Electronic Supplementary Information

The role of ozone in the ozonation process of graphene oxide: oxidation or decomposition?

Feng Yang,[a] Meilian Zhao,[a] Zhen Wang,[a] Hongyun Ji,[c] Baozhan Zheng,[a] Dan Xiao,[a,c] Li Wu,[b]* and Yong Guo*[a]

1. Experimental section

1.1 Materials

All chemicals used were of analytical grade. Graphite Powder (> 99.85%, Shanghai Huayi Company, China). Hydrogen peroxide (H_2O_2, 30%) was bought from Guangdong Chemical Reagent Engineering-technological Research and Development Center (Guangdong, China). Phosphorus pentoxide (P_4O_{10}), sodium hydroxide (NaOH, > 99%), sulfuric acid (H_2SO_4, > 98%), potassium permanganate ($KMnO_4$, > 99.5%) and ethanol absolute (C_2H_5OH, > 99.7%) were obtained from Kelong technological Co. (Chengdu Sichuan, China). Potassium peroxydisulfate ($K_2S_2O_8$, > 99.5%) was purchased from Sinopharm chemical Reagent Co. (Sichuan, China). All chemicals were used as received without further purification, and all solutions were prepared fresh daily in deionized (DI) water. The water used in the experiments was freshly deionized using a deionized (DI) water system (SZ-93, Shanghai Yarong Company, China).

1.2 Materials preparation

GO dispersed mixture was produced using a modified Hummers' method from graphite powder by our previous work.[1] As-synthesized graphene oxide mixtures were dispersed in deionized water to obtain the resultant stable suspension (~ 0.5 mg/mL) at pH 2.00 with the assisted-ultrasonication. To obtain the fluorescence graphene oxide, we bubbled ozone to re-oxidize the graphene oxide dispersed mixtures in ice-bath. The ozone (being generated by OZ-7G Ozone Generator) was bubbled through the suspensions to treatment different time, respectively.

1.3 Characterizations

Transmission electron microscopy (HR-TEM) observations were performed with one drop of the aqueous nanosheet suspension deposited on a holey carbon film on a TECNAL G2 F20 (bought from FEI Company) electron microscope operating at 200 KV. X-ray diffractions (XRD) were obtained with a Tongda TD-3500 X-ray powder diffractometer (Liaoning, China) using Cu Kα radiation (λ = 0.154 nm). The XRD patterns were recorded from 5° to 50° with a scanning rate of 0.03 °/s. Samples were measured in a 1 cm path-length quartz cuvette using a UV 1750 instrument (Shimadzu, Japan). Fluorescence measurements were done with F-7000 Hitachi spectrometer. This spectrometer uses a pulsed xenon arc lamp illumination source and wavelength selection was accomplished using a scanning monochromator. Fluorescence experimental conditions: the photomultiplier tube (PMT) voltage was set at 700 V, and the slit width of excitation and emission was 10 nm and 10 nm, respectively. X-ray photoelectron spectroscopy (XPS) spectra of samples were measured by a Kratos XSAM800 system taking an Al K as source for determining the composition and chemical bonding configuration. Raman microscope instrument (HORIBA Jobin Yvon S.A.S.) equipped with laser (λ = 532 nm, λ = 633 nm and λ = 785 nm). The instrument was calibrated against a Si crystal. Raman spectra were collected on Lab RAM HR with 633 nm wavelength laser. Samples were scanned from 1000 to 2000 cm^{-1} to visualize the D and G bands. Spectra were collected with a 5 s exposure time and 2 accumlation unmber with 50 objective.

2. Morphology, composition and properties of specimens

Figure S1 shows TEM images of GO and O-GO. The morphology of specimens has remarkably changed. The edges of the GO film always folded back and were corrugated and scrolled. Unlike GO, the surface of the O-GO was much more smoothed silk veil waves with better transparent and monolayer.

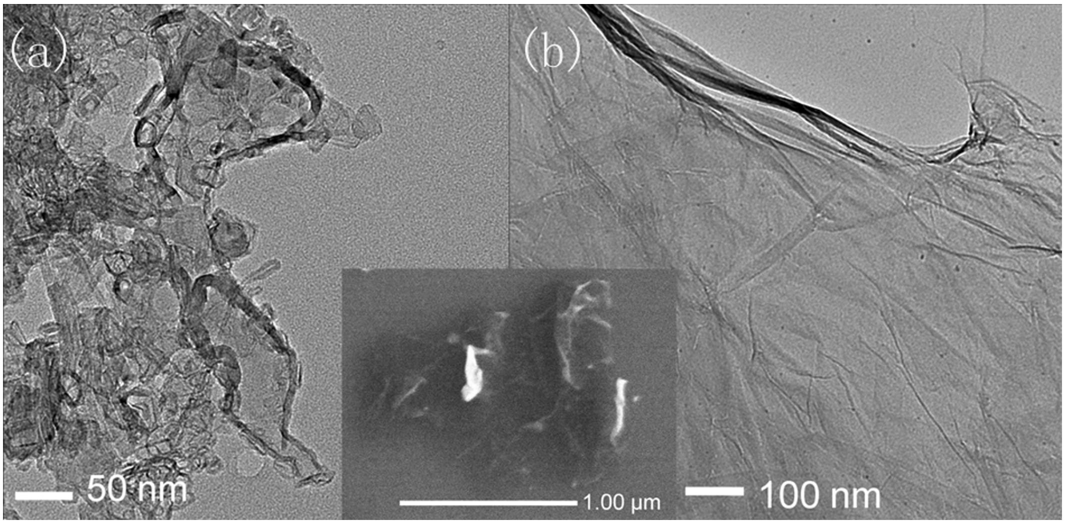

Figure S1 The TEM images of GO (a) and O-GO (b); inset: the SEM image of GO.

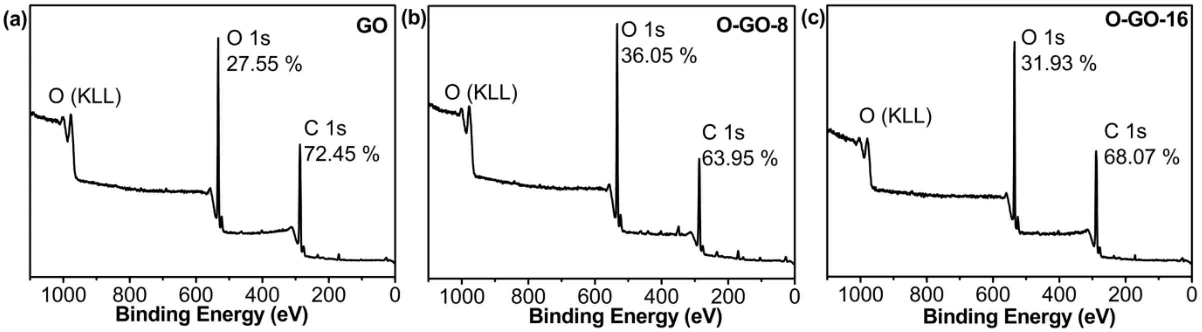

Figure S2 The XPS spectra of (a) GO, (b) O-GO-8, which was treated for 8 h and (c) O-GO-16,which was treated for 16 h.

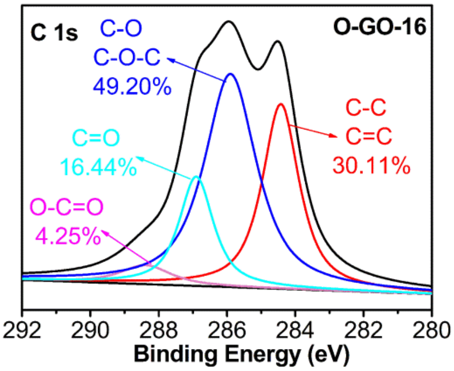

Figure S3 The high-resolution XPS spectra of ozonized graphene oxide, which was treated in ozonation system for 16 h.

Raman spectroscopy is a powerful tool to analyze carbon-based materials structures and provide a better understanding of structural changes. The Raman spectrum is fitted by two Gaussian peaks: the D-peak (1300 - 1360 cm^{-1}) and G-peak (1580 - 1600 cm^{-1}).[1] The D-peak was related to the structural disorder coming from amorphous carbon and any defects. The intensity is dependent on the presence of six-fold aromatic rings and the width is correlated to a distribution of sp^2 bonded clusters with different ring sizes. The G-peak occurs at all sp^2 sites and the width can be used as a measure of quality of the graphene planes.[2] The ratio of intensities of the D and G bands, $R = I_D/I_G$, can be used to evaluate the disorder density of the carbon materials and interesting information on the structure of carbon materials.

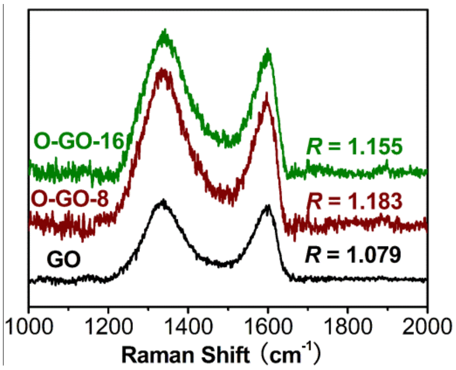

Figure S4 The Raman spectra of the specimens, which were treated in ozonation system for 0 h (black line), 8 h (wine line), and 16 h (olive line).

As shown in Figure S4, the *R* value increased from 1.079 for GO to 1.183 for O-GO-8, and decreased to 1.155 for O-GO-16. While, the D-peak gradually broadened with prolonging treatment time. It demonstrates that the structure of graphene oxide changes greatly in functional oxidation and exfoliation processing with the decomposition of oxygen-containing functional groups. The ozonation treatment affects the nano-crystalline graphite size and defects. The oxygen-containing functional groups occupy the lattice points, which can behave as defects for Raman scattering. Additionally, broadening D-peak could be influenced by the smaller number of electrons in oxygen which caused a redistribution of π-bonding resulting in bond length differences comparing with the ordinary C-C vibrations in precursors. The results are consistent with XPS results.

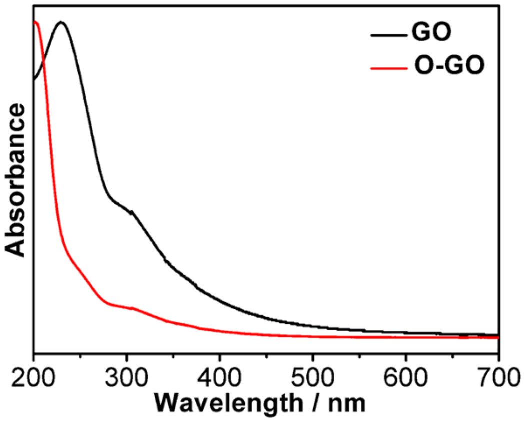

Figure S5 The UV-vis absorbance spectra of GO and O-GO. The broad absorption bands in the visible region are due to conjugated π electrons. The O-GO detected with a noticeable blue shift of the UV absorption and a decrease in visible absorption, indicating a higher degree of oxidation for O-GO compared to GO.

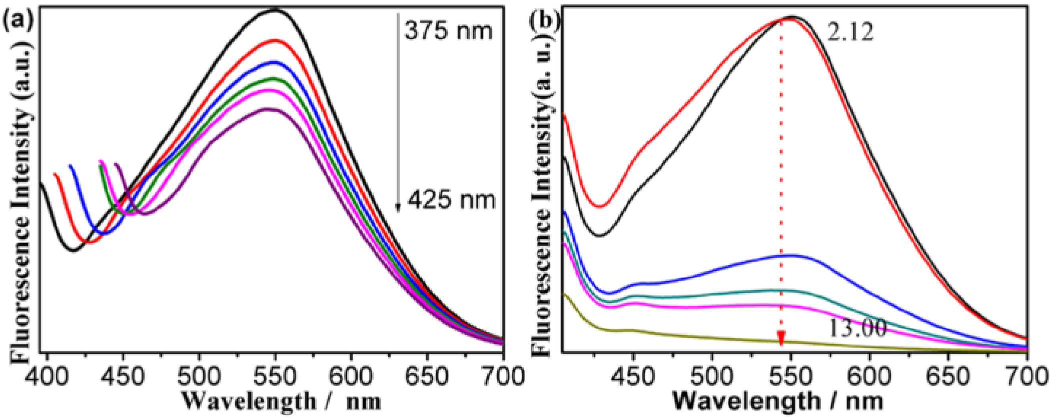

Figure S6 (a) Fluorescence emission spectra (with progressively longer excitation wavelengths from 375 nm on the left in 10 nm increment) of O-GO in an aqueous solution. (b)The pH-dependent fluorescence spectra of O-GO. Emission spectra measured with 380 nm excitation for sample pH values between 2.12 and 13.00.

As Figure S6a shown, the fluorescence weakened gradually, but without obviously shifted with progressively longer excitation, which differed from the excitation-dependent of graphene quantum dots. As pH was increased from 2.12 toward 13.00, we observed a monotonic decreasing in emission intensity with no significant change in shape (Figure S6b). Meanwhile, the fluorescence intensity tended to decrease as the pH increase, especially pH was higher than 6.00, the fluorescence intensity sharply decreased. While, when the pH was switched between 13.00 and 2.12, the fluorescence intensity was irreversibly. The fluorescence originated from the quasi-molecular fluorophores on the surface of graphene oxide.[3, 4] The changes in fluorescence properties were completely irreversible with pH in the measured range, indicating that the structure of O-GO was destroyed in high pH system. According to the pH-depended features of O-GO, we inferred that the structure and groups on O-GO surface were damaged in alkaline system. To prove this hypothesis, we investigated the XRD spectra of GO treated in different concentration of sodium hydroxide system. As shown in Figure S7, the diffraction peak of GO gradually disappeared and the diffraction peak of graphene sheets gradually appeared with the increase of sodium hydroxide concentration. Namely, the graphene oxide was reduced gradually under alkaline conditions. The fluorescence of O-GO is structured and pH dependent, which indicates that the fluorescence properties originate from the quasi-molecular fluorophores on the surface of GO. As As identified previously, the fluorophores are the oxygenated functionalities associated with the sp^3 carbons of graphene oxide.[3]

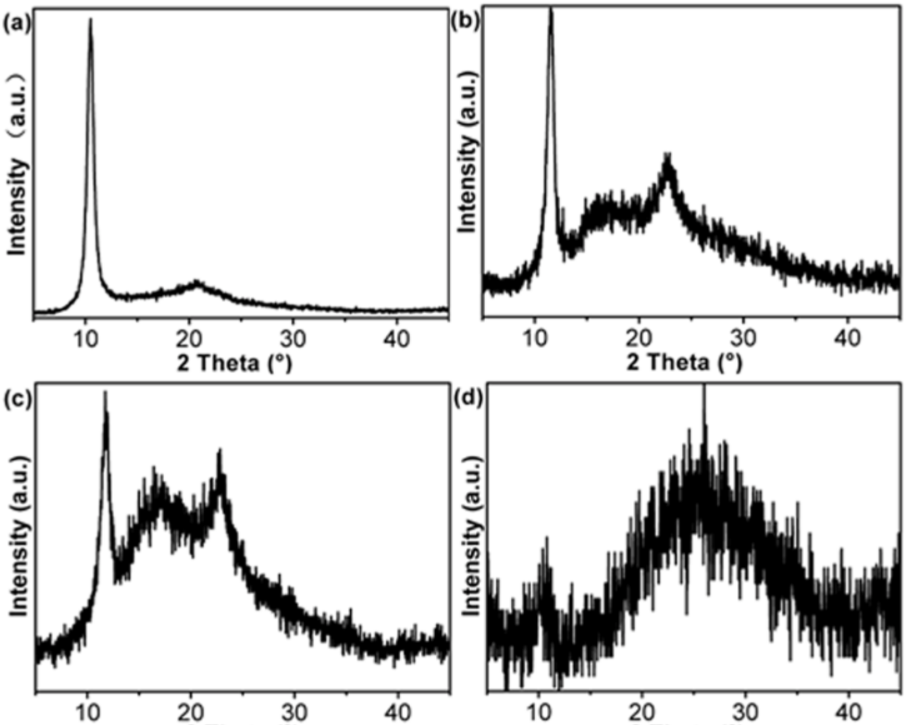

Figure S7 XRD spectra of GO, which was treated in H_2O (a), 0.1 M NaOH solution (b), 1.0 M NaOH solution (c), 10.0 M

NaOH solution (d) for 2 min, respectively.

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2. S. Urbonaite, L. Hälldahl and G. Svensson, *Carbon*, 2008, **46**, 1942.
3. B. Konkena and S. Vasudevan, *J. Phys. Chem. Lett.*, 2013, **5**, 1.
4. C. Galande, A. D. Mohite, A. V. Naumov, W. Gao, L. Ci, A. Ajayan, H. Gao, A. Srivastava, R. B. Weisman and P. M. Ajayan, *Sci. Rep.*, 2011, **1**, 1.