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## Supplementary Information

### One- and Two-Photon Luminescence in the Graphene

#### Oxide Quantum Dots

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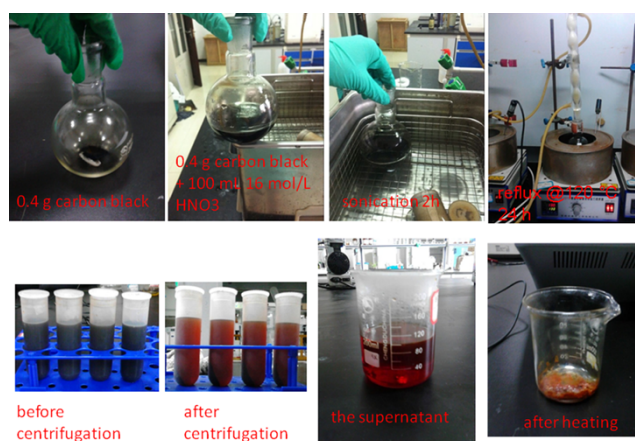
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#### Table of Contents

S1.	Experimental synthesis (Fig. S1).....	2
S2.	Characterization of GOQDs.....	2
S3.	Optical properties of GOQDs (Fig. S 2-Fig. S 5).....	3
	1) PL with different amounts of acid and alkali(Fig. S2).....	3
	2) Two-photon Luminescence with different excitation wavelengths (Fig. S3).....	4
	3) PL in different solvents (Fig. S4).....	5
	4) Photoluminescence excitation (PLE) spectra of GOQDs (Fig. S5).....	6
S4.	Decay curve of GOQDs (Fig. S6).....	6
S5.	Theoretical modeling and discussion (Fig. S7).....	7
	1) Theoretical methods:.....	7
	2) The calculation analysis and discussion:.....	7
References	.....	8

## S1. Experimental synthesis (Fig. S1)

Graphene oxide quantum dots (GOQDs) were obtained using the modified Hummers methods<sup>1</sup> with the following procedures. First, 0.40 g purchased CX-72 carbon blacks were added into 100mL concentrated 16mol/L HNO<sub>3</sub>. The solution was sonicated for two hours (80 W, 100kHz) and then kept refluxing for 24 hours at the temperature of 120 °C. During the reflux, no additional water were added. The solution was slowly cooled to room temperature and then was centrifuged at 9000 rpm for 10 min to separate a supernatant and sediment. After the supernatant was heated at the temperature of 200 °C to remove the water and residual HNO<sub>3</sub>, a light-red solid of about 0.10g was obtained. Then the solid is dissolved in deionized (DI) water with sonication for two minutes. Finally the red-orange solution is obtained. All the chemical products were purchased from Sigma Aldrich. The photographs of the synthesis progress were taken and listed in Fig. S1.



**Fig. S 1** The photographs for the experimental synthesis progress.

## S2. Characterization of GOQDs

1)The TEM images were obtained on a JEM-2100 field emission electron

microscope at an acceleration voltage of 200 kV. The sample was prepared by dropping 1  $\mu$ L GOQD solution onto a 400 mesh carbon-coated copper grids (TEM PELLA, USA).

2) XRD data were obtained on a Japan Rigaku D/Max-3C using Cu K $\alpha$  radiation.

3) Atomic force microscopy (AFM) image was obtained by a Nanoscope IIIa Multimode AFM (Digital Instruments) with NSC15 tips (silicon cantilever, MikroMasch). The sample was prepared by dropping and casting 1  $\mu$ L GOQD solution on a mica surface and dried in air.

4) FTIR spectra were obtained on a Nicolet 6700 FTIR spectrometer (Thermo Scientific).

5) Photoluminescence characterization was gained by a spectrofluorophotometer (SHIMADZU, RF-5301PC) with xenon lamp as the source of excitation.

6) UV-vis absorption was characterized by a UV-VIS spectrophotometer (SHIMADZU, UV2550).

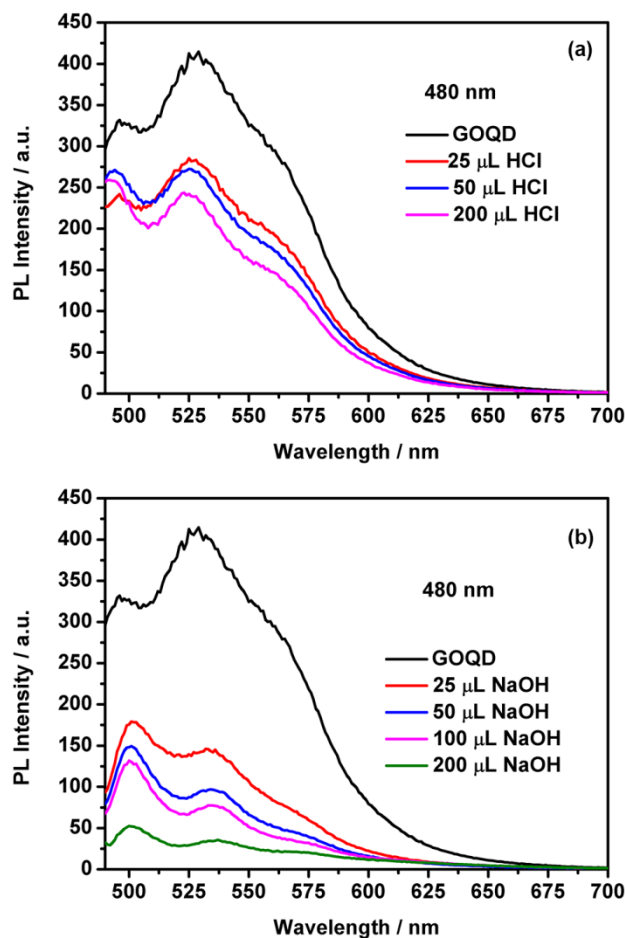
7) Time resolved photoluminescence was recorded with a time-correlated single photon counting technique (Edinburgh FLSP-920 spectrometer) using picosecond laser diodes as the source of excitation at 488 nm.

### **S3. Optical properties of GOQDs (Fig. S 2-Fig. S 5)**

#### **1) PL with different amounts of acid and alkali (Fig. S2)**

With the excitation wavelength of 480 nm, the one-photon luminescence intensities of GOQD solution have been shown in Fig. S 2 with the addition of acid/alkali. It is clearly illustrated that the PL intensities are reduced with acid/alkali. The peaks have been slightly red-/blue-shift

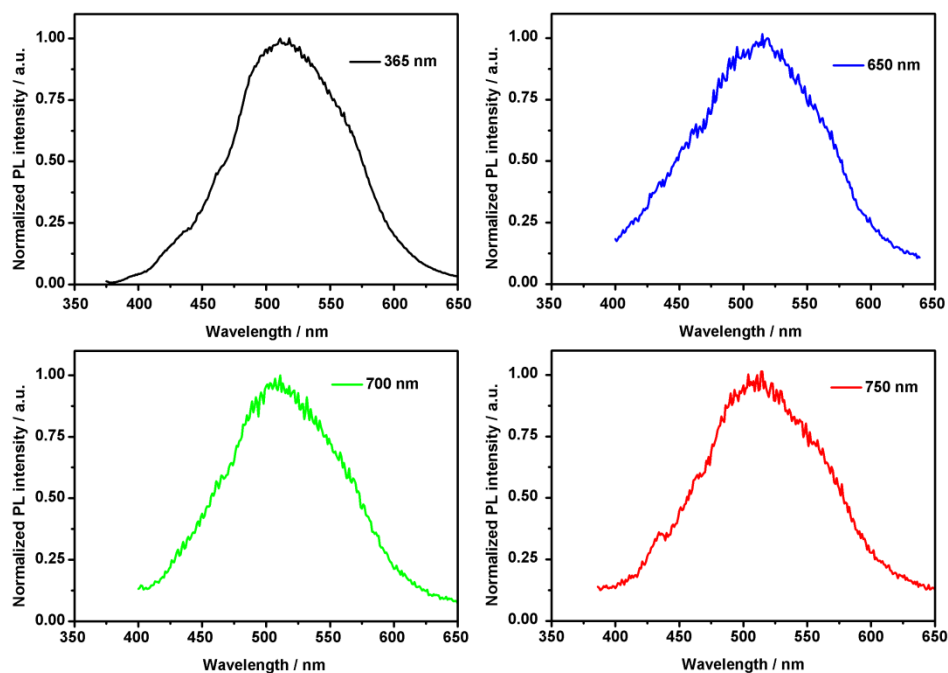
with acid/alkali. But with enough acid/alkali, the peaks cannot move again but reduce the luminescence intensities.



**Fig. S 2** One-photon luminescence intensities of GOQD solution with different amounts of (a) HCl (3mol/L)and (b) NaOH(3mol/L).

## 2) Two-photon Luminescence with different excitation wavelengths (Fig. S3)

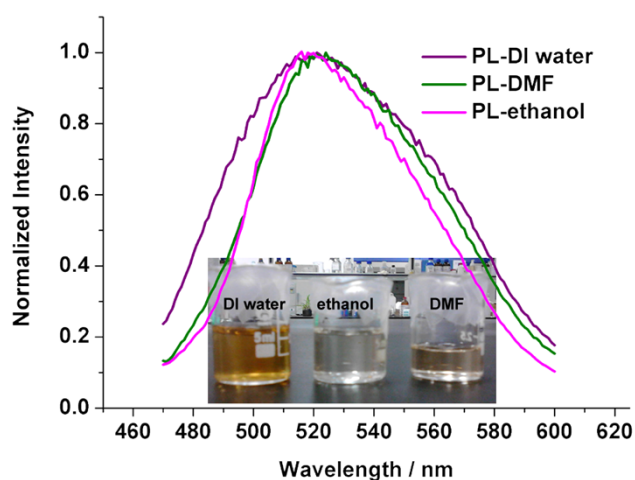
One- and two-photon luminescence of GOQD solution have been measured in Fig. S 3. The emission curve of the one-photon progress with excitation of 365 nm and two-photon ones with excitation of 650 nm, 700 nm, and 750 nm are quite similar.



**Fig. S 3** (a) One-photon progress with the excitation of 365 nm. Two-photon progresses with the excitation of (b)650 nm, (c)700 nm, and (d)750 nm

### 3) PL in different solvents (Fig. S4)

The PL peaks of GOQDs shift in the dimethylformamide (DMF) and ethanol demonstrating the solvent-dependent behaviours. The inset is the image of GOQDs in different solvents.



**Fig. S 4** PL spectra of GOQDs in the DI water, dimethylformamide (DMF) and ethanol.

#### 4) Photoluminescence excitation (PLE) spectra of GOQDs (Fig. S5)

The PLE spectra shows one strong transition peak at 456 nm and three shoulders at 388 nm, 337 nm and 282 nm, respectively. The PLE spectra display red and blue-shift phenomena with the treatment of acid and alkali.

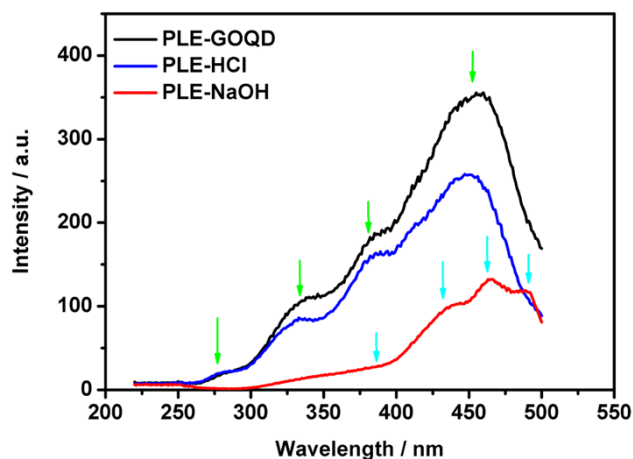
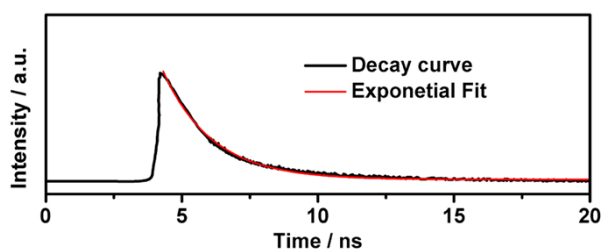


Fig. S 5 PLE spectra of GOQDs with emission at 520 nm.

#### S4. Decay curve of GOQDs (Fig. S6)

The decay time of the luminescence have been measured, and its lifetime data can be obtained by the exponential fitting ( $\tau=1.8$  ns).



**Fig. S 6** Decay time of GOQDs while monitoring the emission at 550 nm upon 488 nm excitation wavelength (black line). Exponential fitting line is plotted in red.

## **S5. Theoretical modeling and discussion (Fig. S7)**

### **1) Theoretical methods:**

The theoretical density functional theory (DFT) calculations are performed with DMol3<sup>2</sup>. Generalized gradient approximation (GGA) with Perdew-Burke-Ernzerh (PBE) functional was used for exchange and correlation, and the double numeric basis with d-functions (DND) is used as the atomic basis set. The tolerance of density convergence in self-consistent field(SCF), energy change, force, and displacement were  $1 \times 10^{-6}$  eV/atom.,  $2 \times 10^{-5}$  Ha, 0.004 Ha/Å, and 0.005 Å, respectively. All these structures are fully optimized.

### **2) The calculation analysis and discussion:**

To confirm the proton effects, three simple GOQD models with the sizes of 2.2 nm are chosen and schematically illustrated in Fig. S 7 (a)-(c). Three simple models have the band gaps of 0.04, 0.60 and 0.81 eV, respectively. Obviously, the band gaps can be controlled during the protonated and deprotonated progresses. To analyze the electronic structures, the wavefunctions of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are plotted in Fig. S 7 (d)-(f). Both HOMO and LUMO of deprotonated GOQD locate near oxygen region, while those of protonated GOQD mostly cover the carbon  $sp^2$  network. In normal GOQD, the most contributions of HOMO and LUMO come from the carbon  $sp^2$  network and oxygen region respectively. Therefore, with the decrease of the protonation of GOQD, the domination of electronic properties originates from the carbon  $sp^2$  network to the oxygen region. Moreover, through theoretical calculations, most oxygen groups of GOQDs in this work may attached on the edges except on the surfaces that is why acid and alkali have more influences than those

previous GQD works. During the preparation of our works, Kozawa et al.<sup>45</sup> reported similar one-photon luminescence observations in graphene oxides originated from nanodisc states and also demonstrated the effects of protonation and deprotonation experimentally and theoretically. In addition, since two-photon absorption can let the electron go to the second excited singlet state ( $S_2$ ), a smaller wavelength of the emission light can be observed in NaOH GOQDs, as shown in Fig. 3 (c). Thus, the treatment of acid/alkali is modified oxygen groups of GOQDs during the progress, and finally the optical properties are influenced.

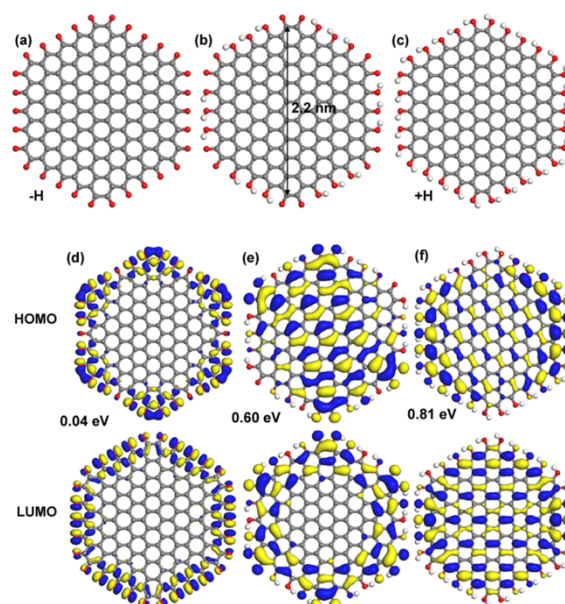


Fig. S 7. Schematically illustrations of (a) deprotonated, (b) normal and (c) protonated GOQDs. (d)-(f) HOMOs and LUMOs for three structures respectively. The iso-surfaces of HOMOs and LUMOs are selected as 0.01 a.u.

## References

1. W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339.
2. Dmol3 is available as part of Materials Studio. Accelrys Inc., Suite 100 San Diego, CA 92121, USA.