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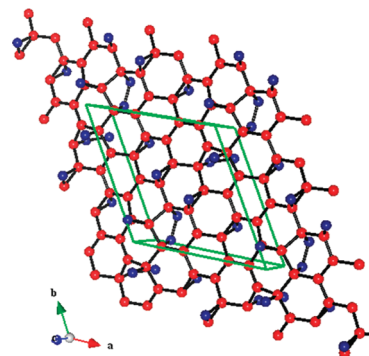
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# Investigation of the Local Structure of Graphene Oxide

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**ABSTRACT** A study of the local structure of graphene oxide is presented. Graphene oxide is understood to be partially oxidized graphene. Absorption peaks corresponding to interlayer states suggest the presence of pristine graphitic nanoislands in graphene oxide. Site-projected partial density of states of carbon atoms bonded to oxygen atoms suggests that the broadening of the peak due to interlayer states in the carbon K-edge spectrum of graphene oxide is predominantly due to formation of epoxide linkages. Density functional theory suggests that multilayers of graphene oxide are linked by peroxide-like linkages.

**SECTION** Nanoparticles and Nanostructures



Graphene oxide<sup>1</sup> (GO) is currently an intense area of research due to its electronic properties. Preliminary investigations have demonstrated its potential applications in technologically important multidisciplinary research such as the development of transparent and flexible electronic<sup>2</sup> devices and nanomechanical devices,<sup>3</sup> and functionalized GO has been used in drug delivery of water-insoluble cancer drugs.<sup>4</sup> Recent studies have shown nonlinear effects in GO in the nanosecond and picoseconds domains,<sup>5</sup> indicating its application in optoelectronic nanodevices. Partially reduced GO samples have also demonstrated the ability to absorb gases<sup>6</sup> at low concentrations. GO has also shown potential application for hydrogen storage for fuel cell applications<sup>7</sup> and in green energy production by enhancing the photoelectrochemical water splitting.<sup>8</sup> GO in its own right is an important material to study not only because it shows interesting and extraordinary properties by itself, but the underlying graphene sheet also shows excellent properties from the perspectives of both fundamental and applied research.<sup>9–11</sup> GO is synthesized by the oxidation of graphene causing changes in the electronic structure of pristine graphene. The local structure of graphene oxide needs to be investigated to understand its properties. In this Letter, the local structure of GO sheets has been investigated using X-ray absorption near-edge spectroscopy (XANES). The insight into the local structure will enable exploration of the potential applications of GO in areas of nanodevices and nanomedicine.

GO samples were synthesized by oxidation of large-area graphite flakes using a modified Hummers method,<sup>12</sup> resulting in large-area sheets that can be seen in TEM images, as shown in Figure 1a. The sample was deposited on copper tape to study the local electronic structure. X-ray absorption spectroscopy (XAS) spectra were acquired in total electron yield (TEY) mode as a function of X-ray photon energy at the beamline U4B of the National Synchrotron Light Source at the Brookhaven National Laboratory. XANES is strongly sensitive to the oxidation state and coordination chemistry of the

absorbing atom and hence may be used to understand the local structure. In the band theory approach, the near-edge structure is the sum of transition rates of all possible unoccupied one-electron states.<sup>13</sup> Each transition can be understood as composed of two components, (1) the terms of the matrix element between the initial and final states and (2) the partial density of states (PDOS) along the  $k_z$  direction. Although detailed investigations may also be performed by using techniques like multiple scattering theory, previous studies have suggested the need to include the core hole for spectral shapes in XAS spectrum for simple metals<sup>14,15</sup> and graphite.<sup>16</sup> Thus, a simple investigation of carbon and oxygen K-edged absorption spectra by using site-projected partial density of states (DOS) obtained from density functional theory (DFT) calculations will enable in understanding qualitatively the contribution of the C–O bonding in the XANES spectrum and hence the local atomic structure of GO. K-edge absorption enables one to sample the PDOS.

DFT within the local density approximation was used to calculate the PDOS for which a unit cell with 33 atoms was taken such that the C/O ratio was 2.66:1. This constraint on the carbon and oxygen ratio was obtained using an analytical technique (CHNS (O) measurement) which determines the ratio of simple elements such as hydrogen, carbon, nitrogen, sulfur, and oxygen in bulk samples using combustion (pyrolysis for oxygen) techniques.<sup>17</sup> The C/O ratio so obtained is in agreement with the previously reported results.<sup>18</sup> The DFT<sup>19–21</sup> calculations reveal that GO is a partially oxidized puckered graphene sheet with oxygen bound to the sheets in the form of epoxide and oxygen bridges (C–O–O–C peroxide and R–O–O–R endoperoxide) as seen in Figure 1b. On the basis of these calculations, multiple layers GO are understood to be linked by peroxide-like linkages. Previous DFT investigations of single oxygen atom

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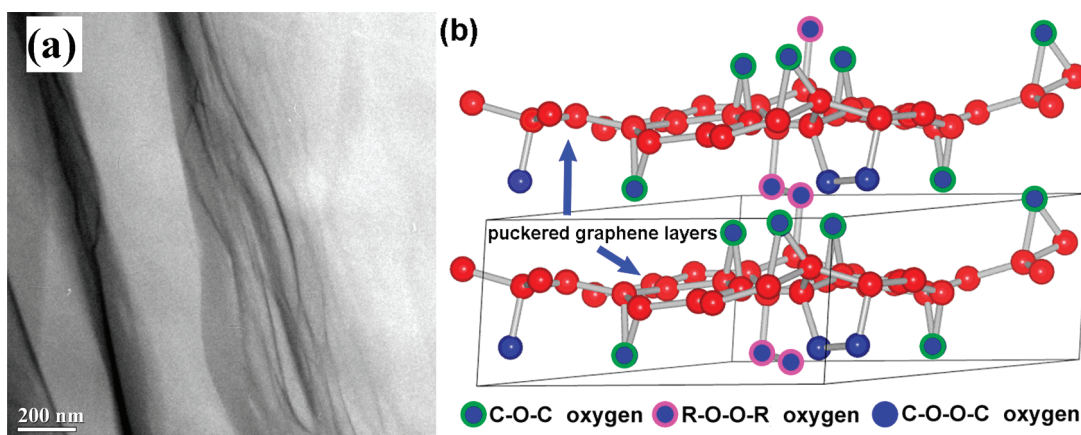


Figure 1. (a) TEM image of a large-area sheet of GO. (b) Ground-state structure of GO obtained from DFT.

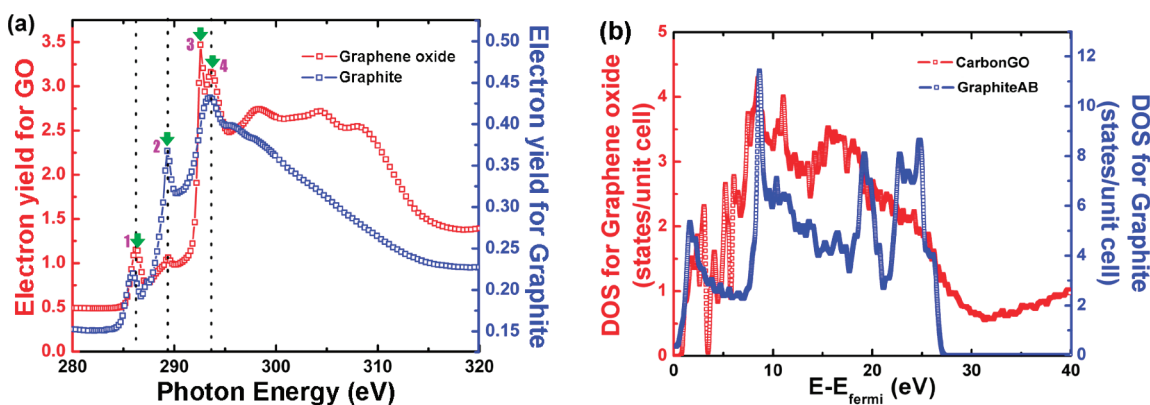
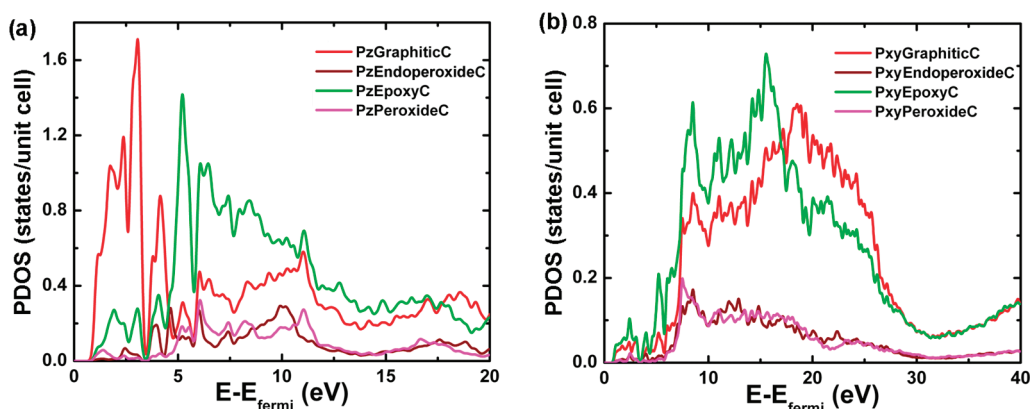


Figure 2. (a) The carbon K-edge XANES cross section of GO and graphite. The peaks are labeled 1–4. The absorption edge at 286.2 eV, marked as 1, is due to  $1s \rightarrow \pi^*$ . The broadening of absorption peak in GO at  $\sim 289.3$  eV, marked as 2, corresponds to epoxide linkages, while the absorption peaks at around 292.5 and  $\sim 293.5$  eV, marked as 3 and 4, respectively, indicate the presence of  $\sigma^*$  and high-energy  $\pi^*$  resonances. (b) Calculated DOS for carbon atoms in the relaxed GO and the AB stacked graphite structure.

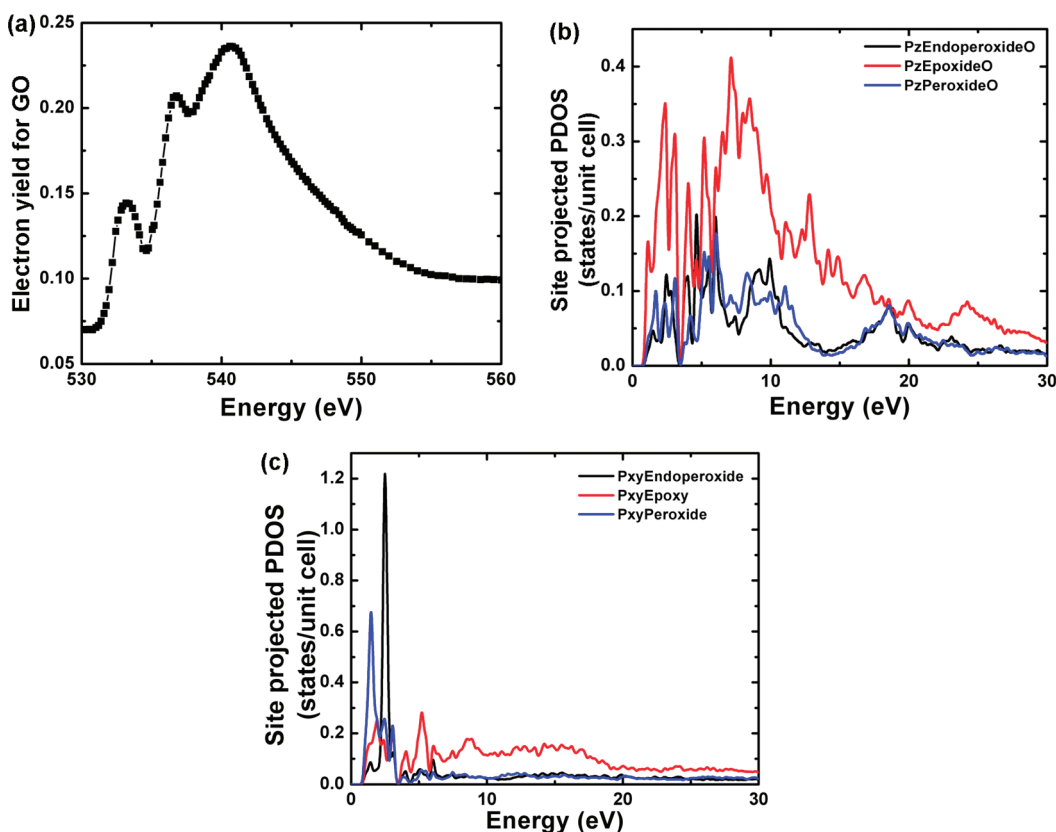
absorption on a graphene lattice in a supercell with a C/O ratio of 50:1 have suggested the formation of epoxide bonds.<sup>22</sup> Similar cluster calculations on  $C_{54}H_{17} + O + (OH)_3 + COOH$  have shown formation of epoxide linkages.<sup>23</sup> Site-projected DOS obtained from DFT calculations for graphene oxide and graphite have been used to interpret the XANES spectrum for GO.

Comparing the site-projected DOS with the XANES spectrum, the absorption edge in the GO sample at  $\sim 286.2$  eV can be assigned due to the out-of-plane  $1s \rightarrow \pi^*$  transition mostly due to graphitic carbon atoms. The absorption edge at  $\sim 293.5$  eV can be assigned to the in-plane  $\sigma^*$  resonance in graphite carbon as also measured for graphite samples in Figure 2a. The absorption peaks observed in the XANES spectrum for reference graphite samples are in good agreement with those obtained using electron energy loss spectroscopy on graphite samples.<sup>24</sup> These absorption peaks are also visible as van Hove singularities at  $\sim 1.5$  and  $8.6$  eV in the DOS for AB stacked graphite in Figure 2b. The DOS contributions for GO in Figure 2b has been plotted only from the carbon atoms. The additional peak at 289.3 eV in the experimental XANES spectra for the graphite sample in Figure 2a possesses neither  $\sigma$  nor  $\pi$  symmetry. The assignment of this peak to interlayer

states has been discussed in detail based on FLAPW calculations.<sup>25</sup> The peak corresponding to the interlayer states at  $\sim 289.3$  eV in GO samples is much broadened and is understood to arise due to graphitic regions in GO. In order to understand the broadening of this peak further, site-projected DOS were decomposed for carbon atoms which could be classified as graphitic carbon carbon-bonded to epoxide bonds and carbon-bonded to oxygen bridges (endoperoxide and peroxide-like linkages). From a comparison of site-projected PDOS of the above-classified carbon atoms in Figure 3, we see that the carbon K-edge at 286.2 in GO can be assigned to primarily due to  $1s \rightarrow \pi^*$  transitions in graphitic carbon atoms in GO, as seen in Figure 3a. The broadening of the absorption peak at 289.3 eV can be assigned to the  $1s \rightarrow \pi^*$  transitions in the carbon involved in bonding with oxygen atoms. Analyzing the site-projected PDOS for carbon atoms involved in different kinds of bonding, it appears that the higher-energy broadening of the 289.3 eV peak may be assigned primarily due to the presence of epoxy bonds. The  $p_z$  and averaged  $p_{xy}$  components as seen in Figure 3a and b suggests that the higher-order  $\pi^*$  and  $\sigma^*$  resonances in GO at  $\sim 292.5$  and  $\sim 293.5$  eV may be assigned mainly to the presence of carbon atoms bonded to oxygen atoms by epoxide



**Figure 3.** Site-projected PDOS plot for carbon atoms involved in different bonding environments for the (a) out-of-plane  $\pi^*$  and (b) averaged in-plane  $\sigma^*$  components.



**Figure 4.** (a) Oxygen K-near-edge XANES spectrum for the GO sample shows absorption resonances at  $\sim 533.2$ ,  $\sim 536.7$ , and  $\sim 540.5$  eV. (b) Site-projected PDOS ( $p_z$ ) for oxygen atoms bonded to the basal puckered graphene plane by different kinds of bonds. (c) Site-projected PDOS ( $p_{xy}$ ) for oxygen atoms bonded to the basal puckered graphene planes by different kinds of bonds.

bonds. Significant contributions of graphitic carbon also need to be considered for  $\sigma^*$  resonances. We note the qualitative similarity of the computed and measured C K-edge spectra in Figure 2, indicating the soundness of the structural model.

The oxygen K-edge near-edge X-ray absorption (XAS) spectrum was also used to investigate the nature of oxygen bonding with the graphene sheet in GO. Three distinctive features in the O K-edge XAS spectrum at  $\sim 540.5$ ,  $\sim 536.7$ , and  $\sim 533.2$  eV are observed in Figure 4a, in agreement with

the previously reported data.<sup>26</sup> Detailed analysis of the PDOS of the out-of-plane  $p_z$  and in plane  $p_{xy}$  orbitals for oxygen atoms in Figure 4b and c shows that the absorption peaks at  $\sim 540.5$  eV may possibly be due to higher-order  $\pi^*(p_z)$  resonance of all oxygen atoms and higher-order  $\sigma^*(p_{xy})$  resonance of the 1,2-epoxy linkages in the GO sample. The absorption peak at  $\sim 536.7$  eV seems to arise from  $\sigma^*(p_{xy})$  and higher-order  $\pi^*(p_z)$  resonances of only epoxy bonds, whereas the absorption peak at 533.2 eV is believed to



possibly be a contribution from the  $\sigma^*(p_{xy})$  resonance of the peroxide and endoperoxide linkages. Significant contributions from the  $\pi^*(p_z)$  resonance of epoxide bonds need to be considered. The O K-edge XANES spectrum is expected to be modified for purely monolayer sheets of graphene with the disappearance of peaks corresponding to  $\sigma^*(p_{xy})$  resonances due to the disruption of peroxide-like linkages.

No absorption edges corresponding to that of molecular oxygen<sup>27</sup> are observed, suggesting that the possibility of intercalation of molecular oxygen can be safely ignored. Spectra measured on both CuO and Si substrates reveal the same profile, and these spectra are consistent with the DFT simulations.

To summarize, we have shown that oxidation of graphene leads to the formation of nanoislands of pristine graphene in graphene oxide. The XANES data exhibit spectral features reflecting absorption features due to the unoccupied DOS corresponding to that of graphite. A comparison of the XANES spectra of GO with PDOS explains the evolution of the electronic states due to oxidation and broadening of states corresponding to interlayer states.

## COMPUTATIONAL METHODS

First-principles spin-restricted calculations were performed using the Vienna Ab initio Simulation Package<sup>19,28</sup> (VASP), which implements the pseudopotential approximation and plane wave basis set into the framework of density functional theory. A high-energy cutoff of 550 eV was chosen for the plane wave basis. The atoms were relaxed using the conjugate gradient algorithm such that the forces on each atom were smaller than 0.001 eV/Å. Highly accurate projected augmented wave (PAW) potentials using exchange correlation of Ceperley and Alder were used. The irreducible Brillouin zone was sampled using K points generated by the Monkhorst Pack scheme.

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