Electronic Supplementary Information

Facile synthesis of P-doped carbon quantum dots with highly efficient photoluminescence

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1. The experimental details

**Synthesis of P-doped carbon quantum dots.** 1.73 mL of PBr₃, 2.0 g of hydroquinone, 0.36 g of NaOH and 5.0 mL of acetone were placed into a 25 mL Teflon equipped stainless steel autoclave, and then the mixture was heated solvthermally at 200 °C for 1 h using a blast oven. When the autoclave cooled down to room temperature, the solution was condensed by rotary evaporation and the obtained product was P-doped CQDs. This product was denoted as PCQDs-1. The samples produced with the ratio of 2:1 PBr₃ and hydroquinone were obtained using the similar procedure, and were denoted as PCQDs-2, PCQDs-3, PCQDs-4 and PCQDs-5 respectively depending on their different reaction time of 1 h, 3h, 5 h and 9 h.

**Synthesis of pristine carbon quantum dots.** 5.0 mL of CCl₄, 5.71 g of hydroquinone, 2.07 g of NaOH and 5.0 mL of ethanol were placed into a 25.0 mL Teflon equipped stainless steel autoclave, and then the mixture was heated solvthermally at 200 °C for 1 h using a blast oven. When the autoclave cooled down to room temperature, the solution was condensed by rotary evaporation and the obtained product was pristine CQDs.

**Characterization methods.** The morphologies of the products were characterized by transmission electron microscopy, which was performed on a JEOL-2100F instrument with accelerating voltage of 200 KV. Samples were prepared by dropping ethanolic or aqueous suspensions of the separated fractions of oxidized products onto Cu TEM grids coated with a holey amorphous carbon film and following solvent evaporation in a dust protected atmosphere. The X-ray photoelectron spectroscopy analyses were conducted using a Kratos Axis ULTRA X-ray photoelectron spectrometer with a 165 nm hemispherical electron energy analyzer. The incident radiation came from monochromatic Al X-ray (1486.6 eV) at 15 kV and 3 mA. Wide survey scans were taken at an analyzer pass energy of 160 eV over a 1400 eV binding energy with 1.0 eV step and a dwell time of 100 ms, while narrow multiplex higher resolution scans were performed at a pass energy of 20 eV with 0.05 eV step and a dwell time of 200 ms. The pressure in analysis chamber was less than 7.5 × 10⁻⁹ Torr during sample analysis. Atomic concentrations were calculated using Vision software and a Shirley baseline. The UV-Vis spectra were carried out on a Perkin Elmer Lambda 950 spectrometer, in which the products were dispersed in solvent after ultrasonication for 30 min. The photoluminescence spectra were conducted on a PerkinElmer LS-55 fluorescence spectrometer, and lifetimes were determined using a FLS920 fluorescence spectrophotometer.

**Determination of the quantum yields.** Determination of the quantum yields of these oxidized products was accomplished by comparison of the wavelength integrated intensity of these functionalized products to that of the standard quinine sulfate. The optical density was kept below 0.05 to avoid inner filter effects. The quantum yields of these oxidized products were calculated using

\[ \Phi = \Phi_s [(I \cdot A \cdot n^2)/(I_s \cdot A \cdot n_s^2)] \]

where \( \Phi \) is the quantum yield, I is the integrated intensity, A is the optical density and n is the refractive index of the solvent. The subscript S refers to the standard reference of known quantum yield. Quinine sulfate was chosen as the standard, whose quantum yield is 0.577 and nearly constant for excitation wavelength from 200 nm to 400 nm.

**Cellular toxicity test.** Human Hela cells (105 cells mL⁻¹) were cultivated in Dulbecco’s modified Eagle’s medium (DMEM) containing 10% fetal bovine serum and 100 µg mL⁻¹ penicillin/streptomycin first for 12 h in an incubator (37 °C, 5% CO₂). Then suspensions of P-doped GQDs with different dose were added, which kept final concentrations of P-doped GQDs with 0, 12.5, 25, 50, 75 and 100 µg mL⁻¹ respectively. The cells were cultivated for 24 h and then 20 µL of 5 mg mL⁻¹ MTT solution was added to every cell well. After the cells were further incubated for 4 h, the culture medium was removed and then 150 µL of DMSO was added. The resulting mixture was shaken for 15 min at room temperature without
light. The optical density (OD) of the mixture was measured at 570 nm. The OD values were determined using Thermo multiskan spectrum microplate spectrophotometer. The cell viability was estimated according to the following equation

\[
\text{Cell viability (\%) = } \frac{OD_{\text{Treated}}}{OD_{\text{control}}} \times 100\%
\]

where \(OD_{\text{control}}\) was obtained in the absence of GQDs, and \(OD_{\text{Treated}}\) was obtained in the presence of P-doped GQDs.

**Cellular imaging.** The human Hela cells were cultivated for 12 h in culture medium containing DMEM supplemented with 10% fetal bovine serum and 100 \(\mu\)g mL\(^{-1}\) penicillin/streptomycin. Suspensions of P-doped GQDs from the stock solution were prepared with Dulbecco’s phosphate buffer saline (DPBS). The suspension was added to the well of a chamber slide, and the final concentration of GQDs was 75 \(\mu\)g mL\(^{-1}\), followed by incubating at 37 °C in a 5% CO\(_2\) incubator for 24 h. Prior to inspection with Leica laser scanning confocal microscope, the excess GQDs were removed by washing 3 times with warm DPBS. The fluorescence images were obtained at the excitation wavelength of 355 nm.

![Figure S1 Raman spectra of the PCQDs-3](image-url)
Figure S2. UV-Vis and fluorescence spectra of PCQDs-1

Figure S3. UV-Vis and fluorescence spectra of P-CQDs-2

Figure S4. UV-Vis and fluorescence spectra of PCQDs-3
Figure S5. UV-Vis and fluorescence spectra of PCQDs-4.

Figure S6. UV-Vis and fluorescence spectra of PCQDs-5.

Figure S7. Fluorescence lifetimes of CQDs and PCQDs measured by the TCSPC technique.
Figure S8 The change of ultraviolet absorption intensity of PCQDs in water solution with time from 0 to 72 hours under Xe lamp. The result indicated that as-prepared PCQDs have strong resistance ability to UV light and are very stable in aqueous solution.

Figure S9 The change of luminescence intensity of CQDs and PCQDs in water solution under Xe lamp with time from 0 to 84 hours.
Figure S10 Effect of pristine CQDs on human Hela cells

Fig. S11 Laser scanning confocal microscopy images of human Hela cells without CQDs. Images for A and B were captured in bright field and at excitation wavelength of 355 nm (collecting emission: 420 – 460 nm) respectively.
Fig. S12 Laser scanning confocal microscopy images of human Hela cells with pristine CQDs. Images for A and B were captured in bright field and at excitation wavelength of 355 nm (collecting emission: 420 – 460 nm) respectively.