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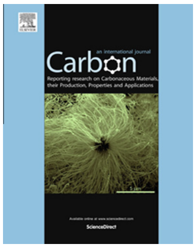

Band gap engineering of graphene oxide by chemical modification

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ABSTRACT

The method with which one creates a sample of graphene oxide paper has a strong impact on its electronic structure. Using X-ray emission spectroscopy and X-ray absorption spectroscopy to indirectly measure the band gap, we have found that intercalation with hexylamine increases the band gap, while replacing water with dimethyl sulfoxide (DMSO) decreases the band gap. Reduction with hexylamine sharply decreases the band gap as expected, but we have also found that heating the sample reduces the band gap to the same degree. This band gap reduction is due to defunctionalization of graphene oxide *via* reaction with water that produces CO_2. Direct current four-probe conductivity measurements show that the decrease in band gap width leads to a lower-than-expected increase in conductivity, likely because the heat-induced defunctionalization process destroys the graphene sheet and reduces overall carrier mobility.

1. Introduction

Graphene is a stable two-dimensional crystal [1] that shows a distinct characteristic in its band structure: the bands near the Fermi level form a Dirac cone that results in massless charge carriers near the Fermi level that propagate through the crystal at the speed of light [2]. The vertex of this cone sits at the Fermi level, which means graphene is a zero band gap semiconductor, and thus has suggested for use in many different electronic and technological applications [3–5]. If one requires graphene to conduct charge carriers, it is perfectly suited for this task. However, the lack of band gap means that graphene cannot be used in devices designed to perform digital logic because a band gap is required to provide distinct ‘on’ and ‘off’ conduction states [6]. Oxidizing graphene to introduce this necessary band gap is an obvious choice, particularly because reducing and repairing graphene oxide (GO) to produce graphene still promises to be first among the methods of graphene manufacture that will provide the highest yields for industrial-level manufacturing. Thus, GO is not only a useful product in its own right, but is also the precursor for graphene. Understanding how the electronic structure of GO changes with chemical treatment is therefore an extremely important question.

We present here a study of the electronic structure of graphene oxide as a function of the chemical modification of GO. Others have looked at chemically modifying GO to engineer the band gap [7], however, here we probe the electronic properties of six differently-synthesized samples of graphene oxide using X-ray absorption near-edge fine structure (XANES), to probe the conduction band (CB), and non-resonant X-ray emission spectroscopy (XES), to probe the valence band (VB). These techniques boast site- and chemical-specificity that other techniques do not possess, allowing for a detailed study of the carbon states that populate the near-Fermi energy regime. In addition to detailed chem-

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ical information about the samples, these spectra indirectly provide the band gap because the band gap is the energy difference between the top of the VB (highest energy state in the XES spectrum) and the bottom of the CB (lowest energy state in the XANES spectrum). Others have accurately determined the band gaps of various materials using a combination of XANES and XES [8–10]. Changes in our experimental band gaps are compared to changes in the conductivities of the samples, as measured by the direct current (DC) four-probe conductivity measurement technique.

2. Experimental

2.1. XES measurements

The GO XES spectra were performed at Beamline 8.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory using the soft X-ray fluorescence (SXF) endstation [11]. Emitted radiation was measured using a Rowland circle type spectrometer with a large spherical grating and a photon-counting area detector. The total experimental resolution was 0.3 eV FWHM. The fluorescence measurements were made using a depolarized configuration, which means that the vector E of the incidence beam lies at the scattering plane. The SXF endstation is configured such that the path of the emitted photons and the incident beam are perpendicular.

2.2. XANES measurements

High-resolution C 1s XANES spectra on the C K edge were measured at the Spherical Grating Monochromator (SGM) beamline at the Canadian Light Source [12]. The incident light had a resolution of 0.1 eV. The spectra were measured in both total electron yield and total fluorescence yield modes. Instead of normalizing to an upstream mesh current, however, the spectra were instead normalized to the current generated in a photodiode [13]. This photodiode current spectrum was not taken simultaneously with the sample spectrum, but rather directly afterwards. This technique allows one to directly measure the light intensity hitting the sample as a function of energy, which allows one to correct for the problem of a carbon-contaminated mesh introducing false features into carbon spectra.

3. Results and discussion

As mentioned previously, we experimented on six samples, each prepared slightly differently. The samples are called graphene oxide sample A, B, C, D, E, and F (shortened to GOa, GOb, GOc, GOd, GOe, GOf, respectively). All six samples were made from the same base material, then five were subjected to some additional treatment. The samples were further subdivided into three sets of two; in each set, two samples were made in exactly the same manner, but one sample of the set was subjected to an additional procedure to which the other was not, thus making one sample a control used to study the effects of the additional procedure. The details are summarized in Table 1.

Fig. 1 shows the results of our experiments, as well as our analysis of the spectra for the purpose of determining the band gap. In this figure, the non-resonant XES spectrum and the XANES spectrum is plotted on the same energy axis, each in a separate panel for each sample. The XES spectra were measured at Beamline 8.0.1 at the Advanced Light Source [11], while the XANES spectra were measured at the SGM beamline at the Canadian Light Source [12]; abbreviated details on the experimentation apparatuses are included in the Experimental section. The XANES spectra were measured in both total electron yield (TEY) and total fluorescence yield (TFY) modes. The TFY spectra that are displayed have been treated using the method of Eisebitt *et. al*, which takes into account, and partially counteracts, the effects of saturation that can severely distort the lineshape of TFY spectra [14,15]. As an added benefit, in the weak near-Fermi energy range, this method suppresses the even weaker noise component, thus allowing for unambiguous determination of real features.

The shapes of the spectra from the six samples hold much information, which will be discussed later. Let us first discuss the band gaps of the samples. As with other spectroscopic methods for determining the band gap, the question of where the bands actually start is central to the accuracy of the analysis. The method chosen here to find the band edges the second derivative method, because weak sharp features, such as localized molecular orbitals and sharp band onsets, show much more prominently than broad features. This is true even if the broad feature has much greater spectral weight. This property helps to extract details from the near-Fermi portions of the XES and XANES spectra. The centroids of peaks in a spectrum become local minima in the second derivative of that spectrum. Thus, the band gap is defined as the energy difference between the highest-energy local minimum in the second derivative of the XES spectrum (denoted d^2XES/dE^2) and the lowest-energy minimum in second derivative of the XANES spectrum (denoted either d^2TEY/dE^2 or d^2TFY/dE^2, as appropriate). The second derivative method has proven to be an accurate and highly reproducible way to determine experimental band gaps from X-ray spectra [16–19]. Whether the gap is direct or indirect cannot be determined from this method without the aid of other analysis techniques.

The second derivatives of the XES, TFY, and TEY spectra of the six samples were computed for the purpose of determining the band gap, and all are displayed in the appropriate insets in Fig. 1. As one can see in the insets, for no sample does its d^2TEY/dE^2 and d^2TFY/dE^2 agree as to the placement of local minima. Invariably, the d^2TFY/dE^2 has the lowest-energy feature, and in many cases, the d^2TFY/dE^2 has more local minima. This particular problem has been addressed in previous work, and the feature at roughly 284.6 eV that makes such a prominent minimum in the d^2TFY/dE^2 spectrum for each sample is due to AA-stacking interactions between GO sheets, whereas the feature that sits somewhere between 285.3 and 285.5 eV is due to AB-stacking [20]. The latter is the preferred stacking arrangement in graphite. As we have established, the lowest-energy peak, due to AA-stacking interactions in GO, determines the upper boundary of the band gap.