Carbon monoxide-induced reduction and healing of graphene oxide

Published in:

DOI:
10.1116/1.4803839

Published: 01/01/2013

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
- A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):
Carbon monoxide-induced reduction and healing of graphene oxide
Badri Narayanan, Stephen L. Weeks, Bhavin N. Jariwala, Bart Macco, Jan-Willem Weber et al.

Citation: J. Vac. Sci. Technol. A 31, 040601 (2013); doi: 10.1116/1.4803839
View online: http://dx.doi.org/10.1116/1.4803839
View Table of Contents: http://avspublications.org/resource/1/JVTAD6/v31/i4
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Related Articles
Low temperature oxidation of plutonium
Reaction mechanisms for atomic layer deposition of aluminum oxide on semiconductor substrates
Reduction of thin oxidized copper films using a hot-filament hydrogen radical source
Reversible nanochemical conversion
Acid–base reactions in a positive tone chemically amplified photoresist and their effect on imaging

Additional information on J. Vac. Sci. Technol. A
Journal Homepage: http://avspublications.org/jvsta
Journal Information: http://avspublications.org/jvsta/about/about_the_journal
Top downloads: http://avspublications.org/jvsta/about/about_the_journal
Information for Authors: http://avspublications.org/jvsta/about/information_for_contributors

ADVERTISEMENT
LETTERS

Carbon monoxide-induced reduction and healing of graphene oxide

Badri Narayanan (a) Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, Colorado 80401

Stephen L. Weeks (a) and Bhavin N. Jariwala (a) Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado 80401

Bart Macco and Jan-Willem Weber Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Somil Kumar J. Rathi Department of Materials Science and Engineering, Arizona State University, Tempe, Arizona 85287

Mauritius C. M. van de Sanden Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Peter Sutter Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973

Sumit Agarwal (b) Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado 80401

Cristian V. Ciobanu (b) Department of Mechanical Engineering and Materials Science Program, Colorado School of Mines, Golden, Colorado 80401

(Received 2 April 2013; accepted 22 April 2013; published 7 May 2013)

Graphene oxide holds promise as a carbon-based nanomaterial that can be produced inexpensively in large quantities. However, its structural and electrical properties remain far from those of the graphene sheets obtained by mechanical exfoliation or by chemical vapor deposition—unless efficient reduction methods that preserve the integrity of the parent carbon-network structure are found. Here, the authors use molecular dynamics and density functional theory calculations to show that the oxygen from the main functional groups present on graphene oxide sheets is removed by the reducing action of carbon monoxide; the energy barriers for reduction by CO are very small and easily overcome at low temperatures. Infrared and Raman spectroscopy experiments confirm the reduction in CO atmosphere and also reveal a strong tendency for CO to heal vacancies in the carbon network. Our results show that reduced graphene oxide with superior properties can be obtained through reduction in CO atmosphere.

© 2013 American Vacuum Society.

I. INTRODUCTION

The reductive processing of graphene oxide (GO) has been intensely investigated because it could lead to the inexpensive, large-scale production of graphene.1–4 The reduction avenues pursued so far rely either on thermal desorption of oxygen and oxygen-containing species,5–10 or on the chemical action of a reducing agent such as, for example, hydrazine,11,12 nitric oxide,13 and others.4,14–18 After any of the reductive processes pursued thus far, there remains a certain amount of oxygen on the sample, ranging from ~8% (Refs. 8 and 19) to ~12%.2,20 Because of these remnant oxygen groups, the electronic, optical, and mechanical properties of the graphene derived from thermal or chemical reduction of GO are not nearly as exciting as those of pure graphene (obtained by more expensive and less scalable methods).21,22 and the resulting nanomaterial is termed reduced graphene oxide (rGO).

Improvement of the electronic, optoelectronic, or mechanical properties of rGO, while clearly possible to an extent,7,8,11,23 is ultimately hindered by two main factors, (i) the ubiquitous presence of oxygen functional groups on the graphene sheet at the end of reduction, and (ii) the presence of defects such as large holes, isolated missing atoms or pairs of atoms, or local reconstructions of the carbon network. A vast portion of these defects are, in fact, introduced during the thermal reduction at high temperatures.5,6 Therefore, the properties of rGO will remain far from those of pure graphene, unless efficient reduction methods that preserve the integrity of the parent carbon-network structure are found.

In this article, we show that carbon monoxide can reduce the main oxygen functional groups that are present on the...
GO basal plane. Using molecular dynamics (MD) simulations based on a reactive force-field (ReaxFF) and density functional theory (DFT) calculations, we have determined the atomic-scale mechanisms and the energy barriers for the reduction of each of the oxygen-containing groups on graphene oxide with gas-phase CO. The barriers for the reduction by CO are lower than 0.1 eV and can be overcome at low temperatures. A recent theoretical study focused on the reaction of nitric oxide (NO) with the epoxide species suggests that the reduction of epoxide could occur in NO atmosphere at 500 K. Our study shows that CO reacts rapidly not only with the epoxide group, but with all the predominant oxygen-containing functional groups present on GO. Furthermore, our infrared and Raman spectroscopy measurements confirm that reduction of GO by carbon monoxide readily occurs at low temperatures. By studying the action of carbon monoxide on samples of monolayer graphene with controlled content of defects (vacancies), we have found that the vacancies heal nearly completely in the presence of CO. Our study therefore demonstrates an efficient, chemically facile, and reproducible way to remove oxygen from the graphene basal plane while restoring the integrity of the parent carbon-network structure.

The remainder of this paper is organized as follows. The next section describes our simulation and experimental results and discusses their relevance not only in terms of the reduction processes via CO, but also in terms of healing of vacancies in pure (unoxidized) graphene. Our conclusions are given in Sec. III. In order to improve the flow of this letter, we have opted to present the full details of our simulations and experimental techniques in Appendix, rather than inside the main text.

II. RESULTS AND DISCUSSION

In order to gain insight into the reduction mechanisms of GO by CO, we have first performed MD simulations of a single graphene sheet with O-containing groups, the most common of which are shown in Fig. 1. Recent work has evidenced that the most prevalent of these groups are epoxides, hydroxyls, and ketone pairs on the basal plane of the GO sheet, and phenols, carboxylics, cyclic ethers, ketones, and others at the edges. To identify the reduction mechanism associated with the removal of each individual oxygen-containing group (epoxide, hydroxyl, or ketone pair), we performed the first set of simulations using a single type of functional group on a graphene sheet without holes or vacancies in CO atmosphere at 900 K; this temperature was chosen such that no thermal desorption of oxygen occurs. The simulations were performed using a ReaxFF potential to reproduce well the formation and breaking of bonds in similar systems (see Appendix).

Fig. 2(a) illustrates the evolution of a selected epoxide group (C–O–C) on a GO sheet containing 8 at.% oxygen in the form of epoxide groups alone. In the initial configuration [to which we assign the time instant \( t = 0 \)], wherein the CO molecules are far away from the GO sheet, the C–C and C–O bond lengths in the epoxide were found to be 1.72 and 1.48 Å, respectively. Initially, the CO molecule experiences thermal motion before coming in the vicinity of any epoxide; the GO sheet oscillates, but at 900 K, these oscillations leave all the epoxide bonds intact. Subsequently, during thermal motion, a CO molecule comes within the interaction range of one of the epoxide groups and attacks it. This attack consists of breaking one of the C–O bonds of the epoxide, with the formation of a bond between the surface O and the C atom of the incoming CO [Fig. 2(ii)]. The carbon atoms that originally formed the epoxide group relax decreasing in their spacing to 1.51 Å, thereby restoring the local planarity of the sheet. The epoxide oxygen, however, remains attached to the GO sheet (and to the incoming CO) before eventually desorbing as part of a free CO\(_2\) molecule [Fig. 2(iii)].

Our simulations show that the CO environment is particularly effective in abstracting hydroxyl groups (OH) from a GO sheet via the reduction mechanism illustrated in panel

![Fig. 1. (Color online) Common oxygen-containing groups present on GO away from edges (epoxide, hydroxyl, and ketone pair) and at the edges (phenol, carboxyl, ketone, and cyclic ether). The hydroxyl group on the basal plane is sometimes called surface phenol or basal-plane phenol.](image-url)
(b) of Fig. 2, in which one CO molecule eventually removes two –OH groups from the GO sheet. The C atom of the CO molecule attacks a hydroxyl group forming a bond with the oxygen of the –OH [Fig. 2(v)]. The COOH radical formed does not remain chemically bonded to the sheet, but migrates freely due to thermal fluctuations. This COOH radical attacks another hydroxyl group on the GO sheet; the O–H bond in COOH dissociates leading to the formation of CO2 and H2O, as shown in Fig. 2(vii–viii). Motivated by recent DFT work, 31 which shows that an epoxide and hydroxyl that are present on neighboring carbon atoms have lower energy than when they are farther apart, we have also considered cases in which two or more O-containing groups are present in combination. For example, the hydroxyl-epoxide combination on neighboring carbons is more stable by ~60 meV per O. For a coverage of 20 at. % O (half epoxide and half hydroxyls), we have found that CO molecules can still attack and abstract first either the epoxide or the hydroxyl with the reduction proceeding by one of the mechanisms shown in panels (a) and (b) of Fig. 2. Carbon monoxide reduces the epoxide-hydroxyl combination by attacking each group sequentially, and the improved stability 31 of the combination on the GO sheet does not affect the reduction by CO.

Panel (c) in Fig. 2 shows the GO sheet containing ketone pairs (16 at. % O) undergoing reduction in a CO environment via a number of intermediate steps [Fig. 2(ix–xiii)]. Initially [Fig. 2(ix)], the carbon atoms belonging to the yet-unreacted ketone pair (i.e., C1–O1 and C2–O2) were 2.44 Å apart and C1–O2 distance measured 2.59 Å. As the CO molecule approaches this ketone pair, the carbon atom of CO, i.e., C3, attacks the C1–O1 bond of the upper ketone leading to the formation of a C3–O1 bond [1.22 Å in Fig. 2(x)]. The O1 atom remains attached to the GO sheet; the atoms C1 and O2 come close to each other to a separation of 1.65 Å, assisted by thermal fluctuations, eventually resulting in a chemical bond between them [Fig. 2(xi)]. Later, the bond between C1 and C2 begins to heal as shown by the decrease in their spacing to 1.72 Å with the formation of an epoxide, C1–O2–C2 [Fig. 2(xii)]. Finally, the O1 atom is removed from the GO sheet via a CO2 molecule, which desorbs.

Thus, the results of the MD simulations reveal that

1. CO reduces the three main oxygen containing species that are present on GO by abstracting an oxygen atom;
2. the reaction product is either CO2 (for epoxides and ketone pairs), or CO2 and H2O (for hydroxyls);
3. with each such abstraction reaction, the local planarity and sp2 bonding are restored;
To distinguish thermally induced changes in GO from those induced by exposure to CO, a drop-cast GO film on a ZnSe internal reflection crystal was annealed at 423 K in vacuum, in a surface analysis chamber. The initial changes in absorbance during low-temperature annealing were primarily due to the removal of residual H2O and thermal decomposition of carboxyl groups. Once the GO surface was thermally stable, different IR spectra were recorded after 5 min, as well as at longer durations of exposure (Fig. 4). In Fig. 4, the decreases in absorbance over ~1600–1750, ~3000–3500, and ~1070 cm−1 were attributed to the stretching modes of C=O, –OH, and C–O, respectively, in carboxyl and hydroxyl groups. In addition, the broad decrease in absorbance centered at ~1240 cm−1 indicates the removal of surface epoxides. The increase in absorbance at ~1010 cm−1 was attributed to the C–O–C stretching mode in agglomerated edge cyclic ethers, which were most likely formed due to the reaction of CO with edge sites. Finally, the increase in absorbance at ~1530 cm−1 was attributed to C=C stretching modes, indicating the simultaneous restoration of the sp2-hybridized carbon network of graphene. This restoration of the basal plane of graphene occurred because of the combined effect of the reduction of surface oxides (Fig. 2) and the healing of point defects such as single-carbon vacancies on the GO sheet. We have also measured the changes in absorbance after 60 min of CO exposure and have found no significant differences with respect to the absorbance changes corresponding to the 5-min exposure (Fig. 4). This means that virtually all reactions of CO with the oxidized graphene occur in less than 5 min, which is consistent with the low energy barriers (fast kinetics) for the reduction reactions determined from our DFT calculations.

Fig. 3. (Color online) Energy change as a function of reaction coordinate $\epsilon$ during DFT relaxations started from $d = 1.4$ Å, the spacing between the carbon atom of the incoming CO and the oxygen atom on the graphene sheet. The reaction coordinate $\epsilon$ varies from 0 (initial) to 1 (final configuration, in which either CO$_2$ or COOH has formed and moved away from the sheet).

Fig. 4. (Color online) Infrared absorbance change for GO during exposure to carbon monoxide. Interaction of covalently bonded surface oxygen with CO results in an absorbance decrease for surface phenols (OH stretching, 3000–3800 cm$^{-1}$), carboxylic acid (OH stretching, ~3000–3800 cm$^{-1}$), C=O stretching, 1550–1750 cm$^{-1}$; C–O stretching, ~1070 cm$^{-1}$), and epoxides (C=O–C stretching, ~1250 cm$^{-1}$). Carbon monoxide also reacts with the vacancies and edges of GO, which results in an increase in absorbance due to sp$^2$ hybridized C (C=C in-plane stretching, ~1500–1600 cm$^{-1}$), and cyclic ethers (C=O–C stretching, ~1010 cm$^{-1}$).
In order to understand the extent of healing of point defects alone (i.e., in the absence of edges and O-containing functional groups), we have performed another set of experiments on a single-layer pristine graphene sheet (not oxidized, see Appendix). First, graphene was transferred onto the ZnSe internal reflection crystal. The Raman spectrum of as-synthesized, single-layer graphene showed the characteristic G band at \( \sim 1580 \text{ cm}^{-1} \), and a strong, long-range-order-related 2D band at \( \sim 2680 \text{ cm}^{-1} \) (see Fig. 5). Second, defects were controllably introduced in pristine graphene through plasma-induced hydrogenation at room temperature followed by dehydrogenation at 773 K. The Raman spectrum in Fig. 5, obtained after the annealing step, confirmed the presence of defects; specifically, a wide disorder-related 2D band at \( \sim 2930 \text{ cm}^{-1} \) emerged along with a widened overlapping G band centered at \( \sim 1580 \text{ cm}^{-1} \). Moreover, the 2D band no longer appeared in the Raman spectrum. Finally, to heal these defects, the ZnSe crystal with the defective graphene layer was placed in the surface analysis chamber and exposed to CO for 4 h, and the healing process was monitored with both ex situ Raman spectroscopy and in situ real-time \( p \)-polarized ATR-FTIR spectroscopy. The Raman spectrum after CO exposure unambiguously shows the healing of the graphene sheet through the restoration of the features that are characteristic of long-range order: the 2D band was restored at \( \sim 2660 \text{ cm}^{-1} \), and the D + G band also appeared at \( \sim 2930 \text{ cm}^{-1} \). Furthermore, the D and G bands at \( \sim 1340 \) and \( \sim 1580 \text{ cm}^{-1} \), respectively, were separated and narrower than in the Raman spectrum of damaged graphene, consistent with healing. Based on the ratio of the intensities of the D and G bands before and after healing, we have followed the approach of Lucchesse et al. to estimate that \( \sim 98% \) of the defects in the graphene sheet were healed after CO exposure with an average defect spacing of 9.6 nm after healing.

Consistent with the Raman data, IR spectra recorded during graphene exposure to CO (Fig. 6) show an increase in absorbance in the in-plane C=C stretching region at \( \sim 1590 \text{ cm}^{-1} \), indicating the restoration of the graphene network. This strong band at \( \sim 1590 \text{ cm}^{-1} \) can obscure changes in other vibrational bands in this region due to oxygen-related defects. However, in a nearly planar graphene layer, this vibrational band only shows a weak absorbance for \( p \)-polarized IR radiation. Consequently, we were able to observe an additional broad absorbance increase over the spectral range extending from \( \sim 900 \) to 1550 cm\(^{-1} \), which indicates that CO reacts with graphene to form oxygen-related species on the surface. Specifically, the increase in absorbance over 1300–1550 cm\(^{-1} \) was attributed to ketones, while the increase in absorbance over \( \sim 900–1300 \text{ cm}^{-1} \) was attributed to cyclic edge ethers, with some contribution from ketones; both these functional groups are likely formed at the edges of larger holes in the sheet. The barrier for abstraction of oxygen atoms from these edge ketones is reported to be over the range of 1.5–8.0 eV, which makes such abstraction events unlikely at 423 K. The cyclic ethers are also known to be thermally stable with a binding energy reported over the range of 4.9–9.1 eV and it is again unlikely that CO will abstract oxygen atoms from these sites.

III. CONCLUSION

In conclusion, we have determined the atomic-scale mechanisms for the reduction of GO by carbon monoxide and have found that the reduction proceeds without...
significant energy barriers for all of the prevalent oxygen-containing groups (epoxides, hydroxyls, and ketone pairs) that are away from the edges of the graphene sheets. The results of the atomic scale calculations are consistent with our vibrational spectroscopy experiments. At the same time, exposure to CO heals the parent graphene network by largely eliminating point vacancies on the sheet. Exposure to CO, however, stabilizes the edges of the holes in the GO sheets by forming cyclic ethers and ketones, which means that the extent of healing by CO is reduced to point vacancies or divacancies within the basal plane. The presence of extended defects in the carbon network (created during solution synthesis of GO or during subsequent thermal annealing) remains particularly acute because the edges of the holes are very reactive and become stabilized by oxygen provided during the synthesis of GO or during its exposure to CO. This suggests that future work in this area will be focused on producing GO with intact or nearly intact carbon network, from which oxygen can readily be removed in CO atmosphere.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the following sources of support: the U.S. National Science Foundation (NSF) through Grants Nos. CMMI-084858 and CBET-0846923, U.S. Dept. of Energy through Grant No. DE-FG02-07ER46397, and the Netherlands Organization for Scientific Research (NWO), which funds the research program of the Foundation for Fundamental Research on Matter (FOM). Computational resources were provided by the Golden Energy Computing Organization at Colorado School of Mines.

APPENDIX: DESCRIPTION OF THE METHODS

1. MD studies of the reduction mechanisms

The molecular dynamic simulations were performed using a reactive force field (ReaxFF)\textsuperscript{28} as implemented in the \textsc{lammmps} package.\textsuperscript{45} ReaxFF is a general bond-order interatomic potential that has been found to provide an accurate description of bond dissociation/formation, intermediate states, reaction pathways and reactivity trends in hydrocarbon systems.\textsuperscript{28,30} The simulation box consisted of a graphene sheet with 512C atoms (4.12 nm × 3.56 nm) and randomly distributed functional groups on both sides of the sheet that were either all (a) epoxide (8 at.% O conc.), (b) hydroxyl (8 at.% O conc.), or (c) ketone pairs (16 at.% O conc.).

Periodic boundary conditions were applied along the two directions (at 60° from one another) in the plane of the graphene sheet, while fixed boundary conditions were applied in the direction normal to the sheet. The graphene oxide sheets were then thermalized at 900 K for 10 ps in a canonical ensemble (NVT) with a Nosé–Hoover thermostat. A timestep of 0.25 fs was used for all the MD simulations. After thermalizing the GO sheets at 900 K, two CO molecules were introduced, one on each side of a given GO sheet, at random positions far away from the sheet. Two reflective walls were employed parallel to the GO sheet at a distance of 1 nm above and below it to simulate a CO atmosphere. These sheets were further annealed in the reducing CO environment in a NVT ensemble for 400 ps, and the reactions of CO with the oxide species on GO were monitored.

2. Optimized reaction pathways using DFT calculations

The computational supercell for the density functional theory (DFT) calculations consisted of a graphene sheet containing 50 carbon atoms; a functional group that could be either (a) an epoxide, (b) a hydroxyl group, or (c) a ketone pair; and a CO molecule away from the sheet but directly above the functional group. Periodic boundary conditions were employed along all the directions, and a vacuum of 15 Å was introduced in the direction normal to the graphene layer. Total energy DFT calculations were performed within the framework of the spin-polarized generalized gradient approximation, using the projector-augmented wave potentials\textsuperscript{46} as implemented in the \textsc{ab-initio} simulation package \textsc{vasp}.\textsuperscript{47,48} The atomic coordinates were relaxed using a conjugate gradient algorithm until the force components on any atom were smaller than 0.02 eV/Å. The exchange-correlation was described by the Perdew–Burke–Ernzerhof functional,\textsuperscript{49} which has been reported to describe well the bonds in graphene oxides.\textsuperscript{5} The plane wave energy cutoff was set to 450 eV. The Brillouin zone was sampled with a Monkhorst–Pack\textsuperscript{51} \(5 × 5 × 1\) k-point grid.

3. Experimental procedures

The evolution of GO surface vibrational modes upon introduction of CO was monitored in a surface analysis chamber equipped with an \textit{in situ} ATR-FTIR spectroscopy setup. An aqueous dispersion of GO (Graphene Supermarket) was drop cast on the surface of a ZnSe internal reflection crystal (IRC). The GO dispersion on the IRC was dried by annealing \textit{ex situ} at 448 K for 6 h and subsequently placed in the IR beam path in the surface analysis chamber. The \textit{ex situ} annealing step removed most of the water present in the dispersion. To ensure the observed spectral changes were not due to thermal annealing but to CO exposure, the ZnSe substrate with the GO layer was heated \textit{in situ} at 423 K. Prior to the exposure of GO to CO, the change in absorbance due to the surface IR modes was monitored until no further spectral changes were observed for 30 min. Once the surface was thermally stable, a fresh reference spectrum was collected. CO was introduced into the chamber at a pressure of 850 mTorr and a substrate temperature of 423 K. IR spectra with respect to the reference spectrum were collected by evacuating the vacuum chamber to the base pressure (\(\sim 10^{-6}\) Torr). After collecting the difference spectra, CO was reintroduced into the chamber at the same pressure, continuing the reduction process.

We have also performed analysis of a single-layer of graphene after introducing defects. Single-layer graphene was grown on Cu, using a procedure similar to the one reported by Li et al.\textsuperscript{50} A 40-μm-thick, 5 × 2 cm\textsuperscript{2} Cu foil...
H₂ was introduced at 110 mTorr, and the Cu-foil was heated 30 min while slowly heating to 1065 °C for 24 h. After this step, we recorded an IR and the PMMA transfer layer were immersed in acetone and annealed in vacuum at this polymer residue, the IRC was rinsed in methanol respectively, due to residual PMMA. Second, to remove crystal. The sample was blow dried with N₂ and baked at 5 min at 130 °C. During the hydrogenation step, the monolayer graphene (on C stretching regions at 1750 cm⁻¹, respectively, due to residual PMMA. Second, to remove this polymer residue, the IRC was rinsed in methanol and annealed in vacuum at ~10⁻⁶ Torr and 573 K for 3 h. The IR spectrum recorded after the annealing step, again referenced to the bare IRC, showed no C = O stretching vibrations at ~1750 cm⁻¹ indicating the removal of PMMA.

Defects were controllably introduced into the graphene sheet by hydrogenation in a plasma followed by annealing. During the hydrogenation step, the monolayer graphene (on the IRC) was placed on the grounded electrode in a radio-frequency, capacitively coupled H₂/Ar (1:4:1 flow ratio) plasma operated at 40 W and 13.56 MHz for 20 s. The IRC was heated to 423 K with the chamber pressure maintained at 150 mTorr. During the annealing step, which induces defects due to the dehydrogenation of graphene, the IRC was heated at 773 K and ~10⁻⁶ Torr for 5.5 h. A Raman spectrum was collected for this defective graphene layer using 532 nm excitation.

To heal the defects induced in graphene, the ZnSe IRC was heated to 423 K and exposed to CO at 850 mTorr for 4 h. Changes in the vibrational modes of the graphene layer due to interaction with CO were measured by only sampling the  𝑝-polarized radiation. This prevented the large absorbance increase associated with the in-plane C = C stretching modes in graphene at ~1590 cm⁻¹ (Refs. 5, 32, 35, 36, and 43) from overwhelming the absorbance due to other O-related species formed in the healing process. After the CO exposure step, another Raman spectrum was collected to determine the structural changes in graphene.
50 X. Li et al., Science 324, 1312 (2009).