Graphene Sensors

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All-Organic Vapor Sensor Using Inkjet-Printed Reduced Graphene Oxide**

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Described herein is a flexible and lightweight chemiresistor made of a thin film composed of overlapped and reduced graphene oxide platelets (RGO film), which were printed onto flexible plastic surfaces by using inkjet techniques. The RGO films can reversibly and selectively detect chemically aggressive vapors such as NO_2, Cl_2, etc. Detection is achieved, without the aid of a vapor concentrator, at room temperature using an air sample containing vapor concentrations ranging from 100 ppm to 500 ppb. Inkjet printing of RGO platelets is achieved for the first time using aqueous surfactant-supported dispersions of RGO powder synthesized by the reduction of exfoliated graphite oxide (GO), by using ascorbic acid (vitamin C) as a mild and green reducing agent. The resulting film is has electrical conductivity properties ($\sigma \approx 15\ S\,cm^{-1}$) and has fewer defects compared to RGO films obtained by using hydrazine reduction.

Graphene has emerged as an environmentally stable electronic material with exceptional thermal, mechanical, and electrical properties because of its two-dimensional sp^2-bonded structure.[1,2] Although individual graphene sheets have been synthesized on various surfaces using chemical vapor deposition,[2,3] an important chemical route to bulk quantities of RGO involves the conversion of graphite into GO using strong oxidants, and then subsequent reduction of the dispersed GO into RGO using strong reducing agents (e.g., hydrazine).[4,5] The large available surface area of graphene makes it an attractive candidate for use as a chemiresistor for chemical and biological detection. There are a few reports on vapor detection using graphene films on interdigitated arrays,[6–9] and one interesting report on single-molecule detection.[9] In recent reports on reversible NO_2 vapor detection using graphene, either the response/recovery time of the signal is long,[7] or efforts to improve the recovery cycle by increasing the temperature was complicated by a smaller sensor response.[6] Herein we describe a rugged and flexible sensor using inkjet-printed films of RGO on poly(ethylene terephthalate) (PET) to reversibly detect NO_2 and Cl_2 vapors within an air sample at the parts per billion level, and demonstrate the use of ascorbic acid as a mild and effective alternative to hydrazine to reduce GO into RGO.

Ascorbic acid reduction of dispersed graphene oxide into RGO is carried out by first preparing GO from graphite using the method reported by Hummers and Offeman,[10] and then dispersing it in water containing 1% polyethylene glycol. Ascorbic acid powder (3 g) is added to a 3 $mg\,mL^{-1}$ aqueous GO dispersion and heated to 80 °C for 1 hour, at which point the color changes from yellow-brown to black, signaling the conversion into RGO platelets (Figure 1a). This RGO powder is suction filtered and washed with water, and then

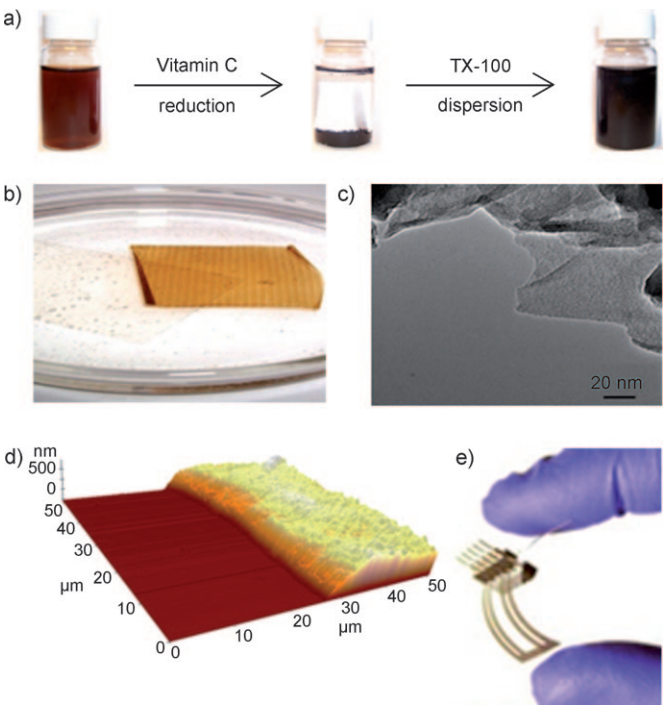

Figure 1. (a) Digital images of the vials containing GO and RGO dispersions. (b) Inkjet-printed graphene oxide film lifts off the PET surface. (c) TEM image of the RGO powder. (d) AFM image of RGO film obtained by reduction of the film in (b) with ascorbic acid. (e) Digital image of inkjet-printed RGO/PET four-probe sensor.

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dried at 60 °C under dynamic vacuum for 12 hours ($\sigma_{RT} \approx 15\ S\,cm^{-1}$, pressed pellet).

The electrical conductivity is similar to RGO films obtained using a hydrazine reduction,[11] which shows that ascorbic acid is an effective green chemistry alternative to hydrazine and aggressive reducing agents that could introduce defects into the RGO film. For example, hydrazine reduction of GO has been shown to result in covalently linked C–N species which are observed in X-ray photoelectron spectra (XPS).[5] In contrast, XPS analysis of RGO films obtained using ascorbic acid show fewer peaks (e.g., there are no C–N peaks), which is consistent with a mild, but effective reduction reaction (Figure 2c). Thermogravimetric analysis

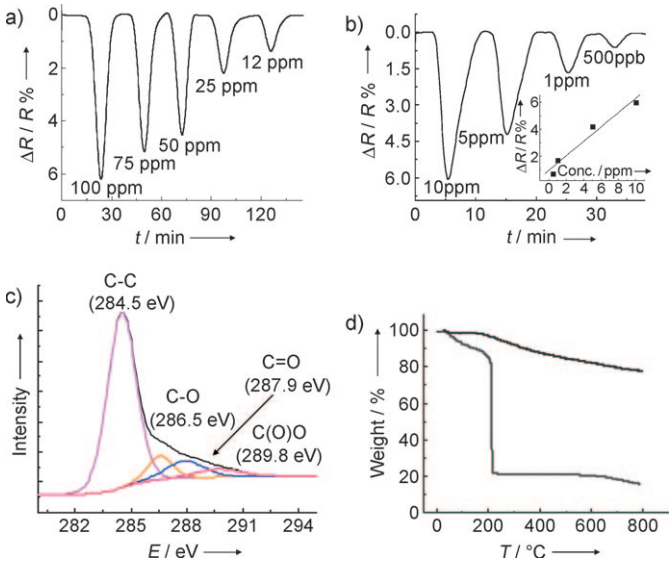

Figure 2. Vapor sensing and characterization of RGO films obtained by ascorbic acid reduction of graphene oxide films. Plot of resistance versus time for of inkjet-printed RGO/PET when exposed to NO_2 vapor using (a) a thicker bottom strip, (b) a thinner bottom strip (Inset: plot for resistance versus vapor concentration). The vapor desorption cycle initiated by UV irradiation is indicated by the troughs. (c) XPS (E = binding energy) and (d) TGA data for GO (grey) and RGO (black).

also suggests a more stable product, because unlike the RGO film obtained using hydrazine, which shows a continuous weight loss during the heating cycle (possibly from C–N species),[5] the RGO film obtained using ascorbic acid shows no significant weight loss below 200 °C.

For inkjet printing, the cartridge ink of a commercial inkjet printer is emptied and refilled with a freshly prepared aqueous dispersion of GO and printed directly on commercial PET (see the Supporting Information). Relatively thick (ca. 700 nm) graphene oxide films spontaneously lift off the PET surface when immersed in water for a few minutes. These graphene oxide films are readily reduced to free-standing RGO films when treated with ascorbic acid. Although these films can be placed on gold electrodes and used directly for chemical vapor sensing, we found more consistent results with RGO films inkjet printed on PET from Triton-X100-supported dispersions of RGO in water. We have previously used Triton-X100 to disperse single-walled carbon nanotubes in water to obtain films on PET for vapor sensing studies[12] and in this study its use also ensures uniformity of graphene films during the inkjet-printing process. The inkjet-printed RGO/PET films are subsequently sonicated and then washed in toluene to remove any residual surfactant. Inkjet printing allows control of the film thickness by altering the number of passes and also by using the gray scale on the computer. The active sensor area is made of a thin rectangular strip of RGO (bottom strip) with four thicker strips that function as the leads for the four-probe measurements (see Figure S3 in the Supporting Information). An active sensor area composed of thinner RGO films facilitates low-concentration vapor detection, for example, less than 10 ppm.

When inkjet-printed RGO/PET films are exposed to electron-withdrawing vapors the conductivity increases sharply, which is consistent with an increase in the number of charge carriers (Figure 2, Figure 3). For example, when

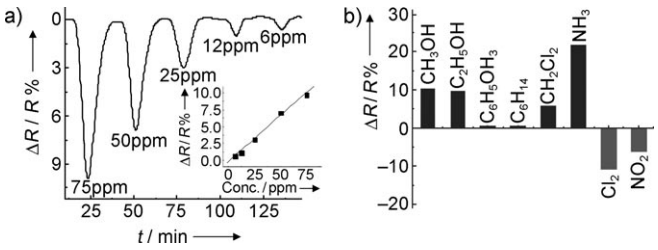

Figure 3. Vapor sensing by inkjet-printed RGO/PET obtained by ascorbic acid reduction of dispersed graphene oxide. (a) Plot for resistance versus time when the film was exposed to a Cl_2 vapor. Inset: Plot of resistance versus vapor concentration. (b) Selectivity plot: sensor exposed to saturated organic vapors, NH_3 (100 ppm), NO_2 (100 ppm), and Cl_2 (100 ppm).

exposed to successively decreased concentrations of the NO_2 vapor in the range of 100 ppm–500 ppb, the conductivity increases in a linear fashion. Although an NO_2 concentration of 500 ppb is the lowest experimentally determined value to date (using RGO/PET films), the theoretical detection limit or resolution limit is much lower, approximately 400 ppt, based on the signal-to-noise ratio (see the Supporting Information). Signal recovery is slow when the sensor is removed from the chamber, consistent with previously published studies showing strong chemisorption of NO_2 vapor upon a graphene surface.[7] However, the signal recovers completely when the film is exposed to 254 nm UV light and there is no noticeable damage to the RGO film or the PET support, thereby suggesting that there is no covalent bond formation. A similar signal recovery upon exposure to UV irradiation has been observed in NO_2 vapor detection using carbon nanotubes wherein the formation of long lived NO_3 species was postulated.[13] We recently reported UV-induced signal recovery in polythiophene/PET nanofiber films that were exposed to NO_2, Cl_2, and SO_2 suggesting that the phenomenon is not unique to the NO_2 vapor.[14] Our RGO/PET films behave similarly, that is, when exposed to Cl_2 vapor, the signal can return to the baseline using UV irradiation (Figure 3a). XPS data on the RGO/PET films before and after prolonged exposure to Cl_2 vapor shows no Cl

peaks, which suggests that Cl_2 is not chemically reacting with the various active sites present in the RGO film. The signal response is consistent with a strong physisorption of the Cl_2 vapor which is accompanied by an increase in the number of charge carriers in the RGO/PET film. Signal recovery upon exposure to UV irradiation is consistent with photodesorption of adsorbed gases observed previously in carbon nanotube films.[15] We have considered other mechanisms to account for the sensor response, namely, the formation of an insulator/conductor composite resulting from residual surfactant or ascorbic acid adsorbed onto the RGO film.[16] However, we can rule this out based on: 1) a similar signal response/recovery to Cl_2 vapor in a free-standing RGO film that was previously never exposed to surfactants or ascorbic acid, 2) a similar signal response/recovery to Cl_2 vapor in a hydrazine reduced RGO/PET film, and 3) vibrational spectra (FTIR) that show no residual Triton-X100 surfactant in films washed with toluene (see the Supporting Information).

The increase in conductivity when the RGO/PET sensor is exposed to highly oxidizing vapors is to be contrasted to the increase in resistance when it was exposed to saturated organic vapors, for example, $CHCl_3$, CH_3OH, hexanes, etc., as well as NH_3 (Figure 3), which is consistent with a recent study using RGO[6] and our polythiophene/PET sensors.[14] In this regard, RGO/PET sensors can be viewed as being selective towards a general class of electron-withdrawing vapors. Notably, the response/recovery times are slow (minutes) compared to commercial vapor sensors. This time could result in part from the large film size, which slows down vapor adsorption. For example, preliminary results using very thin films show a significantly faster signal response and recovery.

In summary, we have demonstrated for the first time: 1) a rapid, one-step conversion of exfoliated graphite oxide into RGO using aqueous vitamin C as a mild and green reducing agent, 2) inkjet printing of free-standing and substrate-supported films of graphene oxide and RGO, and 3) an all-organic RGO-based chemiresistor to detect chemically aggressive vapors at the parts per billion level using an air sample at room temperature.

Experimental Section

Synthesis of GO dispersion for inkjet printing: Graphene oxide was synthesized using the Hummers method.[10] To obtain dispersions for inkjet printing, the dried GO powder (60 mg) was first added to deionized water (20 mL) contained within a vial, which was then sonicated for 12 h. The resulting crude dispersion was centrifuged and the supernatant containing the highly dispersed GO was transferred to another vial. Polyethylene glycol 200 (0.2 mL) was added and the resulting mixture was sonicated for 30 min to obtain a very fine GO dispersion which was suitable for inkjet printing.

Synthesis of RGO dispersion using ascorbic acid as a reducing agent for inkjet printing: Ascorbic acid (5 g) was added to a stirred yellow-brown dispersion of GO (3 mg mL^{-1}) in water (5 mL), and the resulting mixture was heated to approximately 80 °C for 1 h. The color of the dispersion changes to black, gradually over a period of approximately 10 min, signalling the reduction of GO into RGO, which is accompanied by flocculation of RGO. The RGO was centrifuged and washed with deionized water (15 mL) for 5 cycles and centrifuged after each wash. The black RGO powder was added to water (5 mL) containing Triton-X100 nonionic surfactant (40 mg), and probe sonicated for 25 min (5 cycles, 5 min each cycle), resulting in a fine dispersion.

Sensor measurements: The cartridge ink in a commercial inkjet printer was replaced with the RGO dispersion prepared above and a four-probe sensor pattern was printed onto a 3M overhead transparency (PET). The RGO/PET film was sonicated and then washed in toluene to remove the adsorbed Triton-X 100 (see the Supporting Information). Sip socket leads were used to establish connections to the RGO film, and then the sensor was connected to an Agilent 34980 A multifunction switch/measure unit. The sensor was placed in a test chamber (460 cc) and it's resistance was monitored continuously over time. After about 10 min, the desired concentration of the vapor was purged into the test chamber. For the 100–12 ppm concentration range an Environics gas dilution system was used, and for lower concentrations (<10 ppm), the vapor was injected into the test chamber using a plastic syringe of air. For example, for a 10 ppm of a vapor to be detected, an injection volume of 46 mL of 100 ppm NO_2 or Cl_2 vapor is required. The resistance decreases sharply and begins to saturate in about 2–3 min. The vapor in the test chamber is then pumped out using a DryFast (2010B-01) vacuum pump. The signal begins to recover slowly to attain its original baseline during the pumping cycle, and this can be as long as 2 h or more depending on the film thickness (see the Supporting Information). The recovery is accelerated to approximately 5 min when the sensor is exposed to 254 nm UV irradiation. After the signal returned to the original baseline value, the sensor was re-exposed to the vapor at different a concentration (as described in Figure 2, 3) with UV irradiation after each exposure cycle to effect signal recovery.

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