Electronic Supplementary Material (ESI) for RSC Advances.

Facile hydrothermal method to prepare graphene quantum dots from graphene oxide with different photoluminescence

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Experiment

GQDs were prepared from GO by hydrothermal treatment with hydrogen peroxide. GO was purchased from Nanjing Jicang Nanotechnology Co., Ltd. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used without further purification. In a typical experiment, 5 mL 30% hydrogen peroxide was mixed with 20 mL of 1 mg/mL GO aqueous solution first and then the mixture was diluted with 10 mL deionized water. After stirring for 10 min, the brownish mixture was transferred into a Teflon-lined stainless-steel autoclave. Next, the autoclave was placed in an oven at 170℃ and heated for 60 minutes. After completion of the reaction, the autoclave was naturally cooled down to room temperature. Inevitably the solution after hydrothermal reaction still contained certain amount of hydrogen peroxide, so a simple dialysis process was designed to remove it. Specifically, the brown-blackish solution after hydrothermal reaction was first filtered through a 0.22-μm microporous membrane and then dialyzed in a dialysis bag (retained molecular weight: 3500 da). Meanwhile, 0.1 g of manganese dioxide powder was washed by deionized water and separated by centrifugation. The washing process repeated for three times. Then the powder, acting as a dialysate (catalyzing the decomposition of hydrogen peroxide), was added in the beaker outside dialysis bag; the excess hydrogen peroxide in the bag diffused through the bag to beaker and decomposed continuously under the catalysis of manganese dioxide. As long as there was a concentration difference in this system, the dialysis would continue. Eventually, all hydrogen peroxide was decomposed. Then the manganese dioxide suspension in beaker was replaced by deionized water to further dialyze the possible existence of trace amount of dissolved manganese dioxide molecular. The whole process only took several hours to allow GQDs solutions with good purity to be obtained.

Characterization

UV-Vis spectra were measured on an Agilent Technologies Cary-100 UV-Vis spectrometer. Raman spectra were conducted on a Horiba Aramis Raman spectrometer system. PL spectra were obtained on a Fluorescence spectrometer (Horiba Jobin Yvon FL3-TCSPC). The height information and topographic image of GQDs were taken on an atomic force microscope (Dimension Icon) with taping mode. TEM images were carried out on TECNAI G2 20. PL lifetimes of GQDs were recorded using transient fluorescence spectrometer (Horiba Jobin Yvon FM-4P-TCSPC) at room temperature.

Discussion of the relationship between low impurities, PL spectrum, and quantum yield

The low impurities, PL spectra and the quantum yield are all decided by the preparation method. First, the reagents used in the reaction are all easy to be removed thoroughly. So it is different with other preparation methods, the product in this work processes high purity. The size change of GQDs in this work is a process from non-uniform to uniform, so in GQDs1, there are large and small graphene oxide segments at the same time with diameters ranging from 50-200 nm, as shown in TEM images. The size differences of these graphene oxide segments lead to different PL spectra in intensity and the position of maximum peak. The overlap of these spectra may explain why we see broad and rough PL spectra in Figure 5a. The quantum yield of GQDs1 is obviously lower than GQDs2, which is also affected by the size distribution of GQDs1. As we know, for different size of GQDs, the peaks of PL and PLE spectra are different. When a certain wavelength is chosen to measure quantum yields, for some sizes of GQDs, this wavelength is not their maximum excitation wavelength. We obtained a lower PL intensity and then calculated a lower quantum yield. Therefore, for GQDs2, narrow size distribution leads smooth PL spectra and similar maximum excitation wavelength. High quantum yield can be obtained at this wavelength.

Table S1 Quinine sulfate in 0.1M sulfuric acid solution (QYs=57.7%) was chosen as a standard. GQDs' QYs in water were calculated according to

$$Yu = Ys * \left(\frac{Fu}{Fs}\right) * \left(\frac{As}{Au}\right) * \left(\frac{Gu^2}{Gs^2}\right)$$

In this formula, Y refers to the quantum yields while F refers to the integrated emission intensity,

A means UV-vis absorption in the detective wavelength and G means the refractive index of the solvent. The subscript “u” and “s” means the sample and the reference standard with known QYs, respectively. For the as-prepared GQDs, the excitation wavelength was 350 nm.

Sample	Integrated emission intensity (F)	Abs. at 350 nm (A)	Refractive index of solvent (G)	Quantum yields (Y%)
Quinine sulfate	6419187680	0.0846	1.33	57.7
GQDs1	454428020	0.0957	1.33	3.6
GQDs2	530259090	0.0948	1.33	5.3

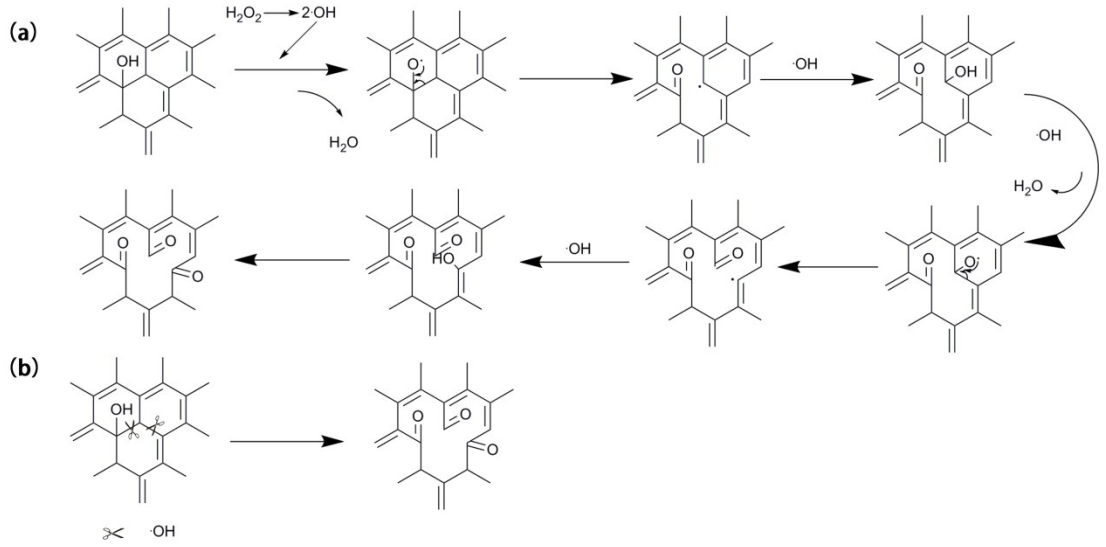

Figure S1. (a) The reaction mechanism between ·OH and hydroxyl. (b) Schematic diagram of ·OH as scissor to break C-C bond.

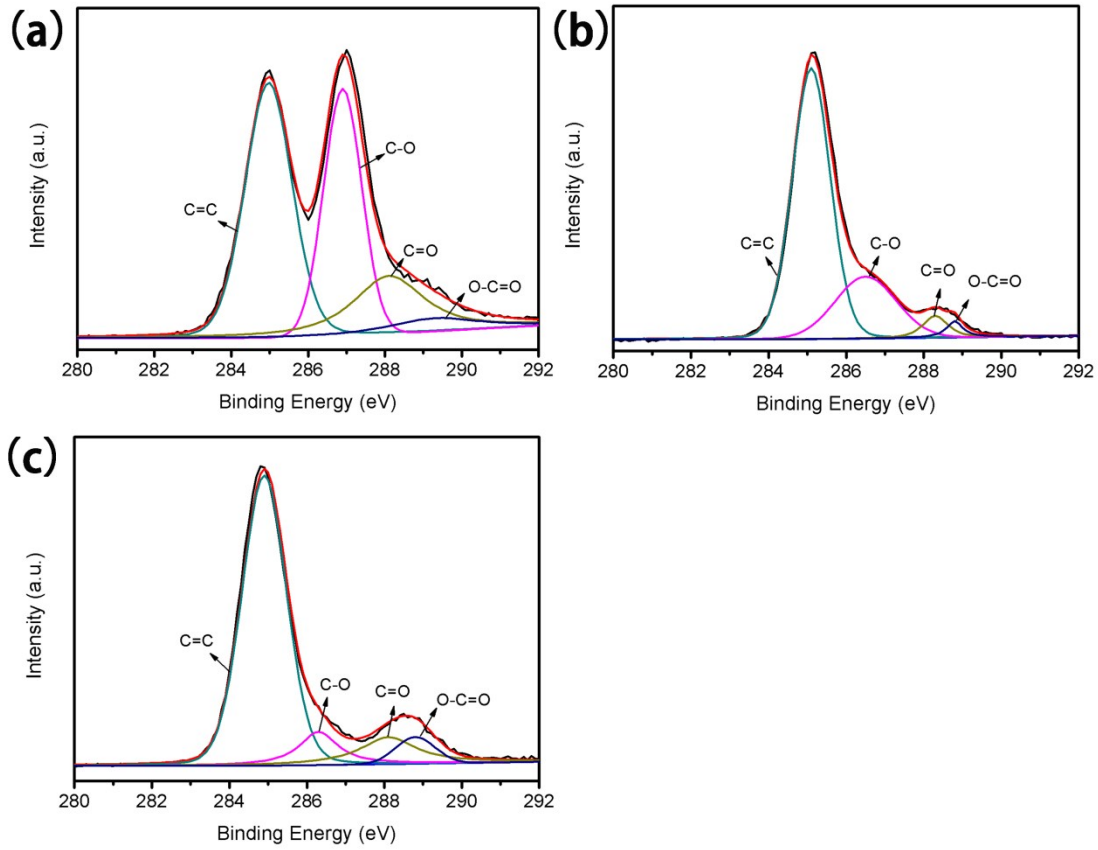

Figure S2. XPS images of GO (a), GQDs1 (b) and GQDs2 (c)

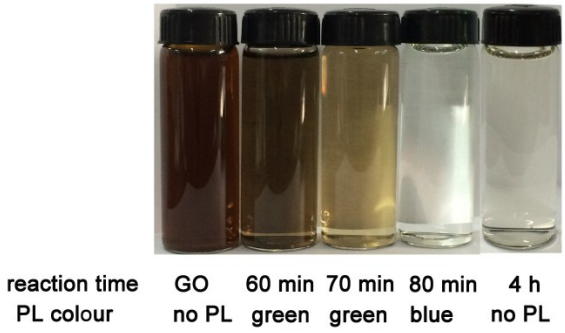

Figure S3. Photos and PL changes of GQDs with different reaction time.

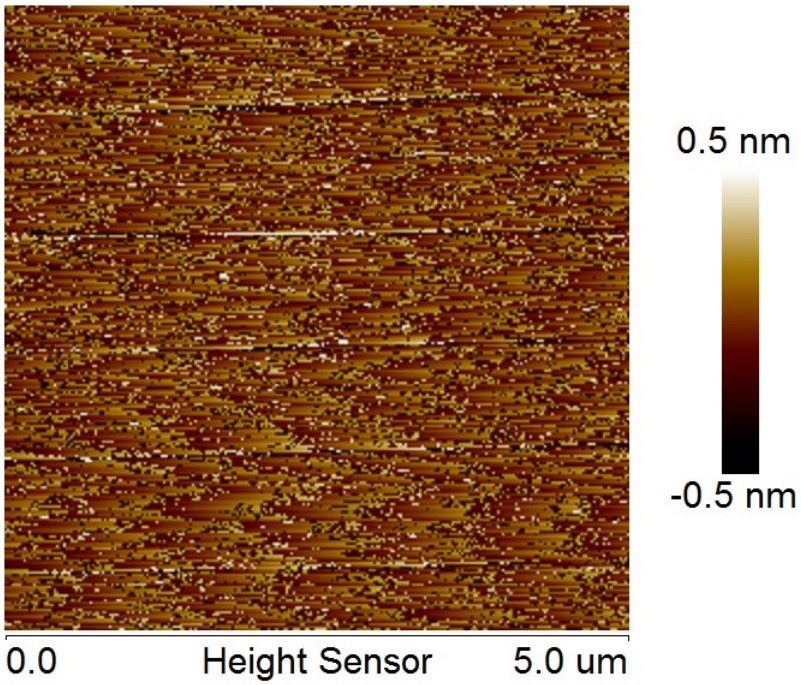

Figure S4. AFM image of product after 4 h of hydrothermal treatment.

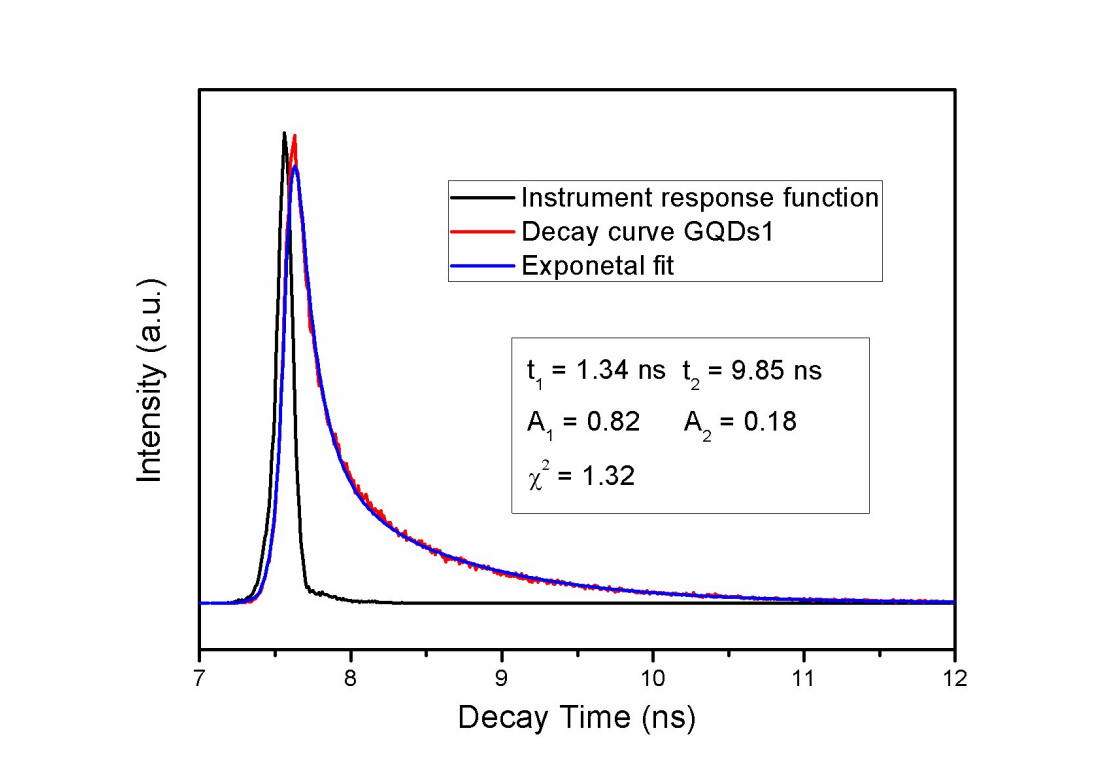

Figure S5. PL decay profile of GQDs1 measured at room temperature. The lifetime data and parameters generated by exponential fitting are also presented in the inset.

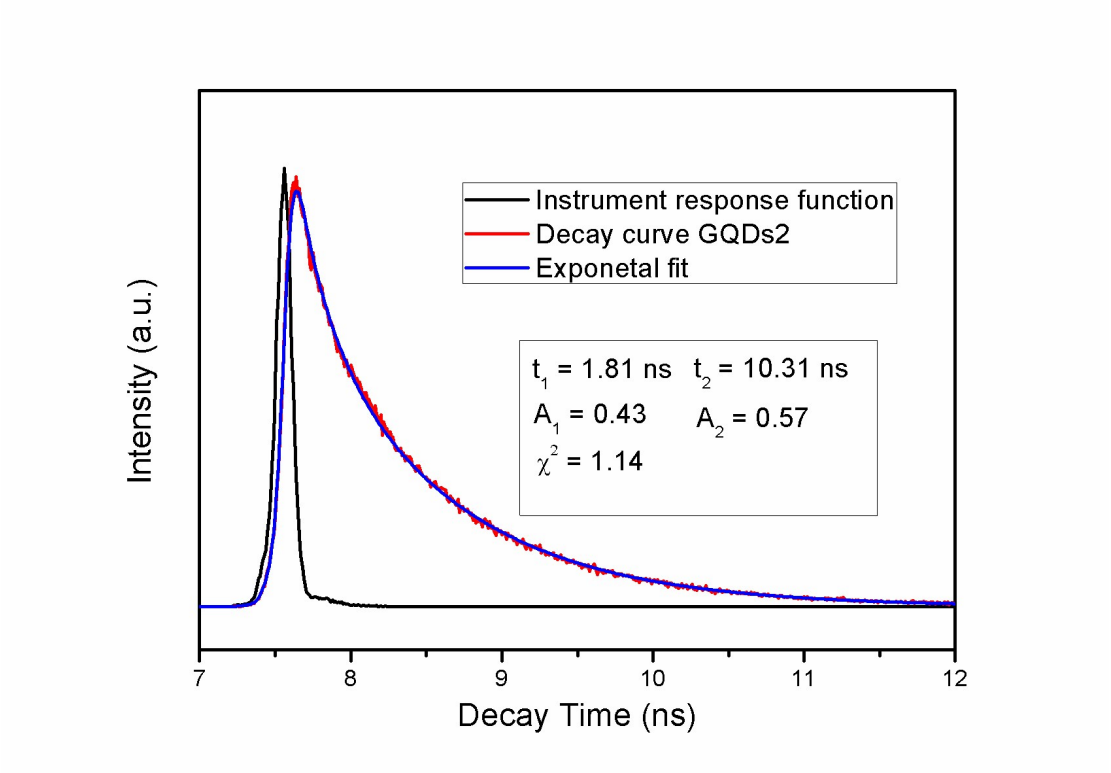

Figure S6. PL decay profile of GQDs2.

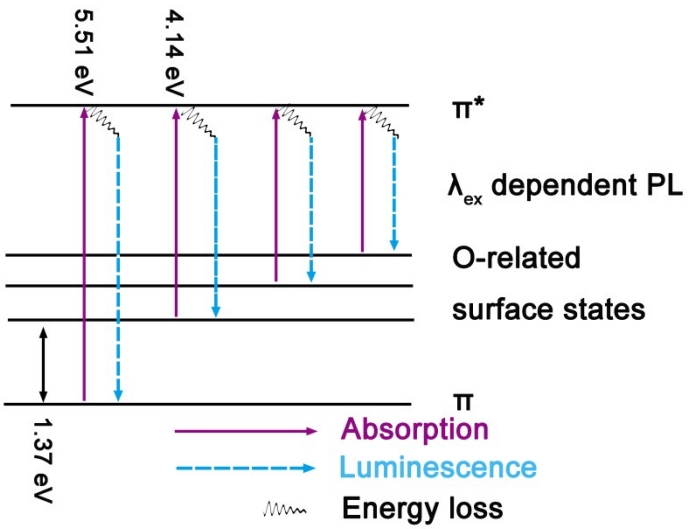

Figure S7. The diagrammatic sketch of PL mechanism for GQDs.