

Sub-ppt gas detection with pristine graphene

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Sub-ppt gas detection with pristine graphene

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Graphene is widely regarded as one of the most promising materials for sensor applications. Here, we demonstrate that a pristine graphene can detect gas molecules at extremely low concentrations with detection limits as low as 158 parts-per-quadrillion (ppq) for a range of gas molecules at room temperature. The unprecedented sensitivity was achieved by applying our recently developed concept of continuous *in situ* cleaning of the sensing material with ultraviolet light. The simplicity of the concept, together with graphene's flexibility to be used on various platforms, is expected to intrigue more investigations to develop ever more sensitive sensors. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4742327>]

Sensing ultra-low concentration of chemical and biological molecules becomes more and more important for today's modern world.^{1–3} The discovery of graphene has opened unprecedented opportunity that promises ultrasensitive and ultrafast electronic sensors due to graphene's high surface-to-volume ratio, low electrical noise, and exceptional transport properties associated with its unique high crystalline single-atom thick two-dimensional structure.^{4,5} Our recent studies showed that continuous *in situ* cleaning of a carbon nanotube's (CNT) surface could dramatically improve its gas sensitivity.⁶ Here by applying continuous *in situ* ultraviolet (UV) light illumination during the course of detection, we demonstrate that a simple two-terminal graphene based sensor can achieve a detection limit (DL) as low as 158 ppq to nitric oxide (NO) molecules at room temperature. This sensitivity is even $\sim 300\%$ better than what we had achieved on CNTs under analogical conditions.⁶ The ultrasensitivity of pristine graphene was further confirmed by the low level detection of other common gas species including NO₂, NH₃, N₂O, O₂, SO₂, CO₂, and H₂O.

Among explored designs with different sensing mechanisms, sensors based on conductance/resistance change as the output are the easiest to build, test, and calibrate. The graphene sample used in this work was synthesized by chemical vapor deposition.^{7,8} The detailed synthesis conditions,⁹ as well as how gas sensing experiments were done in a controlled environment,⁶ had been published previously (see the supplemental material).³⁷ Fig. 1(a) shows a Raman spectrum averaged from 50 different spots of the sample with 532 nm laser excitation (laser spot size $\sim 1 \mu\text{m}$ on the sample). The data were taken with minimum power in order to avoid laser heating. The observation of weak D-band ($\sim 1330 \text{ cm}^{-1}$) and D'-band ($\sim 1620 \text{ cm}^{-1}$) indicates high quality of the sample. The 2D to G peak ratio and the linewidth of 2D peak suggest that our sensor is mainly composed of a monolayer graphene.^{10,11} Typical current versus voltage characteristics of the device is shown in Fig. 1(b). Linear ohmic I-V relationship had been observed throughout the present study without obvious hysteresis for any of the gas sensing experiments. The effect of UV light illumination on graphene under flow-

ing N₂ is shown in Fig. 1(c). The sensor response, i.e., $\sim 10\%$ of conductance change, was very reproducible with UV light on and off. Analogical response had been observed when the graphene was in vacuum ($\sim 10^{-3}$ Torr). Similar to the case of CNTs, we attribute the observed phenomena to graphene's ultrasensitivity to potential contaminations from the surrounding environment that would dope graphene and make its conductance increase after the UV light was turned off. The origin of contaminations could be extremely low level of interfering impurities in a 99.9999% pure N₂ carrier gas or that leaked into the sensor chamber due to imperfection of the device sealing system. Either way the effect seems to be able to be reversibly removed by the UV light illumination. In order to investigate the intrinsic sensing potential of graphene, except otherwise marked, in the present study, all sensing experiments had been performed under an inert atmosphere (flowing Ar or N₂) with continuous *in situ* UV light illumination in order to dynamically "clean" the graphene surface during the course of detection.

Fig. 2 shows the electrical response of graphene to NO molecules. The DL is estimated to be 158 ppq with a signal-to-noise ratio of 3 (see the supplemental material).³⁷ This result demonstrates the feasibility of a pristine graphene-based sensor capable of detecting beyond parts-per-trillion (ppt) concentration of a gas molecule; an amazing level even surpassed the capability of a specially trained dog that can detect gas molecules in the ppt range. To further verify this super high sensitivity as well as the reliability of the obtained results, we recorded the sensor response by cycling between pure N₂ and the mixture of 10 ppt NO in N₂ (Fig. 2 inset). Very reproducible result with a signal of ~ 0.014 or 1.4% was observed. Furthermore, the sensor shows fast response and 80% of recovery on average in a few minutes. Due to the importance of NO gas in environmental pollution and more recently recognized as a signaling molecule that involves in many biological functions and cellular processes, there has been much interest to develop better NO sensors with graphene, where current state-of-the-art results achieved are reported to be in the ppb range.¹²

Similar sensing curve had been observed for NO₂ molecules in a N₂ flow (Fig. 3). The conductance increased $\sim 1\%$ with 40 ppt of NO₂ exposure in 5 min. The DL is estimated to be 2.06 ppt. In comparison, several groups had achieved a

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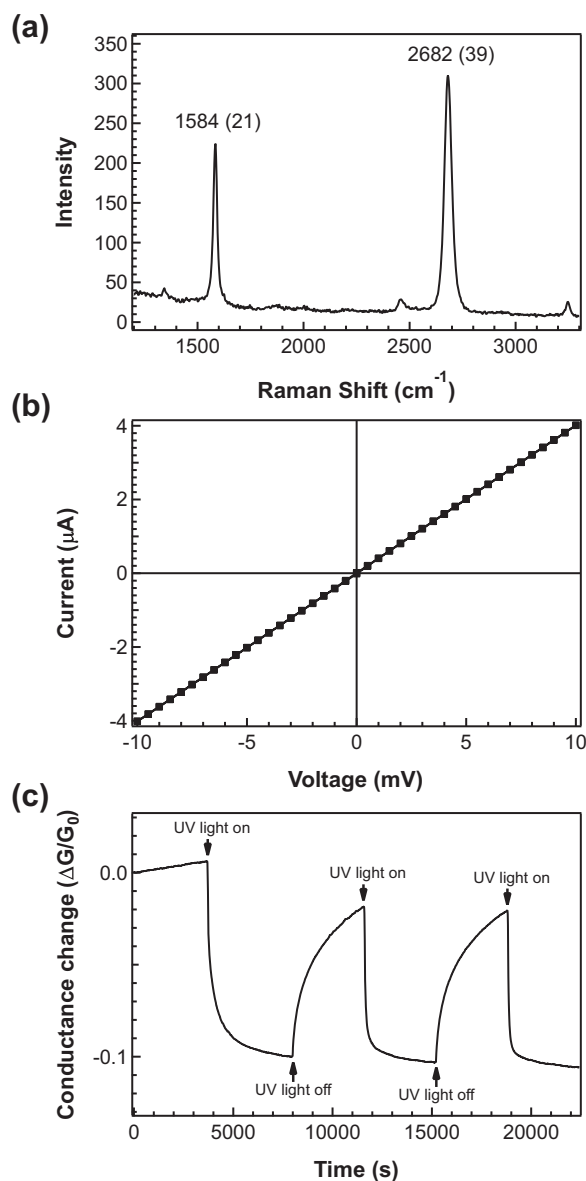


FIG. 1. Sensor characterization and the effect of UV light. (a) Raman spectrum of the graphene. Position and full width at half maximum of the peaks based on a single Lorentzian curve fit were marked for the G and 2D bands. (b) I-V characterization in vacuum. (c) Typical sensor response to the UV light.

DL ranging from a few ppm^{13,14} down to 1 ppb¹ detection of NO₂ on graphene. Compared with those results, the sensor reported here with the application of continuous *in situ* cleaning shows much better sensitivity with a detection level very close to what we had achieved on CNTs recently.⁶ In analogy to the detection of NO molecules, the sensing and recovery experiment at 40 ppt of NO₂ exposure also shows excellent reversibility and reproducibility. This astonishing ultrasensitivity further confirms the impact of *in situ* cleaning to a sensor's performance.

Intrigued by the CNT studies,⁶ it was interesting to see how graphene would behave to NH₃ exposure. In analogy with CNTs, the conductance response of graphene under *in situ* UV light illumination also reversed the direction (Fig. 4). Because conductivity is proportional to the product of carrier density and mobility, the relative contribution of these two factors is unclear without further experimental and theoretical investigations.¹⁵ Nevertheless, like CNTs,¹⁶ since

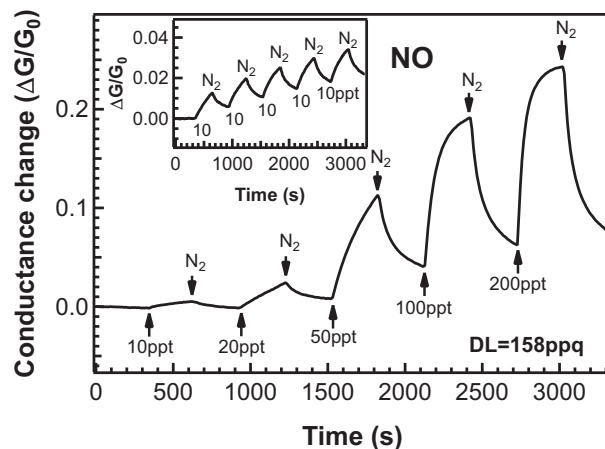


FIG. 2. Relative change of conductance ($\Delta G/G_0$) versus time recorded with NO exposures ranging from 10 to 200 ppt. The inset shows the reproducibility of sensor response at 10 ppt of NO exposure. The detection limit is estimated at 158 ppq.

as-prepared graphene is often p-doped in air,¹ we believe this change of direction is due to the initial conducting state of graphene and the subsequent sign of charge transfer, e.g., adding free electrons by NH₃ adsorption will improve its conductance if the sensor was initially at or close to the carrier neutral point due to UV light induced surface cleaning (Fig. 4(a)), while its conductance will decrease if the sensor was initially p-doped (Fig. 4(b)). Besides the change of direction, note that cleaning with UV light improved the DL of NH₃ on the same graphene device under otherwise identical conditions from 83.7 ppb to 33.2 ppt. Compared with reported results of ppm level NH₃ detection by other groups,^{13,17,18} the pristine graphene exploited here again has drastically enhanced sensitivity.

Furthermore gas sensing had been performed on other interesting species including N₂O, O₂, SO₂, CO₂, and H₂O under flowing N₂ carrier gas, where the estimated DLs range from 38.8 to 136 ppt (Table I). These DLs are well below the lowest detection levels reported in other prototype nano sensors. We should emphasize that all these DLs were achieved in an inert atmosphere, while many practical applications involve an environment with interfering species. Attempting

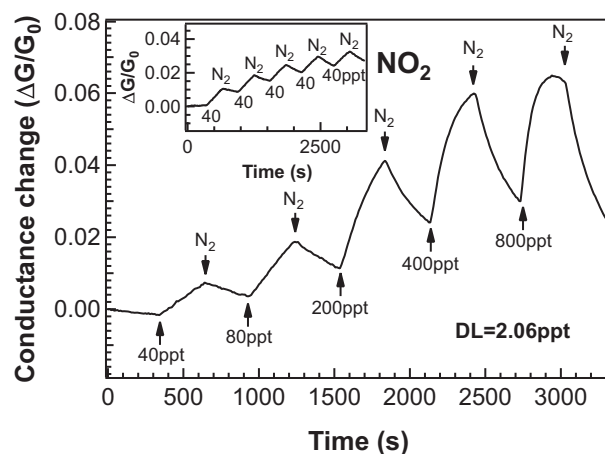


FIG. 3. Conductance change versus time recorded with NO₂ exposures ranging from 40 to 800 ppt. The inset shows the reproducibility of sensor response at 40 ppt of NO₂ exposure. The estimated detection limit is 2.06 ppt.

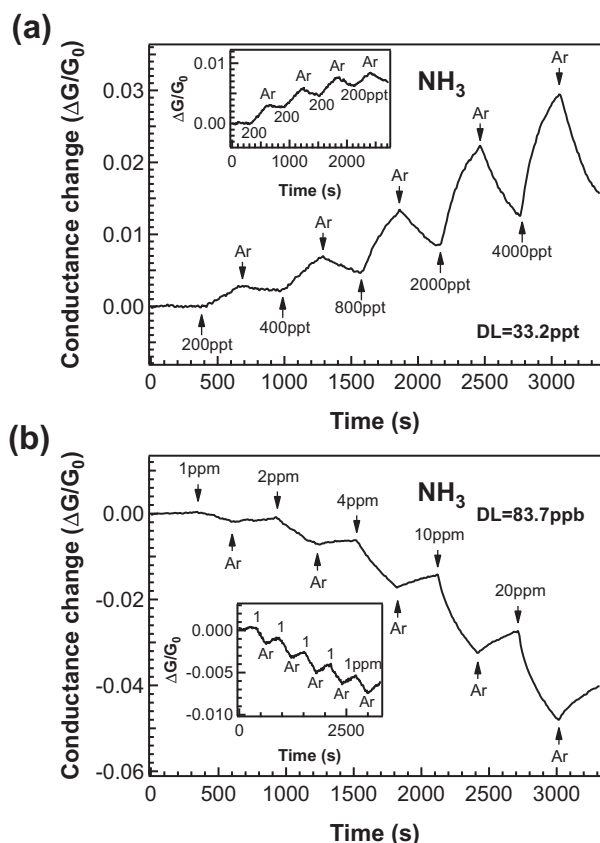


FIG. 4. (a) Response to NH_3 under *in situ* UV light illumination. The inset shows the reproducibility of sensor response at 200 ppt of NH_3 exposure. The detection limit is estimated at 33.2 ppt. (b) Response to NH_3 without UV light illumination, where the detection limit is estimated to be 83.7 ppb.

to address this issue, comparative studies of NO detection had been carried out in air (Fig. S2). We observed a 20-fold sensitivity enhancement with a DL down to ppb level by using *in situ* UV light illumination under the same sensing conditions. These results have further demonstrated the ultra-sensitivity of pristine graphene regardless of the detection environment.

Although the field of graphene-based electronic sensor is still in its infancy, the interest is growing rapidly.⁵ The reported DLs for several gases have already been comparable to what have been achieved on CNTs, a more mature

TABLE I. Summary of molecule sensing to NO, NO_2 , NH_3 , N_2O , O_2 , SO_2 , CO_2 , and H_2O . The lowest gas concentration (C_{\min}) used for each gas species is listed. The detection limit is calculated by $DL = 3 \times \text{rms}_{\text{noise}} / \text{slope}$, where the slope refers to a line fit to the signal versus concentration in the sensor's quasi-linear response region. DLs achieved with CNTs recently by our group were also listed for comparison.⁶

Gas	C_{\min}	RMS noise	Slope	DL	DL with CNTs
NO	10 ppt	1.32×10^{-4}	2.51×10^{-3}	158 ppq	590 ppq
NO_2	40 ppt	8.87×10^{-5}	1.29×10^{-4}	2.06 ppt	1.51 ppt
NH_3	200 ppt	1.10×10^{-4}	9.95×10^{-6}	33.2 ppt	27.8 ppt
N_2O	200 ppt	1.07×10^{-4}	3.11×10^{-6}	103 ppt	—
O_2	200 ppt	1.15×10^{-4}	8.87×10^{-6}	38.8 ppt	—
SO_2	200 ppt	1.32×10^{-4}	5.88×10^{-6}	67.4 ppt	—
CO_2	200 ppt	1.25×10^{-4}	2.75×10^{-6}	136 ppt	—
H_2O	200 ppt	1.07×10^{-4}	3.14×10^{-6}	103 ppt	—

allotrope of carbon which has dominated nano applications in recent years.¹⁹ However, the future of pristine graphene as an active sensing material is widely divided in the scientific community. On one hand, Novoselov and coworkers reported single molecule detection of NO_2 with pristine graphene annealed close to the neutrality point in order to achieve maximum chemical sensitivity.¹ On the other hand, Johnson and coworkers concluded that the intrinsic sensitivity of graphene was very low and contamination from device fabrication actually increased the sensitivity towards a particular analyte.¹⁷ Another report from Masel *et al.* suggested that chemiresistors made from defective graphene ribbons offered superior performance than that from a high-crystalline graphene.²⁰ In addition, it is obvious from the work to date that much effort had been focused on ways to functionalize graphene or its derivatives with nanoparticles, DNA, polymers, and so on in order to improve its interaction to the sensing process.^{21,22} Because these approaches are not only complicated but also dramatically alter a graphene's transport and chemical properties, apparently this is not an ideal route when it comes to making electronic sensors. In the current study, by applying continuous *in situ* UV light illumination, we have clearly shown that pristine graphene is actually an extremely sensitive material without chemical modification. UV light had been used to clean metal surface,²³ CNTs,²⁴ and to recover graphene properties.¹ Although the exact mechanism of cleaning requires further studies, photo induced molecular desorption had been proposed for CNTs and graphene.^{25,26} Of course, for practical applications, many challenges still exist such as how to achieve selectivity on a pristine graphene based sensor. Recent progress in this direction includes using the low-frequency noise spectra of graphene as an indicator for selective gas sensing.²⁷ Functionalization of graphene can also be utilized to tailor a graphene's chemical selectivity,²⁸ and furthermore using a matrix based method with an array of sensors where each individual sensor is tuned to a certain molecule.

Since graphene is atomically thin, very flexible, highly transparent,²⁹ and in general can be transformed to various platforms, many potential sensor applications that were unimaginable before become feasible now. While the physical process involved in gas adsorption on graphene is still unclear,^{30,31} the fact that a pristine graphene based sensor could have tremendous sensitivity is sure to be encouraging. As demonstrated in the current work, incorporation of continuous cleaning into a graphene based sensor is expected to dramatically improve its performance. In addition, graphene has many practical advantages for a diverse range of sensors too, e.g., it is chemically stable and can be subsequently "cut" to the desired shape and size to alter its catchment area so as to achieve a practically desirable sensitivity,³² and it can also be integrated into a conventional lithographic process with potential advantage of rapid and low cost production of miniature sensors that require low power consumption. With recent success on high yield production³³ and large area synthesis of high quality graphene,^{7,34–36} although much work still needs to be done, unique application of such sensors should be foreseeable in the coming years.

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