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<td>Author(s)</td>
<td>Lee, Dongwook; Seo, Jiwon; Zhu, Xi; Cole, Jacqueline M.; Su, Haibin</td>
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Magnetism in graphene oxide induced by epoxy groups

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We have engineered magnetism in graphene oxide. Our approach transforms graphene into a magnetic insulator while maintaining graphene’s structure. Fourier transform infrared spectroscopy spectra reveal that graphene oxide has various chemical groups (including epoxy, ketone, hydroxyl, and C-O groups) on its surface. Destroying the epoxy group with heat treatment or chemical treatment diminishes magnetism in the material. Local density approximation calculation results well reproduce the magnetic moments obtained from experiments, and these results indicate that the unpaired spin induced by the presence of epoxy groups is the origin of the magnetism. The calculation results also explain the magnetic properties, which are generated by the interaction between separated magnetic regions and domains. Our results demonstrate tunable magnetism in graphene oxide based on controlling the epoxy group with heat or chemical treatment. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4919529]

Graphene, a two-dimensional structure, is composed of honeycombed benzene rings; in this structure, each benzene ring acts like a diamagnetic domain, where π-electrons circulate around the ring and generate a magnetic field in opposition to the external applied field. Consequently, diamagnetic behavior in graphene-based materials with no d or f electrons is commonly accepted, but diverse magnetism has been reported based on non-trivial mechanisms, such as zigzag edges, defects, vacancies, adatoms, negative Gaussian curvature, and terminal groups at edges.1–15 The magnetic properties in graphene-based materials have attracted interest because of their potential applications to spintronics for which these properties could incubate high mobility, flexibility, and transparency. Conversely, the magnetic properties of insulating graphene oxides (GO) have not been studied so much, despite versatile applications for these materials in, for example, DNA detectors, high dielectric capacitors, batteries, and so on.16–20 Research on magnetism in GO was carried out on a simplified edge-oxidized graphene nanoribbon (GNR) model21 although GO is composed of crystalline region and non-graphitic region.22–24 If the magnetic properties of GO could be exploited together with its other intriguing characteristics, such as its highly porous properties and high surface charge, graphene oxides could serve as a brand new range of multifunctional materials. In the present study, we report magnetic properties of GO, and our findings indicate the possibility of manipulating the magnetism by controlling the extent of material oxidation. The magnetic behavior reproduced by LDA calculations is found to match to our experimental results, surprisingly well. The similarity between these results provides insights into the origin of the unexpected and non-trivial magnetism in insulating GO.

GO was synthesized using the Brodie method.25 To investigate the magnetic properties of GO, some of the GO was heated up to 180° for 24 h (H-GO) and some was reacted with 0.5M NaOH solution (NaOH-GO).

A FEI Philips XL30 sFEG and a Perkin Elmer Fourier transform infrared spectrometer (FT-IR) were used to characterize the structural properties of GO. Electronic properties of GO were investigated with Quantum 2000 X-ray photoemission spectrometer. The magnetic properties of the sample were also investigated using a Quantum Design superconducting quantum interference device (SQUID). In the present study, all calculations were performed within spin-polarized density functional theory for which the generalized gradient approximation of the local density approximation (LDA) functional and plane-wave basis sets were implemented in the Vienna Ab Initio Simulation Package (VASP).26–29 The interactions between ions and electrons were addressed using the frozen-core projector augmented wave (PAW) approach.30,31 The energy cutoff was 500 eV, and the Monkhorst-Pack 1×1×1 k-point grid was used to sample the Brillouin zone.

GO retains a layered structure with partially distorted layers,22–24 and this material is composed of two regions: an unreacted graphitic (sp2) region and a reacted (sp3) region. In the reacted regions, there are various chemical groups, such as epoxy and hydroxyl groups. The epoxy groups are not thermally stable;22,32 these groups are also vulnerable to NaOH.33,34 Consequently, the epoxy group in GO can be controlled with heat treatment (H-GO) and/or chemical reaction with NaOH (NaOH-GO).

We modified the structure of GO using both heat treatment and reaction with NaOH in order to investigate the
magnetic properties of GO and the origin of these properties. The Raman spectrum of GO shows two distinct peaks at 1380 and 1600 cm\(^{-1}\) corresponding to the D and G bands, respectively. (See supplementary material.\(^{35}\) Figure 1 illustrates transmission electron microscopy (TEM) images of GO. The insets of the figures are electron diffraction (SAED) patterns in the selected area. There are areas with distinct circular patterns in the inset of Fig. 1(b), implying that two phases [crystalline (graphitic region) and amorphous (reacted region)] coexist in GO. Diffuse halo-like patterns and distinct spots are visible in the insets of Fig. 1(c), indicating that the amorphous phase and crystalline phase are present together in GO. Fig. 1(d) is the schematic structure for GO synthesized in this study. Graphitic regions are separated by chemical groups.

The chemical groups in GO, H-GO, and NaOH-GO that result from oxidation were investigated using Fourier transform infrared (FT-IR) spectroscopy. Figure 2(a) shows the FT-IR spectra of the samples with different magnifications for clear comparison and that there are four main IR peaks centered at 1050, 1380, 1650, and 3470 cm\(^{-1}\) in all three materials; represent the epoxy group (C-O-C), C-O-C asymmetric stretching of the epoxy groups (C-O), ketone (C=O), and hydroxyl (C-OH), respectively. While the peaks exist in all materials, the IR intensity varies. The destruction of epoxy, ketone, and C-O groups, causal on exposing GO to heat treatments, is indicated by a decrease in their associated peak intensity. In contrast, NaOH treatment of GO induces an increase in the amount of ketone and C-O groups but a decrease in epoxy groups; this finding implies the decomposition of the epoxy group into ketone and C-O groups, which results from reactions with NaOH. Fig. 2(b) illustrates the XPS spectra of the samples. All spectra were decomposed into three components; \(sp^2\) carbon around 284 eV, C-O bonded carbon at 286 eV, and an additional carboxyl group (C(O)O) near 289 eV.\(^{20}\) The ratio of \(sp^2:sp^3\) orbitals of the carbon atoms in the samples were extracted from the XPS spectra and given in Table I. GO is composed of two kinds of carbon orbitals and the ratio of \(sp^2:sp^3\) carbon is 2.8:1. As for heat-treated GO (H-GO), the ratio is 6.5:2:1. NaOH-GO has the lowest ratio of \(sp^2:sp^3\) carbon orbitals.

The magnetic properties of GO, H-GO, and NaOH-GO as a function of temperature were probed using DC susceptibility measurements. Figure 3(a) shows the magnetization

FIG. 1. TEM images of (a) GO, (b) H-GO, and (c) NaOH-GO and (d) the schematic structure of GO. The scale bars represent 100 nm. The insets are SAED patterns.

FIG. 2. (a) FT-IR spectra of GO, H-GO, and NaOH-GO. The peak at 1050 cm\(^{-1}\) results from epoxy groups (-O-), and another peak at 1380 cm\(^{-1}\) arises from stretching between C and O. The other peak centered at 3470 cm\(^{-1}\) is produced by hydroxyl groups (-OH). (b) XPS spectra of the samples. GO (bottom), Heat-treated GO (H-GO, middle), and NaOH-GO (top).

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The effective Bohr magneton numbers ($n_B$) per atom are found by fitting the susceptibility curves using the Curie-Weiss law. For this process, it is assumed that the chemical value of GO is C$_6$O$_2$H, and this assumption is based on the Weiss law. For this process, it is assumed that the magnetic susceptibility curves using the Curie-Weiss equation $\chi = C/(T - \theta_C)$, where $C$ is the Curie constant and $\theta_C$ is the Curie temperature. The Curie constant is described as follows: $C = (n_B^2 \mu_B^2) / M_B$, where $n_B$ is the effective Bohr magneton number, $\mu_B$ is the Bohr magneton, and $k_B$ is the Boltzmann constant.

In the exclusively full carbonic system, it has been predicted that graphene could host a carbon magnetic domain caused by carbon radicals. In GO, the epoxy group can dictate that graphene could host a carbon magnetic domain in GO as in graphene nanobud analogues. Figure 4 shows two typical structures of GO with corresponding band structures for the magnetic carbon domains that contain epoxy groups. To examine the effect of oxygen coverage on magnetism, the oxygen coverage (the ratio of O/C) was varies: 17% and 34% in Figs. 4(a) and 4(b), respectively. Based on this analysis, it was determined that, as the number of epoxy groups increase, the magnetic moment also increases. In this instance, oxygen coverage of 34% is very close to the experimental value of 37% O/C = 6.22 (in Table II), which allowed for direct comparison between experimental and calculated values.

<table>
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<th>TABLE I. XPS peak analysis of the data in Fig. 2(b).</th>
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<td>Area (%)</td>
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</tr>
<tr>
<td>GO</td>
</tr>
<tr>
<td>H-GO</td>
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<td>NaOH-GO</td>
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<th>TABLE II. Atomic ratios by energy dispersive X-ray (EDX) analysis and effective Bohr magneton numbers ($n_B$) of GO, H-GO, and NaOH-GO.</th>
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<td>$n_B$</td>
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In the low oxygen coverage structure shown in Fig. 4(a), the C-C bond length of the epoxy group is 1.52 Å, which is quite similar to the length of that reported in graphene oxide structures. The metallic character is evident of this structure by the nature of its band structure. As shown in Fig. 4(c), the spin densities of this low oxygen coverage structure are located mainly in the carbon atom, whose electron in the 2pz orbital (with a small fractional amount of spin) is localized because of the sp² to sp³ bond character transformation of adjacent carbon atoms, caused by the formation of epoxy groups. The carbon atoms in area I of Fig. 4(c) have 0.02 μB in total, i.e., each carbon atom has 0.0011 μB.

For the high oxygen coverage structure shown in Fig. 4(b), more epoxy groups are present on the graphene surface. So, the gap between majority and minority spins widens and the unpaired spins in the and carbon 2pz orbitals orthogonal to oxygen 2p are in the parallel alignment through Hund’s coupling mechanism as presented in regions I and II in Fig. 4(d). This magnetic state exhibits the same character as that in the nanobud structure. The carbon atoms in areas I and II of Fig. 4(d) have approximately 1μB per carbon atom (for carbon atoms with a spin). In addition to a minor contribution from the epoxy groups, the structure in Fig. 4(b) (including eighteen carbon and six oxygen atoms) exhibits 4μB in total, which indicates that the average magnetic moment per carbon atom in GO is 4μB/18 = 0.22μB. The experimental data such as TEM and XPS reveal that GO is composed of two regions (unreacted graphitic and reacted non-graphitic regions) and the ratio of sp²:sp³ carbon orbitals is 2.8:1. Since epoxy groups are not uniformly located all over the sample and placed only in the reacted non-graphitic region of the sample, only carbon atoms in the regions surrounded by epoxy groups are able to hold a magnetic moment. Hydroxyl groups in GO are also non-uniformly distributed. And the atomic ratios by EDX analysis in Table II reveal that the ratio of epoxy groups to hydroxyl groups in GO is almost 1, implying that the regions surrounded by only epoxy groups in GO are not so much that only some of the carbon atoms in these regions hold magnetic moments.

The structure of GO also depends on the preparation methods25,39,40 and the preparation time41 because different oxidizing agents and preparation time produce varying amount of chemical groups in GO and random distribution of carbon grid formed by benzene and aliphatic rings. Thus, the extent and distribution of the regions I and II in GO rely on the way and time of preparation, leading to different magnetic moment of GO irrespective of similar ratio of C to O. Therefore, the magnetism of GO is very hard to interpret and this is the reason the study on GO has not been reported so much.

Clearly, the magnetic moments in GO originate from unpaired spins in the presence of epoxy, which are presented in the regions I and II in Fig. 4(d). These unpaired spins in the carbon atoms form clusters (like regions I and II) and finally produce magnetic behaviors.

The magnetic properties of GO have been investigated. Magnetic moments obtained from both experiments and first principles calculations show good agreement, suggesting that the origin of this magnetism is the unpaired spins on the carbon radicals, caused by the presence of epoxy groups. Our results indicate the utility of GO as a spintronic device. In detail, by introducing CVD growth methods for large-scale graphene sheet, instead of the graphite powder we used here, the amount and distribution of the epoxy groups are precisely manipulated. Accordingly, it is possible to engineer the magnetism of the GO sheet and consequently employ GO for spintronic device applications.

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