Low-temperature thermal reduction of graphene oxide: *In situ* structural, thermal desorption and electrical transport measurements

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ABSTRACT

Elucidation of the structural transformations in graphene oxide (GO) upon reduction remains an active and important area of research. We report the results of *in situ* heating experiments, during which electrical, mass spectrometry, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and transmission electron microscopy (TEM) measurements were carried out correlatively. The simultaneous electrical and temperature programmed desorption (TPD) measurements allowed us to correlate the onset in the electrical conductivity change of GO by five orders of magnitude at about 150 °C with the maxima of the rates of desorption of H₂O, CO and CO₂. Interestingly, this large conductivity change happens at an intermediate level of the reduction of GO, which likely corresponds to the point when the graphitic domains become large enough to enable percolative electronic transport. We demonstrate that the gas desorption is intimately related to (i) the changes in the chemical structure of GO sheets revealed by TEM. These *in situ* observations provide a better understanding of the mechanism of the GO thermal reduction.

KEYWORDS Graphene oxide, thermal reduction, in situ experiments, temperature programmed desorption, X-ray photoelectron spectroscopy, transmission electron microscopy, electrical measurements

Chemical oxidation and exfoliation of graphite to form graphene oxide (GO) is an important process to produce bulk quantities of easily processable and inexpensive graphene-like materials for various applications, such as composites, energy storage devices, conductive thin films, gas sensors, and others.¹⁻³ The as-synthesized GO is an electrical insulator, but its conductivity can be improved by several orders of magnitude *via* chemical reduction.⁴⁻⁷ Since electrical conductivity is the key property for a number of applications, the process of chemical reduction of GO to reduced GO (rGO) has received a great deal of attention.^{7, 8} The conversion can be achieved by several means, including reducing agents (such as hydrazine or sodium borohydride), annealing in vacuum or hydrogen, and various combinations of chemical and thermal treatments.⁸

Verification of the exact structure of GO and rGO remains an active research topic.⁹⁻¹⁵ However, it is generally agreed that GO has an irregular structure that consists of few nanometers wide graphitic domains separated by heavily oxidized regions,¹⁶ which explains its low electrical conductivity.⁴ In contrast, the rGO sheets contain larger graphitic regions that are responsible for the improved electrical conductivity,⁴ as well as clusters of residual oxygen-containing functional groups and nanoscopic holes. The described structures are in agreement with transmission electron microscopy (TEM) observations^{17, 18} and spectroscopy with high spatial resolution.¹⁵ Theoretical simulations suggest that the complete oxidation of graphite to GO, as well as its complete reduction to pure graphene, are both difficult to achieve.¹⁹ The irregular structure also explains the fact that the electronic transport in rGO materials is well described by the two-dimensional variable range hopping (VRH) mechanism.^{4, 20-22}

Numerous investigations focused on achieving the highest degree of GO reduction possible and compared properties of the starting material, GO, and the final reaction product, rGO. In other studies, reduction was performed stepwise and properties of intermediate products have been considered as well.²¹⁻²⁶ For example, Larciprete *et al.* studied the kinetics of thermal reduction of oxidized graphene by *in situ* X-ray photoelectron spectroscopy (XPS) using synchrotron radiation and temperature programmed desorption (TPD) measurements.²⁷ Jung *et al.* reported experiments, in which the kinetics of thermal reduction of GO in vacuum was studied by electrical measurements of individual GO flakes as well as by TPD measurements of few-layer GO films.²⁴ The electrical measurements revealed a gradual decrease in resistivity of a GO flake during thermal reduction, while the TPD experiments on a GO film identified CO₂, CO and H₂O as the primary desorption/decomposition products at temperatures up to 300 °C; the evolution of these gases from GO is consistent with the observation of nanoscopic holes in rGO by high-resolution TEM.^{15, 16}

Since measurements of different physical properties of GO were performed in different experiments, it often remains unclear how the kinetics of structural changes, gas evolution, restoration of electrical conductivity and other processes, correlate with each other. Given the large number of studies on GO reduction, a lot of important information can be obtained by correlating data from different reports. However, a direct comparison of experimental results on GO reduction from different studies is not always straightforward for the following reasons. First of all, different studies often employed different protocols for GO reduction. Second, due to the existence of five major synthetic approaches for GO synthesis, including the Brodie,²⁸ Staudenmaier,²⁹ Hofmann,³⁰ Hummers³¹ and Tour³² methods, as well as their multiple variations, the starting GO materials for such experiments could vary considerably in their properties.³³ The use of different graphite sources for GO synthesis can be another source of variability in properties of GO.³⁴

In order to correlate changes in different physical properties of GO, we studied samples from the same batch and designed experiments in which several analytical methods, including mass spectrometry (MS), electronic transport measurements, XPS, Raman, and transmission electron microscopy (TEM), were used simultaneously, or in similar conditions. The GO was synthesized according to the Tour method by oxidizing graphite flakes with a mixture of KMnO4, H₂SO₄ and H₃PO4;³² the details of characterization of this GO material can be found in our previous work.³⁵ Figure 1a shows the scheme of *in situ* MS experiments and electrical measurements that were performed in this study during the thermal reduction of GO. Shown in this image is a two-terminal device, in which a film of GO flakes bridges two metal electrodes on a Si/SiO₂ substrate. The device is placed in the ultrahigh vacuum (UHV) chamber of a home-built setup, in which heating and *simultaneous* physical measurements (electrical conductivity and mass spectrometry of evolving gases as a function of temperature) can be performed.



Figure 1. Electrical characterization and temperature programmed desorption (TPD) measurements of a GO film. (a) Scheme of the experimental setup; see text for details. (b) An optical photograph of an aqueous solution of GO. (c) An SEM image of a representative GO flake that was drop-casted onto Si/SiO₂ substrate from the suspension shown in panel (b). (d) An optical photograph of a multielectrode chip with a film of GO flakes deposited on the Pt electrodes. (e) An SEM image of the edge of the GO film on a multielectrode chip. (f) Results of simultaneous electrical and TPD measurements of the GO devices taken at the heating rate of $\beta = 19$ °C/min. The legend displays masses (in atomic mass units, amu) and interpretation of the gas species that were observed by mass-spectrometry; the background signal (60 amu) is labelled "BG". The colored scattered curves show partial pressures of different gas species. The purple solid lines show electric conductance measurements of six selected segments of the multielectrode chip. The blue area corresponds to the time when the heaters were turned off and the chip was rapidly cooling down.

Figure 1b shows an optical photograph of a ≈ 0.1 g/mL aqueous GO suspension. Since we did not use sonication during the synthesis, a considerable number of GO flakes were larger than 10 µm across, as shown in the scanning electron microscopy (SEM) image in Figure 1c. This suspension was drop-casted on the active area of a multielectrode chip similar to the ones that were used in our previous works ^{35, 36} (Figure 1d). The active area of the chip consists of a 8 mm ×10 mm Si/SiO₂ substrate (a green rectangle in Figure 1d) with 39 Pt electrodes (100 µm ×3000 µm each) separated by ≈ 70 µm gaps and two thermocouples located at the edges. The back side of the chip is equipped with four independent Pt meander heaters. Once the droplet of the GO suspension dried on the chip, it formed a continuous multilayer film of overlapping GO flakes,³⁷ which bridged

the Pt electrodes, see the arrow in Figure 1d. An SEM image of a fragment of the GO film on the active area of the multielectrode chip is shown in Figure 1e. The described preparation procedure results in 38 GO devices that are similar to the one schematically shown in Figure 1a; each of these devices can be measured independently.

The multielectrode array chip with the as-deposited GO film was kept at ≈ 95 °C overnight in vacuum to remove weakly bound water and other surface adsorbates. By the start of the measurements, the pressure was $\approx 10^{-5}$ Pa. Then, the Pt heaters on the back side of the multielectrode array chip were used to ramp the temperature of the GO devices at the rate of $\beta =$ 19 °C/min. The temperature was read out using two thermocouples that were fabricated directly on the chip, providing accurate measurements of the temperature of the GO film. The mass spectrometry data were recorded every 2.5 s and the resistance of each of the 38 GO devices was measured every 15 s; both measurements were synchronized with the temperature readings.

Figure 1f demonstrates the results of temperature-dependent electrical and mass spectrometry measurements. While changes in the structure, composition and electrical conductivity of GO upon heating have been reported previously in separate experiments,²¹⁻²⁶ it is informative to monitor them correlatively in a single experiment. Figure 1f shows that major volatile species that are observed in the TPD experiment have mass numbers of 18 amu, 30 amu and 44 amu, corresponding to H₂O, CO and CO₂, respectively. The evolution of H₂O is observed through the entire heating process, and at first is likely associated with the desorption of water molecules that are bound to the GO material via hydrogen bonding,³⁸ although at higher temperatures should include water produced by decomposition of oxygen-containing functional groups in GO. At about 125 °C, the desorption of CO and CO₂ becomes noticeable, suggesting structural changes in the GO carbon framework. The rates of desorption of all three gases, H₂O,

CO and CO₂, increase with the heating and peak at the same temperature of about 150 °C. This means that closer to this temperature the release of these three species is correlated and that the water molecules that desorb from GO at higher temperatures likely originate from the same functional groups as CO and CO₂.

While the rates of desorption of H₂O, CO and CO₂ increase with temperature, the GO film remains nonconductive until about 150 °C, when the conductance abruptly increases by nearly 5 orders of magnitude. Representative conductance-temperature dependencies for six segments of the multielectrode chip are shown in Figure 1f; all 38 segments demonstrated qualitatively the same behavior. The conductivity onset occurs at the same temperature when the maximum rates of H₂O, CO and CO₂ evolutions are observed. This can be rationalized as follows. The as-prepared GO is nonconductive due to the presence of heavily oxidized regions that separate sp^2 graphitic domains. While the removal of CO and CO₂ is observed already at \approx 135 °C, the initial reduction of GO is insufficient to decrease the distances between the graphitic domains to enable hopping of charge carriers between them. However, at ≈ 150 °C, when the rates of evolutions of H₂O, CO and CO₂ peaks, the graphitic domains grow in size to the point when the percolative electronic transport becomes possible, and the GO film abruptly transitions from nonconductive to conductive. Noteworthy, because of its irregular structure, GO can be considered as amorphous material, and physical properties of amorphous materials often gradually change with temperature. In this particular case, however, the conductance of GO changes abruptly by nearly 5 orders of magnitude within a narrow temperature range. It should be noted that the exact temperatures of the start of CO and CO₂ evolutions, the abrupt conductivity increase, etc., should depend on the heating rate, as was also reported for the mass loss curves obtained for GO by thermogravimetric analysis (TGA).³⁹ Thus, a good correlation between the results of TPD and conductivity measurements



(Figure 1f) was possible because the data were collected in the same experiment, which means that all experimental conditions including the heating rate were identical.

Figure 2. C1s XPS spectra of GO recorded at (**a**) room temperature, (**b**) 135 °C, (**c**) 185 °C and (**d**) 200 °C. (**e**) Temperature dependencies of the peak areas of the C1s XPS fitting components (solid lines) and the I_D/I_G ratio in the Raman spectra (dotted line). (**f**) Raman spectra of GO films annealed at different temperatures.

In order to correlate the TPD results with the composition changes in the gradually reduced GO, we performed *in situ* XPS analysis of the GO film. Similarly to the sample preparation of the GO-covered multielectrode array chips, the same GO suspension was drop-casted onto a Si wafer coated with a 100 nm thick Au film. After drying in air, the sample was placed in an multiprobe XPS UHV chamber and degassed overnight at a pressure of $\approx 5 \cdot 10^{-7}$ Pa. Next, the sample was slowly annealed in front of the electron energy analyzer, and C1s as well as survey XPS spectra were recorded sequentially as a function of temperature.

Figure 2a-d shows the curve-fitted C1s XPS signals of GO and rGO at different temperatures. The C1s signal was fitted by four components with a full width at half maximum (FWHM) of \approx 1.9 eV: C=C&C-C (284.99(5) eV), C-O (286.91(14) eV), C=O (288.67(8) eV) and O=C-OH (290.57(13) eV). The numbers in brackets represent average peak positions with a standard deviation of fitted signals across all temperatures. These fitted features are consistent with the previous studies.^{40, 41} As demonstrated in the spectrum shown in Figure 2a, as-prepared GO is heavily oxidized: epoxy and hydroxyl groups at 286.9 eV constitute 46 % of the C1s peak area. The peak shape remains almost unchanged up to 185 °C when a qualitative change occurs and the C-C&C=C signal at 285.0 eV becomes a dominant component of the C1s peak area. To quantitatively illustrate the evolution of the GO XPS spectra during the reduction we plotted the temperature dependencies of peak areas in percent for all four fitting components (Figure 2e). The dramatic change occurs between 135 °C and 185 °C when the C-C&C=C component increases from 38 % to 51 % while the C-O component decreases from 44 % to 30 % of the C1s peak area. These observations are consistent with the results of correlated electrical and TPD measurements (Figure 1f), confirming structural changes in the GO carbon framework in this temperature range. On the other hand, the peak areas of carbonyl and carboxyl carbons (288.6 eV and 290.6 eV,

respectively) remain stable throughout the entire temperature range of up to 200 °C. The temperature dependencies of these components are consistent with the previously reported XPS data on the low-temperature thermal reduction of GO,²² which appears to be primarily associated with the reduction of hydroxyl and epoxy groups. A higher degree of reduction could be achieved at higher temperatures by removing the carbonyl and carboxyl groups.

The XPS data also show that the annealing of GO at 200 °C does not achieve the highest possible degree of reduction. For example, XPS C1s spectra of the GO that was chemically reduced using hydrazine³⁹ have less pronounced features associated with the oxygen-containing functionalities than the spectrum in Figure 2d. Interestingly, a hydrazine reduced GO, despite its higher degree of reduction, was also found to be five orders of magnitude more conductive than the starting GO material.³⁹ This agrees well with the observation that the largest conductivity change happens at an intermediate level of reduction (Figure 1f), likely when the graphitic domains grow large enough so that the percolative electronic transport becomes possible, and further reduction has a much smaller effect on the conductivity increase.

Raman spectroscopy was also used to monitor the reduction of GO.^{8, 39, 42, 43} Representative Raman spectra of GO samples that we annealed at different temperatures in the 85-200 °C range are shown in Figure 2f. These spectra show two broad features at about 1355 and 1554 cm⁻¹, which are known as D and G bands respectively.⁴⁴ It was previously demonstrated that while in the asprepared GO the intensity of the G band (I_G) is slightly higher than the intensity of the D band (I_D), this reverses upon GO reduction.^{8, 39, 42, 43} In general, I_D/I_G has a nonlinear dependence with a maximum on the size of sp² domains,⁴⁴⁻⁴⁶ and the ratio increase upon reduction is consistent with the growth of sp² domains that are originally only a few nm in size.^{4, 17} We plotted the I_D/I_G ratios extracted from the Raman spectra of GO (Figure 2f) as a function of reduction temperature in Figure 2e, and the beginning of the rise of the I_D/I_G ratio agrees well with the changes in the fractions of XPS components, as well as the results of the TPD experiment (Figure 1f).



Figure 3. (a) An optical micrograph showing the central portion of an *in situ* heating device. **(b-f)** TEM images recorded during the thermal reduction of GO. (b) A TEM image of the pristine GO (before heating). (c-f) TEM images recorded *in situ* during the heating experiments at (c) 155 °C, (d) after 7 min, and (e) 18 min at 170 °C, and (f) after 10 min at 250 °C.

Transmission electron microscopy (TEM) has been employed in several studies to visualize the structural transformations in GO upon reduction.^{17, 18} Here, in order to correlate the TEM data with the results of temperature-dependent conductivity, TPD and XPS measurements, we used the *in situ* heating capability of a commercial specimen holder. The same aqueous GO

solution was dried on interdigitated heating devices, which were calibrated for each experiment. Figure 3a shows SEM image of the central portion of a device, in which a GO flake is suspended over an array of holes. Similarly to other experiments, the TEM analysis of GO was performed in UHV conditions, although the heating rates $\beta = 0.3$ °C/min – 1°C/min were lower than in the electrical conductivity/TPD and XPS measurements.

Figures 3b-f show a series of TEM images recorded *in situ* at various temperatures during the heating experiments, except in Figure 3b, where the pristine GO (before heating) is shown with a uniform and amorphous like structure. At 155 °C, disruptions in the structure of GO can be noticed (Figure 3c), becoming more prominent with longer heating times and at higher temperatures. This is clearly noticeable in the images recorded after seven minutes (Figure 3d) and eighteen minutes at 170 °C (Figure 3e). The most noticeable feature in these images is the progressive development of nanoscopic holes. Based on the results of TPD measurements, the most active evolution of CO and CO₂ is observed in the temperature range of 130 °C to 170 °C. Therefore, when the temperature reaches 170 °C, a substantial amount of CO and CO₂ is desorbed, leaving nanoscopic holes in the GO sheets. Images recorded at slightly higher temperatures, such as 250 °C (Figure 3f), do not show signs of further evolution of the GO structure, suggesting that most structural changes in GO correlate with the active phase of gas desorption observed between 130 and 170 °C.

In summary, we performed several *in situ* experiments, in which electrical transport, mass spectrometry, XPS and HRTEM measurements of GO were performed in similar vacuum conditions as a function of temperature. The simultaneous electrical and TPD measurements allowed us to correlate the abrupt change in the electrical conductivity of GO by five orders of magnitude with the maxima of the desorption rates of H₂O, CO and CO₂, which are all observed at ≈ 150 °C. The desorption of these gases is in a good agreement with (1) the changes in the chemical composition of GO detected by XPS, and (2) the formation of the nanoscopic holes in GO sheets. The correlation of the results of these *in situ* experiments provides a clearer picture of the low-temperature thermal reduction of GO.

See supplementary material for experimental details.

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