

Supporting Information

Narrowing and Blue-shifting Photoluminescence of Carbon Dots by Enhancing sp^3 -C Hybridization Using a Microreactor

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Experimental Section

Reagents

Reagent grade of glucose was bought from Aladdin Chemicals Co. Ltd (Shanghai, China). Formamide, sulfuric acid and phosphoric acid were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All chemicals were used as received without further purification unless otherwise specified. Deionized (DI) water was used throughout this study.

Preparation of UV-CDs and UV-CDs-2

Typically, 3.664 g of glucose was dissolved in 200 mL of formamide, followed by the addition of 2.0 mL of sulfuric acid. The resulting clear and transparent solution was loaded into a syringe connected to a Teflon capillary ($\phi=1$ mm). The syringe was set to a syringe pump and the solution was pushed into the capillary with a constant rate. The capillary was heated to 180 °C on an oil bath, and the resident time of solution in the capillary (reaction time) was set to 2 minutes (calculated based on the flow rate, inner diameter and length of the capillary). The obtained brown solution was allowed to cool down to room temperature naturally, and then filtered using a polycarbonate membrane filter (from Filter-Lab) with pore sizes of 0.22 μm , and followed by dialysis against DI water for 96 hours using a dialysis membrane with a molecular weight cutoff of 1000 Da. Finally, the purified product was placed into a lyophilizer for freeze-drying, yielding UV-CDs powder for further use. The preparation of UV-CDs-2 was conducted in the same manner as UV-CDs, except that sulfuric acid was replaced with phosphoric acid.

Preparation of TA-CDs and TA-CDs-2

Typically, 0.916 g of glucose was dissolved in 50 mL of formamide, followed by the addition of 0.5 mL of sulfuric acid. The resulting clear and transparent solution was transferred into a poly(tetrafluoroethylene)-lined autoclave and heated at 180 °C in an oven for 3 hours. After cooling down to room temperature naturally, the resulting brown solution was filtered using a polycarbonate membrane filter (from Filter-Lab) with pore sizes of 0.22 μm , and then dialyzed against DI water for 96 hours using a dialysis bag with a molecular weight cutoff of 1000 Da. Finally, the purified product was placed into a lyophilizer for freeze-drying, yielding TA-CDs powder for further use. The preparation of TA-CDs-2 was conducted in the same manner as TA-CDs, except that sulfuric acid was replaced with phosphoric acid.

Determination of the band gap (E_g), conduction band (CB), and valence band (VB) of CDs

The bandgap (E_g) of the CDs was determined using a method reported in the literature (Ref. 19), based on the Tauc plot. This plot represents the curve of converted $(\alpha h\nu)^r$ versus $h\nu$, derived from the UV-vis spectrum, where α is the absorption coefficient, h is Planck's constant, ν is the light frequency, and $r=2$ for a direct band gap material, $r=1/2$ for an indirect band gap material, respectively. The E_g value for the CDs was obtained by measuring the x-axis intercept of the tangent at the first inflection point of the curve. The valence band (VB) of the CDs was determined through ultraviolet photoelectron spectroscopy (UPS) by measuring the x-axis intercept of the tangent at the first inflection point of the UPS curve. Finally, the conduction band (CB) of the CDs was estimated by subtracting the E_g value from the VB value.

Equipment and Characterization

Transmission electron microscopy (TEM) observations were performed on a JEM-2100plus microscope. Atomic force microscopy (AFM) pattern was recorded from Dimension Fast Scan (Bruker, German). X-ray diffraction (XRD) patterns were recorded on an X-ray powder diffractometer (D8, Bruker AXS GmbH, Germany) using Cu $K\alpha$ (1.5406 Å) radiation (40 kV, 40 mA) at room temperature. X-photoelectron spectroscopy (XPS) spectra were carried out with AXIS SUPRA X-ray photoelectron spectrometer (Kratos, Shimadzu, Japan). Ultraviolet photo-electron spectroscopy (UPS) were measured using Thermo ESCALAB 250XI (Thermo Fisher Scientific U.S.A). Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 FT-IR spectrometer. UV-vis absorption spectra were recorded on a SHIMADZU UV-2600 spectrophotometer. Photoluminescence (PL) emission and excitation spectra were measured using F-7000 spectrometer (Hitachi, Japan). PL lifetimes were measured using FLS1000 (Edinburgh Instruments). Raman spectra were measured by LabRAM HR Evolution (HORIBA Jobin Yvon S.A.S. France). PL quantum yields (QYs) were measured on a QE-2100 quantum efficiency measurement system (Japan Otsuka Electronics). Photographs of sample was taken using a Canon camera (EOS 550) under daylight. Photographs of PL were taken using a UV camera (ARTCAM-4070V-VOM, Xi'an Leading Optoelectronic Technology Co., Ltd) under excitation by UV light (295 nm from F-7000 spectrometer (Hitachi, Japan)).

Supporting Figures and Tables

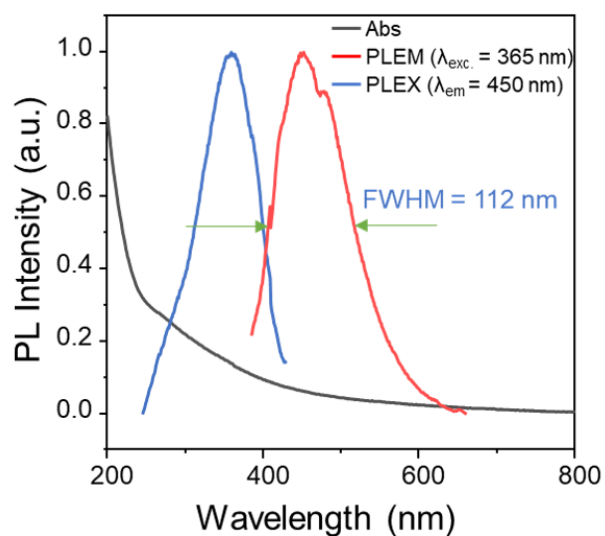


Figure S1. The UV-Vis absorption (black line), optimal PL emission (red line) and excitation (blue line) spectra of TA-CDs.

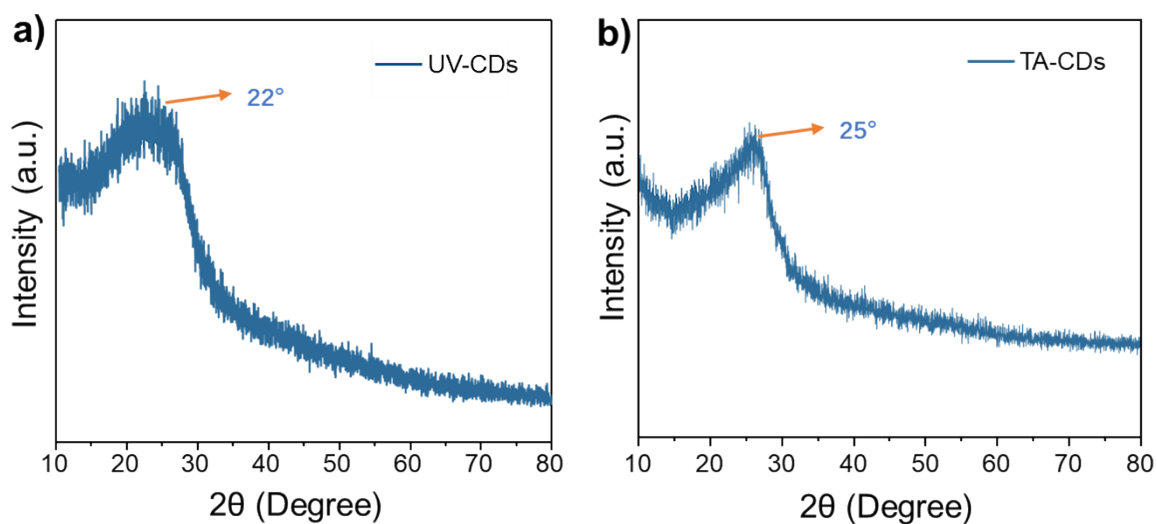


Figure S2. The XRD patterns of a) UV-CDs, b) TA-CDs.

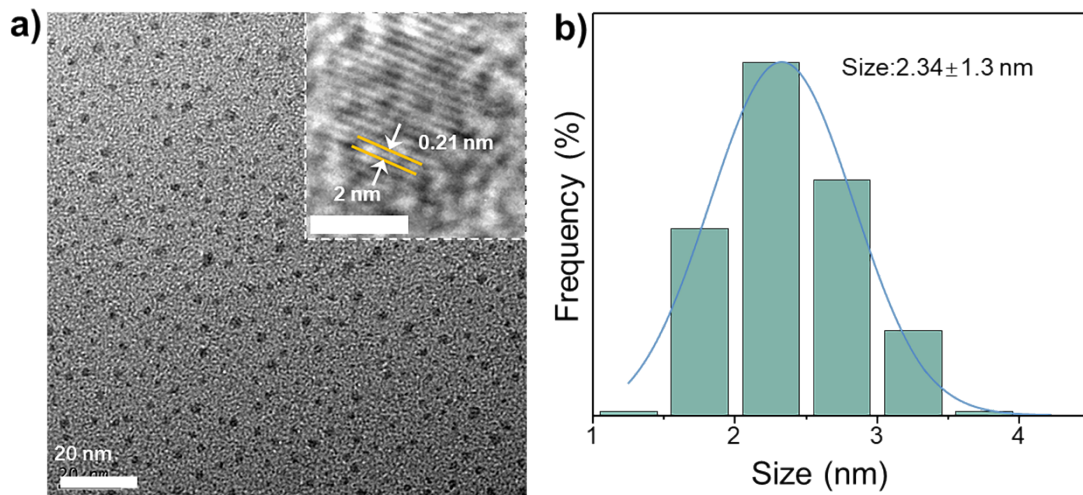


Figure S3. a) The TEM and high-resolution (HR) TEM of UV-CDs. b) Size distribution based on the TEM images of UV-CDs.

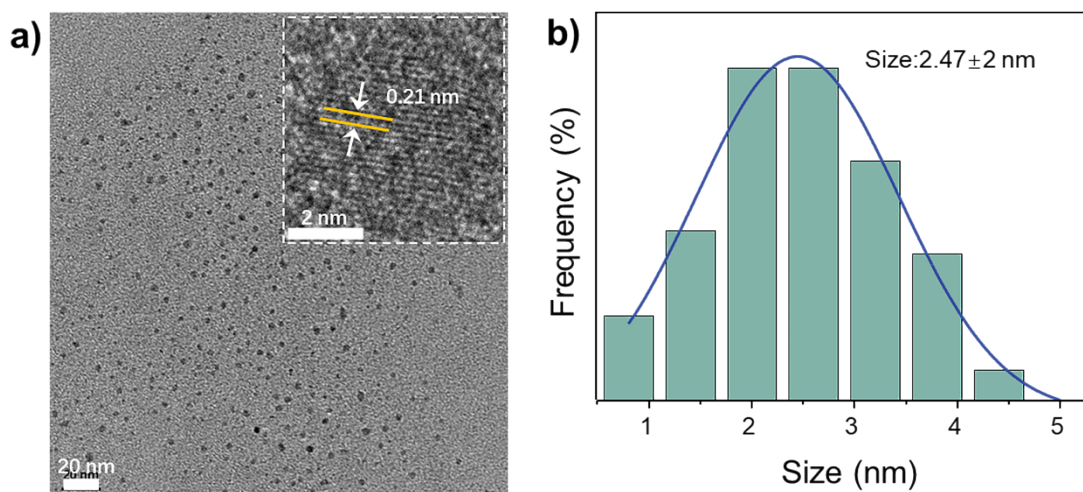


Figure S4. a) The TEM and HR TEM of UV-CDs. b) Size distribution based on the TEM images of UV-CDs.

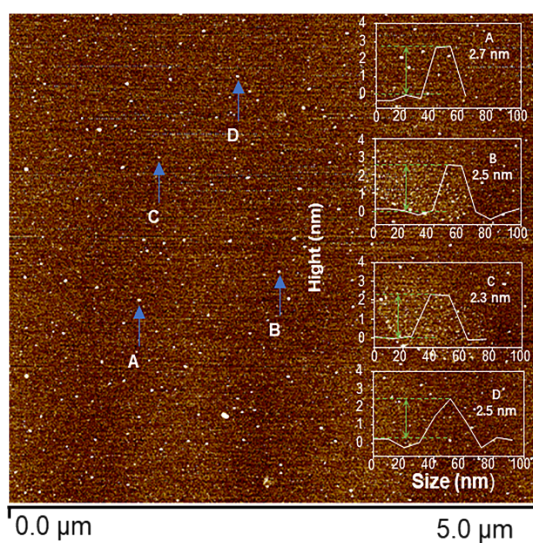


Figure S5. The AFM image of UV-CDs.

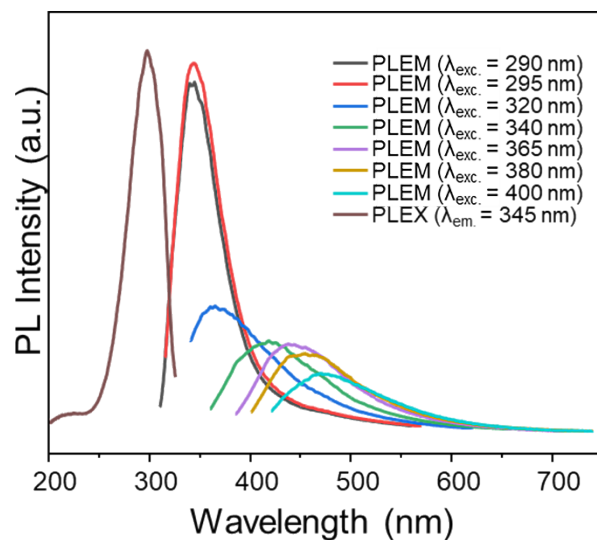


Figure S6. The PL emission spectra at different excitation wavelengths and excitation spectrum at 345 nm of UV-CDs.

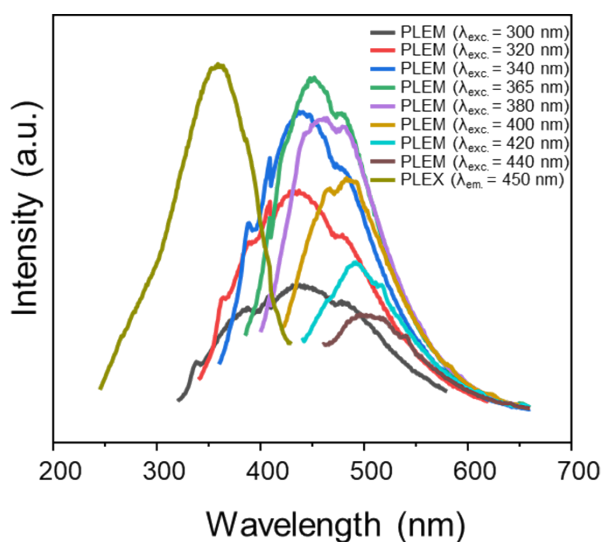


Figure S7. The PL emission spectra at different excitation wavelengths and excitation spectrum at the optimal emission wavelength of TA-CDs.

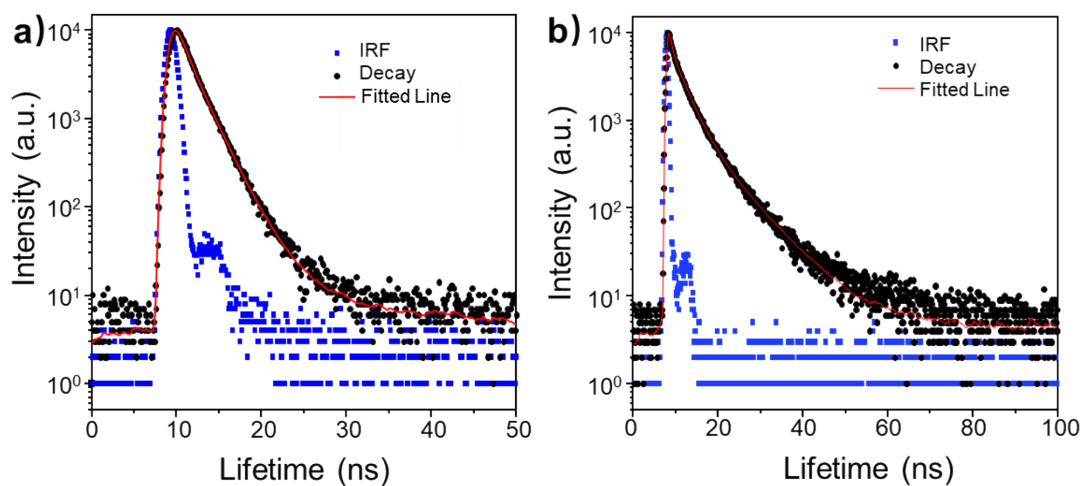


Figure S8. The PL decay spectra and fitting curves of a) UV-CDs ($\lambda_{exc.}=295$ nm, $\lambda_{em}=345$ nm), b) TA-CDs ($\lambda_{exc.}=365$ nm, $\lambda_{em}=450$ nm),.

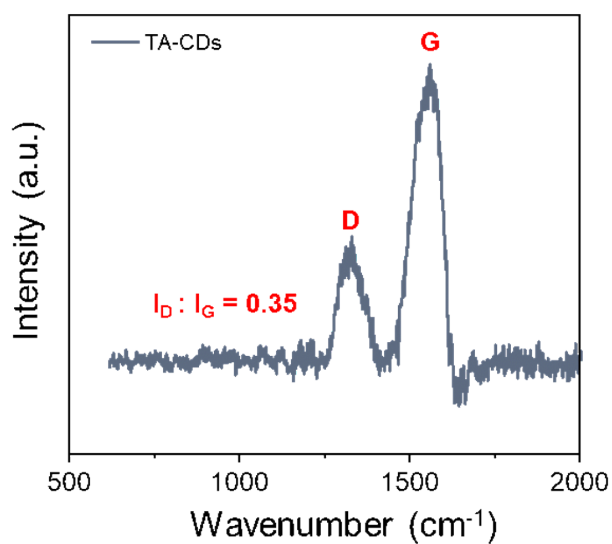


Figure S9. Raman spectrum of TA-CDs.

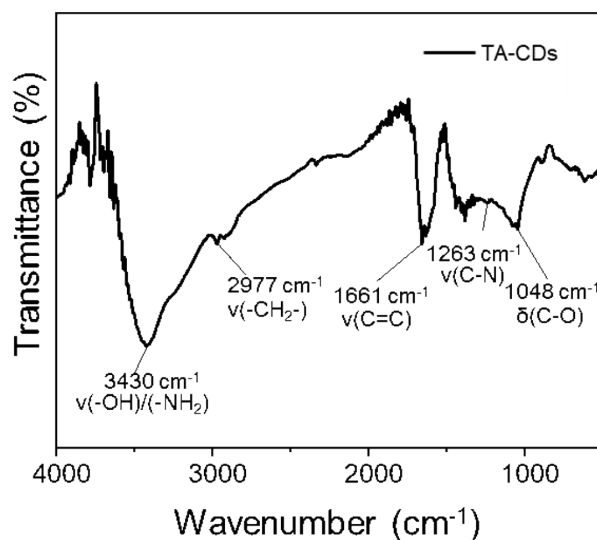


Figure S10. The FTIR spectrum of TA-CDs.

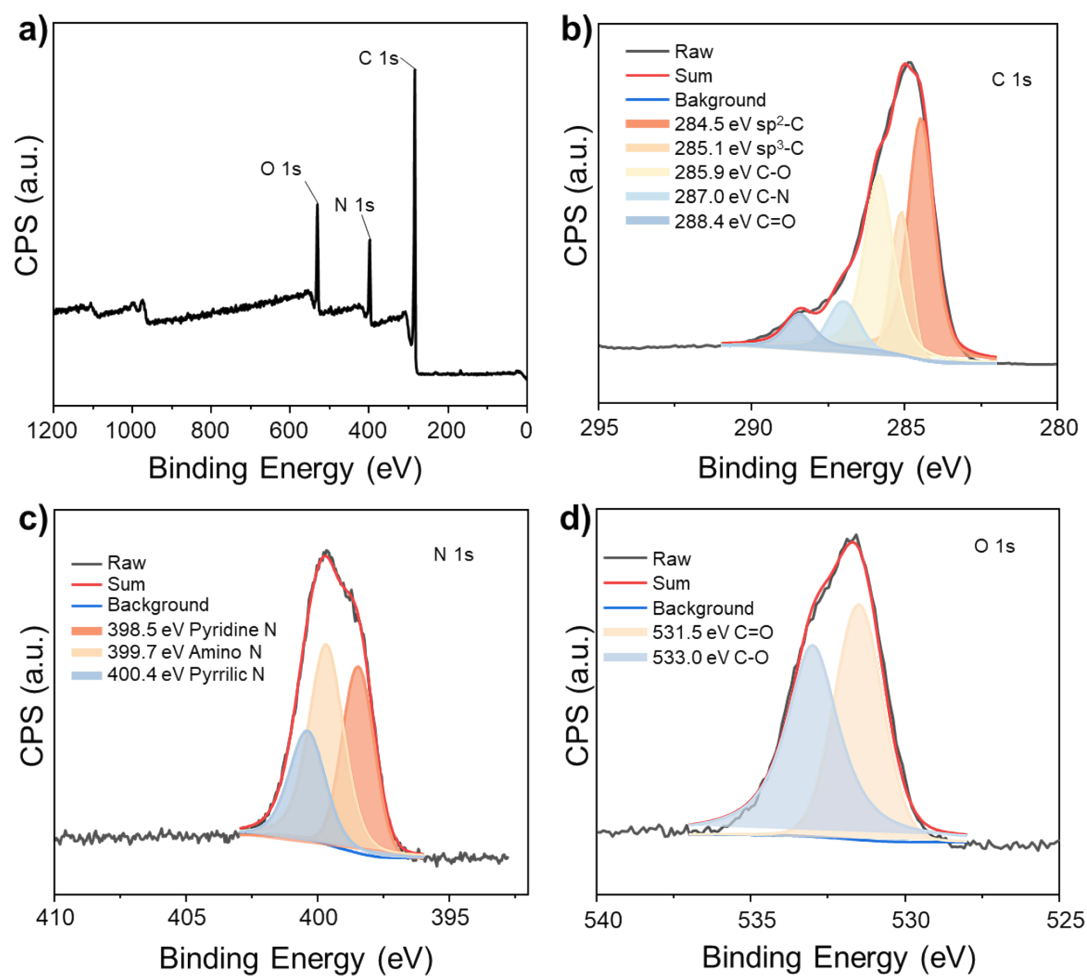


Figure S11. a) The XPS spectrum of TA-CDs. b–d) The HR XPS spectra and the corresponding fitting curves of the b) C 1s, c) N 1s, and d) O 1s of the TA-CDs.

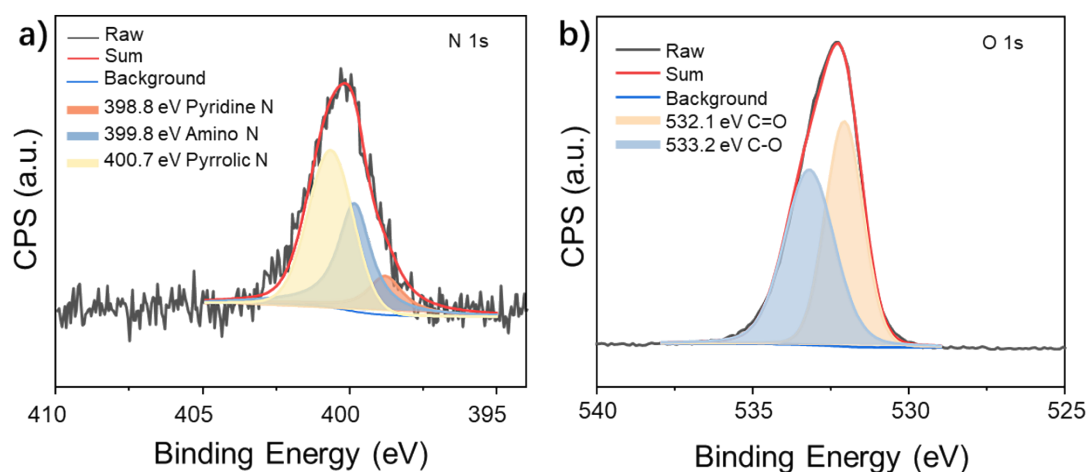


Figure S12. The HR XPS spectra and the corresponding fitting curves of the a) N 1s, and b) O 1s of the UV-CDs.

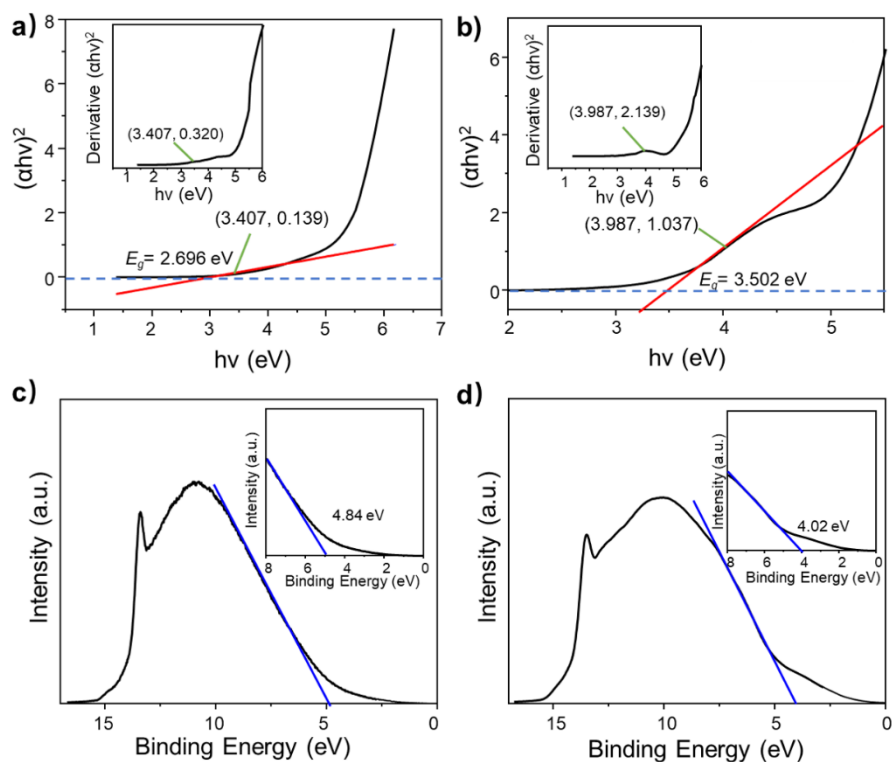


Figure S13. The $(\alpha hv)^2$ versus hv curves of a) TA-CDs and b) UV-CDs, and the UPS spectra of c) TA-CDs and d) UV-CDs.

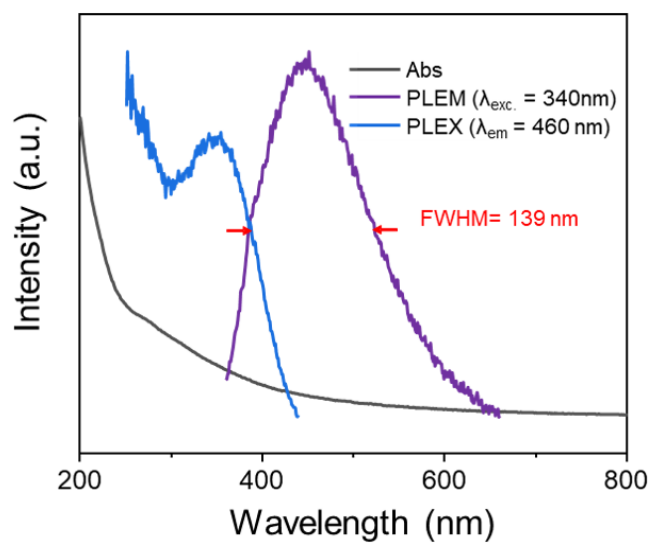


Figure S14. The UV-Vis absorption (black line), PL emission (purple line) and excitation (blue line) spectra under the corresponding wavelengths of TA-CDs-2.

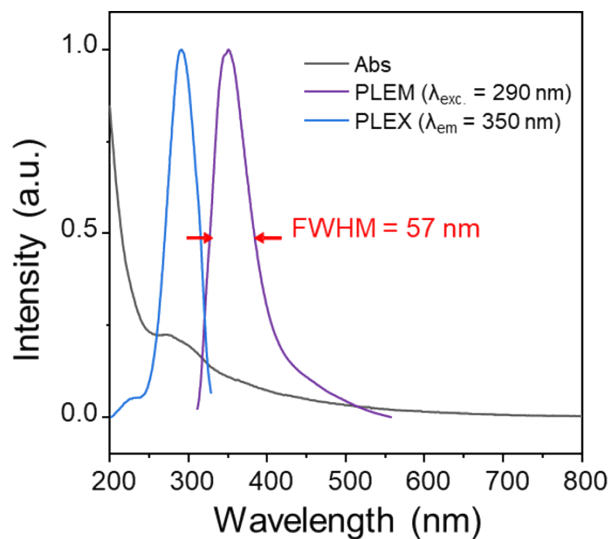


Figure S15. The UV-Vis absorption (black line), PL emission (purple line) and excitation (blue line) spectra under the corresponding wavelengths of UV-CDs-2.

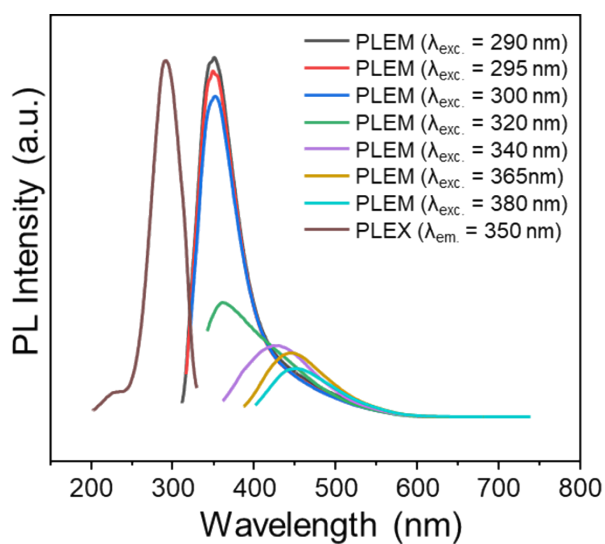


Figure S16. The PL emission spectra at different excitation wavelengths and excitation spectrum at 350 nm of UV-CDs-2.

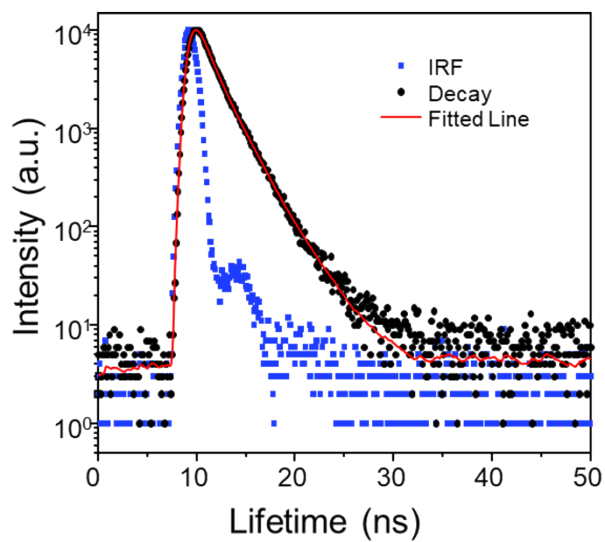


Figure S17. The PL decay spectrum and fitting curve of UV-CDs-2 ($\lambda_{\text{exc.}}=290$ nm, $\lambda_{\text{em}}=350$ nm).

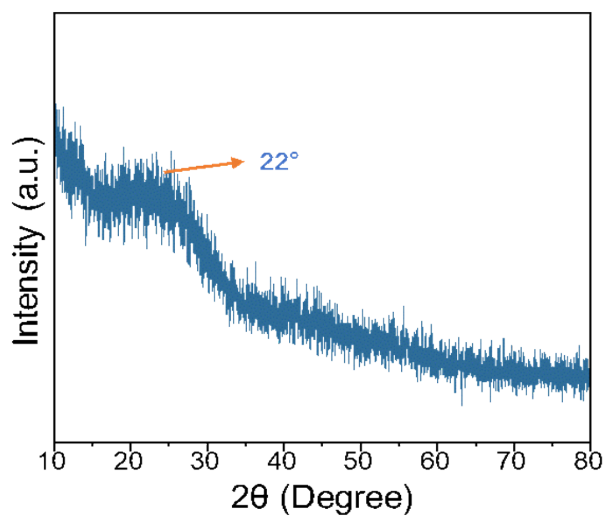


Figure S18. The XRD pattern of UV-CDs-2.

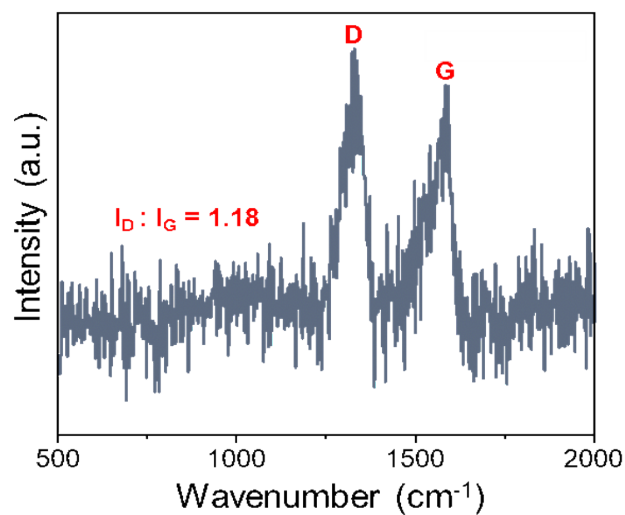


Figure S19. The Raman spectrum of UV-CDs-2.

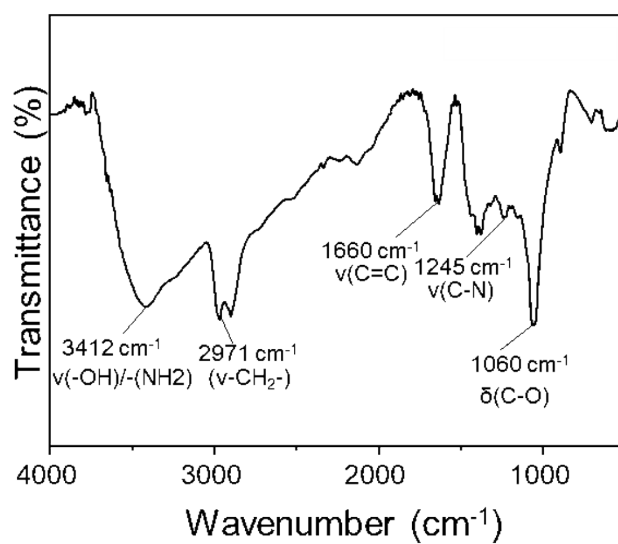


Figure S20. The FT-IR spectrum of UV-CDs-2.

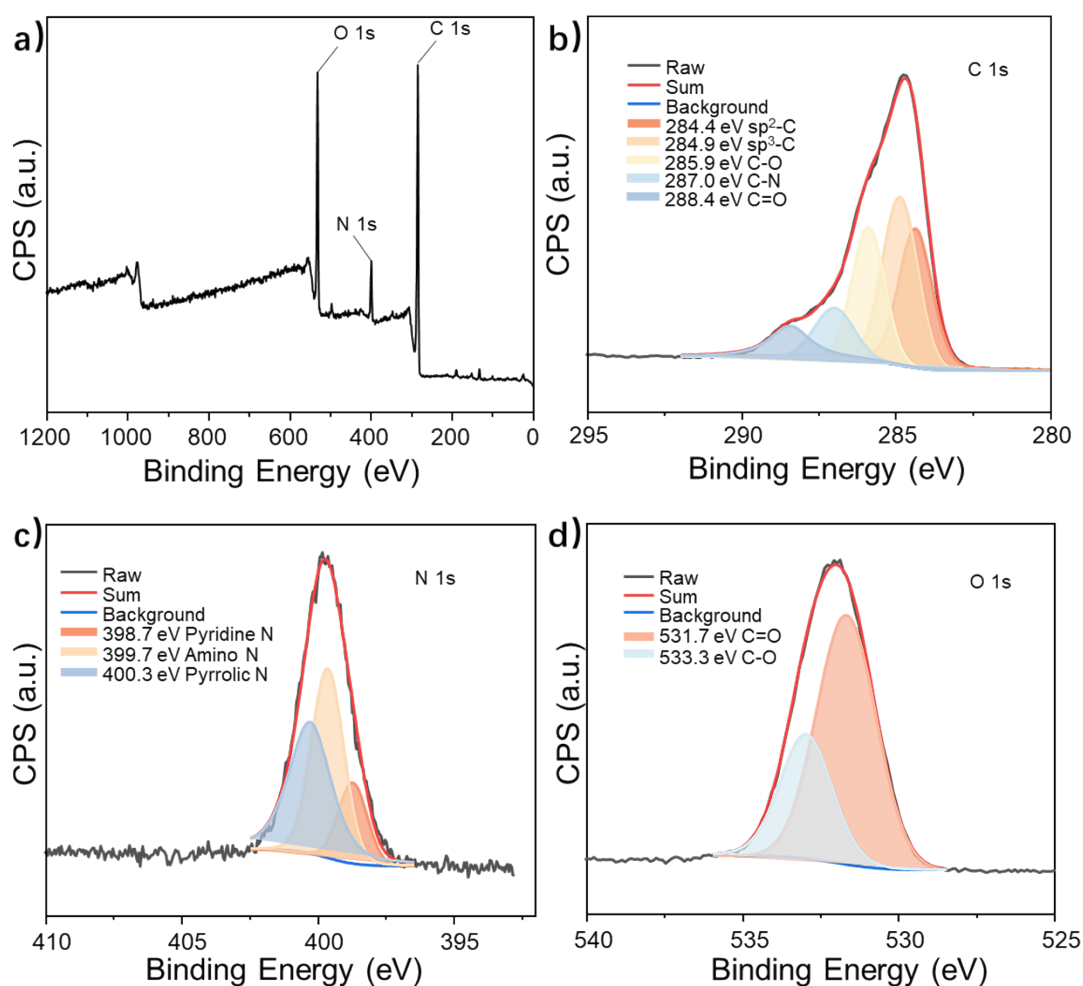


Figure S21. a) The XPS spectrum of UV-CDs-2. b–d) The HR XPS spectra and the corresponding fitting curves of b) C 1s, c) N 1s, and d) O 1s of the UV-CDs-2.

Table S1. The fitted parameters of the PL decay curves of CDs.

Sample	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ_3 (ns)	B_3 (%)	τ_{avg} (ns)	χ^2
UV-CDs	1.37	46.77	2.28	52.59	13.89	0.64	1.47	1.30
TA-CDs	0.41	11.61	2.90	56.77	8.05	31.62	4.24	1.34
UV-CDs-2	1.31	45.64	2.42	54.36	-	-	1.92	1.26

Table S2. Relative contents of C, N and O elements on the basis of the XPS data.

Sample	C (%)	N (%)	O (%)
UV-CDs	68.95	2.20	27.95
TA-CDs	76.86	12.34	10.80
UV-CDs-2	72.55	7.61	19.84

Table S3. Relative contents of different functional groups in CDs are determined based on the HR XPS spectra and the corresponding fitting curves.

Sample	C 1s (%)					N 1s (%)			O 1s (%)	
	sp ² -C	sp ³ -C	C-O	C-N	C=O	Pyridine N	Amino N	Pyrrolic N	C=O	C-O
UV-CDs	25.80	31.18	18.36	15.81	8.85	14.78	35.96	49.26	46.63	52.37
TA-CDs	39.90	14.25	32.82	7.29	5.74	31.97	43.93	24.10	45.45	54.55
UV-CDs-2	26.23	31.20	22.81	10.46	9.30	15.15	40.80	44.05	68.40	31.60