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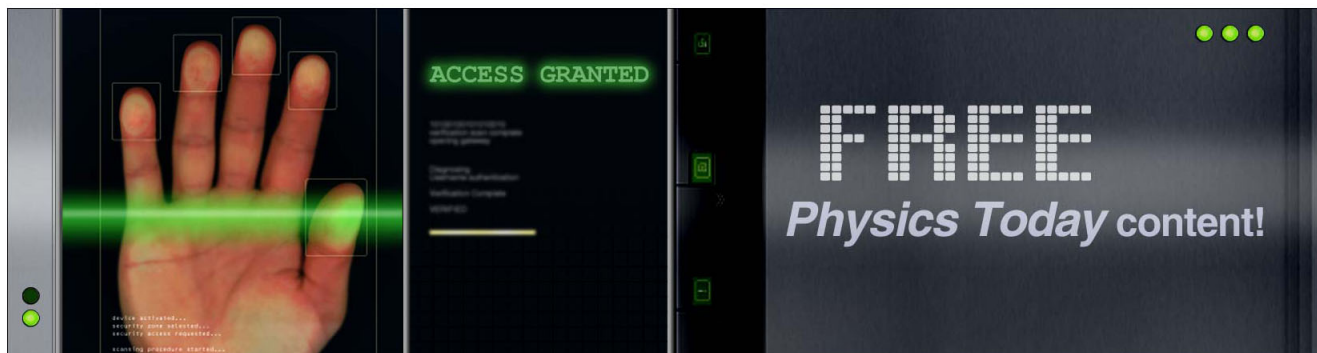
Investigation of structural and electronic properties of graphene oxide

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The local atomic structure of graphene oxide has been probed using synchrotron radiations. Detailed investigations of recently proposed simplistic model of graphene oxide using x-ray absorption near edge spectroscopy have been performed. X-ray diffraction measurements and calculations indicate loss of coherence between graphene-like layers. However, larger in-plane structural coherence is understood to be present. Selected area electron diffraction measurements indicate the presence of graphitic regions in graphene oxide which is expected to produce interesting confinement effects in graphene oxide which could be important for the development of tunable electronic and photonic devices. © 2011 American Institute of Physics. [doi:10.1063/1.3607305]

The unusual and exotic properties of functionalized graphene have made it a promising material for fundamental advances as well as an attractive platform for development of nanodevice technologies. One such functionalized graphene material is graphene oxide and is obtained by oxidation of graphene using strong oxidants. Graphene oxide has shown promising device applications[1–3] and is being explored vigorously particularly due to the challenges in determining its structural and electronic properties. Therefore, a detailed investigation providing insight into the atomic structure of graphene oxide will provide helpful information in tailoring its properties and unleashing its potential device applications. The atomic structure of graphene oxide has repeatedly been investigated using different experimental techniques.[4–6] One of the earliest models of graphite oxide was proposed as early as 1934 by Hofman *et al.*[7] Subsequently several models were proposed by Ruess[8] in 1947, Scholz and Boehm[9] in 1967, and by Lerf *et al.*[10] in 1998. These models have been based mostly on the analysis of spectroscopic measurements until density functional theory was used by Kudin *et al.*[11] to investigate the essential the findings of these models by computing the Raman spectrum. The computed Raman[11] spectra have suggested the need to significantly improve the model of graphene oxide to correctly interpret the spectroscopic data.

In light of above models, the most commonly agreed conclusion that can be derived suggest that graphene sheets get oxidized by the formation of epoxy (C-O-C) bonds during oxidation to form graphene oxide. Our recently proposed simplistic model of graphene oxide has been able to predict the local electronic structure of graphene oxide in very good agreement to highly accurate synchrotron based x-ray absorption near edge measurements[12] and has motivated this research further to investigate the atomic structure of this interesting material.

The electronic and atomic structure of graphene oxide has been investigated based on the molecular ratio of C:O as 2.66:1 obtained from experimental measurements. Spin restricted density functional theory as implemented in Vienna ab-initio simulation package (VASP) was used to relax the structure. The electron localization function was plotted to visualize the bond strengths in graphene oxide using the formulation of Savin and Silvi.[13] The functionalization of graphene due to bonding of oxygen atoms produces ripples on graphene sheet straining the lattice with C-C bond lengths up to ~1.52 Å. The atomic structure suggest that oxygen gets bonded to the graphene sheets through epoxide bonds as seen in Fig. 1(a). The formation of epoxide bonds is well supported by the presence of NMR measurements[6,14] and in density functional calculations of single oxygen atom absorption in supercells with C:O ratio of 50:1 on graphene lattice.[15] Linking of oxygen molecules in form of peroxide and endoperoxide bonds is also observed as seen in Figs. 1(b) and 1(c). Linking of oxygen dimer in form of endoperoxide bonds has been reported in carbon nanotube[16] systems. The experimental investigations of the presence of peroxide and endoperoxide bonds have been difficult to verify from the x-ray absorption near edge spectroscopy (XANES) due to the absence of very well resolved peak ~289.3 eV region as observed in Fig. 1(d). Graphene oxide samples were synthesized by chemical exfoliation using modified Hummer's method[17] which uses harsh oxidizing agents such as conc. H_2SO_4 and H_2O_2 are the important constituents in peroxide synthesis, hence supporting the formation of endoperoxide and peroxide linkages as observed in our density functional calculations. The presence of pristine graphitic domain as predicted by density functional theory is expected to produce interesting confinement effects leading to control of optical emissions in the UV and near UV region of the electromagnetic spectrum and has been verified experimentally recently.[18]

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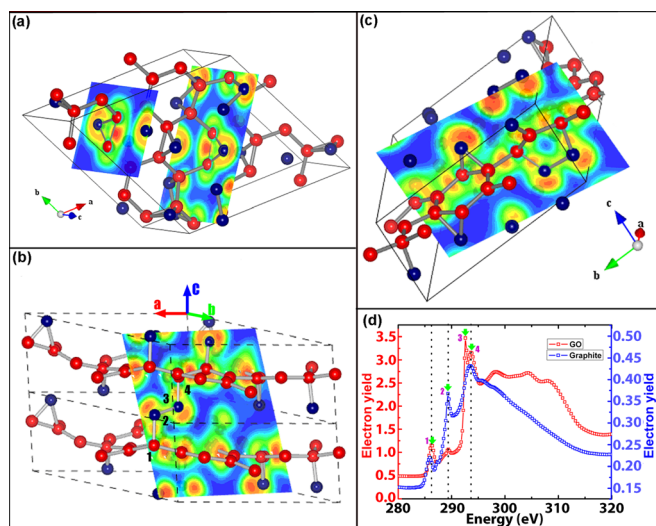
FIG. 1. (Color online) Slices showing the ELF for (a) 1, 2 – epoxide bonds, (b) peroxide like linkages linking weakly different sheets, (c) 1, 3 – endoperoxide, and (d) XANES measurement of graphene oxide and graphite (for reference).

The structural coherence of the sample was investigated using transmission electron microscopy (TEM). The TEM and selected area electron diffraction (SAED) measurements have been performed using JOEL, JEM2010. Graphene oxide sample was deposited on the standard holey-carbon-film covered copper grids and loaded into the microscope for TEM measurements to study graphene oxide lattice. The TEM images show large surface area graphene oxide sheets. The TEM image shown in Fig. 2(a) illustrates large folded sheet of graphene oxide. The electron diffraction rings obtained from SAED measurements as seen in Fig. 2(b)

yielded "d" spacing of about 1.2 Å and 2.1 Å corresponding to "d" spacing in graphene, suggesting the presence of graphitic regions within the graphene oxide in agreement to the predictions of density functional calculations. X-ray diffraction (XRD) measurements were performed on the X14A beamline at the national synchrotron light source at Brookhaven national laboratory using synchrotron source with a wavelength of 0.72838 Å for powdered samples of graphene oxide and graphite. The finely powdered samples were placed in Kapton capillary tubes for XRD measurements. The XRD pattern of the Kapton tube which was used as sample holder is shown in Fig. 2(c). The XRD pattern of graphite shows sharp peaks indicating highly crystalline structure of graphite in Fig. 2(d), while that of graphene oxide in Fig. 2(e) shows a combination of broader peaks at higher "d" spacing along with few sharp features at smaller d values. The peaks marked as "1" and "2" in Fig. 2(e) correspond to the "d" spacing of 1.2 Å and 2.1Å as also obtained from SAED measurements. The XRD pattern calculated for the graphene oxide structure using DFT is found to be in qualitative agreement with the measured pattern as shown in Fig. 2(f). The presence of broader diffraction peaks in the diffraction pattern indicates very short range atomic coherence. There is a loss of coherence between graphene-like layers. However, in-plane peaks are sharper, showing larger in-plane structural coherence. A representative high resolution transmission electron microscopy image (HRTEM) of the sample is shown in Fig. 2(g).

The sample synthesized was characterized using UV-Vis absorption spectroscopy. UV-Vis-NIR absorption spectrum of suspension of graphene oxide in distilled water was recorded to estimate the transitions from ground state to the
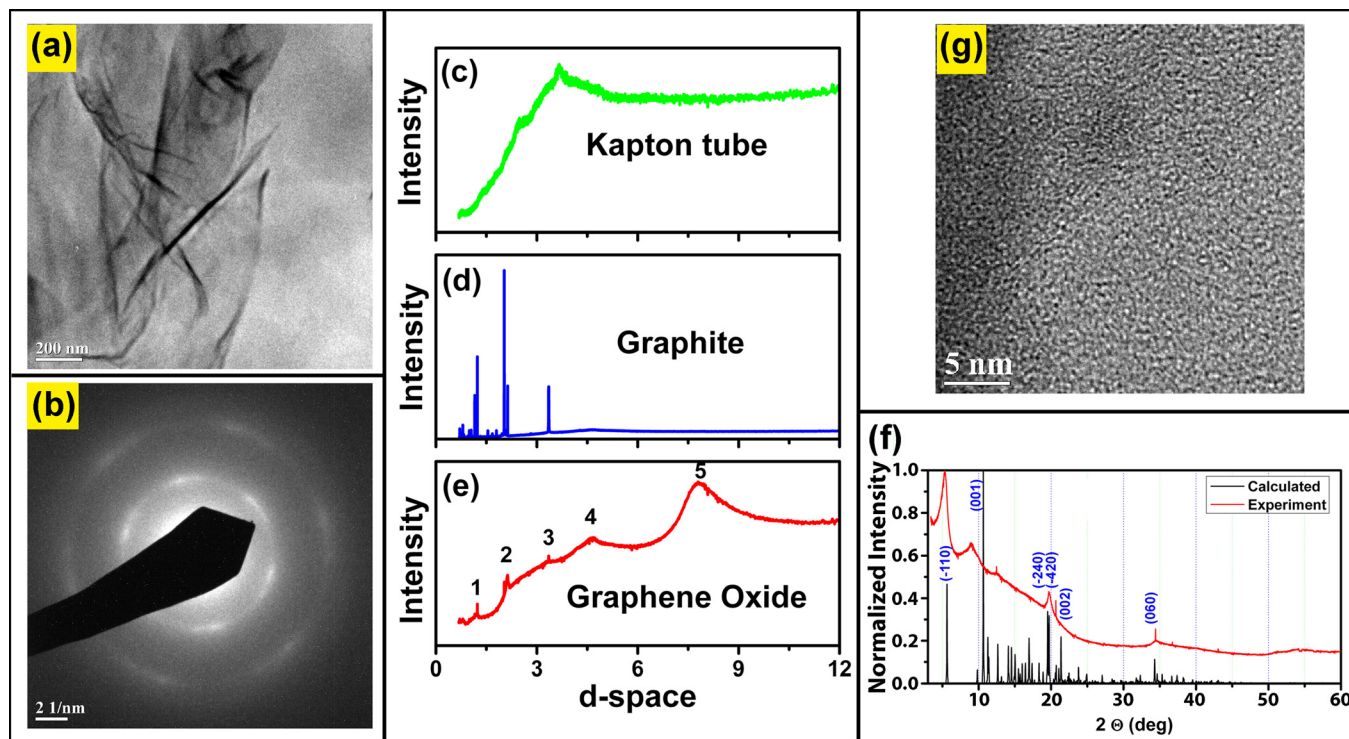

FIG. 2. (Color online) (a) TEM micrograph of graphene oxide nano sheets (b) electron diffraction pattern from SAED measurements for graphene oxide sample. X-ray diffraction pattern for (c) Kapton tube (sample holder), (d) graphite, and (e) graphene oxide sample measured using wavelength of 0.72838 Å. The peak positions marked "1" through "5" corresponds to d pacing of 1.2 Å, 2.1 Å, 3.35 Å, 4.65 Å, and 7.89 Å, respectively. (f) Comparison of calculated (black) and measured (red) x-ray diffraction pattern. (g) HRTEM image of graphene oxide.
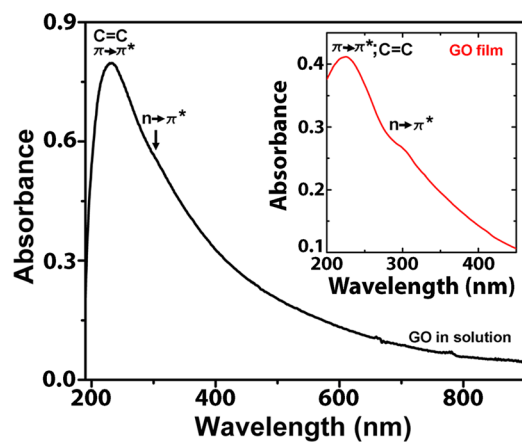
FIG. 3. (Color online) UV-Vis absorption spectra of aqueous graphene oxide solution in a quartz cuvette with sharp absorption peak at ∼233 nm and a shoulder in the range ∼295 nm–305 nm. The inset shows the absorption spectra for a graphene oxide film on quartz substrate indicating that the shoulder becomes more prominent in the graphene oxide film.

excited states of the chromophores in the sample. The spectrum obtained is in agreement with the previously reported results with characteristic sharp absorption peak at about 233 nm and a broad shoulder at ∼290 – 305 nm as seen in Fig. 3. The absorption peak at ∼233 nm has been assigned to the $\pi \rightarrow \pi^*$ transition of the C = C bonds in the previously reported results. This assignment of the absorption peak at ∼233 nm to the $\pi \rightarrow \pi^*$ transition of the C = C bonds seems reasonable in accordance with the predicted structure of our density functional calculation and are logical when compared to the UV-Vis absorption spectrum of graphene which shows absorption peak ∼270 nm.[19]

This blue shift of the absorption peak can be understood due to the reduced electronic conjugation increasing the HOMO and LUMO further away. We assign this broad shoulder in the range 295 – 305 nm to the $n \rightarrow \pi^*$ transitions due to the presence of epoxide (C – O – C) and peroxide (R – O – O – R) like linkages which is also in accordance to our *ab initio* calculations. The broad shoulder becomes very prominent when the spectrum was recorded for a film sample due to the formation of large number of peroxide like linkages in multilayered graphene oxide. The broadening of the peaks is also observed with the ageing of the sample over a long period. However on ultrasonicating and vortexing the aged solution, the shoulder diminishes indicating the formation of monolayer graphene oxide sheets.

The structural and electronic properties of graphene oxide have been investigated in light of our recently proposed simplistic model of graphene oxide. The presence of broadened peaks in x-ray diffraction pattern together with TEM

and HRTEM images lead us to the conclusion that graphene oxide has small structural coherence due to random functionalization of the puckered graphene sheet by oxygen atoms. Based on the density functional studies, the broad shoulder in the range 295–305 nm observed in the UV-Vis measurements is assigned to the $n \rightarrow \pi^*$ transitions due to the presence of epoxide (C – O – C) and peroxide (R – O – O – R) like linkages. The oxidation of graphene sheets will lead to confinement effects thereby opening up the possibility to tune the optical emission from graphene oxide by controlling oxidation. The insight developed in this study will help in tailoring the properties and unleashing the potential applications of graphene oxide.

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