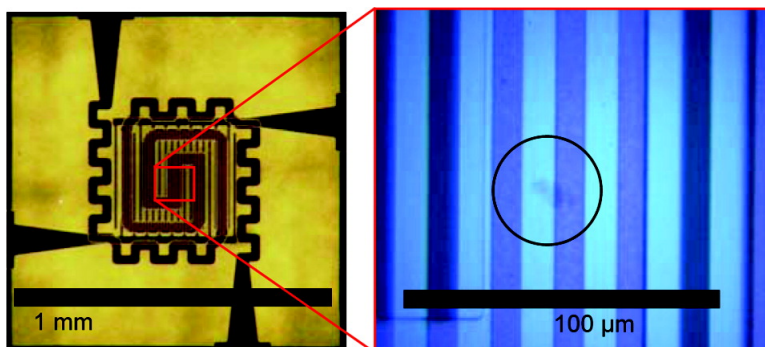


Article

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Practical Chemical Sensors from Chemically Derived Graphene

Jesse D. Fowler,^{†,‡} Matthew J. Allen,^{*,‡} Vincent C. Tung,[§] Yang Yang,[§] Richard B. Kaner,^{*,§,*} and Bruce H. Weiller^{†,*}

[†]Materials Processing and Evaluation Department, Space Materials Laboratory, The Aerospace Corporation, P.O. Box 92957/M2-248, Los Angeles, California 90009,

[‡]Department of Chemistry & Biochemistry and California NanoSystems Institute, University of California, Los Angeles, California 90095-1569, and [§]Department of Materials Science and Engineering and California NanoSystems Institute, University of California, Los Angeles, California, 90095. [‡]These authors contributed equally to this work.

Graphene has long been interesting as a two-dimensional model for carbon-based electronic materials as well as being a fundamental building block for buckyballs, carbon nanotubes, and graphite. Recent results on device performance from single sheets of graphene showing high carrier mobility at room temperature have further intensified interest in this material.¹ Unfortunately, until now, the method for producing single sheets of graphene has been limited to a laborious process of mechanically peeling graphite layers and subsequent electrode attachment with electron beam lithography.² This has severely limited the study and applications of graphene. Recently, chemists have shown that by using chemical methods it is possible to generate device quality graphene flakes coated on a wafer scale.^{3–6} Often this involves the chemical oxidation and exfoliation of graphite to produce graphite oxide and its subsequent reduction to graphene. The effectiveness of this reduction step appears to have a large affect on the quality of the resulting graphene, and most recently, it has been shown that liquid anhydrous hydrazine is a very effective reducing agent and solvent for dispersion of large, high quality graphene flakes.⁷ This has opened the door to a wide range of possible applications, one of which is for chemical sensors.

Preliminary chemical sensor experiments with mechanically exfoliated graphene flakes have shown very high sensitivity, with single molecule detection claimed for NO₂ in a high vacuum chamber.⁸ The high sensitivity was explained as resulting from the extraordinary mobility of carriers in graphene, which enabled extremely low noise sensing at room temper-

ABSTRACT We report the development of useful chemical sensors from chemically converted graphene dispersions using spin coating to create single-layer films on interdigitated electrode arrays. Dispersions of graphene in anhydrous hydrazine are formed from graphite oxide. Preliminary results are presented on the detection of NO₂, NH₃, and 2,4-dinitrotoluene using this simple and scalable fabrication method for practical devices. Current *versus* voltage curves are linear and ohmic in all cases, studied independent of metal electrode or presence of analytes. The sensor response is consistent with a charge transfer mechanism between the analyte and graphene with a limited role of the electrical contacts. A micro hot plate sensor substrate is also used to monitor the temperature dependence of the response to nitrogen dioxide. The results are discussed in light of recent literature on carbon nanotube and graphene sensors.

KEYWORDS: hydrazine · micro hot plate · nitrogen dioxide · ammonia · 2,4-dinitrotoluene

ature. The mechanism for sensing appears to be similar to that for carbon nanotubes, with both NO₂ and NH₃ producing an increase in conductivity consistent with p-type and n-type doping, respectively.^{9–13} Recent work has also been published using chemically produced graphene as a chemical sensor.¹⁴ Here we report the development of useful chemical sensors based on chemically converted graphene using spin-coating of hydrazine dispersions on interdigitated planar electrode arrays, as shown in Figure 1. Preliminary results are presented on the detection of NO₂ and NH₃ using this simple and scalable fabrication method for practical devices. Current *versus* voltage data are presented for a range of conditions including presence of analyte and electrode metal. The temperature dependence of the NO₂ response is presented using a micro hot plate sensor to accelerate the response rates. We also present data on the detection of dinitrotoluene, a volatile component of explosives. The results are discussed in light of literature results and calculations for carbon nanotube and graphene sensors.

*Address correspondence to kaner@chem.ucla.edu, bruce.h.weiller@aero.org.

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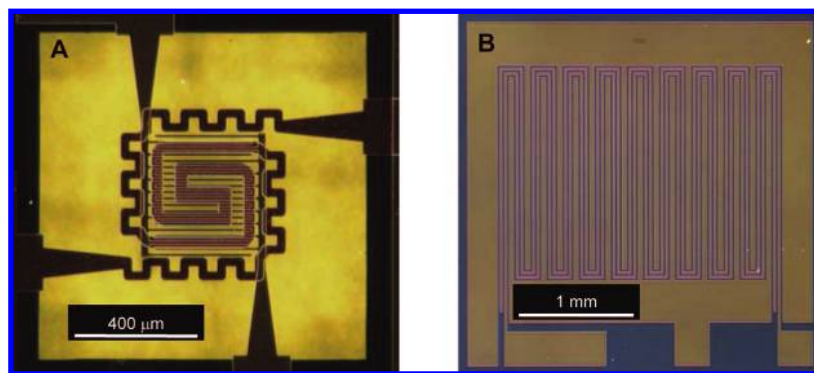


Figure 1. Photographs of the sensor substrates used. (A) Micro hot plate (MHP) sensor showing interdigitated electrodes layered over heater leads. The electrode array is a 400 μm square with individual electrodes 10 μm wide with 10 μm gaps. The sensor is suspended on a thin silicon nitride membrane. (B) Four-point interdigitated electrode sensor. Two serpentine electrodes between the interdigitated electrodes are used for four-point resistance measurements. The electrode array is 2.4 mm \times 1.9 mm with 20 μm serpentine electrode widths, 40 μm interdigitated electrode widths, and 20 μm electrode gaps as described in the text.

RESULTS AND DISCUSSION

Figure 2 shows a scanning electron micrograph (SEM) of graphene as deposited on the electrodes of the sensor substrate. One can clearly see isolated, single-layer flakes of graphene. The material was deposited using a centrifuged solution to achieve well-dispersed, single-layer graphene flakes. Figure 3 shows the Raman spectrum of the reduced graphite oxide as deposited on a sensor substrate. The spectrum shows the D and G bands in the ratio expected for reduced graphite oxide and is consistent with data previously reported for chemically converted graphene.^{3,15} The spectrum was taken using a single isolated flake (as in the material shown in Figure 2) directly on the sensor substrate at room temperature. We have also used thicker multilayer films deposited by drop-casting, but they do not respond as well as the single flake material.

Figure 4 shows the sensor response from a spin-coated graphene film exposed to 5 ppm of NO_2 in dry nitrogen. The material was spin-coated directly onto a

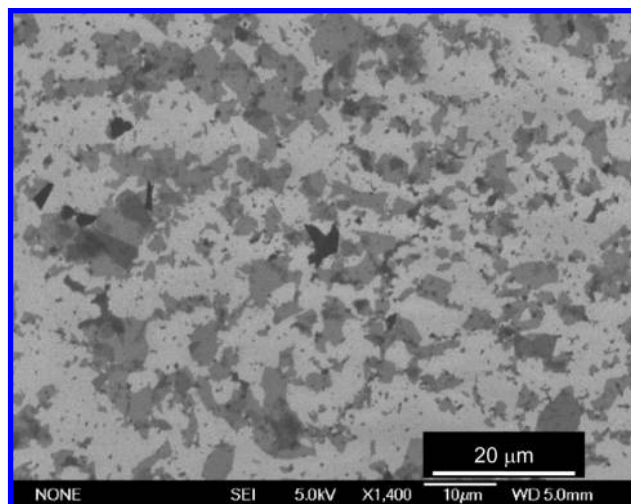


Figure 2. Spin-coated graphene film as deposited on the chemical sensor, 1400 \times magnification.

mounted sensor chip as described in the Methods section. The baseline resistance of the film at room temperature varied from 70 to 700 ohms, based on proportion of multi-layer to single-layer graphene flakes present and how effectively the electrode gap is bridged. Single-layer graphene flakes presented a higher baseline resistance and stronger sensitivity. Four-point resistance was measured using an excitation current of 500 μA , with an electrode gap of 20 μm . The data are plotted as R/R_0 where R_0 is the resistance just prior to gas exposure. The dotted line tracks the gas exposure where the exposure time is 10 min, followed by 10 min of purge with nitrogen. The sensor gives a large initial decrease in resistance of about $\Delta R/R_0 = -13\%$, followed by partial recovery at room temperature over the

10 min purge time. The full scale response is estimated to be $\sim 30\%$ for 5 ppm. In comparison, using single-crystal, mechanically exfoliated graphite with directly deposited metal contacts, Schedin *et al.* found that a drop in resistivity of 300% occurred over an hour when exposed to a constant flow of “ppm concentration” of NO_2 , as outlined in their Supporting Information.⁸ The fast response shown in the main text of that paper is explained as being due to the limited number of gas molecules available in a sealed chamber and may not be indicative of the true sensor response. Given the ease with which our sensors can be produced, the magnitude of the unoptimized response reported here is very encouraging.

Figure 5 shows the sensor response to 5 ppm of ammonia measured as described above. In this case, we observe an increase in resistance with an initial response of about $\Delta R/R_0 \sim +2.5\%$. The full scale response is estimated to be $\sim 10\%$. This response is significantly smaller and opposite sign from the response when exposed to NO_2 , while Schedin *et al.* showed a similar response magnitude for NH_3 and NO_2 exposure.⁸ The fact that we observe responses for NO_2 and NH_3 with opposite polarities is consistent with the charge transfer mechanism proposed for graphene.¹⁶ Schedin *et al.* used Hall measurements during their sensing experiments to determine the identity of the carriers. They concluded that NO_2 induced hole conduction, while NH_3 induced electron conduction. Under their vacuum conditions, one expects a similar drop in resistance for hole and electron doping because the material initially has no carriers in its conduction band. Residual epoxide and carboxylic groups expected in chemically produced graphene are electron-withdrawing and promote some holes into the conduction band. Additional p-type dopants, such as NO_2 , should enhance hole conduction and generate a significant decrease in resistance, and n-type dopants, such as NH_3 , actually cause

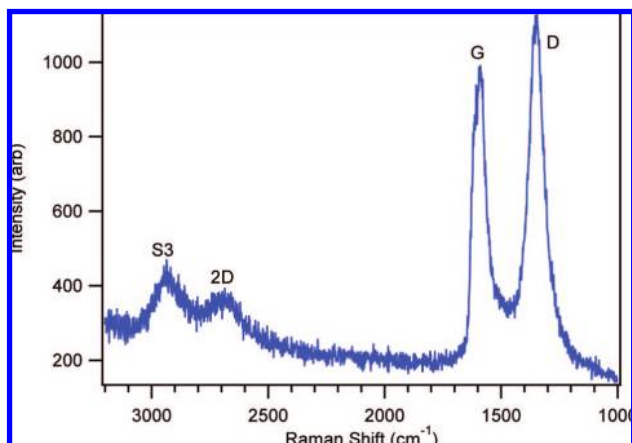


Figure 3. Raman spectrum of the graphene film as deposited on the sensor showing the D band at 1350 cm^{-1} , the G band at 1584 cm^{-1} , the 2D band at $\sim 2700\text{ cm}^{-1}$, and the S3 peak at $\sim 2930\text{ cm}^{-1}$.

depletion of holes from the conduction band and hence raise the resistance of our material.

There has been some discussion in the literature on carbon nanotube sensors regarding the possible role of electrical contacts in sensor response.^{16–21} The majority of the more recent literature, including theoretical studies, conclude that charge transfer between the adsorbed gas and nanotubes is the primary response mechanism, although gas effects at the electrical contacts have not been ruled out in all cases. In regard to graphene, theoretical calculations on the interaction with various molecules, including NO_2 and NH_3 , draw the conclusion that charge transfer is responsible for sensor response.^{22,23}

The following data indicate that the charge transfer mechanism is operative at the graphene surface with a limited role of the electrical contacts. First, the measurements presented in Figures 4 and 5 were made using the four-point sensors in Figure 1B, which eliminates the contact resistance of our sensing devices and also the area nearest to charge injection. In this geometry, sensor response is dependent only on changes in resistivity of the graphene between the inner two electrodes. In this way, our devices were insensitive to any

changes in trap states that might be formed near the injection of charge at the outer electrodes. In addition to the four-point measurements, we also looked for any dependence of electrical or sensor response on the work function of the electrodes. Current *versus* voltage (I – V) measurements using gold electrodes show only linear ohmic behavior in both nitrogen and dilute NO_2 exposure, as shown in Figure 6. Similar I – V curves on platinum electrodes are also linear in both nitrogen and in dilute NO_2 , and there was no significant difference in time response or sensitivity using platinum electrodes. These similarities and the lack of any Schottky behavior lead us to believe that the electrical contacts do not play a significant role in our devices. While we cannot make a definitive conclusion without more elaborate

methods to encapsulate the contact areas, our data are most consistent with simple charge transfer at the graphene. This understanding of our observations will guide further optimization of the operating conditions necessary to maximize sensitivity to individual analytes. This may include chemical modification of the residual oxygen containing functionalities and incorporation of a gate bias.

We have also found a good response of graphene to a molecule relevant to explosive detection, 2,4-dinitrotoluene (DNT). DNT is the relatively volatile component found in trinitrotoluene (TNT) explosives, which makes it a reliable signature for gas sensors.^{24,25} It is also an electron-withdrawing molecule that is expected to give a response similar to that of NO_2 . Figure 7 shows the response of a spin-coated graphene film to room temperature, low concentration of DNT, measured in a two-wire configuration. With 10 min exposures to 52 ppb flow of DNT at room temperature (21°C), we find a response of $\Delta R/R = -0.028\%$. The signal-to-noise ratio of $S/N = 5.6$ implies a limit of detection of 28 ppb ($S/N = 3$). This is well below the room temperature vapor pressure of DNT, which is 173 ppb.²⁶ The sensor had gold electrodes with isolated flakes of graphene, as

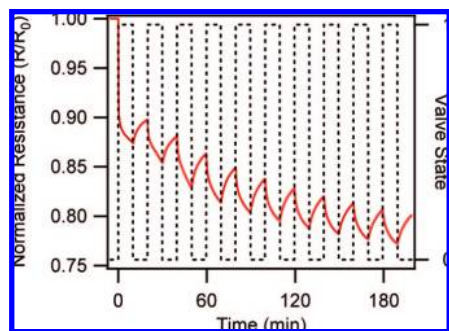


Figure 4. NO_2 detection using a graphene film. The sensor has gold electrodes and measurement used a four wire method with $500\text{ }\mu\text{A}$ driving current. The NO_2 concentration is 5 ppm in dry nitrogen.

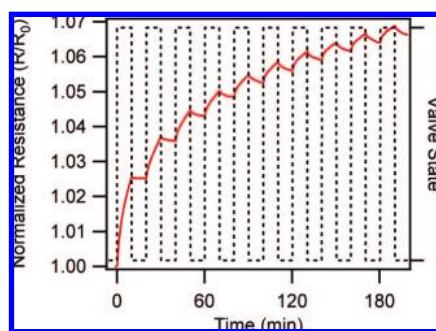


Figure 5. NH_3 detection using a graphene film. The sensor has gold electrodes and measurement used a four wire method with $500\text{ }\mu\text{A}$ driving current. The NH_3 concentration is 5 ppm in dry nitrogen.

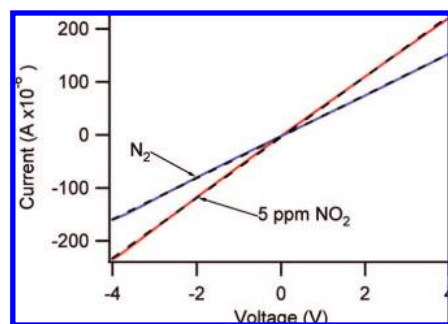


Figure 6. Current versus voltage traces for graphene on gold electrodes in nitrogen and in dilute NO_2 gas (5 ppm).

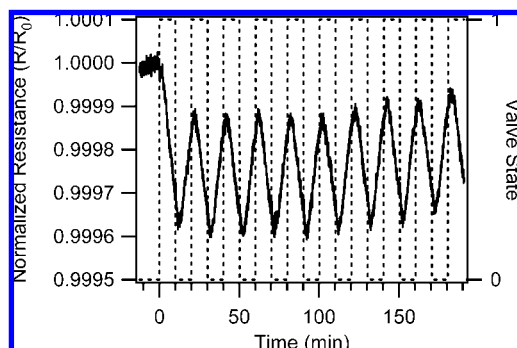


Figure 7. Response of the graphene sensors to 2,4-dinitrotoluene. The graphene sensors were exposed to room temperature flows of 30% DNT (52 ppb). Note that the full scale signal is $\Delta R/R_0 = -0.028\%$.

shown in Figure 1. In order to achieve this sensitivity, the temperature of the sensor and associated gas lines was controlled to $\pm 0.1^\circ\text{C}$.

A recent publication reports the use of chemically reduced graphite oxide for chemical sensors.¹⁴ In that work, films of graphite oxide were deposited on silicon wafers using spin-coating, interdigitated metal electrodes were deposited on top of the graphite oxide, and the graphite oxide was subsequently reduced using hydrazine vapor at elevated temperatures. They found excellent sensitivity using this approach, better than carbon nanotube sensors for some molecules including DNT, although NH_3 or NO_2 were not measured. From our experience with reducing graphite oxide us-

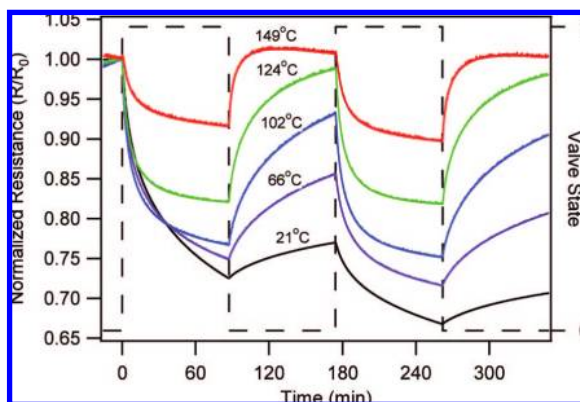


Figure 8. NO_2 detection (5 ppm) on the micro hot plate (MHP) sensor at temperatures ranging from 21 to 149°C as indicated.

ing vapor phase hydrazine,^{5,7} liquid hydrazine is much more effective, giving higher conductivity graphene with fewer defects. The fact that metal electrodes were deposited onto the graphite oxide may raise some concern regarding the nature of the electrical contacts. It is interesting to note that Robinson *et al.*¹⁴ also observed relatively slow response times that were attributed to oxygen defects in the reduced graphite oxide. We believe that the use of liquid hydrazine to spin-coat graphene flakes directly onto metal electrodes gives better graphene with fewer defects and should lead to superior devices. Further work is required to determine the optimum approach for graphene chemical sensor development including detection methodology.

Figure 8 shows the temperature dependence of the response to 5 ppm of nitrogen dioxide. For this measurement, MHP sensor substrates were used as described in the Methods section. The temperature was varied from room temperature to 149°C . In this case, the two-electrode geometry was used and the resistance was measured using constant current excitation ($96\ \mu\text{A}$). There is a clear trend from larger response and slower response times at room temperature to smaller response and faster response times at higher temperature. With long exposures and well-dispersed, single-flake graphene, we observe a response of $\Delta R/R_0 = -27\%$ at room temperature, which decreases to $\Delta R/R_0 = -7\%$ at 150°C . Using the initial slope of the off cycle to calculate sensor recovery rates, an activation energy of $5.7\ \text{kcal/mol}$ ($250\ \text{meV}$) can be determined for sensor recovery. While this result is preliminary, it may be related to the adsorption energy of NO_2 on the reduced graphite oxide. This value is much larger than the calculated adsorption energy of $67\ \text{meV}$ ($1.5\ \text{kcal/mol}$) for NO_2 on pure graphene.²³ Residual oxygen defects such as carboxylic acids or epoxides in the reduced graphite oxide film should result in higher binding energies and may be responsible for the longer response times; this has been proposed earlier in the response of carbon nanotube sensors.²⁷ The micro hot plate sensor provides very fast temperature control and modulation and is a very useful tool in characterization of sensor materials and as an important enhancement to sensor response, recovery, and data interpretation.

In conclusion, we have shown that chemically converted graphene provides a simple, practical, and effective method for producing chemical sensors for NO_2 , NH_3 , and dinitrotoluene. Current versus voltage data support the view that electrical contacts do not play a significant role in chemical response and that charge transfer is the primary mechanism. The time response is relatively slow at room temperature but can be accelerated at elevated temperatures at the expense of sensitivity. There are still open questions about the time response and sensitivity of this material versus single-

crystal graphene and other forms of reduced graphite oxide. Experiments are underway to further un-

derstand this material and to enhance its performance as an effective chemical sensor.

METHODS

Graphite oxide (GO) was prepared *via* Hummer's method from graphite powder.²⁸ Upon exfoliation, dispersions were typically 2% w/v GO in water. To obtain a dry product, dispersions were diluted to 1 g/L and subsequently filtered through a 0.22 μm alumina membrane to produce GO paper. The filtration process required approximately 24 h, after which the resultant films were left to dry completely under ambient conditions. The dry, matte black GO films were then carefully peeled from their membranes to produce free-standing, robust GO paper.

The use of hydrazine vapors to both reduce GO and restore the planar structure of native graphene is well-known. In this case, GO paper was dispersed directly in 98% anhydrous hydrazine to produce an opaque black suspension of hydrazinium graphene (HG). The resulting HG suspensions were typically 1 g/L and stable for months without aggregation.

HG suspensions could be readily spin-coated onto a variety of substrates in order to form uniform depositions of large ($10 \times 10 \mu\text{m}$) single sheets. Just prior to deposition, suspensions were centrifuged at 1500 rpm to remove any higher density aggregates from solution. For deposition on Si/SiO_2 , the substrates were pretreated for 2 min with an oxygen plasma at 20 mW. Such treatment modifies the hydrophilicity of the substrates and ensures adequate wetting by hydrazine suspensions. Spin-coating was carried out at 1300 rpm for 1 min in a nitrogen-filled glovebox.

The substrates coated were of two types: micro hot plates and four-point electrode sensors. The MHPs (Figure 1A) were produced at the University of Neuchâtel, Institute of Microtechnology (IMT).²⁹ Four-point electrode sensors (Figure 1B) were produced at The Aerospace Corporation and consisted of gold interdigitated electrodes (where source current is applied) with a serpentine electrode pair wound between them (where sense voltage is read).³⁰ The four-point electrodes were deposited on top of thermally grown silicon dioxide to isolate them from the bulk silicon, while the MHP electrodes were deposited on top of low-stress silicon nitride. Both types of sensors were mounted in 24-pin dual in-line packages (DIPs) and cleaned with acetone, isopropanol, and an oxygen plasma prior to being spin-coated with HG. In the case of dinitrotoluene, current was applied and voltage was read using the interdigitated electrodes in a two-point configuration.

Deposited graphene flakes were examined with techniques most often used to characterize native graphene, including atomic force (AFM) and scanning electron microscopy (SEM), Raman spectroscopy, and electrical measurements. Microscopies confirmed the presence of large single sheets ($\sim 10 \times 10 \mu\text{m}$) with an overall thickness of less than 0.6 nm. Raman measurements were consistent with literature studies of reduced graphite oxide, with prominent D, G, and 2D peaks indicating moderate restoration of graphitic structure. Electrical characterization of the graphene flakes was carried out as described elsewhere.⁷

Sensor measurements of MHPs were performed using a high-resolution voltmeter (Keithley 2002) through a multiplexer (Keithley 7001). Sensor measurements of four-point sensors were performed using a current source (Keithley 2400 set at a constant current of 500 μA) and a voltmeter (Keithley 2002). These measurements were multiplexed through an Agilent 34970A scanner. Gas flow was controlled using mass flow controllers, and all measurements were recorded to computer through the use of LabVIEW over the GPIB interface. Calibrated gas mixtures (Scott Specialty Gases) were delivered through stainless steel or PFA tubing. Dinitrotoluene was delivered using a room temperature saturated vapor stream and calculated concentrations based on literature vapor pressure data.²⁶

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