

Carbon Nanotube Sensors for Gas and Organic Vapor Detection

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ABSTRACT

A gas sensor, fabricated by the simple casting of single-walled carbon nanotubes (SWNTs) on an interdigitated electrode (IDE), is presented for gas and organic vapor detection at room temperature. The sensor responses are linear for concentrations of sub ppm to hundreds of ppm with detection limits of 44 ppb for NO₂ and 262 ppb for nitrotoluene. The time is on the order of seconds for the detection response and minutes for the recovery. The variation of the sensitivity is less than 6% for all of the tested devices, comparable with commercial metal oxide or polymer microfilm sensors while retaining the room-temperature high sensitivity of the SWNT transistor sensors and manufacturability of the commercial sensors. The extended detection capability from gas to organic vapors is attributed to direct charge transfer on individual semiconducting SWNT conductivity with additional electron hopping effects on intertube conductivity through physically adsorbed molecules between SWNTs.

Single-walled carbon nanotube (SWNT)-based sensors have been demonstrated for the detection of small gas molecules such as NO₂ and NH₃.¹ A detection level on the order of ppm can be readily reached at room temperature with SWNT sensors in a transistor configuration, but it requires a temperature of >350°C for conventional metal oxide microfilm sensors. The room-temperature sensitivity of the SWNT sensors, which are fabricated like chemical field effect transistors, is attributed to drastic changes in the electrical conductivity of semiconducting SWNT induced through the charge transfer of gas molecules. However, it is generally difficult to obtain semiconducting SWNTs from as-grown samples, which are typically mixtures of both metallic and semiconducting SWNTs. Even when nanotubes are directly grown on the platform by chemical vapor deposition, there is no control over the growth of semiconducting or metallic tubes' selectivity. This often results in fabrication complexity, low sensor yield, and poorly reproducible sensor performance. Recently, a multiple SWNT transistor array coated with a polymer film has been reported² to improve sensitivity and selectivity at zero gate voltage. The fabrication process and need of a 3-terminal electronic testing setup make the carbon nanotube transistor a more costly platform for chemical sensor applications. Also, it is not clear if the gating effect itself makes a significant contribution to the sensitivity. Sensors based on carbon nanotube films, in contrast, are less complex and thus less expensive but exhibit poor sensitivity. For example, the resonant-circuit sensors^{3,4} using multiwalled carbon nano-

tubes (MWNTs) showed a sensitivity of only a few percent with a detection limit of 100 ppm for NH₃. The low sensitivity of this sensor may be attributed to fewer semiconducting nanotubes in the MWNT film that can be modulated by gas molecules as well as to the poor electric contact between nanotubes and electrodes. A thermoelectric "nanonose" fabricated from the film of SWNTs bundles⁵ also showed a sensitivity of only a few percent for gas molecules. The sensitivity of this type of sensor may be affected by the effectiveness of the thermoelectric conversion.

Here, we demonstrate a simple SWNT sensor platform that combines the advantages of both single nanotube transistors and film-based nanotube sensors with extended applications to the sensitive detection of organic vapors. In this platform, SWNTs form a network or mesh on interdigitated electrodes (IDE) using a solution casting process (Figure 1), providing a large enough density of nanotubes for sensor performance. The IDE configuration enables effective electric contact between SWNTs and the electrodes over large areas while providing good accessibility for gas/vapor adsorption to all SWNTs including semiconducting tubes. This relatively simple fabrication is important to developing inexpensive sensor systems for the cost-conscious chemical sensor market.

The interdigitated electrode was fabricated using a conventional photolithographic method (Figure 1a) with a finger width of 10 μm and a gap size of 8 μm. The IDE fingers were made by thermally evaporating 20-nm Ti and 40-nm Au on a layer of silicon dioxide (SiO₂) thermally grown on top of a silicon wafer. The sensing material consists of SWNTs purified using a two-step purification procedure.⁶ SWNTs produced by the high-pressure carbon monoxide

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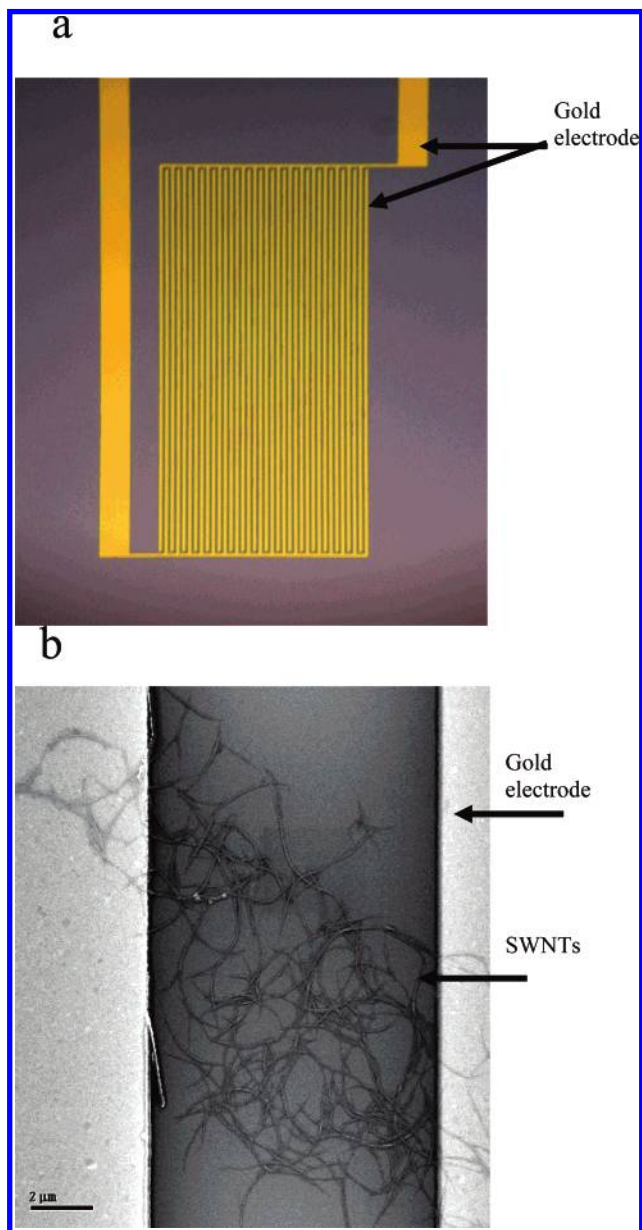


Figure 1. (a) Interdigitated electrodes. (b) SEM image of SWNTs across two gold electrodes.

disproportionate (HiPCo) process⁷ were purified with acid to remove the residuals of the metallic catalyst, followed by air oxidation at high temperature to remove the graphitic carbons. The final purified SWNT has a purity of >99.6% and a surface area of 1587 m²/g, both of which are the highest values reported for SWNTs to the best of our knowledge. Such a high purity level is critical to ensuring that the sensor response is from the nanotubes and is not affected by the metal and amorphous carbon impurities.

The purified SWNTs were then dispersed in dimethylformamide (DMF) to form a suspension. An SWNT–DMF solution (3 mg/L, 0.05 μL) was drop-deposited onto the interdigitated area of the electrodes. After the DMF evaporated, a network of nanotubes lay on the electrodes to bridge the fingers (Figure 1b). The DMF was chosen to debundle the SWNT ropes because the amide group can easily attach to the surface of the nanotubes, providing a uniformly

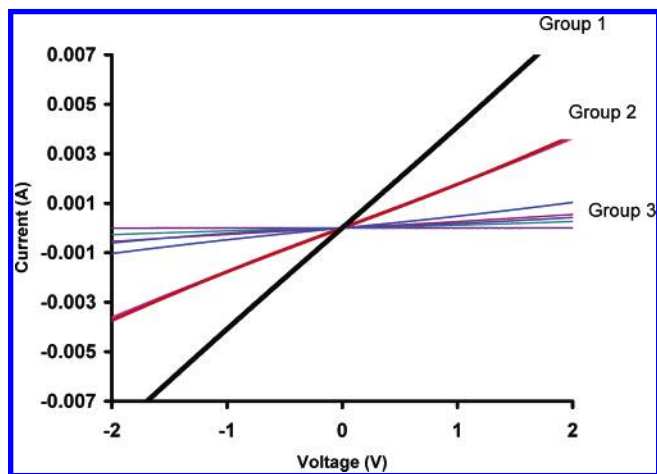


Figure 2. *I*–*V* curves of different sensors. Group 1: three droplets of 0.05 μL SWNT–DMF solution were deposited on the IDE; each droplet was added after the previous one dried. Group 2: two droplets of 0.05 μL SWNT–DMF solution were deposited on the IDE; the second droplet was added after the first one dried. Group 3: one droplet of 0.05 μL SWNT–DMF solution was deposited on the IDE. The initial sensor resistance values were 244 Ω, 568 Ω, and 5.4 ± 2.2 kΩ, respectively, for groups 1–3.

suspended SWNT solution. This ensures good-quality SWNT deposition on top of the interdigitated area. The SWNTs on the IDE were then dried under vacuum to get rid of the DMF residue. The density of the SWNTs across the IDE fingers can be adjusted by varying the concentration of the SWNT–DMF solution. The total interdigitated area is 0.72 mm × 1.5 mm, which is big enough to hold about 0.05 μL of solution within the space. The large interdigitated area also ensures enough carbon nanotubes to give reproducible sensor performance. Figure 2 shows three distinct groups of *I*–*V* curves resulting from three different concentrations of SWNT–DMF solution. Each group consists of results from several sensors. It can be seen from Figure 2 that conductivity (slope) is the same for all devices within groups 1 and 2, but it varies a little for the group 3 devices fabricated from the same low concentration. The highly concentrated solution has denser SWNTs bridging the IDE fingers, which yields the highest conductivity of the sensing film. Obviously, the device yield and reproducibility, measured by the consistency of sensor performance from device to device, would decrease with decreased concentration or increased microelectrode spacing. The asymptotic case of the lowest concentration is the single-tube transistor device that actually lacks the statistical significance required for chemical sensor applications.

The assembled devices from all three groups were exposed to NO₂, acetone, benzene, and nitrotoluene, respectively, at different concentrations to demonstrate sensor performance. Here we show results from NO₂, a molecule that has been extensively studied for nanotube sensors, and from nitrotoluene, an organic vapor molecule with a nitrogen oxide group in benzene. The optimal resistance for sensor performance is about 10 kΩ from our previous experience. Group 3 sensors fall in this range and therefore are the subject of discussion in the remainder of this paper. Figure 3 shows that the SWNT sensor gives strong responses to NO₂ at four

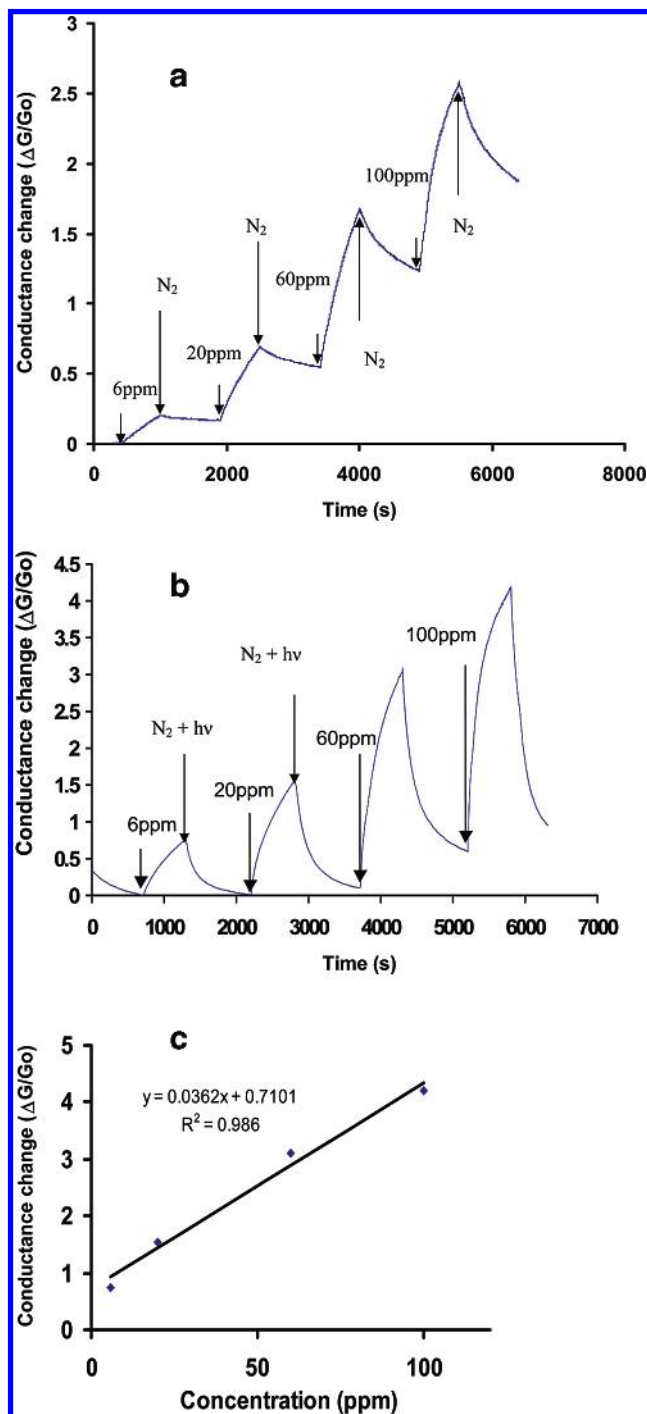


Figure 3. Representative sensor response from group 3 for NO₂. Various concentrations of the sample gas and the pure gas injections are shown by arrows. The sample gas is NO₂ in a 400 cm³/min nitrogen flow at room temperature. Ultrapure nitrogen is used for dilution and purging. (a) Without UV light in the recovery. (b) With UV light for sensor recovery. The UV illumination and N₂ purging start simultaneously. (c) Calibration curve obtained from b.

different concentrations. The recovery time is very long, on the order of 10 h, because of the higher bonding energy between SWNTs and NO₂. This long recovery time is the same as that previously reported for carbon nanotube sensors.¹ The recovery time is accelerated to about 10 min by ultraviolet (UV) light illumination (Figure 3b). The UV exposure decreases the desorption-energy barrier to ease the

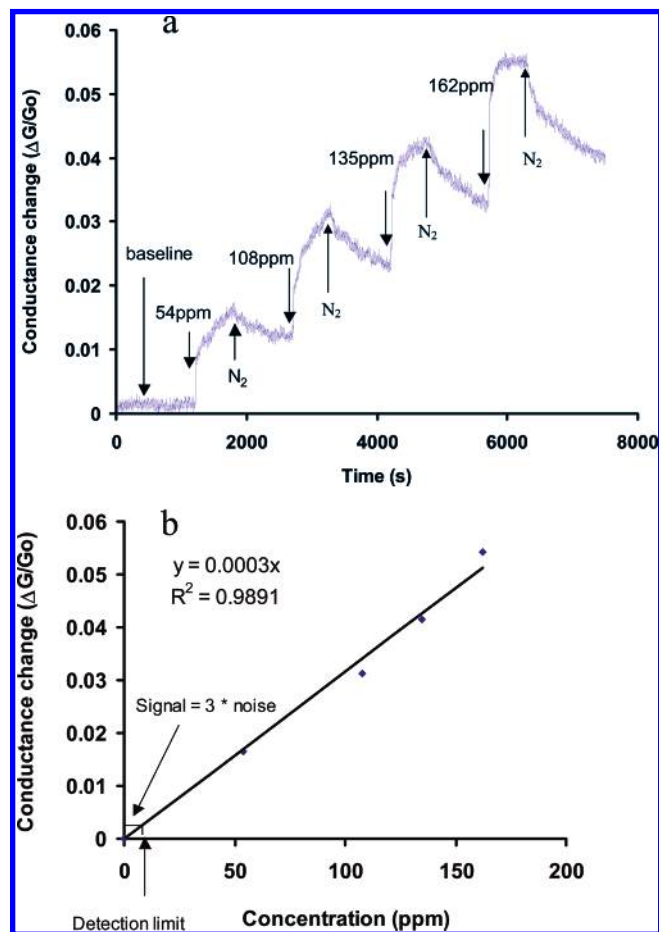


Figure 4. Representative sensor response from group 3 for nitrotoluene. (a) Sensor response is a step function of concentration. (b) Calibration curve from a. The nitrotoluene vapor was evaporated using a bubbler with a 100 cm³/min flow rate of ultrapure nitrogen at room temperature, and this vapor stream was further diluted by nitrogen to a total flow rate of 400 cm³/min. The purge gas is nitrogen as well.

NO₂ desorption.⁸ Indeed, UV illumination for 2 h prior to sensor testing helps to reduce the baseline, initial conductivity of the nanotube. Figure 3c shows a good linear dependency between the response and the concentration of NO₂. The sensor response to nitrotoluene (Figure 4) shows a faster and more reversible response than that for NO₂. However, the response is smaller because of weak bonds and less partial electron transfer between SWNTs and nitrotoluene molecules. The sensor response is linear with respect to concentration in the range investigated.

In the above investigations, the lowest detectable concentration was limited by the present experimental setup. We can derive the detection limit from the sensor's signal processing performance as described below. The sensor noise can be calculated using the variation in the relative conductance change in the baseline using the root-mean-square deviation (rmsd).⁹ For example, in Figure 4a, we took 10 data points at the baseline before the nitrotoluene exposure. After plotting the data, a fifth-order polynomial fit, which gives not only the curve-fitting equation but also the statistical parameters of the polynomial fit, was executed within the data-point range.

$$V_{\chi^2} = \sum (y_i - y)^2$$

where y_i is the measured data point and y is the corresponding value calculated from the curve-fitting equation. The rms noise is calculated as

$$\text{rms}_{\text{noise}} = \sqrt{\frac{V_{\chi^2}}{N}}$$

where N is the number of data points used in the curve fitting.

The sensor noise is 0.00026 for the nitrotoluene sensor in Figure 4a. The average noise level is 0.00050 ± 0.00028 for all of the nitrogen oxide sensors. According to the IUPAC definition,¹⁰ when the signal-to-noise ratio equals 3, the signal is considered to be a true signal. Therefore, the detection limit can be extrapolated from the linear calibration curve when the signal equals 3 times the noise.

$$\text{DL}(\text{ppm}) = 3 \frac{\text{rms}}{\text{slope}}$$

Using the above equation, the NO_2 detection limit is calculated to be 44 ppb from the average sensitivity of the three NO_2 sensors in Figure 5 and the average noise level. The nitrotoluene detection limit is similarly calculated to be 262 ppb.

We have also carried out reproducibility studies for our SWNT sensors. An example is shown in Figure 5 in which three sensors with the most variation in their conductivity from group 3 in Figure 2 were tested for NO_2 at concentration levels of 6, 20, 60, and 100 ppm. All responses are linear, showing a consistent sensitivity of 0.034 ± 0.002 defined by the slope or $(\Delta G/G)/\Delta(\text{concentration})$. The overall variation in the sensitivity for the fabricated devices is about 6%, which is comparable to and even better than that of metal oxide or polymer-based sensors.^{11,12} This shows the excellent reproducibility of our SWNT sensors.

A striking feature emerges from Figure 4b for nitrotoluene detection and Figure 3c for NO_2 detection when we extrapolate the linear sensitivity curve to zero concentration. This leads to nonzero and zero responses for NO_2 and nitrotoluene, respectively, suggesting two sensing mechanisms for the electrical response to molecular adsorption in SWNTs. One type of adsorption results in direct charge transfer between a donor or acceptor type of molecule (or group) and an individual SWNT, leading to the modulation of the Fermi level in the semiconducting tubes (intratube modulation), which causes a conductivity change.¹³ This occurs for NO_2 and the nitrogen oxide group in nitrotoluene molecules. However, such intratube modulation from nitrotoluene molecules will be less significant than that for pure NO_2 because the stronger hydrophobic interaction between SWNTs and benzene groups will leave the nitrogen oxide groups farther away from the SWNTs. Another type of adsorption occurs in the interstitial space between SWNTs to form an SWNT–molecule–SWNT junction, leading to a hopping mechanism for intertube charge transfer between

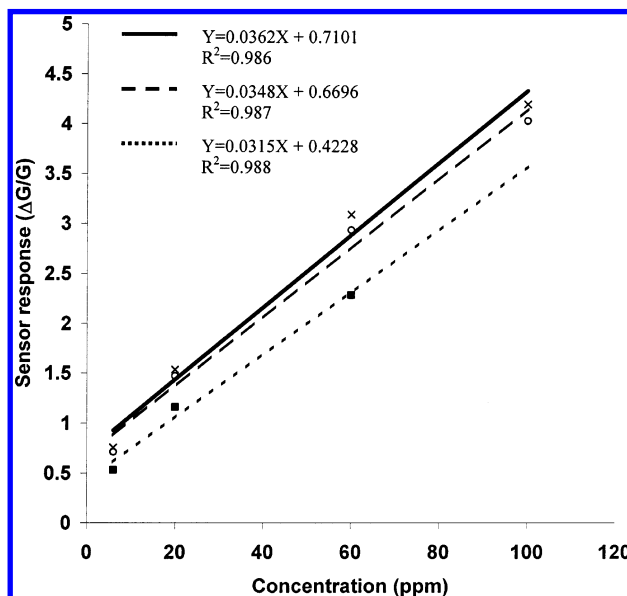


Figure 5. Calibration of three SWNT sensors' response to NO_2 concentration. In the curve-fit equation, y is $\Delta G/G_0$, and x is the gas concentration. R^2 represents the quality of the curve fit.

SWNTs and an intertube modulation of the SWNT network in lieu of a conductivity change. This occurs for all types of molecules and for both metallic and semiconducting SWNTs. The intratube modulation is similar to that of the interaction between semiconductor metal oxides and donor or acceptor types of molecules, showing a nonlinear (power law) response and a large slope (sensitivity) feature at low concentrations.¹⁴ The intertube modulation is similar to that of the interaction between conductive polymers and physically adsorbed molecules, showing nearly linear and smaller slope (sensitivity) behavior over a broad range of concentration.¹⁴

The above phenomenological model explains our experimental observations. In nitrotoluene detection, the intertube modulation plays a key role.

In NO_2 detection, nonlinear behavior should be observed if the response is extended to very low concentrations (in the Henry's law regime) because it should reach zero at zero concentration. The electrical response is contributed from both the inter- and intratube modulation of electronic states in our experimental conditions but should be dominated by an intra effect at low concentrations. Such a nonlinear feature has been observed previously using SWNT transistor array sensors,² where each sensor was made of many metallic and semiconducting SNWTs between two electrodes. The behavior in ref 2 can be characterized with two linear response regions with a slope of about 0.2 below 2 ppb and 0.03 for higher concentrations, indicating that the sensitivity from intratube modulation is at least 1 order of magnitude higher than that from intertube modulation. Clearly, our sensors show similar response behavior (sensitivity of 0.034 at higher concentrations) and would show higher sensitivity if they were applied to lower concentrations. Therefore, we estimate that our detection limit can reach another order of magnitude lower concentration from the current 44 ppb derived from higher concentrations.

An important feature of our sensor platform is the extended detection capability to organic vapors such as benzene, acetone, and nitrotoluene whereas most previous approaches were restricted to small molecules.¹⁻⁵ In principle, semiconducting metal oxides as well as semiconducting SWNTs are not sensitive to many organic vapors, especially to nonpolar molecules such as benzene because of no or less-significant charge transfer. Even with donor or acceptor types of groups, organic molecules still cannot give or take away charge from an SWNT simply because the hydrocarbon groups in the molecules would prefer to adsorb on the SWNT sidewall. However, the detection of such molecules is made possible in our sensor platform mainly through the intertube electron modulation effect, leading to the observation in this work of a linear response down to zero concentration with a lower sensitivity, for example, 0.003 for nitrotoluene shown in Figure 4b. This shows a difference in sensitivity of 2 orders of magnitude resulting from intratube modulation. Such sensitivity has also been observed for acetone and benzene. Acetone is a polar molecule with a carbonyl group that might withdraw electrons from SWCNTs, the same as NO₂ that caused the intratube modulation. We have seen a sensor response from 1 ppm acetone in the direction of a conductance increase. However, benzene is a nonpolar molecule and therefore may have no charge transfer for the intratube modulation effect. As a result, we have observed a small sensor response to 20 ppm benzene, which we believe results from the intertube modulation effect. These observations are preliminary. A systematic study of the response dynamics over a wide range of concentration is in progress for acetone and benzene and also other volatile organic compounds; these results will be summarized in a future article.

In summary, we have developed a simple, reliable, and reproducible SWNT sensor platform for gas and organic vapor detection at room temperature. The electrical response shows well-defined and reproducible linear behavior and a detection limit of <44 ppb for NO₂ and 262 ppb for

nitrotoluene. The electronic molecular sensing in our sensor platform can be understood by intra and intertube electron modulation in terms of charge-transfer mechanisms.

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