# **Supporting Information**

## Influence of pH on the Fluorescence Properties of Graphene Quantum Dots Using Ozonation Pre-oxide Hydrothermal Synthesis

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#### 1 Morphology of Precursors

In order to gain insights into the chemical structures of GO and treated GO (O-GO and RGO), some analysis and testing tools (such as FT-IR, XRD, TG, TEM) were employed to analyze the existence of functional groups and their changes after a series of treatment.

There were marked changes involving surface morphology, surface functional groups and interlayer spacing after ozonation re-oxidation and thermal reduction. As a nonstoichiometric compound, the specific synthetic process strongly affects the chemical structure of graphene oxide (GO). Morphologic changes were observed by TEM (Fig. 2). As shown in Fig. 2, O-GO sheets were ultrathin with fewer ripples than the GO. The transparency revealed that the sheets consisted of ozonized graphene oxide (O-GO) with only a few layers and were fully extended.

As is well-known, oxygen-containing groups primarily contain carboxylic group, epoxy group, carbonyl group and hydroxide group in GO sheets.<sup>1</sup> In this paper, hydroxyl and epoxy groups were the primary functional groups in the GO, while hydroxyl and epoxy groups were changed into carboxylic group or carbonyl group after ozonation (show in Fig. S1 and Fig. S2). It was possible that the release of  $H_2O$  and  $CO_2$  or CO gas occurred upon the "collision" of oxygen-containing functional groups in the basal plane of O-GO when it was treated in a tube furnace in argon atmosphere and the appearance of the samples had been significantly eroded (Fig. S2c). From the experimental phenomena we could speculate that the oxygen-containing groups created defects as chemically reactive sites which allowed O-GO to be thermal-reduced into black powder (RGO).



Fig. S1 FTIR results (a), XRD patterns (b) and TG (c) results of GO, O-GO, RGO, respectively. All the samples were dried at 45 °C in a vacuum desiccator for two weeks.

In order to analyze the existence of functional groups and composition changes of samples, we employed the drift mode FTIR, XPS and XRD. In Fig. S1a, the peaks at ~ 3430, ~ 2360, ~ 1630, and ~ 1070 cm<sup>-1</sup> signified the presence of -OH, C=O, C=C and C-O-C, respectively. After ozonation treatment, the intensity of the absorption at ~ 3430 cm<sup>-1</sup> (hydroxyl) and ~ 1060 cm<sup>-1</sup> (epoxy) decreased for O-GO, while the peaks at ~ 2360 cm<sup>-1</sup> (C=C=C, C=C=O,C=C) and ~ 1960 cm<sup>-1</sup> (=C=C-) increased for O-GO, because ozonation of the hydroxy groups changed to C=C=C, C=C=O or C=C (Fig. S1a). As shown in Fig. S1a, the peaks at ~1630 cm<sup>-1</sup> were still present after ozonation, while the absorption at ~ 3400 cm<sup>-1</sup> and ~ 1070 cm<sup>-1</sup> greatly decreased in intensity for samples as a result of decomposition of the hydroxy groups and epoxy groups after the thermal treatment. Other peaks from carbon-carbon double bond (C=C) were still present after the thermal treatment, because they were stable in this condition.<sup>2</sup> Some of the oxygen-containing groups (epoxy, carbonyl) dispersed in the basal plane and at the edges of GO and O-GO, which enlarged the gap between adjacent GO sheets and O-GO sheets (Fig. S1b). As for RGO, the diffraction peak appeared at ~  $24.8^{\circ}$ , and the interplane distance was about 0.350 nm which was very close to the d-spacing (0.335 nm) of natural graphite. For the GO and O-GO sheets, the diffraction peaks appeared at 9.916° and 9.586°, corresponding to an interplane gap of 0.891 nm and 0.959 nm, respectively (Fig. S1b). It indicated that the O-GO sheets had been fully exfoliated and were much better than GO. Oxygen-containing groups and few H<sub>2</sub>O molecules, which were trapped between GO layers, enlarged the interlayer gap. After the thermal treatment in tube furnace, the diffraction peak shifted to  $\sim 25^{\circ}$  belonging to the peak of RGO. The decreased interplane distance indicated that some of the oxygen-containing functional groups and few H<sub>2</sub>O molecules locating in films layers decomposed to form CO<sub>2</sub>, CO and water vapour during thermal treatment. However, there were remaining functional groups on the RGO sheets (0.350 nm). The remaining groups as reactive sites allowed RGO to be pre-oxidized by ozone and prevented it from aggregating back to graphite (0.335 nm).

The thermal stabilities and transformation during thermaltreatment of GO, O-GO and RGO were investigated by thermogravimmetric analysis (TG) in nitrogen atmosphere (Fig. S1c). The RGO was thermally stable in nitrogen atmosphere. The GO and O-GO weight losses below 110  $^{\circ}$ C were assigned to water, and it must be considered when evaluating the composition derived from elemental analysis. Smith<sup>4</sup> heated the ozonized SWNTs leading to the loss of the C=O groups followed by loss of the C-O groups at higher temperatures. For GO and O-GO, there were dramatic weight losses (30.40% and 31.88%, respectively) at 140 - 200  $^{\circ}$ C which were assigned to removal of the carboxylic groups and ketone groups with releasing CO<sub>2</sub>. The GO and O-GO exhibited weights losses of 21.50% and 17.35% at 200 - 300  $^{\circ}$ C which were related to the decomposition of epoxy groups and hydroxy groups. It may surmise that CO<sub>2</sub>, H<sub>2</sub>O, and CO release upon the decomposition resulted in the formation of many fragment sheets. Hence, we set the constant temperature at 300  $^{\circ}$ C during the thermal treatment in the tube furnace. And Boukhvalov and Katsnelson<sup>6</sup> modeled the effect of oxygen and hydroxyl groups on the structure of graphene oxide. They predicted that the carbon-carbon bond length was highly dependent on the types of functional groups and their coverage. On the basis of the above discussion, we took O-GO as the precursor to synthetize the RGO.



Fig. S2 High-resolution C 1s XPS spectra of GO (a), O-GO (b), RGO (c).

The high-resolution C 1s XPS spectra further confirmed the changes of GO during ozonation and thermal treatment. As shown in Fig. S2, there were three types of carbon with different chemical states. The peaks at a binding energy of ~ 284.5 eV were attributed to C-C, C=C, and C-H bonds, and the deconvoluted peaks centered in binding energy ranges of ~ 286.5 eV and ~ 287.8 eV were attributed to C-O (C-O-C and C-OH) and C=O bands, respectively.<sup>3</sup>

#### 2 Morphology of GQDs



**Fig. S3** Morphology of GQDs. Representative HR-TEM (a) - (e) images of the aqueous-dispersible GQD2 - GQD6. (f) FFTs obtained from the marked regions of GQD3 (b).

#### 3 Mechanism for Fluorescence Quenching



**Fig. S4** The schematic illustration of the possible interaction process of GQDs and pyrocatechol, and the conceivable mechanism for GQDs based fluorescence quenching sensor for pyrocatechol. The possible interaction process of GQDs and pyrocatechol was physical process including hydrogen bonding interaction process and physical absorption including electrostatic interaction and  $\pi$ - $\pi$  stacking process. The fluorescence quenching process was the energy transfer with nonradiant relaxation.

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