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Communication

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

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We took ozonation as an effective method to oxidize graphene oxide (GO) and discussed the behaviour of ozone in the ozonation process according to the changes of optical properties, compositions and structures. The results indicate that the ozonation process may involve the oxidation stage and decomposition stage. The research would improve the understanding of the ozonation process and promote the future application of ozonized graphene oxide as the precursor.

As the precursor of multifunctional graphene-based material, the properties of graphene oxide (GO) depend on the compositions, dimension, layer structure, and edge configuration.[1-4] The fluorescence properties of graphene oxide can be drastically modified or fine-tuned by atomistic or chemical doping.[5] The functional groups, including hydroxyls, epoxies, carbonyls, carboxyls, are primarily arose from different treatment processes. Currently, the main approaches for modifying the band structure and modulating the oxidation degree of graphene-based materials include plasma treatment,[6] cutting graphene into nano-ribbons or dots[7, 8] and chemical modification[9, 10]. Oxidation was carried out with strong oxidizing agents such as concentrated HNO_3, mixtures of H_2SO_4 with HNO_3, H_2O_2, or $KMnO_4$, etc.[7, 9-11] The deficiencies of chemical re-treatment are time-consuming and difficult for purification. The chemical versatility and tunability of GO make it attractive for a wide application. Ozone, which produces hydroxyl radical-based advanced oxidation process, is the traditional method to cleave organic and inorganic pollutants with oxidation for practical applications. Meanwhile, compared with previous reports, ozonation system was employed to simplify the synthesis of fluorescent graphene oxide, the simplified purification and controllable process are the distinct advantages.

Ozone as the oxidizing agent to treat the carbon-based materials has been reported.[12-14] Some research works discussed the destructiveness[15] and adsorption[16] of ozone on graphene or adjustment of the electrical and optical properties[17]. Recently, Gao and co-authors[18] showed that the chemical modification of GO by ozone to form ozonized GO as the proton-exchange membrane. Our group has taken ozone as the oxidizing agent to treat GO and reduced GO, and discussed the reaction of ozone and active sites, but the details of ozonation process are not clarified.[19] Namely, up to now, most research used ozone as the oxidizing agent tuning the oxidation degree or the electrical and optical properties of graphene or graphene-based materials, but little work has been detailed the ozonation process and the behaviour of ozone. What role does ozone play in the process of ozonation - oxidation or decomposition? It is essential to study graphene-based materials for further application.

Herein, we focus on the ozonation process, and the optical properties of O-GO and elucidate patterns of fluorescence based upon the oxidation mechanism. We reported a simple ozonation for re-oxidation GO into surface-functionalized GO. The functionalized GO was found to exhibit yellow fluorescence. The yellow fluorescence and UV-vis absorption bands are directly induced by the molecular-like fluorophores on the basal plane and the sheet edges. As-produced specimens, according to TEM and SEM images, were dominated by micrometer-sized rippled graphene oxide sheets (Figure S1).

The graphene oxide was produced from graphite *via* modified Hummers methods[20], then it was re-oxidized by ozone to obtain fluorescent graphene oxide. As-prepared graphene oxide suspension was dispersed in pH = 2.0 acidic system. Emission peaks appeared ~ 550 nm with 374 nm excitation at this pH (Fig. 1), which was different from previously reported.[6, 8, 9]. As we all know, graphene is a zero-gap semiconductor and controllably modifying the electronic band structure remains a major challenge. We took ozone as oxidizing agent to introduce oxygen-containing functional groups onto sheets, open optical band gap of graphene oxide and enhance fluorescence. After ozonation, the fluorescence intensity was significantly enhanced and the solutions changed from brown to yellow, and the yellow fluorescence emissions were observed.

Despite it was micrometer-sized, the fluorescent graphene oxide exhibited obvious fluorescence suggesting that the sheets behaved as indirect bandgap materials. And the broadband fluorescence peaks observed in fluorescent GO were attributed to oxygen-containing groups as the molecular-like fluorophores. Namely, the ozonation processes changed the composition and microstructure of graphene oxide. These changes are further confirmed by X-ray photoelectron spectroscopy, Raman spectroscopy and optical spectra. Interestingly, the fluorescence activity can be tuned and enhanced *via* ozonation to increase the degree of oxidation (as shown in Fig. 1). Hence, it is a facile, simple, economical, efficient and controllable strategy for ozonation graphene oxide with fluorescence properties.

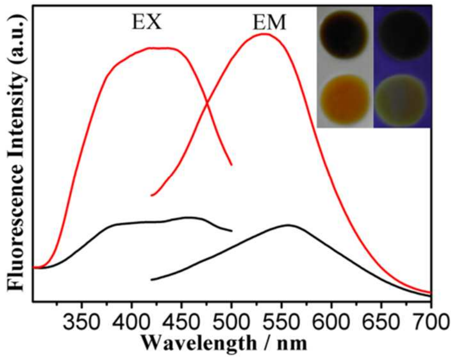

Fig. 1 Fluorescence spectra of GO (black line) and O-GO (red line) dispersed in water with the detection wavelength of ~ 550 nm and fluorescence spectra excited at 374 nm. Inset: Photographs of the GO (up) and O-GO (down) (0.5 mg/mL) aqueous solution were taken under visible light and 365 nm UV-light.

The change of oxidation degree and chemical components of GO was investigated by X-ray photoelectron spectroscopy (XPS) during ozonation process. As shown in Figure S2, the survey spectra clearly reveals that the intensity of O 1s peak increased significantly for the O-GO compared with GO. It indicated that the percentage of oxygen on the specimens increased from 27.55% to 36.05% after ozonation for 8 h. Strangely, the percentage of oxygen decreased, when the graphene oxide was treated in ozone system for 16 h (Figure S2c). In the high-resolution XPS spectra, the C1s peaks at 284.5 eV, 286.5 eV, 287.2 eV and 288.5 eV were assigned to carbon in the form of C-C, C–O or C-O-C, C=O and O-C=O, respectively (Fig. 2). The functional groups at edges and on the basal plane of GO mainly including hydroxyls and epoxies (47.37%). While for O-GO, some of hydroxyls and epoxies were transformed into carboxyl (19.34%) and carbonyl (20.46%) groups as the molecular-like fluorophores. However, it should be noted that the contribution of –O-C=O decreased from 19.34% for O-GO (being ozonized for 8 h, as shown in Fig. 2b) to 4.25% from O-GO-16 (being ozonized for 16 h, as shown in Figure S3). It indicated that the excessive ozonation treatment would lead to the decomposition of the oxygen-containing functional groups. In addition, we employed the Raman spectra to analyse the structures of GO and O-GO, which gives a better understanding of structural changes in the ozonation process (Figure S3). The change of *R* value and width of peaks indicated that oxygen-containing functional groups were introduced to the lattice points along with the decomposition of oxygen-containing functional groups (as shown in Figure S4), which was consistent with XPS results. The detailed results were discussed in Electronic Supplementary Information.

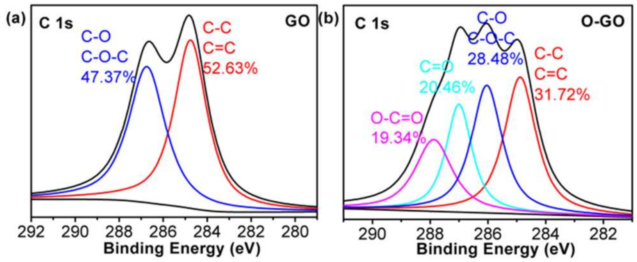

Fig. 2 The high-resolution XPS spectra of (a) GO and (b) O-GO.

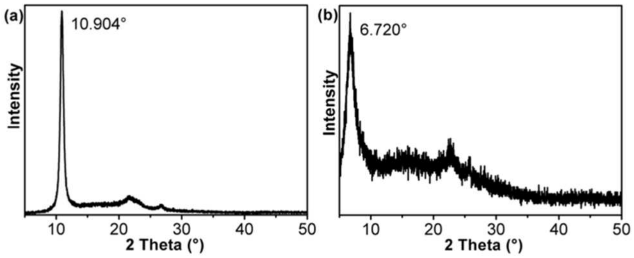

Fig. 3 XRD patterns of (a) GO and (b) O-GO.

We also employed X-ray diffractions (XRD) to investigate the chemical structure of GO and O-GO, which was impacted by the components of materials. Fig. 3 shows the XRD results for both GO and O-GO. The diffraction peak of GO is at ~ 10.904°, and the interplanar distance is 0.811 nm. After ozonation, the diffraction peak of O-GO shifts to ~ 6.720°, corresponding to an interplanar gap of 1.314 nm (Fig. 3). It indicates that the GO was further oxidized to be fully exfoliated and hydrated on the sheets surface, which was consistent with XPS and Raman results.

To further explore the influence of ozonation on the fluorescence properties of graphene oxide and ozonation mechanism, fluorescence and UV-vis absorption spectra were studied (Fig. 4 and 5). GO dispersed systems were ozonized for different time in two system, which was aqueous dispersion without H_2O_2 being designated as system-I and with H_2O_2 being designated as system-II. The gradual transformation of GO is confirmed by fluorescence and absorbance measurements (shown in Fig. 4 and Fig. 5).

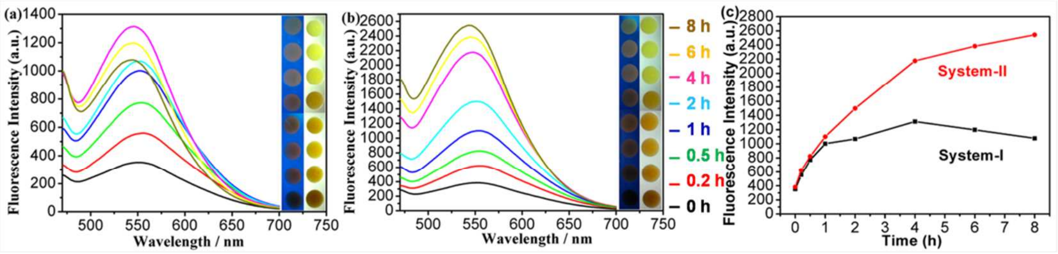

Fig. 4 Fluorescence spectra of progressively ozonized GO dispersed in water. The two system were treated for 0 h, 0.2 h, 0.5 h, 1 h, 2 h, 4 h, 6 h, 8 h, respectively. The fluorescence spectra of GO dispersed water solution without H_2O_2 in system-I (a) and with H_2O_2 (0.5 mL) in system-II (b) were obtained

for excitation at 450 nm; (c) Summary plot showing the fluorescence intensity of O-GO as a function of ozonation time in two system. Insets (a, b): Photograph of progressively ozonation in GO aqueous solution were taken under visible light (right) and UV light (left) at 254 nm.

As shown in Fig. 4, the fluorescence intensity of O-GO could be enhanced with the reaction time increasing. The general trends in fluorescence intensity with ozonation time are summarized in Fig. 4c. It should be noticed that (i) the fluorescence intensity of O-GO was correlated with the ozonation time; (ii) the enhancement rate of system-II was clearly faster than that of system-I, meanwhile the change trends and enhanced fluorescence intensities were different within the time scale; (iii) The fluorescence intensity could be gradually enhanced and the fluorescence emission peaks always shifted blue within the time scale in system-II. Unlike system-II, the fluorescence intensity was gradually weakened but it continually shifted blue after 4 h in system-I.

At low concentration solution, the GO suspension exhibited brown and the colour gradually changed to yellow with ozonation (insets of Fig. 4a and b). The change of colour may result from a higher degree of oxidation for O-GO compared to GO, which was confirmed by UV-vis (Figure S5).

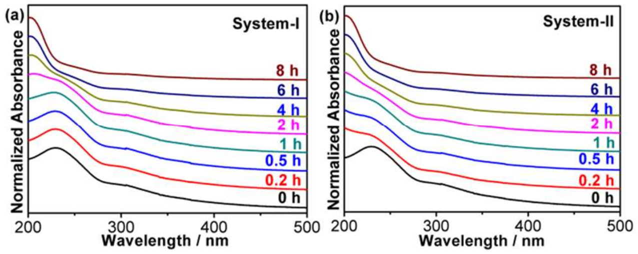

Fig. 4 Absorbance spectra of progressively ozonized GO dispersed in water. The ozonation time for the two system is 0 h, 0.2 h, 0.5 h , 1 h, 2 h, 4 h, 6 h, 8 h.

Fig. 5 shows the UV-vis absorption of GO and O-GO, a typical absorption peak at ~ 230 nm which was assigned to the π-π* transition of aromatic sp^2 domains. It gradually showed a blue-shift with prolonging ozonation time. This indicated that the oxygen functionalities reduced the π-π* domains to open the gap. Thus, the increasing accommodation of oxygen functionalities can change the gap of GO. Clearly, the ozonation rate of system-II was faster than system-I, which was consistent with the evolution of fluorescence results.

As discussed above, we speculated that system-I and system-II experienced different reaction mechanism. In system-I, the dissolved ozone directly reacted with GO slowly. When there is hydrogen peroxide as initiator reaction with O_3 to generate HO· radicals (as shown Eq. 1) in reaction system. The HO· radicals are much more reactive than ozone. Hence, indirect reaction reacted much more rapidly than dissolved ozone with GO. The ozone or HO· radicals attack active sites mechanism similar with previous study.[19]

$$2O_3 + H_2O_2 \rightarrow 2OH\cdot + 3O_2 \qquad (1)$$

Based on XPS and optical properties, we can propose that the composition of ozonized graphene oxide play an important role on the optical properties. Namely, different ozonation times resulted in the O-GO with different degree of oxidation, being consistent with the trend of change of fluorescence and absorbance.The change trends of fluorescence indicate that the ozone plays a different role (oxidation behavior and erosion behavior) in process. Ozonation process undergoes two stage including ozone-oxidation (Stage-I, oxidation-dominated) and ozone-decomposition (Stage-II, erosion-dominated). Thus, we put forward the conceivable ozonation mechanism, which was based on the results of the fluorescence spectra of O-GO. As mentioned above, the ozone acted as oxidation behavior and erosion behavior. As shown in Fig. 6, stage-I was dominated by oxidation behaviour to introduce oxygen-containing groups to the surface, and stage-II was dominated by erosion behaviour to release CO_2/CO and form more defects. That has been verified by the XPS results.

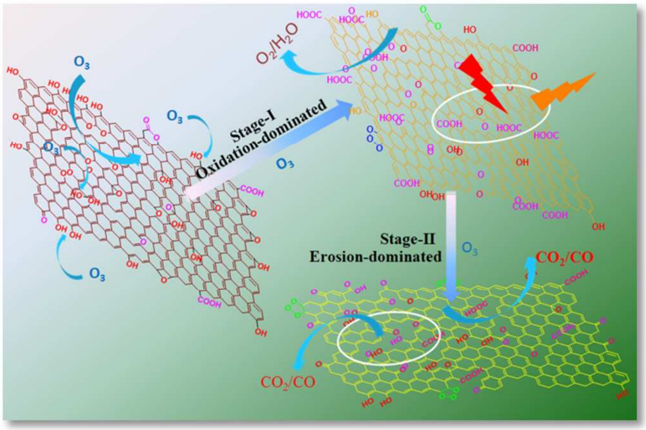

Fig. 5 Schematic of the ozonation process for GO.

There are several mechanisms explaining the unique optical characteristics of nano-carbon materials, such as the size distribution of the carbon nano-particles,[21] a distribution of different emissive trap sites,[22] and the pyrolytic formation of several different polyaromatic fluorophores.[23, 24] According to the theories, the enhanced fluorescence in nano-carbon materials were due to the passivation that stabilized the surface energy traps of nano-carbon and made them emissive. We discussed the fluorescence properties of O-GO (Figure S6). Ozonized graphene oxide exhibited strong pH dependent fluorescence that originates from the oxygen-containing functional groups. The results indicated the fluorescence of graphene oxide dispersions is structured and pH dependent, which have been interpreted as evidence of a quasi-molecular origin of the fluorescence. As identified previously, the fluorophores are the oxygenated functionalities associated with the sp^3 carbons of graphene oxide.[24] More detailed discussions were given in the Electronic Supplementary Information.

Conclusions

In summary, we described yellow fluorescence chemically derived GO by ozonation and discussed the influence of ozonation time on the optical features, compositions and structure. The optical, XPS and Raman results indicated that ozonation mechanism may involve the oxidation stage and decomposition stage. Clearly, it is a simple, economical, efficient, controllable approach to pre-treated GO for appropriate treatment-time. The discovery of the new ozonation process will have a greatly help for future applications of graphene-based materials.

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Notes and references

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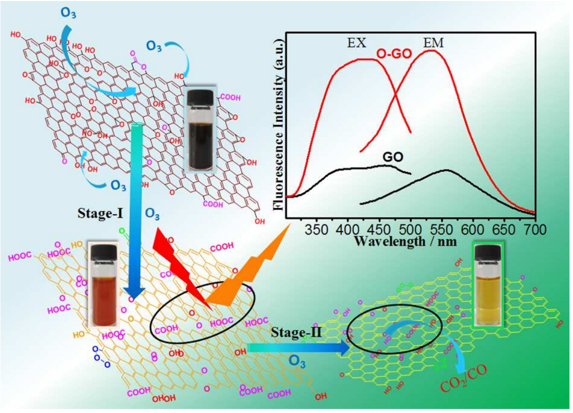

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