

Electronic Supplementary Information

Facile Preparation and Upconversion Luminescence of Graphene Quantum Dots

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Experimental Part

Materials

PEG_{1500N} was purchased from Sigma-Aldrich Chemicals Co. And all other chemicals were purchased from Shanghai Chemical Reagent Co. All chemicals were used as received without any further purification. Doubly distilled water was used in all experiments.

Synthesis

The preparation of GQDs with an oligomeric PEG_{1500N} as the surface passivation agent. GO were prepared from natural graphite powder by a modified Hummers method^{S1,S2}. The sample GO (0.05 g) was treated in an aqueous nitric acid solution (up to 2.6 M) (40 mL) with 70 °C reflux for 24 h. After cooling to room temperature, the suspension was under mild ultrasonication. The pH was tuned to 8 with Na₂CO₃. The suspension was filtered through a 0.22 μm microporous membrane to remove

the large tracts of GO. In a typical reaction, PEG_{1500N} (2g) was mixed with the cutting GO solution, and the mixture was substantially mixed. The mixture solution was heated at 120 °C for 24 h. And then, graphene oxide is reduced by hydrazine hydrate at 100 °C for 24 h. After cooling to room temperature, the resulting solution was filtered and a yellow solution was separated. So, the mixture solution was further dialyzed in a dialysis bag (retained molecular weight: 14,000 Da) for 7~10 days and GQDs were then strongly fluorescent.

Characterization Part

High-resolution TEM images were taken on a JEOL JEM 2011 microscope (JEOL, Japan) at an acceleration voltage of 200 kV. The specimen was prepared by drop casting the sample dispersion onto a carbon-coated copper grid, followed by drying under room temperature. Photoluminescence spectra were measured on a Fluorolog-3-P UV-VIS-NIR fluorescence spectrophotometer (Jobin Yvon, France). UV-vis spectrum of the CDs dispersed in water was obtained using a Unico UV-2102PC spectrophotometer. All spectra were recorded with quartz cells of 10 mm path length.

Quantum Yield (QY) Measurements

Rhodamine B in water (literature^{S3} quantum yield 0.31) was chosen as a standard. The quantum yield of CDs in water was calculated according to:

$$\phi = \phi_r \times \frac{A_r}{I_r} \times \frac{I}{A} \times \frac{n^2}{n_r^2}$$

Where Φ is the quantum yield, I is the measured integrated emission intensity, n is the

refractive index (1.33 for water), and A is the optical density. The subscript “r” refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects, absorbencies in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength of 360 nm.

Table S1 quantum yield of the as-prepared CDs

| Sample | Integrated emission intensity (I) | Abs. at 360 nm (A) | Refractive index of solvent (n) | Quantum Yield (Φ) |
|-------------|-----------------------------------|--------------------|---------------------------------|--------------------------|
| Rhodamine B | 330881926 | 0.04676 | 1.33 | 0.31 |
| GQDs | 31540390 | 0.01864 | 1.33 | 0.074 |

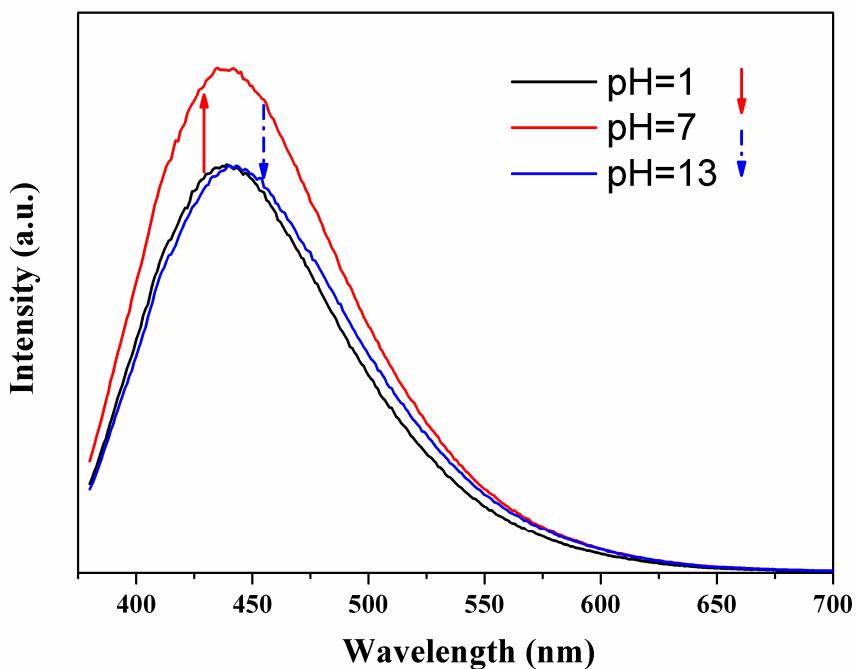


Fig. S1 pH-dependent PL spectra when pH is switched from 1 to 13.

References

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- [S3] D. Magde, G. E. Rojas and P. G. Seybold, *Photochem. Photobiol.*, 1999, **70**, 737.