Supplementary Information

Solvent effect on triphenylphosphine modified graphene quantum dots: spectral modulation for full spectrum of visible light with high quantum yield

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Experimental Section

TEM measurements were carried out on a spherical aberration-corrected TEM (FEI Titan 80-300) at 80 kV.   X-ray photoelectron spectra (XPS) were carried out on a PHI Quantera II system (Ulvac-PHI, INC, Japan). Fourier transform infrared (FTIR) was performed on a BRUKE Vertex 70 (resolution 0.4 cm^{-1}) infrared spectrometer and samples were dispersed in potassium bromide and compressed into pellets.

The UV-vis spectra were obtained on a UV5800 Spectrophotometer. PL and PLE spectra were recorded on a PerkinElmer LS55 luminescence spectrometer (PerkinElmer Instruments, U.K.) at room temperature in aqueous solution. The stability of these products was determined via contrast the fluorescent emission intensity of products aqueous solution under different conservative time at room temperature. Time-resolved fluorescence behavior was measured via the time-correlated single-photon counting (TCSPC) technique (Hydra Harp 400, Pico Quant). The samples were excited by a frequency-doubled titanium: sapphire oscillator laser with approximately a pulse duration of 150 fs, and a repetition rate of 80 MHz (Chameleon, Coherent). Fluorescence emission was sent to a spectrometer (iHR550, Horiba Jobin Yvon) with 300/mm grating and then detected by a photomultiplier tube. The time-resolved PL curves were fitted with a bi-exponential decay.

As the most direct and important index, the quantum yield (φ) of N-GQDs was calculated according to equation 1:[s1]

$$\varphi = \varphi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

(1)

where I is the measured integrated emission intensity, η is the refractive index of the solvent, A is the optical density, and the subscript R refers to the reference standard with a known φ (RhB in ethanol solution, φ_R=0.68). In order to minimize reabsorption effects, absorbance was kept under 0.1 at 460 nm excitation wavelength in 10×10 mm fluorescence cuvette.

Synthesis of graphene oxide quantum dots (GOQDs)

GOQDs were prepared from graphene powder (SIMBATT, Shanghai, China) by a modified Staudenmaier method. Graphene powder (4 g) was put into H_2SO_4 (150 mL) and HNO_3 (80 mL) with stirring at 15 °C, and was kept for 2 h. Then $NaClO_3$ (40 g) was added gradually and the temperature was kept below 5 °C. The mixture was then stirred at 15 °C for 5 h. After that, the reaction was terminated by adding distilled water (80 mL). The pH value was neutralised to 7 by NaOH, before the mixture was filtered using an alumina inorganic membrane with 20 nm pores. The resulting light yellow filtrate was dialysed in a 3500 Da dialysis bag against deionised water for a week to remove excess salt. The resultant solution was freeze-dried to obtain the GOQD powder. The GOQD yield from graphene is approximately 45%.

Table S1 A brief summary of the characteristics of GQDs.

Size	φ	τ / ns	Doping agent (content)	Ref. (Raw material)
1-6 nm	0.64[a]	6.4	P(Ph)₃	This work (graphite)
1-3 nm	0.74[a]	11.5	N (N/C=10.06%)	18 (graphite)
2-5 nm	-	-	N (N/C=4.3%)	S2 (graphite)
3-9 nm	0.16[b]	-	N (-)	S3 (graphite)
2-6 nm	0.24[c]	-	N (N/C=17.88%)	S4 (graphite)
2.6 nm	0.49[d]	-	N and B	S5(graphite)
2.5 nm	0.29-0.19[e]	-	N (N/C=12%)	S6(graphite)
1-7 nm	0.086[f]	-	N (N/C=5.6%)	S7(graphite)
10-35 nm	-	1.29	-	S8(graphite)
2-9 nm	0.11[g]	-	-	S9(graphite)
3-5 nm	0.12[g]	7.7	-	S10(graphite)
4-24 nm	0.28[h]	-	PEG	S11(graphite)
3-9 nm	0.088[i]	-	isopropanol	S12(graphite)
12-17 nm	0.18[j]	-	PEG	S13 (graphite)
1-4 nm	-	5.36	-	S14 (graphite)
2-4 nm	0.71	7.6	N, S	S15 (citric acid and urea)
2-6 nm	0.60	6	PEG	S16 (carbon soot)

[a]:Quantum yield was calculated using those of Rhodamine B (φ=0.68) in EtOH as a standard.

[b]:Quantum yield was calculated using those of Quinine sulfate (φ=0.577) in wateras a standard.

[c]: Quantumyield was calculated using Quinine sulfate (φ= 0.54) in 0.1 M H2SO4 as a standard.

[d]: Quantumyield was calculated using Rhodamine B (φ=0.31) in water as astandard.

[e]:Quantumyield was calculated usingquinine sulphate (φ=0.54) in 0.5 M H2SO4 as astandard.

[f]:Quantumyield was calculated using Quinine sulfate(φ= 0.54)in wateras a standard.

[g]:Quantumyield was calculated using 9,10-Bis(phenylethynyl) anthracene (φ=1) in cyclohexane as a standard.

[h]:Quantumyield was calculated using Rhodamine B (φ=0.31) in water as a standard.

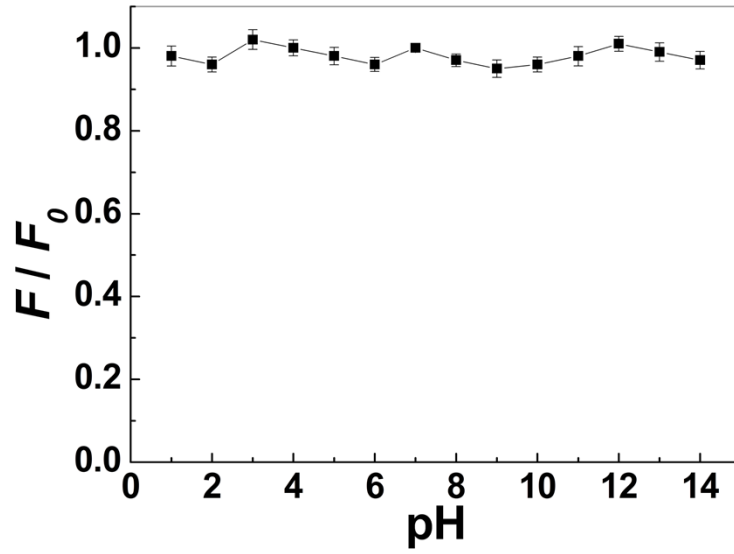[i]:Quantumyield was calculated using Fluorescein (φ= 0.95) in water as astandard.

[j]:Quantumyield was calculated using 9,10-Bis(phenylethynyl) anthracene(φ= 1) in cyclohexaneas a standard.
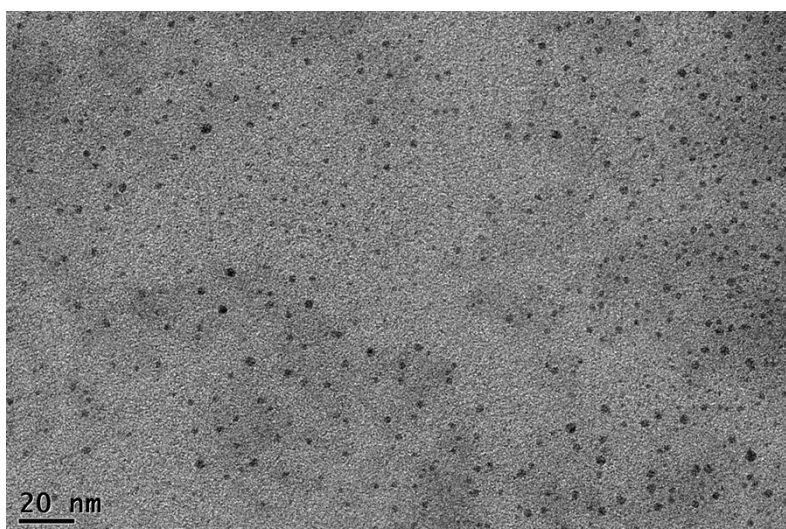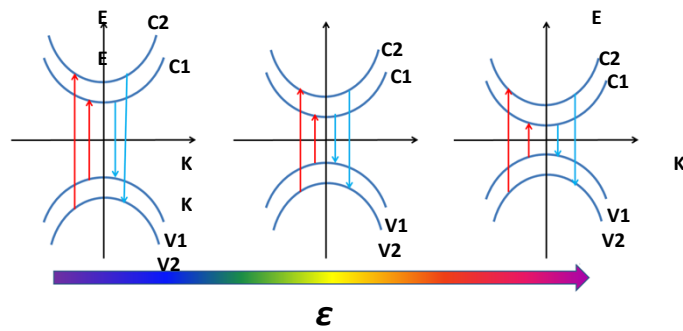

Fig. S1 TEM image of GOQDs
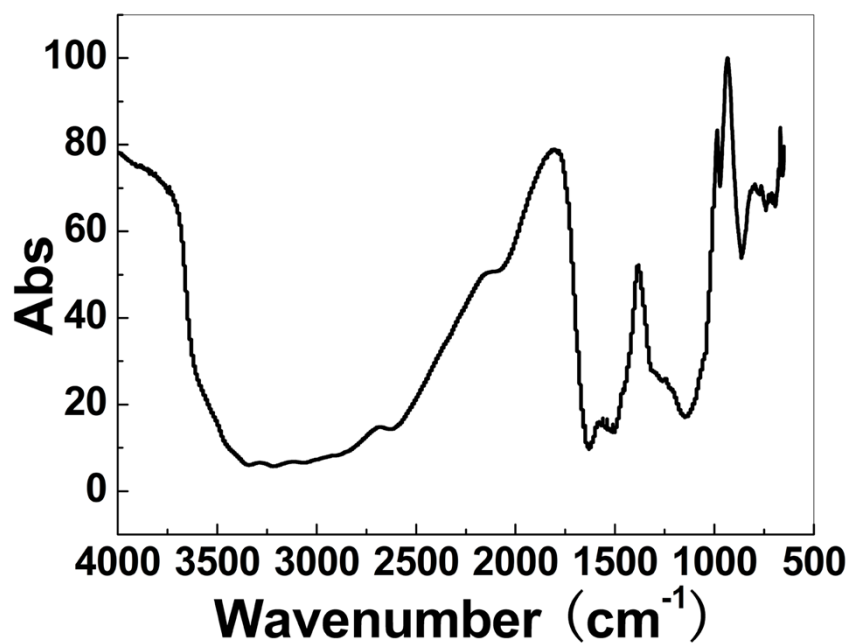
Fig. S2 FTIR spectrum of P-GQDs.

Fig. S3 PL intensity of P-GQDs under different pH. The *F* and *F₀* are PL intensity of P-GQDs when pH=7 and other value, respectively. The concentration of P-GQDs is 0.1 mg/L.

Fig. S4 The schematic diagrams of tunable emission mechanism of P-GQDs.

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