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Water Oxidation behind Photoreduction of Graphene Oxide

Hongjiang Li, Xuedan Song*, Yantao Shi, Yan Gao, Duanhui Si, Ce Hao*

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By means of H₂¹⁸O labeling experiment in combination with mass spectrometry tracking, we study GO photoreduction. The finding of ¹⁸O labeled O₂ provides direct evidence to confirm the water oxidation occurs during GO photoreduction. In combination with DFT calculations, we propose the mechanism of O₂ and CO₂ evolution in the photoreduction of GO.

Graphene oxide (GO), commonly synthesized by strong oxidation of graphite, has a single-atomic layered twodimensional (2D) structure decorated with a large quantity of oxygen-containing groups, such as epoxide (C-O-C), carbonyl (C=O), carboxyl (COOH) and hydroxyl (C-OH), which make GO water-dispersible, insulating, and light brown in color.1-3 Reducing GO to produce reduced GO (rGO) is accomplished by removing a large portion of the oxygen-containing groups, which is a routine procedure in the synthesis of graphenebased materials with high conductivity.4,5 In comparison to thermal 6,7 or chemical reduction, $^{8\mathchar`-11}$ photoreduction of GO 12 aqueous dispersions is an environment-friendly strategy. More importantly, photoreduction is a unique method capable of patterning GO films.^{13,14} Despite many successful applications reported to date, currently there is still no wide consensus regarding the mechanism behind GO photoreduction.

Upon ultraviolet (UV) light irradiation, the color of GO changes from brown into black due to the partial removal of oxygen-containing groups that accompanies recovery of conjugated structure and increase in conductivity. Usually, the contents of different oxygenated functional groups and the change of the sp² π -conjugated domain before and after GO photoreduction can be well analyzed by X-ray photoelectron spectroscopy (XPS) in combination with other methods.^{15,16} As established by many groups, the content of epoxide and

carbonyl decreases while that of hydroxyl increases in GO photoreduction. In recent years, more and more research works imply that water may play a very important role in GO photoreduction. For example, a transient absorption spectroscopy study conducted by Gengler et al.¹⁷ demonstrated that there were two distinct processes during GO photoreduction, which were identified as water excitation (0.5 \sim 1 ps) and GO reduction (1 \sim 250 ps). Subsequently, Koinuma et al.¹⁶ proposed a mechanism whereby epoxides are transformed into C=O and C=C units, while the C=O react with water to produce C-OH and release CO₂ molecules. By using mass spectrometry (MS), Shulga et al detected O₂ and CO₂ as gas products in GO photoreduction.^{18,19} However, there is no experimental evidence to confirm the participation of water in GO photoreduction so far. In addition, the mechanism of oxygen evolution has never been investigated.

Herein, for the first time we report the study of GO photoreduction by ¹⁸O isotope. In our experiment, heavy oxygen water (with an ¹⁸O content of 20%) was used as isotopic tracer and dispersion medium of GO. The welldesigned analysis setup enabled us to detect various gaseous products during GO photoreduction. The detection of ¹⁸O labeled molecular oxygen (m/z = 34 or 36) provided direct evidence to confirm water is oxidized in GO photoreduction. In



Department State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology

Dalian , Liaoning, China

⁺ Electronic Supplementary Information (ESI) available: characterization of GO, Infrared spectra and Raman spectra of GO, modeling information, Scheme of oxygen evolution and decarboxylation reaction See DOI: 10.1039/x0xx00000xAddress here.



Fig. 2 (a) XPS results of GO (top) and rGO (bottom) after UV irradiation for 3 hours. (b) Photographs of GO and rGO aqueous dispersions. (c) The chemical shift of GO (black line) and rGO (red line) obtained by solid-state ¹H NMR.

combination with XPS analysis and DFT calculations, we put forward a mechanism for oxygen and carbon dioxide evolution. Oxygen evolution in GO photoreduction occurs through oxidation of water molecules by two nearby homolateral epoxides. And carbon dioxide is produced through decarboxylation, during which water plays a positive role to lower its energy barrier by altering the reaction pathway. The direct and strong experimental evidence as well as our theoretical analysis can advance our understanding of GO photoreduction.

In our study, the general approach to revealing the mechanism of oxygen and carbon dioxide evolution during GO photoreduction is to collect oxygen and carbon dioxide and identify their sources by means of isotope labeling. As shown in Fig 1, an experimental installation, consisting of reactor, cooling system, light source, carrier gas and MS analysis system, was designed. GO was dispersed by distilled water and then transferred to the quartz reactor. During GO photoreduction, the surrounding temperature of the quartz reactor was maintained at about 25 °C by a water cooling system. Moreover, the residual gas in the GO suspension was thoroughly removed by aeration for 2 h. We initiated GO photoreduction by subjecting the GO aqueous dispersion to UV irradiation.

The GO used in this study was synthesized by the Hummers method and is commercially available. The UV-Vis absorption spectroscopy and Fourier transform infrared (FTIR) spectroscopy analyses of GO are presented in Fig S1, the results are very consistent with those reported by others in the

Table 1. Oxygen content and structural changes after					
photoreduction					

	P _{oxygen}	$P_{\rm GO}$	P _{C=O}	Pepoxide	P _{hydroxyl}
GO	46.8%	62.6%	15.7%	15.8%	15.3%
rGO	35.8%	39.9%	12.1%	4.1%	19.6%



Fig.3 Oxygen signal detected by mass spectrometry. m/z=32, m/z=34 and m/z=36 are ${}^{16}O_2$, ${}^{18}O^{16}O$ and ${}^{18}O_2$ respectively. The zero point of the X axis represents the time we started GO photoreduction. (a) Oxygen signal of GO in normal water under UV irradiation for 3 hours. (b) Oxygen signal of GO in ${}^{18}O$ enriched water under UV irradiation for 3 hours.

literature. As shown in Fig. 2, significant variation can be observed for the sample before and after being irradiation by UV light. The XPS analysis results presented in Fig 2 show that the contents of different oxygen-containing groups varied considerably as the color of the aqueous dispersion changes from brown into black, indicating the conversion of GO into rGO. The analysis of the peaks in the XPS spectrum was performed according to the literature, assigning the peaks at 286.7 eV to C-O (hydroxyl and epoxide), 288.30 eV to C=O and 284.60 eV to C-C, C=C and C-H species.^{15,20,21} Poxygen in Table 1 is the content of oxygen. P_{GO} represent the ratio of oxygen containing carbon atoms relative to the total number of carbon atoms. P_{C=O} is the ratio of carbonyl group. P_{epoxide} and P_{hydroxyl} are the ratio of epoxide and hydroxyl. P_{GO} , P_{oxygen} and $P_{C=O}$ can be obtained from analyzed the XPS spectrum Using P_{GO} , P_{oxygen} and $P_{C=O}$ we can roughly estimate $P_{epoxide}$ and $P_{hydroxyl}$ which is listed in Table 1. (The analysis method is shown in Supplementary Information Section 2.) After photoreduction, the contents of epoxide decreased from 15.8% to 4.1%. At the same time, the content of hydroxyl increased from 15.3% to 19.6%. Moreover, the chemical shift of ¹H (from 5.5 ppm for GO to 5.1 ppm for rGO) solid-state NMR measurement also reflects the increase of hydroxyl content after GO photoreduction.^{22,23} (Fig 2c)

To the best of our knowledge, isotope labeling experiments have rarely been reported in probing into the mechanism of GO photoreduction. In this study, the isotopic tracer used was heavy oxygen water with an ¹⁸O content of about 20%. Since the yields of gaseous products in GO photoreduction were very low, the gas accumulation process was conducted for 3 h in order to clearly observe MS signals. The mass spectrum of overall gas products are shown in Fig S3. Oxygen evolution during GO photoreduction traced by MS is illustrated in Fig 3. In the labeling experiment, the isotope composition of the gaseous product (e.g. the ratio between different oxygen molecules) can provide us valuable clues. In the experiment using normal water (whose ¹⁸O content is about 0.2%) to

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disperse GO, the signal of ${}^{16}O_2$ (m/z = 32) is strong but there is no clear signal of $^{18}\mathrm{O}^{16}\mathrm{O}$ (m/z = 34) or $^{18}\mathrm{O}_2$ (m/z = 36) by comparison. The integration of the peak areas for the three signals revealed that the ¹⁶O₂ accounts for about 98.8% of the evolved oxygen. As shown in Fig 3b, the signals of ¹⁸O¹⁶O and ¹⁸O₂ in the labeling experiment using heavy oxygen water can be clearly observed compared to the above experiment using unlabeled water. The contents of ${}^{16}\text{O}_2$, ${}^{18}\text{O}^{16}\text{O}$ and ${}^{18}\text{O}_2$ in the labeling experiment were determined to be about 78.9, 18.7 and 2.4%, respectively. At this stage, it would be reckless to reach a conclusion confirming the source of molecular oxygen as adequate consideration should be given to some critical issues, such as the oxygen exchange between water and GO. Here, we first made the assumption that there is oxygen exchange occurring between water and GO; the ¹⁸O content of GO at the equilibrium state of oxygen exchange is α (with regard to the overall oxygen atoms of GO). If GO is the only oxygen source during photoreduction, based on above assumption, the ratio of ${}^{16}O_2$, ${}^{18}O^{16}O$ and ${}^{18}O_2$ should be: $(1-\alpha)^2$: $2\alpha(1-\alpha)$: α^2 . Clearly, the actual ratio of the three oxygen molecules (78.9% : 18.7% : 2.4%) is totally inconsistent with above mathematical deduction. This finding leads us to speculate that the evolved oxygen comes from GO and water together. Thus, it is inferred that GO and water contribute equally to oxygen evolution because the actual ratio of ¹⁸O¹⁶O (18.7%) is closer to 20%. In other words, half of the atoms in the evolved molecular oxygen come from GO, while the other half is derived from water. Thus, we can conclude that the occurrence of GO photoreduction in aqueous dispersion is accompanied by water oxidation ²⁴⁻²⁸ as depicted by equation 1:

 $GO + H_2^{18}O \rightarrow rGO + {}^{16}O^{18}O$

(equation 1)

To gain more insight into the possible mechanism of oxygen generation, we additionally performed DFT calculations. According to the results of the XPS analysis, the content of ep-



Fig.4 Minimum energy path for oxygen evolution reaction obtains by DFT calculation. A is the configuration of initiating reactant. We omitted the gray atoms to make the model clearer to see. B, C and D are the configuration of intermediate. E is the configuration of product. TS represent transition state of reaction. C, O and H atoms are illustrated in green, red and white, respectively. The reaction energy curve including activation energy of each step is given in the bottom diagram.



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Fig 5. Carbon dioxide signal detected by mass spectrometry. m/z=44, m/z=46 and m/z=48 are C¹⁶O₂, C¹⁸O¹⁶O and C¹⁸O₂ respectively. The zero point of the X axis represents time of the detection starting. (a) Carbon dioxide signal of GO in normal water under UV irradiation for 3 hours. (b) Carbon dioxide signal of GO in 18O enriched water under UV irradiation for 3 hours.

oxide and carbonyl groups clearly decreased after photoreduction. We compared the possibility of the reactions of epoxide and carbonyl groups with water, as shown in Fig S4. The results indicated that epoxide can directly react with water molecules, while carbonyl and water molecules are difficult to react. Accordingly, we propose a reasonable pathway whereby two nearby homolateral epoxide groups and one water molecule as the starting reactants participate in the oxygen generation process during GO photoreduction. As shown in Fig 4 and Fig S11, the deoxidization reaction consists of four steps: First, the hydrogen atom of water is transferred to the epoxide group to form a hydroxyl group and a hydroxyl radical. Second, the hydroxyl radical attacks the second epoxide group and causes the removal of the epoxide group to produce the •OOH fragment. Then the hydrogen atom of •OOH is transferred between the two oxygen atoms of •OOH. In the last step, the hydrogen atom of •OOH is transferred to the carbon atom in GO to form the C-H bond and at the same time oxygen is produced. The overall reaction process consumes two epoxide groups, one water molecule to generate oxygen, C-H bonds and hydroxyl groups. The activation energy of four steps is listed in Fig 4. The mechanism is consistent with the results of the XPS analysis and isotope labeling experiments. The contrast of the infrared and Raman spectrum intensity before and after photoreaction (Fig S5) reflects the increase of the C-H bond content, which is also consistent with the mechanism we have proposed.

In addition to oxygen, another important gaseous product in the photoreduction of GO is carbon dioxide. Our study also confirms the important role of water in carbon dioxide production, as shown in Fig S6. In this experiment, solid sample with low water content rather than GO aqueous dispersion was put into the quartz reactor. The solid sample was prepared by squeezing 50 mg freeze-dried GO into a tablet (see the insert photo of Fig S6), while the wet tablet sample contained 0.5 ml distilled water. Evidently, under UV

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irradiation more carbon dioxide was released from the wet sample, with its yield twice that released from the dry sample, implying that water may probably participate into the production of carbon dioxide. As shown in Fig 5a, the MS signals of $C^{18}O^{16}O$ (m/z = 46) and $C^{18}O_2$ (m/z = 48) are observable in the unlabeled experiment, and the content of $C^{16}O_2$ is determined to be about 99.3%. In the labelling experiment shown in Fig 5b, the contents of $C^{16}O_2$, $C^{18}O^{16}O$ and $C^{18}O_2$ are about 76.2%, 22.6% and 1.2%, respectively. This result also suggests that water as a reactant participates into the production of carbon dioxide, and one half of oxygen atoms in carbon dioxide may probably derive from water. Online mass spectrometry was used to detect the concentration changing of O₂ and CO₂ with irradiation time. The results are showing in Fig S7. The concentration ratio of O₂ and CO₂ is nonlinear relation with irradiation time, which indicates there is no correlation between the formation of O₂ and CO₂, their formation mechanism should be independent. We calculate the formation mechanism of CO₂ separately. The result is shown in Section 10 of Supplementary Information.

In this work, the mechanism of oxygen and carbon dioxide evolution during GO photoreduction was studied by means of ¹⁸O isotope labeling experiments in combination with MS tracking and DFT methods. The MS signals of ¹⁸O-containing products provided direct evidence to confirm the participation of water into the evolutions of oxygen and carbon dioxide during GO photoreduction. In combination with the results of the XPS characterization and DFT calculations, a new mechanism was proposed to explain GO photoreduction whereby the epoxides played an important role. Oxygen evolution in GO photoreduction was interpreted to take place through oxidation of water molecules by two nearby homolateral epoxides. At the same time, the epoxides or carbonyls at the edge of GO react in pairs with water to form carboxyls. Ultimately, carbon dioxide is generated through decarboxylation, during which the participation of water could lower its energy barrier by altering the reaction pathway. The direct and strong experimental evidence, as well as the results of our theoretical investigation, contribute to advance our understanding of GO photoreduction.

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Conflicts of interest

There are no conflicts to declare.

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