Vacuum, Surfaces, and Films

Review Article:
Fabrication of organic interfacial layers by molecular layer deposition:
Present status and future opportunities

-by Han Zhou and Stacey F. Bent
Carbon monoxide-induced reduction and healing of graphene oxide

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

Stephen L. Weeks and Bhavin N. Jariwala
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

Somilkumar 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 and Dutch Institute for Fundamental Energy Research, 3430 BE, Nieuwegein, The Netherlands

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

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

Cristian V. Ciobanu
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.

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,2,11,12 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, carboxyls, 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, which has been shown 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 \( t = 0 \), Fig. 2(i)], 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 CO2 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](https://example.com/fig1.png)  
**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.
(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;
the reduction reactions occur rather fast, on time scales of the order of 10–100 ps, suggesting a low or absent activation energy barrier.

In order to confirm that the attack of CO is facile, we have also performed DFT calculations (see Appendix) of the energy barriers associated with vertical pathways of the CO molecules toward the various oxygen-containing species on the surface. In these calculations, the carbon of the CO was kept at various distances \( d \) away from the oxygen atom of each particular group on the sheet, and the total energy was computed as a function of \( d \). We have found that for distances \( d > 1.5 \text{ Å} \) the approach of the incoming CO molecule occurs with small energy barriers of 0.06 eV for an epoxide, 0.04 eV for hydroxyl, and 0.09 eV for a ketone pair; these barriers are associated with specific vertical pathways in which incoming CO is aligned above the O atom on a graphene sheet, and, as such, they represent upper bounds. Interestingly, DFT static relaxations from starting configurations with \( d = 1.4 \text{ Å} \) trace similar reaction pathways as those found in ReaxFF MD simulations. Figure 3 shows the change in the total energy of a supercell containing a single functional group on graphene and a CO molecule (initially at \( d = 1.4 \text{ Å} \)), as a function of the reaction coordinate that traces the progress from the initial (\( \epsilon = 0 \)) to the final (\( \epsilon = 1 \)) state in which either CO\(_2\) or COOH has formed and moved away from the sheet. The reactions are strongly exothermic, with energy releases greater than 6.5 eV. The energy decreases monotonically in all three cases [Fig. 3], suggesting that there is no energy barrier for the desorption of the reaction products, and the only energy barrier (lower than 0.1 eV in all cases, for \( d > 1.5 \text{ Å} \)) occurs during the approach of CO.

With this atomic-scale understanding of the GO reduction by CO in place, we have also performed experiments in which we have monitored the reactions of CO with the GO surface using real-time in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (see Appendix). 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 H\(_2\)O and thermal decomposition of carboxyl groups.\(^{5,32}\) 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 \( \sim 1600–1750, \sim 3000–3500\), and \( \sim 1070 \text{ cm}^{-1} \) were attributed to the stretching modes of C–O,\(^{33,34}\) –OH,\(^{33,34}\) and C–O,\(^{34,35}\) respectively, in carboxyl and hydroxyl groups.\(^{5,32,35,36}\) In addition, the broad decrease in absorbance centered at \( \sim 1240 \text{ cm}^{-1} \) indicates the removal of surface epoxides.\(^{5,32,35,36}\) The increase in absorbance at \( \sim 1010 \text{ cm}^{-1} \) was attributed to the C–O–C stretching mode in agglomerated edge cyclic ethers,\(^{35,36}\) which were most likely formed due to the reaction of CO with edge sites.\(^{35}\) Finally, the increase in absorbance at \( \sim 1530 \text{ cm}^{-1} \) was attributed to C=C stretching modes,\(^{5,32,35,36}\) indicating the simultaneous restoration of the sp\(^2\)-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.
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).\(^{37,38}\) Second, defects were controllably introduced in pristine graphene through plasma-induced hydrogenation at room temperature followed by dehydrogenation at 773 K.\(^{39}\) The Raman spectrum in Fig. 5, obtained after the annealing step, confirmed the presence of defects; specifically, a wide disorder-related 2D band at \( \sim 2400 \text{ cm}^{-1} \) emerged along with a widened overlapping G band centered at \( \sim 1580 \text{ cm}^{-1} \).\(^{40}\) 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 \( \sim 2930 \text{ cm}^{-1} \)\(^{37,42}\) Furthermore, the D and G bands at \( \sim 1340 \text{ and } \sim 1580 \text{ cm}^{-1} \), respectively, were separated and narrower than in the Raman spectrum of damaged graphene, consistent with healing.\(^{40}\) 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.\(^{41}\) 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\(=\text{C} \) stretching region at \( \sim 1590 \text{ cm}^{-1} \)\(^{5,32,35,36}\) 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.\(^{43}\) 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,\(^{36}\) 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.\(^{35}\) The barrier for abstraction of oxygen atoms from these edge ketones is reported to be over the range of 1.5–8.0 eV,\(^{44}\) 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,\(^{35}\) 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) as implemented in the LAMMPS package. 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. 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 an 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 as implemented in the ab-initio simulation package VASP. 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 functional, which has been reported to describe well the bonds in graphene oxides, was used. The plane wave energy cutoff was set to 450 eV. The Brillouin zone was sampled with a Monkhorst–Pack 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 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 ex situ at 448 K for 6 h and subsequently placed in the IR beam path in the surface analysis chamber. The 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 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 (~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. A 40-μm-thick, 5 × 2 cm² Cu foil
H2 was introduced at 110 mTorr, and the Cu-foil was heated/C14 30 min while slowly heating to 1065°C/C14. Referenced to the spectrum of the bare IRC. This IR spectrum of the IRC with monolayer graphene, which was (reagent grade) for 24 h. After this step, we recorded an IR spectrum/C24 423 K for 15 min for improved adherence. This polymer residue, the IRC was rinsed in methanol/C14 10 min. The Cu foil was annealed in H2 for 1050°C, giving a total pressure of 430 mTorr. After 2 min, the sample was slowly cooled down (~15 min), while maintaining the gas flow. Polymethylmethacrylate (PMMA, A4, MicroChem) was spin-coated on one side of the sample for 60 s at 2500 rpm, and the sample was cured on a hot plate for 5 min at 130°C. To remove the graphene from the uncoated side, the sample was floated on an aqueous solution of 1M FeCl3·6H2O for 5 min and then rinsed with deionized (DI) water. The sample was reintroduced into the solution to fully dissolve the Cu. The floating PMMA/graphene sheet was rinsed in DI water several times and transferred to the ZnSe crystal. The sample was blow dried with N2 and baked at 423 K for 15 min for improved adherence.

The PMMA transfer layer was removed in a two-step process. First, the ZnSe IRC with the monolayer graphene and the PMMA transfer layer were immersed in acetone (reagent grade) for 24 h. After this step, we recorded an IR spectrum of the IRC with monolayer graphene, which was referenced to the spectrum of the bare IRC. This IR spectrum showed characteristic absorbance due to the C–H and C=O stretching regions at ~3000 and ~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 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.

C. To remove the graphene from the uncoated side, the sample was floated on an aqueous solution of 1M FeCl3·6H2O for 5 min and then rinsed with deionized (DI) water. The sample was reintroduced into the solution to fully dissolve the Cu. The floating PMMA/graphene sheet was rinsed in DI water several times and transferred to the ZnSe crystal. The sample was blow dried with N2 and baked at 423 K for 15 min for improved adherence.

PMMA. The sample was reintroduced into the solution to fully dissolve the Cu. The floating PMMA/graphene sheet was rinsed in DI water several times and transferred to the ZnSe crystal. The sample was blow dried with N2 and baked at 423 K for 15 min for improved adherence.

The PMMA transfer layer was removed in a two-step process. First, the ZnSe IRC with the monolayer graphene and the PMMA transfer layer were immersed in acetone (reagent grade) for 24 h. After this step, we recorded an IR spectrum of the IRC with monolayer graphene, which was referenced to the spectrum of the bare IRC. This IR spectrum showed characteristic absorbance due to the C–H and C=O stretching regions at ~3000 and ~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 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).