Electronic Supplementary Information

Facile synthesis of halogenated carbon quantum dots as an important intermediate for surface modification

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1. The experimental details

Synthesis of halogenated C-dots. 5 mL of CCl_4, 5.708 g of Hydroquinone, 2.0736 g of NaOH and 5 mL of ethanol were placed into a 25 mL Teflon equipped stainless steel autoclave, and then the mixture was heated solvothermally at 200 ℃ for 2 h using a blast oven. When cooled down to ambient temperature, the solution was condensed by rotary evaporation and the obtained product was Cl-CQDs. Then 0.5 g of I_2 and 2 mL of Br_2 were put into 25 mL of Teflon equipped stainless steel autoclaves respectively, which were filled with 0.3 g of Cl-CQDs. Then the autoclaves were sealed and maintained at 200 ℃ for 1 h using a blast oven. After drying by rotary evaporation, the obtained products were donated as Br-CQDs and I-CQDs respectively.

Synthesis of 1,2-ethylenediamine-functionalized carbon dots. 0.02 g Cl-CQDs was added in the 20 ml 1,2-ethylenediamine, and then the mixture was refluxed for 8 h to complete the substitution of halogen with 1,2-ethylenediamine. This procedure was monitored using UV-Vis and fluorescence spectrum. After completion of the reaction, the extra 1,2-ethylenediamine was removed through vacuum rotary evaporation and then the obtained EDA-CQDs-Cl was dried at 80 ℃ overnight. The synthesis of EDA-CQDs-Br and EDA-CQDs-I were achieved using the similar procedure with Br-CQDs and I-CQDs as precursors.

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 hemisphereical 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 1400-0 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. The Fourier transform infrared spectroscopy (FTIR) spectra were measured by a Thermo NEXUS 670 Fourier transform infrared spectrometer.

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

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

where Φ 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.

Preparation of the solutions with additional ions. The products were purified by dialyzing against Milli-Q water with a cellulose ester membrane bag (M_w = 1000) first. In order to eliminate the pH effect induced by metal ions, all the chosen ions solutions were adjusted to pH 1.0. The resulting ions solutions were added to the same amount of Cl-CQDs solutions respectively to obtain the series of mixed solutions, in which the concentrations of the ions in the mixed solutions keep identical. In all the mixed solutions, the concentration of Cl-CQDs was identical to raw solution with pure Cl-CQDs.

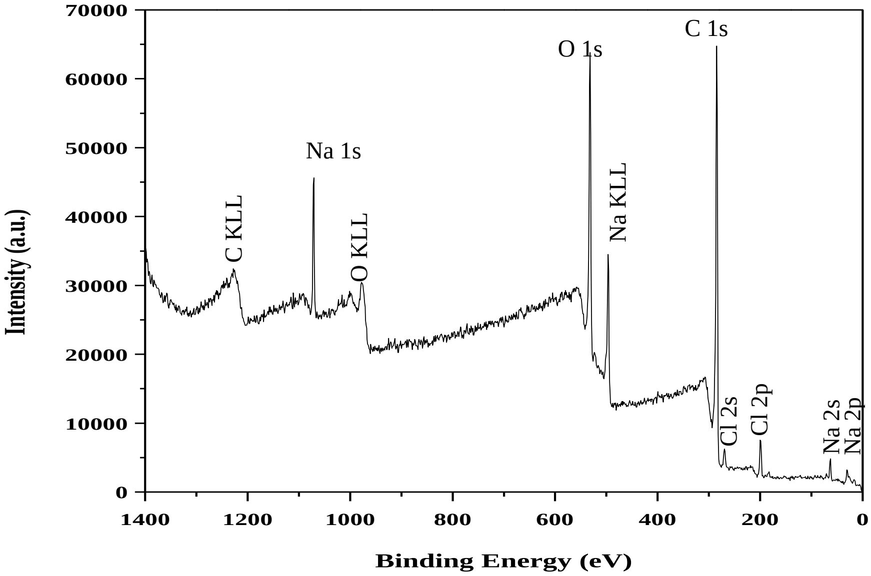

Figure S1. The XPS spectrum of Cl-CQDs.

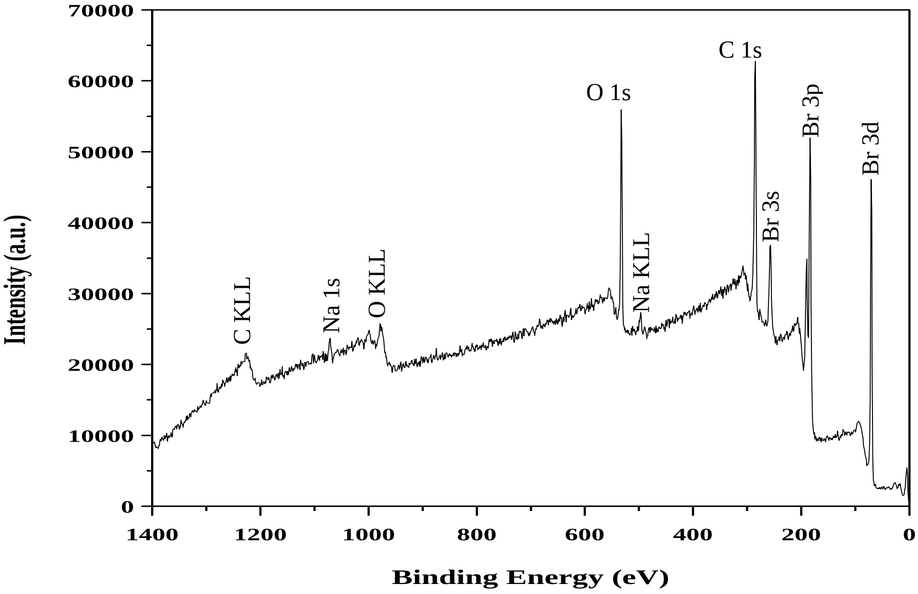

Figure S2. The XPS spectrum of Br-CQDs.

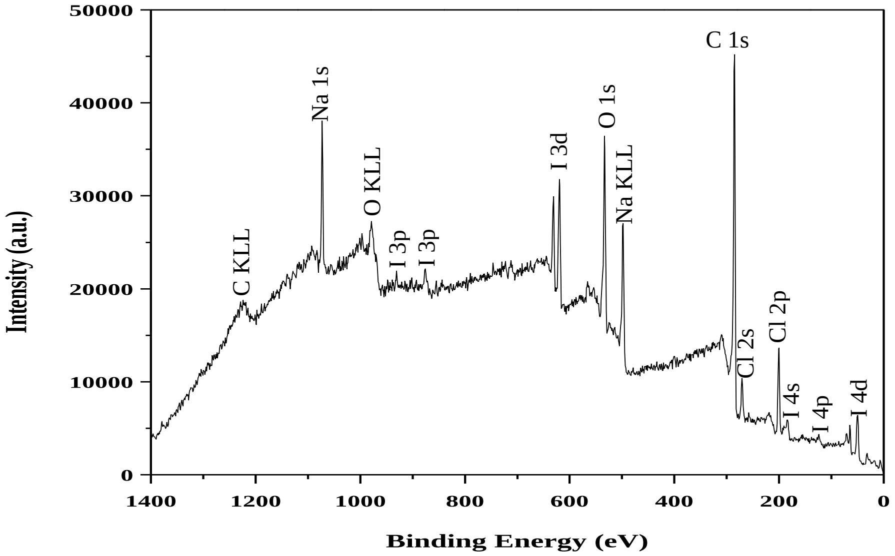

Figure S3. The XPS spectrum of I-CQDs.

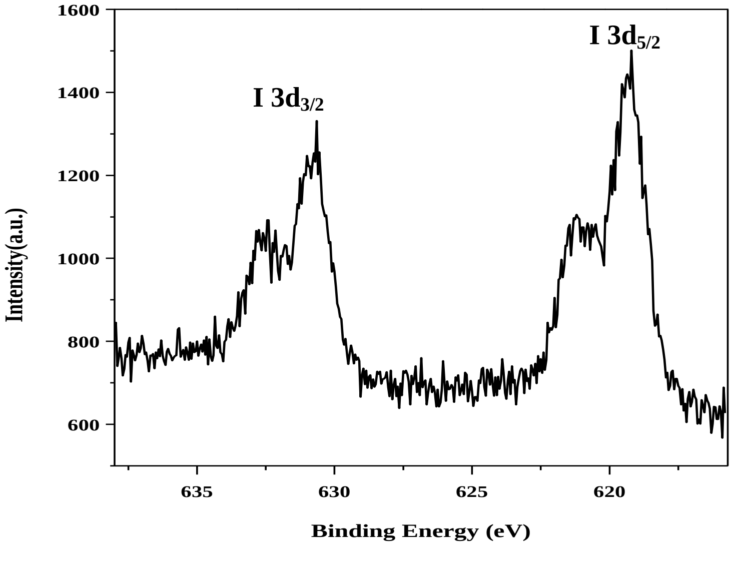

Figure S4. The 3d region of XPS spectrum of I-CQDs.

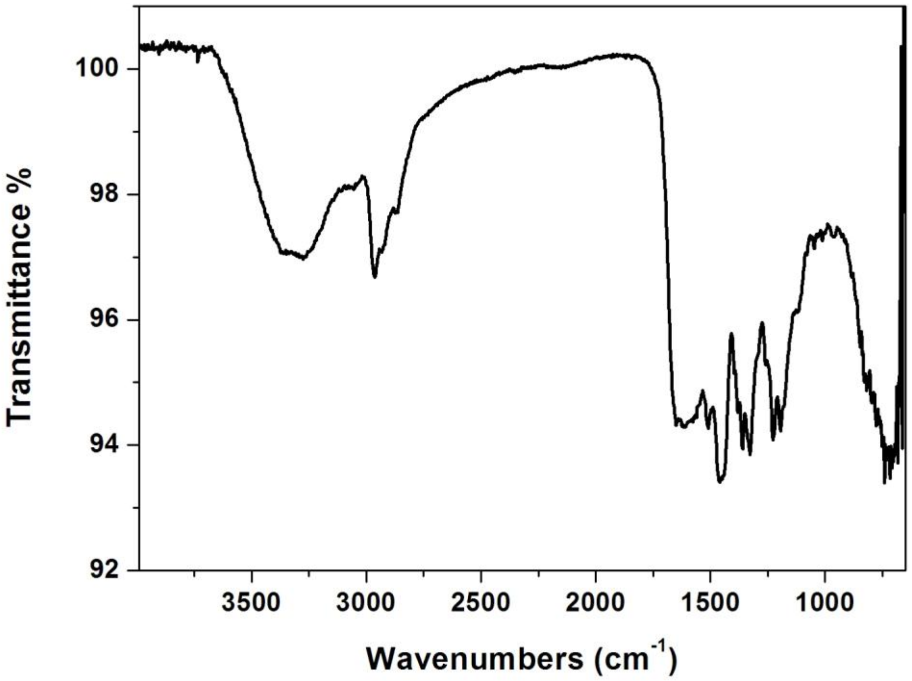

Figure S5. The FT-IR spectrum of EDA-CQDs-Cl

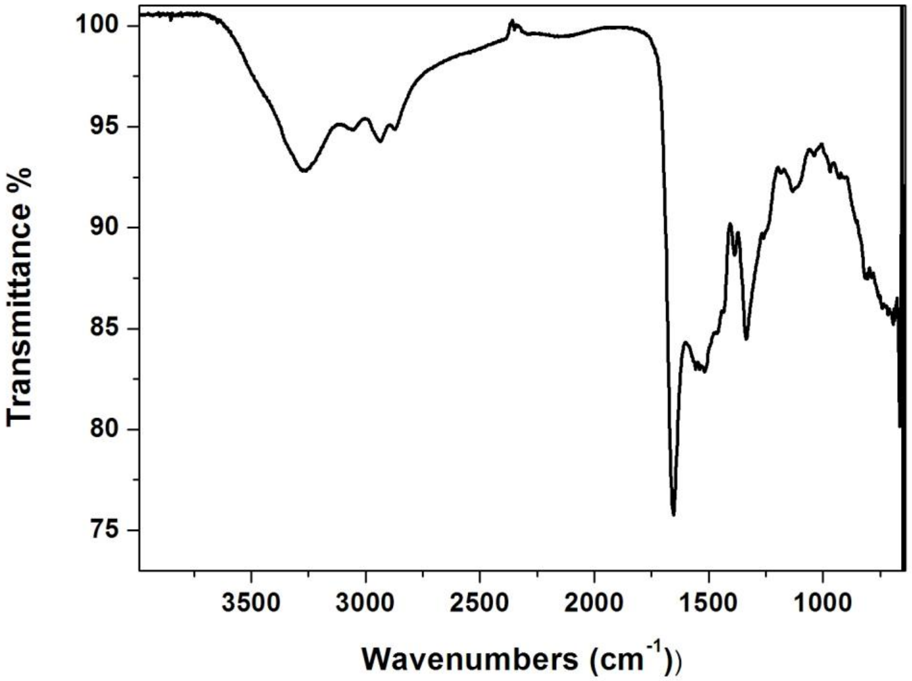

Figure S6. The FT-IR spectrum of EDA-CQDs-Br

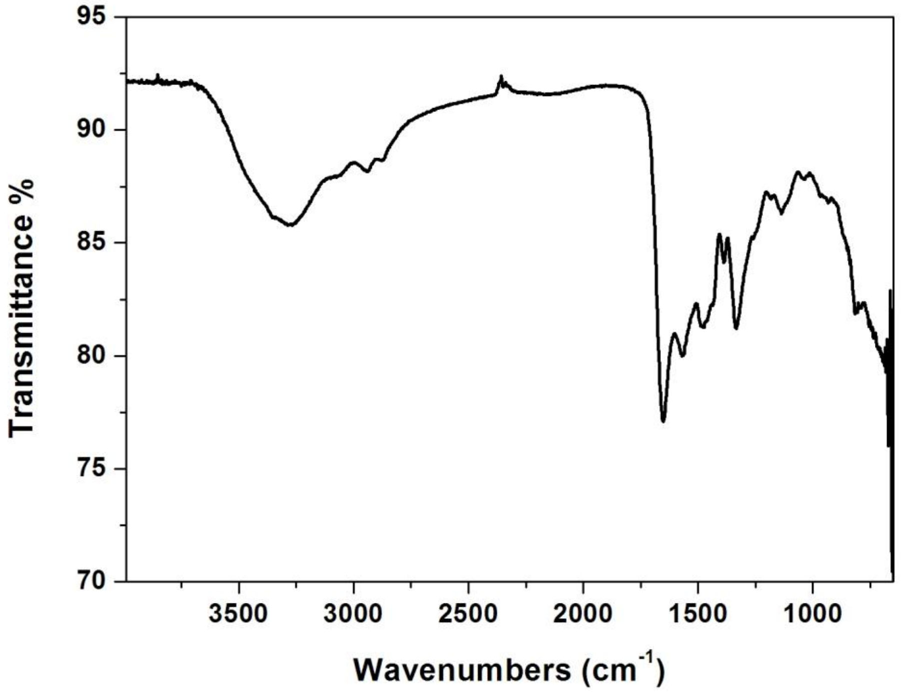

Figure S7. The FT-IR spectrum of EDA-CQDs-I

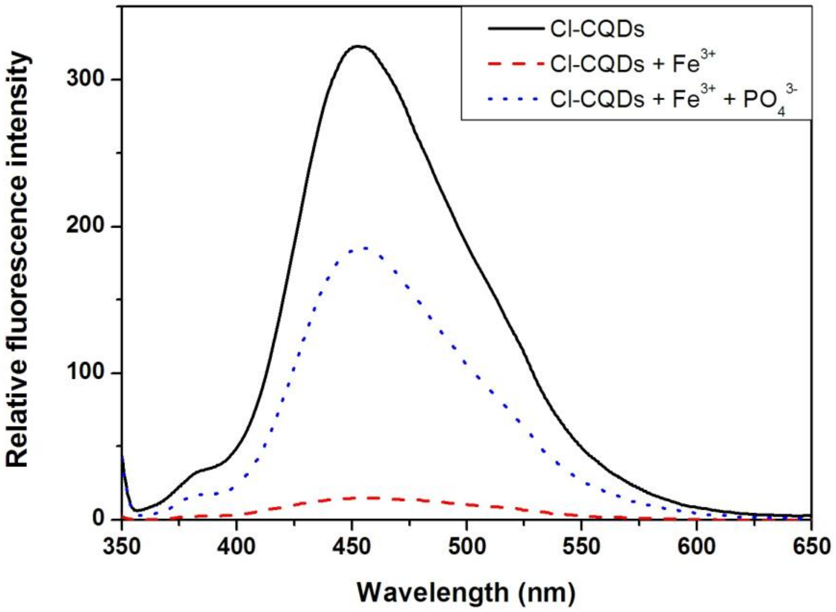

Figure S8. The fluorescence recovery experiment