxide coated multi-walled carbon nanotubes (MWNTs) detected NO down to 2 parts-per-million (ppm) in air<sup>25</sup>. SWNTs wrapped with a 3,4-diaminophenyl-functionalized dextran exhibited selectivity for *in vivo* detection of NO<sup>10</sup>, while polymer coated SWNTs showed DL of 5 parts-per-billion (ppb) compared to 300 ppb for bare SWNTs in an inert atmosphere<sup>11</sup>. Compared to those results and other reports that we are aware of for NO detection under comparable detection environment, the sensitivity of pristine SWNTs as shown here is at least 4 orders of magnitude better. This ultrasensitivity is a strong support of the great potential of SWNTs in sensor applications which has been speculated for many years now. To further verify the reliability and reproducibility of the obtained results we recorded the sensor response by alternating between pure N<sub>2</sub> and 10 ppt of NO in N<sub>2</sub> (Fig. 4b). Very consistent result with a signal around 30% is observed. Furthermore, the sensor shows fast response and significant recovery in the scale of minutes. Note that the baselines in both panels of Fig. 4 are flat before NO exposures, which indicates that a stable dynamic balance has been established between adsorption and UV light induced molecular desorption. However, the baselines exhibit up drift with NO exposures which we attribute to incomplete device recovery since we have restricted both exposure time and recovery time to 5 minutes for all of our gas sensing experiments (unless otherwise marked) in order to have fair comparison of DLs. Moreover, we consider 5 minutes of sensing or recovery to be reasonable for a practical sensor, a number which is also in line with other published works.

Remarkably, the sensor shows very repeatable response even at such a partially recovered state (Fig. 4b), a feature certainly desirable for a sensor.

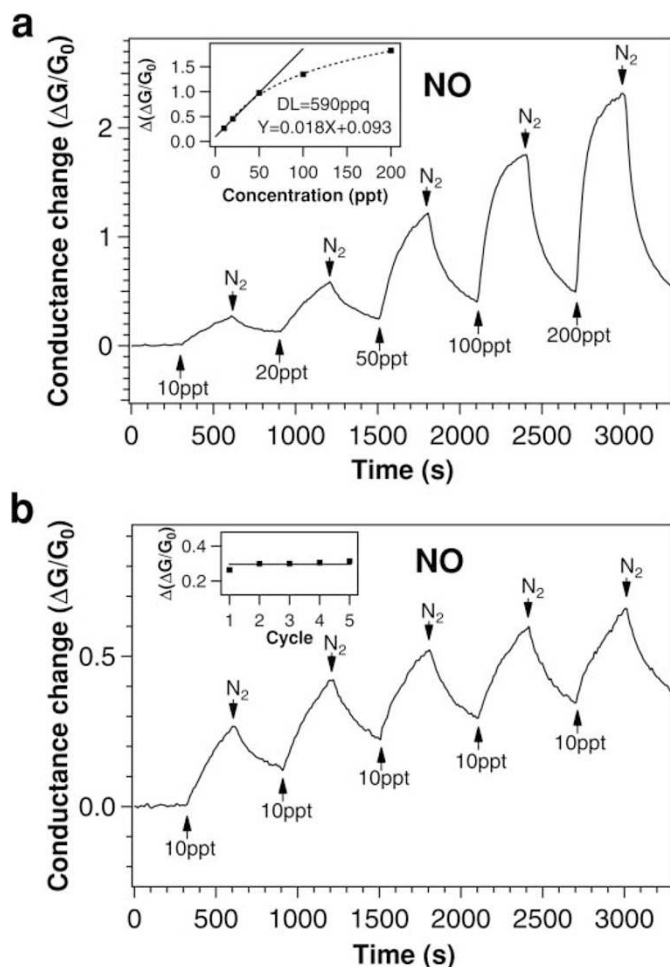
Next we used the same device to investigate the sensing performance of NO<sub>2</sub> molecules under analogical sensor preparation and detection conditions (Fig. 5). Similar to NO detection, a linear response is observed at low NO<sub>2</sub> concentrations. The conductance is observed to increase 25% with 40 ppt of NO<sub>2</sub> exposure in 5 min. The DL is estimated to be 1.51 ppt. As a comparison, an individual semiconducting-SWNT (S-SWNT) demonstrated remarkable sensitivity to 2 ppm of NO<sub>2</sub> in Ar or air<sup>1</sup>, and a DL of 44 ppb was achieved using SWNT-based chemiresistor in ultrapure N<sub>2</sub><sup>24</sup>. DLs down to ppb level had been reported on pristine carbon nanotubes<sup>26,27</sup> as well as gold functionalized SWNTs<sup>12</sup>. NO<sub>2</sub> detection as low as 100 ppt was reported on polyethyleneimine coated SWNTs<sup>13</sup>. PPB level detection of NO<sub>2</sub> was also reported on other nanomaterials under an inert atmosphere<sup>28,29</sup>. Compared with those results, about 2 orders of magnitude better NO<sub>2</sub> detection limit has been obtained in the current work due to dynamic surface cleaning induced by the application of continuous *in situ* UV light illumination. In analogy to the detection of NO molecules, repeated sensings at 40 ppt of NO<sub>2</sub> exposure also show good reversibility (Fig. 5b). It is noticeable that the best detection levels of NO<sub>2</sub> and NO that we have achieved under analogous sensing conditions but without *in situ* UV light illumination are also in the ppb range similar to those lower limits presented in the literature, where the gas sensitivities are about 3 and 4 orders of magnitude worse than what are reported here for the detections of NO<sub>2</sub> and NO, respectively. This comparative study of UV light application



**Figure 3** | Effect of UV light on the electrical characteristics of the SWNT film. (a) Device response to UV light under flowing  $N_2$ . (b) I–V characteristics before and after UV light illumination. The data before UV light illumination was taken in air, while that after UV light was recorded under UV light illumination in an inert atmosphere after thorough cleaning of the nanotubes. The inset shows the curve plotted on an enlarged scale.

clearly illustrates the significant impact of continuous *in situ* cleaning on sensor performance.

Interestingly, the change of conductance to  $NH_3$  exposures reverses its direction, i.e., from decrease of conductance to eventually increase of conductance upon applying *in situ* UV light illumination on the sensor (Fig. 6). This change of sign is attributed to the initial conducting state of the sensor. Carbon nanotubes were found to be p-type in air<sup>15</sup>. In contrast to NO and  $NO_2$  which are electron acceptors,  $NH_3$  is an electron donor. Because of a lone electron pair that can be donated, negative charge transfer from  $NH_3$  adsorption will cancel the existing p-type carriers of an air doped nanotube and thus make its conductance to decrease. After applying UV light illumination, Fig. 6b indicates that the UV light has efficiently removed the p-type dopants so as to shift the Fermi level of a nanotube closer to the carrier neutrality point. Therefore, any charge transfer from subsequent  $NH_3$  adsorption will only increase its conductance by adding free electrons. It is remarkable that simply applying *in situ* UV light illumination improves the DL of  $NH_3$  under otherwise identical sensing conditions from 5.67 ppm to 27.8 ppt, i.e., 5 orders of magnitude sensitivity improvement in this case. There have been significant progresses on ultra-low level detection of  $NH_3$  with both SWNTs and MWNTs<sup>1,7–9,14,24,27</sup>. For example, SWNT and MWNT coated sensors had been found to have similar sensitivity toward  $NH_3$  at concentrations ranging from 100 to 400 ppm<sup>7</sup>. Detection

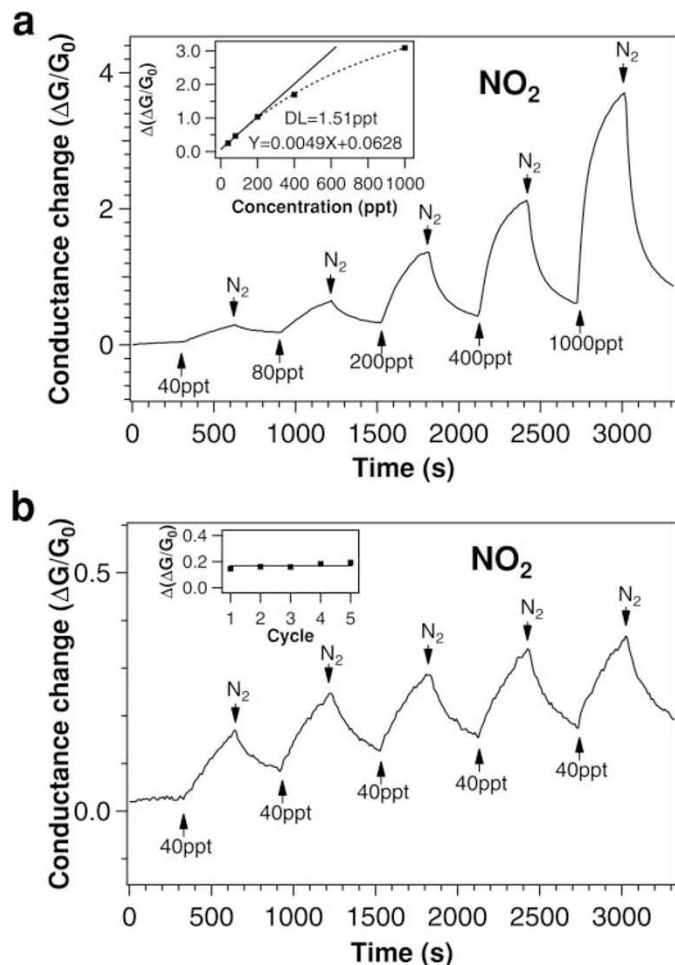


**Figure 4** | Sensor response to NO molecules under *in situ* UV light illumination. (a) Conductance change recorded with NO exposures ranging from 10 to 200 ppt. The inset shows sensor response with concentration. Squares are experimental data, and dashed line is a guide to the eye. In the linear-fit equation, Y and X denote  $\Delta(\Delta G/G_0)$  and NO concentration, respectively. DL is estimated to be 590 ppq. (b) Reproducibility of sensor response at 10 ppt of NO exposure. The inset shows the amplitude of response at each cycle. The experiment was done after device recovery.

of  $NH_3$  at 5 ppm had been achieved with pristine SWNTs in purified air<sup>27</sup> as well as polymer coated SWNTs in  $N_2$ <sup>9</sup>, while a DL of 262 ppb had been derived from a SWNT chemiresistor in  $N_2$ <sup>24</sup>. DL as low as 50 ppb diluted in Ar had been reported on functionalized SWNTs<sup>14</sup>. Compared with those results, our pristine SWNT based sensor has at least 3 orders of magnitude better sensitivity owing to continuous surface cleaning. In addition, the sensor was fully recoverable, and we had not observed any obvious device degradation for these 3 gases (NO,  $NO_2$  and  $NH_3$ ) studied here in an inert atmosphere.

## Discussion

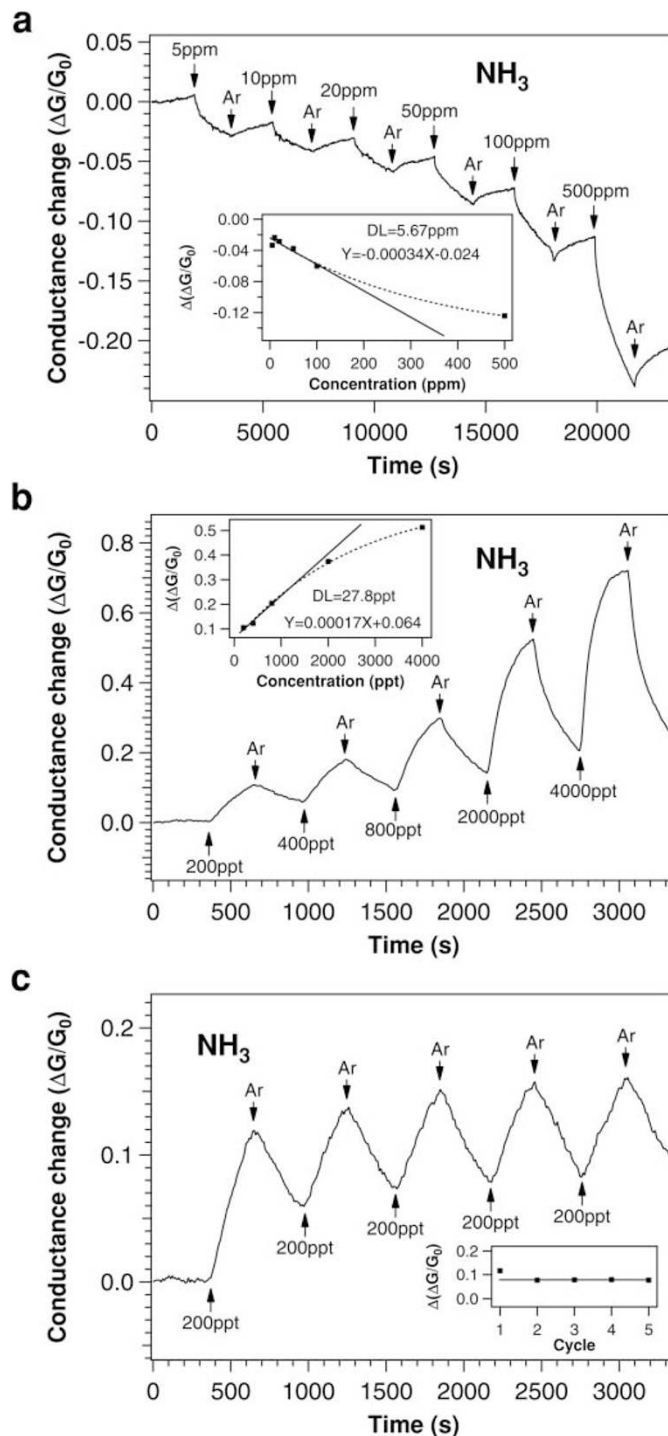
Sensitivity is only one aspect of sensor performance, while selectivity is also required for a practical sensor. As an attempt to address this issue, we have studied the sensitivity dependence of an individual S-SWNT based field effect transistor (FET) device on an applied electrical gate voltage. Importantly, this feature can open the prospect for selective detection. Although the concept is not completely new<sup>1</sup>, here we demonstrate how this can be done at very low level of gas detection (Fig. 7). The basic idea is that you can set up the initial conducting state of an individual S-SWNT through an external gate



**Figure 5** |  $\text{NO}_2$  sensing under *in situ* UV light illumination.

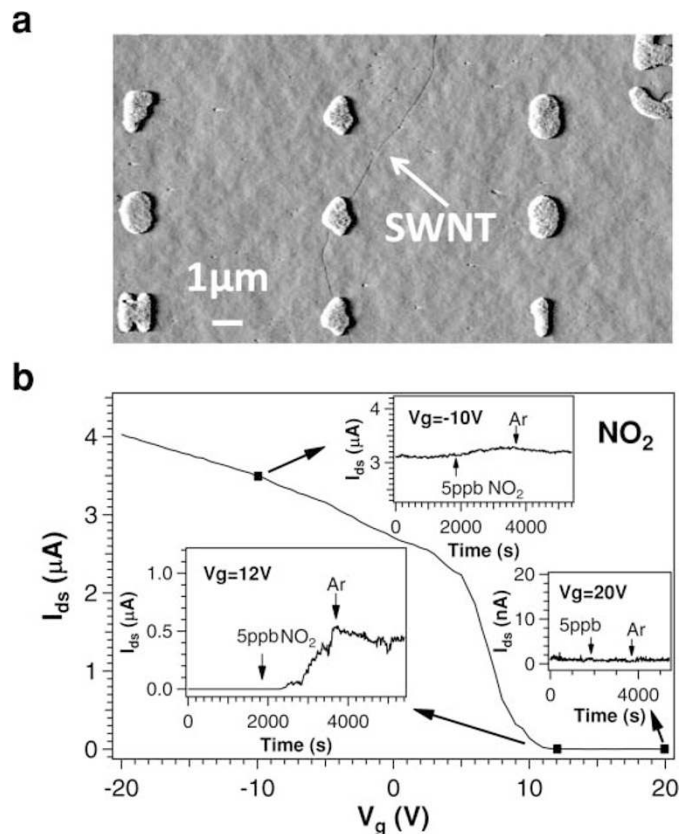
(a) Conductance change versus time recorded with  $\text{NO}_2$  exposures ranging from 40 to 1000 ppt. The inset shows sensor response with concentration. Squares are experimental data, and dashed line is a guide to the eye. In the linear-fit equation, Y and X denote  $\Delta(\Delta G/G_0)$  and  $\text{NO}_2$  concentration, respectively. DL is estimated to be 1.51 ppt. (b) Reproducibility of sensor response at 40 ppt of  $\text{NO}_2$  exposure. The experiment was done after device recovery.

bias which in principle, depending on its gate dependent I-V characteristics profile, determines whether and how sensitive the sensor will respond to an analyte gas. An individual S-SWNT based device was fabricated in FET geometry by e-beam lithography for this purpose<sup>16</sup>, where the heavily doped Si substrate was used as the back gate. Due to the vulnerability of the device, no UV light had been used for this study, while we kept all other conditions (e.g., gas dilution and device cleaning) in analogy to the case of a SWNT film. The utilized nanotube appears to be p-type before molecular sensing (Fig. 7b). Careful device preparation enabled us to use 5 ppb of  $\text{NO}_2$  as the target gas. As an electron acceptor, the adsorption of  $\text{NO}_2$  is equivalent to applying a negative chemical gate voltage. According to the  $I_{ds}$  versus  $V_g$  curve, we expect to see drastically different responses from this device when we apply the following gate voltages: a)  $V_g = -10$  V. We predict the sensor to have weak response since the  $I_{ds}$  versus  $V_g$  profile has a small slope ( $|dI_{ds}/dV_g| < 0.1 \mu\text{S}$ ) at this gate bias. (b)  $V_g = 12$  V. Because this  $V_g$  is on the right-hand side just before the threshold of a sharp slope ( $|dI_{ds}/dV_g| > 0.4 \mu\text{S}$ ), we should see large response due to negative chemical gate effect of  $\text{NO}_2$  adsorption. (c)  $V_g = 20$  V. No obvious response is expected since  $|dI_{ds}/dV_g| \sim 0$  at this gate voltage. The experimental results as shown



**Figure 6** | Comparison of sensor responses to  $\text{NH}_3$ . (a) Conductance change versus time recorded with the sensor exposed to increasing  $\text{NH}_3$  concentrations without UV light illumination. The inset shows sensor response with concentration. DL is estimated to be 5.67 ppm. (b) Sensor response under *in situ* UV light illumination. DL is estimated to be 27.8 ppt. (c) Reproducibility of the sensor response at 200 ppt of  $\text{NH}_3$  exposures under *in situ* UV light illumination. Successive experiments were done after the device had been recovered.

in the insets of Fig. 7b agree pretty well with this analysis, e.g., we have observed very weak response at  $V_g = -10$  V, over 300 fold current increase at  $V_g = 12$  V and no response at  $V_g = 20$  V. This experiment clearly demonstrates that, by setting up the initial conducting state via applying an electrical gate bias, one can tune and maximize



**Figure 7 | Electrical gate effect on the sensitivity of an individual S-SWNT.** (a) AFM image of the SWNT before device fabrication. Numbers and characters were used as a coordinate for e-beam lithography. The nanotube diameter is  $\sim 1.4$  nm. (b)  $I_{ds}$  dependence on gate voltage  $V_g$ , where  $V_{ds} = 1$  V. Squares indicate 3 different gate voltages applied to sense 5 ppb of  $\text{NO}_2$  whose results are shown on the insets. Successive experiments at each gate bias were carried out after the device had been recovered.

the sensitivity of a SWNT-based sensor. Because opposite electron affinities will move the  $I_{ds}$  versus  $V_g$  profile in different directions, this effect can be thoughtfully utilized for selective detection between electron donor and acceptor gas species, but to be more specific will be challenging although possible with well calibrated sensitivity for each gas. As can be seen from this discussion, gate bias dependent gas selectivity seems more feasible from individual S-SWNT based sensor than that based on a film with wide nanotube chirality distribution since where metallic tubes don't have significant response to a gate and the effect from semiconducting tubes will be mostly smeared out due to averaging from tubes of varied electronic transition energies. However, it becomes almost equally promising to address selectivity from a film based sensor after recent success on selective growth of semiconducting SWNTs with narrow chirality distribution<sup>30,31</sup>.

In conclusion we have demonstrated the effect of continuous *in situ* UV light illumination on a SWNT sensor's performance. The comparative studies unambiguously support that UV light induced surface cleaning should be responsible for SWNT's ultrahigh sensitivity reported here. The effect of *in situ* UV light illumination is presumably reflected by: (1) Affecting the background conductance; (2) Cleaning the nanotube surface so that it is more accessible for gas adsorption; (3) Dynamically removing all adsorbed gas species from nanotubes. The first aspect shouldn't affect a sensor's performance dramatically. The second one has the potential to drastically enhance

a sensor's sensitivity, while the third one will only reduce it. It is thus intuitive to assume that optimized UV light illumination can probably further improve a sensor's performance. It seems logic to extend the idea of continuous *in situ* cleaning to other sensing materials where a material-specific method of cleaning may be required. Although UV light induced loss/degradation of active sensing materials hinders long term usage of UV light on SWNTs in air, yet it could still be utilized for fast gas detection at much enhanced sensitivity (2 orders of magnitude in this study). Certainly application of *in situ* cleaning is more powerful in a controlled environment where either the method of cleaning doesn't cause any damage to the sensing material or by removing any problematic species with special filters as well as other technologies, e.g., here we have demonstrated a DL down to ppq level for  $\text{NO}$  detection in  $\text{N}_2$ . Because of its simplicity we believe the concept of continuous *in situ* cleaning can be deployed in existing sensor platforms which has great promise to significantly improve their performance. In the meantime the combination of observed ultrasensitivity from pristine SWNTs with potentially-achievable selectivity can be fully utilized to detect a range of substances that have a significant impact on the betterment of humanity. Although many challenges remain to be addressed, with increased interest and the development of related technologies, SWNTs are still one of the most promising candidates for developing the next generation of ultrasensitive sensors.

## Methods

**Device fabrication.** All SWNT films were as-grown on Si substrates ( $\text{SiO}_2$  thickness 400 nm) by CVD method without any post-synthesis chemical treatment. Typical SEM image of the SWNT network is shown in Fig. 1. Two electrical pads (Au/Ti with thicknesses of 120 nm/30 nm) were applied 2 mm apart on top of a SWNT film through vacuum thermal evaporation. The device was then annealed in a CVD chamber at  $300^\circ\text{C}$  for 3 hours under flowing Ar. For gas sensing in air, two tungsten needle probes (radius: 100  $\mu\text{m}$ ) were applied  $\sim 5$  mm apart on top of the SWNT film as contacts. For individual SWNT based FETs, see reference 16 about the details of device fabrication.

**Electrical conductance measurements.** Electrical measurements were done on a customized flowing cell that has electrical feedthrough connections for both temperature and electrical measurements. The current was monitored with a Keithley 4200-SCS instrument at atmospheric pressure and  $25^\circ\text{C}$  on a sample stage where the temperature was controlled through a temperature controller equipped with automatic resistive heating and liquid  $\text{N}_2$  cooling assemblies (temperature stability better than  $0.1^\circ\text{C}$ ). For experiments involving UV light illumination, a pencil light ( $\lambda = 253.7$  nm, and estimated  $1 \sim 1.7$  mW/cm<sup>2</sup>) was applied  $\sim 5$  mm above the center of the SWNT film through a quartz window.

**Gas sensing experiments.** For gas sensing in air, the carrier gas was from compressed dry air with a dew point of  $-70^\circ\text{C}$  through a desiccant dryer. Certified 1000 ppm mixture gas of  $\text{NO}$  in  $\text{N}_2$  was used for dilution. For gas sensing in an inert atmosphere, research-grade (99.9999% purity)  $\text{N}_2$  or Ar was used as the carrier gas. Certified 50 (200) ppb mixture gas of  $\text{NO}$  ( $\text{NO}_2$ ) in  $\text{N}_2$  was used for dilution, where the concentration was confirmed by chemiluminescence measurements at an error of 5%. For  $\text{NH}_3$  detection, certified 1 ppm of  $\text{NH}_3$  in Ar was used, where the concentration was determined by Gravimetric method at 10% uncertainty. A total flow rate of 1000 ml/min was used for all gas sensing experiments. In order to minimize experimental errors, gas dilution was restricted to a simple one step mixing of carrier and analyte gases controlled by two digital mass flow controllers (MFCs) (Brooks Model # 5850S) with a full scale of 2000 ml/min and 20 ml/min, respectively. Both MFCs were calibrated using a multipoint calibration curve with gas measurement equipment (DHI) accurate to 0.01 ml/min. The flow uncertainty of these MFCs is 0.7% of the flow rate or 0.2% of the full scale, whichever is greater. Based on the accuracy of MFCs, flow rates and certified gas concentrations, assuming these errors are uncorrelated, simple error propagation calculation shows that the error will be  $\sim 21\%$  at 10 ppt of  $\text{NO}$  detection. Therefore, a DL of 590 ppq for  $\text{NO}$  detection has an error of  $\pm 120$  ppq. Similar calculation shows that the DLs would be  $1.51 \pm 0.32$  ppt and  $27.8 \pm 6.2$  ppt for  $\text{NO}_2$  and  $\text{NH}_3$  detections, respectively.

**Detection limit (DL) estimation.** DL can be derived from the signal to noise ( $s/n$ ) ratio. Both  $s/n = 1$  and  $s/n = 3$  have been commonly used in the literature. We have used  $s/n = 3$  for all DL calculations presented here. The noise refers to the root-mean-square (rms) noise of the baseline. To calculate the rms noise, we have used a third-order polynomial equation to fit the data and then the noise is computed by comparing the experimental data with the fitted curve. For gas detection at a constant analyte concentration (Fig. 2), DL is calculated by  $\text{DL} = 3 \text{ Concentration}/(s/n)$ , where a median value of  $s/n$  is used. For gas detection with varied analyte concentrations (Fig. 4–6),  $\text{DL} = 3 \text{ rms/slope}$ , where the slope refers to a line fit to the signal



$\Delta(\Delta G/G_0)$  versus concentration in the sensor's quasi-linear response region.

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## Author contributions

G.C. designed and carried out experiments, and analyzed the data. T.M.P. and E.M.P. synthesized nanotubes and prepared devices. A.R.H. initiated and supervised the research. G.C. and A.R.H. wrote the manuscript.

## Additional information

**Competing financial interests:** The authors declare no competing financial interests.

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