Magnetism in graphene oxide induced by epoxy groups

Lee, Dongwook; Seo, Jiwon; Zhu, Xi; Cole, Jacqueline M.; Su, Haibin

2015

Lee, D., Seo, J., Zhu, X., Cole, J. M., & Su, H. (2015). Magnetism in graphene oxide induced by epoxy groups. *Applied physics letters*, 106(17), 172402-.

<https://hdl.handle.net/10356/79407>

<https://doi.org/10.1063/1.4919529>

© 2015 AIP Publishing LLC. This paper was published in *Applied Physics Letters* and is made available as an electronic reprint (preprint) with permission of AIP Publishing LLC. The paper can be found at the following official DOI: [<http://dx.doi.org/10.1063/1.4919529>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 19:39:36 SGT

Magnetism in graphene oxide induced by epoxy groups

Dongwook Lee, Jiwon Seo, Xi Zhu, Jacqueline M. Cole, and Haibin Su

Citation: [Applied Physics Letters](#) **106**, 172402 (2015); doi: 10.1063/1.4919529

View online: <http://dx.doi.org/10.1063/1.4919529>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/106/17?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Carbon monoxide-induced reduction and healing of graphene oxide](#)

J. Vac. Sci. Technol. A **31**, 040601 (2013); 10.1116/1.4803839

[Graphene hydrogenation by molecular hydrogen in the process of graphene oxide thermal reduction](#)

Appl. Phys. Lett. **102**, 071910 (2013); 10.1063/1.4793484

[Reduced graphene oxide produced by rapid-heating reduction and its use in carbon-based field-effect transistors](#)

J. Appl. Phys. **112**, 033701 (2012); 10.1063/1.4739486

[Temperature-dependent photoluminescence from chemically and thermally reduced graphene oxide](#)

Appl. Phys. Lett. **99**, 041905 (2011); 10.1063/1.3616142

[Ferrimagnetism in zigzag graphene nanoribbons induced by main-group adatoms](#)

Appl. Phys. Lett. **96**, 102503 (2010); 10.1063/1.3327884

An advertisement for COMSOL simulation software. On the left, a dark blue box contains the text "CREATE your best design" in white and yellow. To the right, a white box lists various simulation parameters for a horn antenna, such as "TE11 cutoff frequency (fc): 4.868 Hz", "Frequency: fc*1.2 Hz", "Wavelength (lambda): 0.5205 m", "Flare angle: 17 degrees", "Corrugation thickness: 0.105 m", "Corrugation length: 0.155 m", "Horn thickness: 0.5 m", "Horn length: 4 m", "Waveguide length: 1 m", and "Matching corrugation length: 0.25 m". Below these parameters, it shows "Input waveguide cross pol. ratio: 17.657 %" and "Output aperture cross pol. ratio: 3.025 %", with a checkmark indicating "Target criterion: passed". On the far right, a 3D visualization of a horn antenna is shown with a color-coded electromagnetic field distribution. At the bottom, the text "WITH SIMULATION APPS >>" and the COMSOL logo are displayed.

Magnetism in graphene oxide induced by epoxy groups

Dongwook Lee,^{1,2,a)} Jiwon Seo,^{3,4,b)} Xi Zhu,⁵ Jacqueline M. Cole,^{1,6} and Haibin Su⁵

¹*Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom*

²*Division of Physics and Applied Physics, Nanyang Technological University, Singapore 637371*

³*Department of Physics and IPAP, Yonsei University, Seoul 120-749, South Korea*

⁴*School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, South Korea*

⁵*Division of Materials Science, School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798*

⁶*Argonne National Laboratory, 9700S Cass Avenue, Argonne, Illinois 60439, USA*

(Received 29 January 2015; accepted 20 April 2015; published online 29 April 2015)

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 oxidization. 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 $11 \times 11 \times 1$ 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 (sp^2) region and a reacted (sp^3) 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

^{a)}Electronic mail: dongwookleed1324@gmail.com

^{b)}Electronic mail: jiwonseo@yonsei.ac.kr

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.

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 $6.52:1$. 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. 2. (a) FT-IR spectra of GO, H-GO, and NaOH-GO. The peak at 1050 cm^{-1} results from epoxy groups (C-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).

TABLE I. XPS peak analysis of the data in Fig. 2(b).

	284–285 eV (C=C) Area (%)	286–287 eV (C-O)	288–289 eV (C-(O)-O)	$sp^2:sp^3$
GO	73.7	17.3	9	2.80:1
H-GO	86.7	10.2	3.1	6.52:1
NaOH-GO	55.8	32	12.2	1.26:1

curve of GO in the zero-field-cooled (ZFC) mode for which the measurement is conducted in a field after the sample undergoes cooling in the absence of a magnetic field; in this mode, the curve exhibits a characteristic maximum. Also shown are the field-cooled (FC) results, where the sample is measured in a field after cooling in a magnetic field; here, the curve becomes saturated at low temperatures. A discrepancy between magnetic susceptibilities in the ZFC and FC modes is one of representative properties of inhomogeneous magnetic systems that lack long-range magnetic order, such as spin glass, spin clusters, and superparamagnets.³⁶ Conversely, H-GO and NaOH-GO where epoxy groups have been removed from GO show conventional paramagnetic behaviors. Although the destruction of epoxy groups produced more hydroxyl groups in NaOH-GO and the heat-treatment removed chemical groups in H-GO, the magnetic moments of both materials decreased rapidly. This finding implies that the magnetism in GO is strongly related to its epoxy groups.

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_6O_2H , and this assumption is based on the sample's elemental composition, which was identified using energy dispersive X-ray analysis. Bohr magneton numbers and elemental compositions of both H-GO and NaOH-GO were similarly obtained and are summarized in Table II. This shows that effective number of Bohr magnetons in H-GO and NaOH-GO are tenfold lower than that of GO which contains epoxy groups.

Magnetization curves with respect to the magnetic fields of GO, H-GO, and NaOH-GO are displayed in Fig. 3(b). GO exhibits a nonlinear S-like magnetization curve, while NaOH-GO evinces an essentially linear curve, which is characteristic of conventional paramagnets. H-GO also displays a non-linear curve, but compared with GO, the magnetization of H-GO is much smaller. Both the strong S-shaped curve and the very narrow coercive field support the presence of

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. In the Curie-Weiss equation [$\chi = C/(T - \theta_C)$], C is the Curie constant and θ_C is the Curie temperature. The Curie constant is described as follows: $C = (n_B)^2(\mu_B)^2/3k_B$, where n_B is the effective Bohr magneton number, μ_B is the Bohr magneton, and k_B is the Boltzmann constant.

	GO	H-GO	NaOH-GO
C:O:Na	6:2.2:-	6:1.78:-	6:3.2:0.6
n_B	1.6×10^{-3}	8.34×10^{-5}	2.4×10^{-4}

weak magnetic phenomena such as spin glass, spin clusters, and superparamagnets in GO, and the susceptibility curves with thermal hysteresis in Fig. 3(a) (as a function of temperature) provide corroborating evidence. Magnetic impurities can be excluded as a possible origin of the magnetic properties in GO because neither its heat treatment nor its chemical reaction with NaOH could remove magnetic impurities in GO. The overall experimental results demonstrate that the magnetic moments in GO are closely related to the epoxy groups, and the magnetism is not a form of long-range order but is instead a type of magnetic clustering.

To determine the origin of the magnetism in GO and to compare our findings with experimental data, first-principles calculations were conducted. The destruction of epoxy groups by the heat-treatment and the reaction with NaOH decrease the magnetic moment of GO in Fig. 3 and increasing hydroxyl groups by reacting GO with NaOH does not increase the magnetic moment of GO. Thus, only epoxy groups are considered in this calculation.

In the exclusively full carbonic system, it has been predicted that graphene could host a carbon magnetic domain caused by carbon radicals.³⁷ In GO, the epoxy group can form local structures with carbon atoms on its 2D surface. Therefore, it is possible to form a local magnetic domain in GO as in graphene nanobud analogues.³⁷ 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 varied: 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% C:O=6:2.2 (in Table II), which allowed for direct comparison between experimental and calculated values.

FIG. 3. (a) Magnetic susceptibility curves of GO, H-GO, and NaOH-GO as a function of temperature. The susceptibilities of the samples were measured in ZFC and FC modes with an external field of 500 Oe. (b) Curves showing magnetization with respect to the magnetic field for GO, H-GO, and NaOH-GO. These curves were obtained at 5 K.

FIG. 4. Band structures and spin densities of two GO structures with epoxy functional groups. The calculated magnetic moments for (a) and (b) are 0.02 and $4\mu_B$, respectively. Spin densities are plotted in (c) and (d) with yellow-colored regions. Carbon and oxygen atoms are colored gray and red, respectively.

In the low oxygen coverage structure shown in Fig. 4(a), the C-C bond length of the epoxy group is $1.52 \text{ \AA}$, which is quite similar to the length of that reported in graphene oxide structures.³⁸ 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 $2p_z$ orbital (with a small fractional amount of spin) is localized because of the sp^2 to sp^3 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 $0.02\mu_B$ in total, i.e., each carbon atom has $0.0011\mu_B$.

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 insulating characteristics occur, as depicted via the band structure shown in Fig. 4(b). The metal-insulator transition can be realized by manipulating oxygen coverage, as demonstrated in the present work. The C-C bond length in the epoxy groups of the higher oxygen coverage structure is $1.47 \text{ \AA}$, which is shorter than that of the low oxygen coverage structure; this difference leads to more unpaired spins of the oxygen in the epoxy groups. Moreover, the geometric constraint imposed by the epoxy groups will tend to produce carbon radicals in the structure, i.e., carbon radicals are formed due to the surrounding epoxy groups. Consequently, the unpaired spins in the carbon $2p_z$ 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.³⁷

The carbon atoms in areas I and II of Fig. 4(d) have approximately $1\mu_B$ 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 $4\mu_B$ in total, which indicates that the average magnetic moment per carbon atom in GO is $4\mu_B/18 = 0.22\mu_B$. 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 $sp^2:sp^3$ 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 methods^{25,39,40} 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.^{42,43} Accordingly, it is possible to engineer the magnetism of the GO sheet and consequently employ GO for spintronic device applications.

This work was supported by the National Research Foundation of President Post-doctoral fellowship Program (NRF-2013R1A6A3A060443). The work at Nanyang Technological University was supported by Ministry of Education, Singapore, through a Tier-2 grant (2013-T2-2-049). J.M.C. thanks the Fulbright commission for a UK-U.S. Fulbright Scholar Award hosted by Argonne National Laboratory where work done was supported by DOE office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

- ¹Y. Wang, Y. Huang, Y. Song, X. Zhang, Y. Ma, J. Liang, and Y. Chen, *Nano. Lett.* **9**, 220 (2009).
- ²M. A. H. Vozmediano, M. P. Lopez-Sancho, T. Stauber, and F. Guinea, *Phys. Rev. B* **72**, 155121 (2005).
- ³P. Esquinazi, R. Höhne, K. H. Han, A. Setzer, D. Spemann, and T. Butz, *Carbon* **42**, 1213 (2004).
- ⁴K. H. Han, D. Spemann, P. Esquinazi, R. Höhne, V. Riede, and T. Butz, *Adv. Mater.* **15**, 1719 (2003).
- ⁵P. Esquinazi, D. Spemann, R. Höhne, A. Setzer, K. H. Han, and T. Butz, *Phys. Rev. Lett.* **91**, 227201 (2003).
- ⁶M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, *J. Phys. Soc. Jpn.* **65**, 1920 (1996).
- ⁷H. Yoshioka, *J. Phys. Soc. Jpn.* **72**, 2145 (2003).
- ⁸N. Tyutyulkov, N. Ivanov, K. Müllen, A. Staykov, and F. Dietz, *J. Phys. Chem. B* **108**, 4275 (2004).
- ⁹L. R. Radovic and B. Bockrath, *J. Am. Chem. Soc.* **127**, 5917 (2005).
- ¹⁰D. J. Klein and L. Bytautas, *J. Phys. Chem. A* **103**, 5196 (1999).
- ¹¹K. Kusakabe and M. Maruyama, *Phys. Rev. B* **67**, 092406 (2003).
- ¹²P. O. Lehtinen, A. S. Foster, Y. Ma, A. V. Krasheninnikov, and R. M. Nieminen, *Phys. Rev. Lett.* **93**, 187202 (2004).
- ¹³G. Z. Magda, X. Jin, I. Hagymasi, P. Vancso, Z. Osvath, P. Nemes-Incze, C. Hwang, L. P. Biro, and L. Tapasztó, *Nature* **514**, 608 (2014).
- ¹⁴S. S. Rao, S. N. Jammalamadaka, A. Stesmans, V. V. Moshchalkov, J. V. Tol, D. V. Kosynkin, A. Higginbotham, and J. M. Tour, *Nano. Lett.* **12**, 1210 (2012).
- ¹⁵S. S. Rao, A. Stesmans, Y. Wang, and Y. Chen, *Physica E* **44**, 1036 (2012).
- ¹⁶N. Mohanty and V. Berry, *Nano Lett.* **8**, 4469 (2008).
- ¹⁷C. Liu, Z. Yu, D. Ne, A. Zhamu, and B. Z. Jang, *Nano Lett.* **10**, 4863 (2010).
- ¹⁸Y. Bai, R. B. Rakhi, W. Chen, and H. N. Alshareef, *J. Power Sources* **233**, 313 (2013).
- ¹⁹D. Lee, J. Seo, X. Zhu, J. Lee, H. J. Shin, J. M. Cole, T. Shin, J. Lee, H. Lee, and H. Su, *Sci. Rep.* **3**, 2250 (2013).
- ²⁰D. Lee and J. Seo, *Sci. Rep.* **4**, 7419 (2014).
- ²¹M. Wang and C. M. Li, *New J. Phys.* **12**, 083040 (2010).
- ²²A. Lerf, H. He, M. Forster, and J. Klinowski, *J. Phys. Chem. B* **102**, 4477 (1998).
- ²³T. Nakajima and Y. Matsuo, *Carbon* **32**, 469 (1994).
- ²⁴D. W. Lee, L. D. L. S. Valladares, J. Seo, L. L. Felix, D. A. Bustamante, J. M. Cole, and C. H. W. Barnes, *J. Phys. Chem. B* **114**, 5723 (2010).
- ²⁵B. C. Brodie, *Philos. Trans. R. Soc.* **149**, 249 (1859).
- ²⁶G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ²⁷G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ²⁸G. Kresse and J. Hafner, *Phys. Rev. B* **48**, 13115 (1993).
- ²⁹G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- ³⁰P. E. Bloch, *Phys. Rev. B* **50**, 17953 (1994).
- ³¹G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ³²H. He, J. Klinowski, M. Forster, and A. Lerf, *Chem. Phys. Lett.* **287**, 53 (1998).
- ³³D. W. Lee, J. W. Seo, G. R. Jelbert, L. D. L. S. Valladares, J. M. Cole, C. Panagopoulos, and C. H. W. Barnes, *Appl. Phys. Lett.* **95**, 172901 (2009).
- ³⁴D. Lee, X. Zou, X. Zhu, J. W. Seo, J. M. Cole, F. Bondigo, E. Magnano, S. K. Nair, and H. Su, *Appl. Phys. Lett.* **101**, 021604 (2012).
- ³⁵See supplementary material at <http://dx.doi.org/10.1063/1.4919529> for Raman spectrum of GO.
- ³⁶N. Paunovic, Z. V. Popovic, and Z. D. Dohcevic-Mitrovic, *J. Phys.: Condens. Matter* **24**, 456001 (2012).
- ³⁷X. Zhu and H. B. Su, *Phys. Rev. B* **79**, 165401 (2009).
- ³⁸K. A. Mkhoyan, A. W. Contryman, J. Silcox, D. A. Stewart, G. Eda, C. Mattevi, S. Miller, and M. Chhowalla, *Nano Lett.* **9**, 1058 (2009).
- ³⁹L. Staudenmaier, *Ber. Dtsch. Chem. Ges.* **31**, 1481 (1898).
- ⁴⁰W. S. Hummers and R. E. Oeman, *J. Am. Chem. Soc.* **80**, 1339 (1958).
- ⁴¹D. W. Lee and J. W. Seo, *J. Phys. Chem. C* **115**, 2705 (2011).
- ⁴²Y. Mulyana, M. Uenuma, Y. Ishikawa, and Y. Uraoka, *J. Phys. Chem. C* **118**, 27372 (2014).
- ⁴³S. Huh, J. Park, Y. S. Kim, K. S. Kim, B. H. Hong, and J. M. Nam, *ACS Nano* **5**, 9799 (2011).