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Temperature dependent Raman spectroscopy of chemically derived graphene

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Reduced graphite oxide (GO) has shown promise as a scalable alternative to mechanically exfoliated specimens. Although many measurements show that reduced GO has properties approaching those of pristine graphene, it has been difficult to quantify the extent to which the graphitic network is restored upon reduction. Raman spectroscopy is widely used for the characterization of mechanically exfoliated graphene, but has not been fully explored for reduced GO. In this work, hydrazine suspensions of reduced GO are deposited on micro-hot-plates and examined over a range of temperatures by Raman spectroscopy. The work highlights the benefits of solution processing. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3011030]

Graphene has recently garnered a great deal of attention as a platform for a large variety of experiments.[1–3] In addition to its intrinsic interest, the two-dimensional (2D) carbon network may contribute to our understanding of a wider range of phenomena as graphene is the fundamental building block of both graphite and carbon nanotubes. Recently, chemists have developed a synthetic procedure utilizing aqueous dispersions of the intermediary graphite oxide (GO).[4] This method is scalable and promising for applications, especially given that it has led to the fabrication of graphene based electrical devices by our group and others.[5,6]

The quality of chemically derived graphene is of major importance for many applications, but has not yet been thoroughly characterized. Specifically, the extent to which graphitic regions are restored upon reduction of GO has remained unclear. Thus far the most informative methods of characterization include optical, scanning electron, and atomic force microscopies as well as field effect device performance. Here we present temperature dependent Raman measurements as an additional method of materials characterization for reduced GO. This work highlights the versatility of the solution processing of chemically derived graphene, which enables selective deposition onto micro-hotplates (MHPs)[7] and ultimately Raman characterization across a much larger temperature range (up to 400 °C) than previously accessible.

In order to produce single layer specimens, GO was prepared via Hummers' method, yielding an aqueous dispersion.[8] An aliquot was filtered and left to dry overnight. The resultant GO films were peeled away and placed in anhydrous hydrazine. Bubbling and gradual dispersion of GO indicated both reduction and suspension of the reduced product. After two days, bubbling subsided and no solids were present. The suspension was spin coated at 1300 rpm onto prepared MHPs. The MHPs consisted of a 1-μm-thick silicon nitride membrane with a serpentine platinum resistor and a pair of interdigitated electrodes [Fig. 1(a)]. Current provided to the resistor produces resistive heating through the membrane. The resistance is determined and enables the

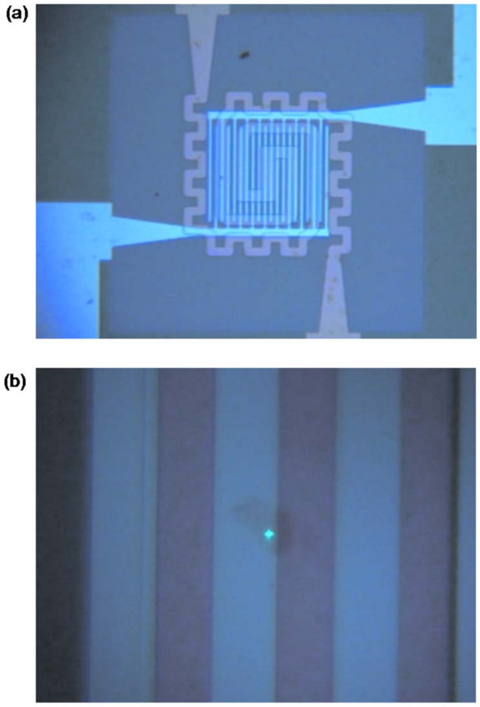

FIG. 1. (Color online) (a) An optical microscope image shows a MHP at 50× magnification. The MHPs are comprised of a silicon nitride membrane with two interdigitated platinum electrodes and a serpentine resistor. Current provided through the resistor causes resistive heating in the membrane. Temperature can be extrapolated from the power dissipated by the membrane and comparison to a calibration curve. (b) A single sheet specimen can be seen positioned beneath the 533 nm focused laser spot.

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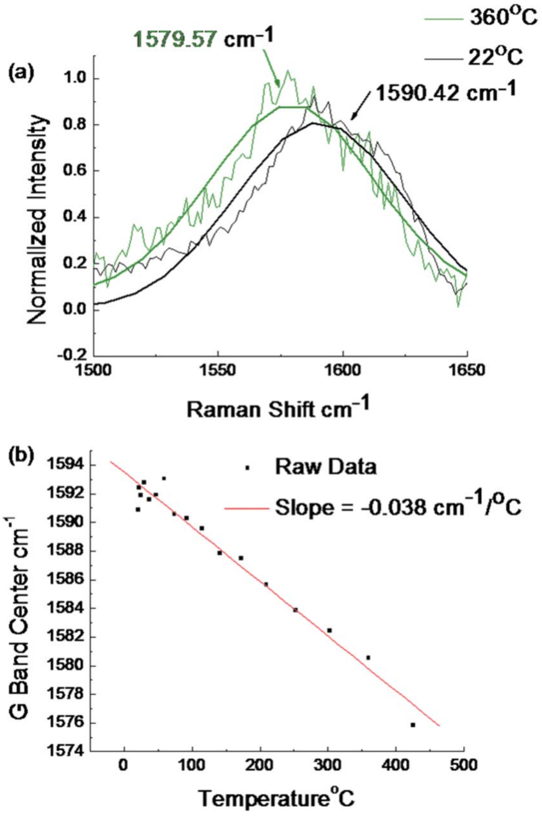

FIG. 2. (Color online) (a) Comparison of spectra taken at high and low temperature extremes shows a gradual redshift in the G band. (b) The center of each G band plotted as a function of temperature gives a linear fit with a slope of of$=-0.038\ \mathrm{cm}^{-1}/{}^{\circ}\mathrm{C}$.

temperature to be determined by comparison to a calibrated power curve. After deposition, MHPs were evacuated to ensure complete removal of hydrazine. Because single and few layer graphene have different properties, it is important to fully characterize layer thickness and electrical performance.[9,10] Detailed characterization of our reduced GO is reported elsewhere.[11] Briefly, Si/SiO_2 substrates coated in a similar fashion to MHPs allowed for atomic force measurements, confirming single sheet step heights of less than 1 nm, which are consistent with the observations of others.[5,6] Top contact, back-gated field effect devices were also fabricated on Si/SiO_2, displaying p-type current modulation under ambient conditions as is commonly observed for reduced GO.

Raman measurements were conducted using a Renishaw inVia instrument equipped with a 532 nm laser and 100× objective. A single layer specimen was located using the attached microscope and carefully aligned before spectra were recorded [Fig. 1(b)]. The data sets presented are plotted with temperatures recorded during excitation. Raman peak locations for chemically converted graphene are consistent with those of mechanically exfoliated samples, but the peaks themselves are substantially broadened.

The location of the E_{2g} vibrational mode, commonly called the G peak, as the temperature is varied from 22 to 400 °C is presented in Fig. 2(a).[12,13] Representative spectra recorded at the low and high extremes of the temperature range are shown in Fig. 2(b). Calizo *et al.*[14,15] recently performed a number of temperature dependent Raman measurements on mechanically exfoliated graphene samples. They observed a comparable dependence for the G band and generated an expression for the peak frequency given in Eq. (1).

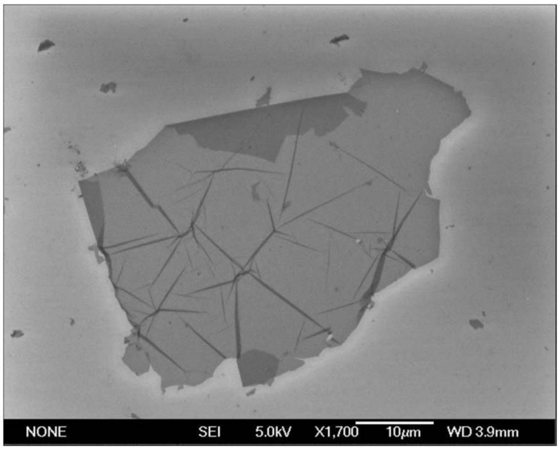

FIG. 3. SEM of a large single sheet of chemically derived graphene displays wrinkling and folding. While such phenomena are rarely observed in mechanically exfoliated samples, they provide evidence of a diminished Young's modulus in chemically produced graphene.

$$w_G = w'_G + X_G T. \tag{1}$$

From Eq. (1), a linear fit of the data in Fig. 2(a) indicates a G band temperature coefficient for reduced GO of $X_G=-0.0267\ \mathrm{cm}^{-1}/{}^{\circ}\mathrm{C}$ over the entire temperature range.

The observed G band temperature coefficient includes contributions from thermal expansion (X_T) and anharmonic coupling of phonons (X_v) such that $X_G=X_T+X_v$.[14] The X_G value ($-0.0267\ \mathrm{cm}^{-1}/{}^{\circ}\mathrm{C}$) for reduced GO is larger than that observed for both mechanically exfoliated single ($-0.0162\ \mathrm{cm}^{-1}/{}^{\circ}\mathrm{C}$) and double layer ($-0.0154\ \mathrm{cm}^{-1}/{}^{\circ}\mathrm{C}$) samples.[14] Calizo *et al.* noted that the magnitude of the temperature coefficient varies inversely with the number of layers present, becoming much larger as one moves from highly oriented pyrolytic graphite (HOPG) to single layer specimens. They suggested that this may be the result of increased contributions from X_T as thin samples enjoy greater freedom for thermal expansion in the a and b directions. Our data agree well with this suggestion, indicating that single sheets of reduced GO undergo more thermal expansion than both HOPG and their mechanically exfoliated counterparts.

The coefficient of thermal expansion (CTE) is inversely proportional to Young's modulus (E) given in Eq. (2), where F is a force applied to an area A, $L(0)$ is the initial length, ΔL is the change in length, and ΔT is the change in temperature.

$$E = \frac{\text{stress}}{\text{strain}} = \frac{FL(0)}{A(0)\Delta L} = \frac{FL(0)}{A(0)\Delta T \times \text{CTE}}. \tag{2}$$

From this relationship and the Raman data, we expect reduced GO to have a lower Young's modulus than samples produced by mechanical exfoliation of graphite. This is not to suggest that chemically derived samples are weak, as measurements of tensile strength performed on similar materials before reduction yield Young's modulus values of greater than 32 GPa. We do, however, commonly observe wrinkling and folding in large single sheets as is evident in the scanning electron microscope (SEM) image in Fig. 3. Such wrinkling is rarely observed in mechanically exfoliated samples and supports the conclusion of diminished Young's modulus for chemically derived graphene.

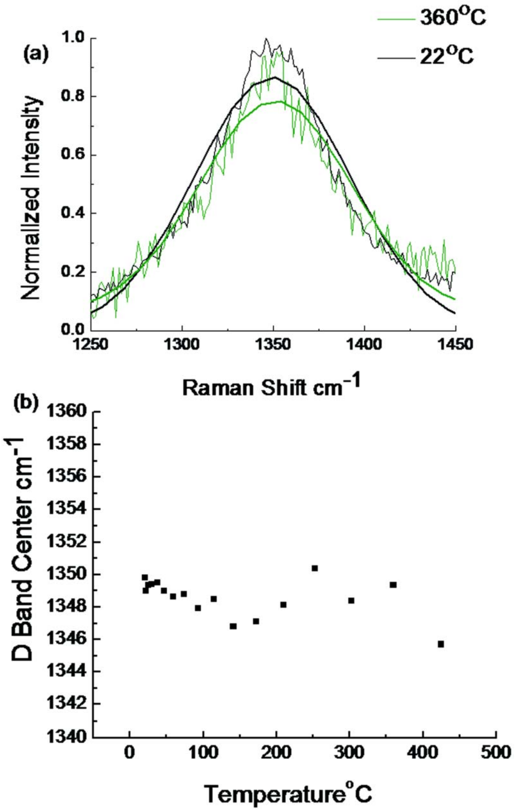

FIG. 4. (Color online) (a) Spectra at high and low temperature extremes show similar *D* bands. (b) *D* band centers are plotted as a function of temperature, but do not show evidence of an obvious trend.

A second important observation is that the *G* band data do not deviate significantly from the linear trend observed for other conjugated carbon based materials. This is of note particularly in relation to temperature dependent measurements of diamond, which become nonlinear at elevated temperatures. Such nonlinear terms serve as an indication of diamond's sp^3 carbon centers and three dimensionality.[14] Our data remain linear upon heating, indicating that there are not a significant number of such regions. This is surprising, given the prominence of the *D* band in reduced GO samples, which is usually attributed to the presence of sp^3 carbons within a specimen.[4] Other forms of disorder, which could include residual carboxylic acids, epoxides, or ketones, may well account for the increased *D* band intensity.

Figure 4 presents the temperature dependence for the *D* peak, located around 1350 cm^{-1}.[12] We do not observe a significant shift with changes in temperature. This is surprising, given that Calizo *et al.* observed a considerable shift in the second order analog to this peak, the so-called 2D peak.[14] A possible explanation is that the width of our *D* peak simply makes any shift difficult to observe.

This study confirms the impact of thermal expansion on the Raman spectrum and suggests that reduced GO has a lower Young's modulus than its mechanically exfoliated counterparts. This conclusion is well supported by the consistent observation of wrinkling in the SEM images of reduced GO.

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