Electronic Supplementary Information

Enhancing the luminescence of carbon dots with a reduction pathway

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Materials: Specpure graphite was a product of the Tianjin Guangfu Fine Chemical Research Institute, sodium borohydride was purchased from Tianjin Huan Wei Fine Chemical Co., Ltd. Dialysis bags (molecular weight cut off = 3500) were ordered from Shanghai Green Bird Science & Technology Development Co., Ltd. Ultra-pure water was prepared using a Milli-Q-Plus system and used in all experiments. All reagents were used as received without any further purification.

Experimental:

1. Synthesis of r-CDs: Graphite oxide was synthesized from spectra-pure graphite powder according to Hummers method.[S1] Briefly, graphite oxide (0.2 g) was added to a solution of HNO_3 (5 mol/L, 150 mL) and the mixture was heated under reflux at 140 °C for 12 h. The dark-brown CDs solution was neutralized with sodium carbonate. The supernatant was collected by centrifugation at 12,000 rpm for 15 min and it was then loaded into dialysis bags for dialysis against ultra-pure water for 48 h. The purified CDs solution was kept at 4 °C until use. For the reduction of the CDs, excess sodium borohydride (0.5 g) was mixed with an aqueous solution of the CDs (about 1×10^{-5} g/mL, 150 mL) and then stirred gently overnight at room temperature. Excess reductant was removed by dialysis as mentioned above.

2. Purification of r-CDs and CDs: The gel column that was used for purification was prepared using commercial Sephadex G-100 gel (Pharmacia). The dried gel (2.5 g) was steeped in ultrapure water and heated at 90 °C for 3 h. The gel suspension was stored overnight. The supernatant was decanted from the suspended gel. Air bubbles were removed from the remaining gel by ultrasonication and then the gel was washed several times until no suspended gel remained. A column (10 mm internal diameter) was filled with ultrapure water and then the gel suspension was added to the column.

The gel-filled column was rinsed with ultrapure water for 6 h until the column height (20 cm) remained unchanged. For purification, the as-prepared r-CDs or CDs (1 mL) were added to the gel column and eluted with ultrapure water. Colored fractions of the r-CDs and the CDs were collected for further investigation.

3. H_2O_2 assays: These experiments were performed in a boiling water bath, r-CDs (about 1×10^{-5} g/mL, 200 μL) and cobalt ions (100 μM) were incubated with H_2O_2 at different concentrations in a phosphate buffer solution (pH = 7.0) for 20 min. Photoluminescence spectra were measured at an excitation wavelength of 280 nm.

4. TEM measurement: r-CDs and CDs samples were prepared by dropping the CDs aqueous solution (5 μL, about 1×10^{-5} g/mL) onto 400-mesh carbon coated copper grids (spi, USA) and dried in a vacuum oven. The size and dispersivity were determined by a field emission TEM (Tecnai G^2 F20 S-TWIN, FEI, USA) operating at 200 kV. The TEM images and HRTEM images were magnified 45,000 and 450,000 times, respectively. The size distribution was determined by measuring the dimensions of 150 particles. The average sizes of the r-CDs and CDs are 3.3 nm (standard deviation is 1.0 nm, n=150) and 3.4 nm (standard deviation is 1.2 nm, n=150), respectively (Figure S1).

5. Optical analysis: The CDs aqueous solutions were air-equilibrated and measured without any other treatment. The absorption spectra and photoluminescence spectra of the two CDs were recorded using a UV-2450-PC spectrophotometer (Shimadzu, Japan) and a F-4500 fluorescence spectrometer (Hitachi, Japan) containing a R928 photomultiplier tube (Hamamatsu, Japan).

6. Quantum yield measurements: The QYs were measured according to "A Guide to Recording Fluorescence Quantum Yields" by Jobin Yvon Horiba Ltd. at

http://www.jobinyvon.co.uk/ukdivisions/Fluorescence/plqy.htm. Quinine sulfate in a 0.1 M H_2SO_4 aqueous solution (quantum yield is 0.54) and fluorescein in 0.1 M NaOH aqueous solution (quantum yield is 0.95) were selected as references for the r-CDs and CDs aqueous solutions, respectively. The QYs were determined by comparing the integrated photoluminescence intensity (excited at 280 nm for r-CDs and 470 nm for CDs) and the absorbance value (less than 0.1 at the excitation wavelength) of the CDs samples with that of the references. The slope method was used to calculate the QYs of two kinds of CDs using the equation:

$$QY_u = QY_s (m_u/m_s) (n_u/n_s)^2$$

where QY is the quantum yield, m is the slope determined by the curves in Figure S1 and n is the refractive index (1.33 for water and a 0.1 M H_2SO_4/NaOH aqueous solution). The subscript "s" refers to the standards and "u" refers to the unknown samples. For these aqueous solutions, $n_u/n_s = 1$. A series of concentrations for the references and the CDs samples were measured to obtain the slopes.

As shown in Figure S3, the m values were calculated to be 392086, 740347, 78912 and 3540690 for r-CDs, quinine sulfate, CDs and fluorescein, respectively. The QY of the r-CDs was 28.6% and the QY of the CDs was 2.4%. We also tested different batches of r-CDs and CDs samples using the same method. The QYs of the r-CDs was consistently higher than 20% (24 ± 3.6%, n = 3, P = 90%) and the QYs of the CDs was about 2% (2.1 ± 0.76%, n = 3, P = 90%) in each batch.

7. Other Characterization: The luminescence lifetime was measured using a Fluorolog-3 fluorescence spectrometer (Horiba Jobin Yvon Inc, France). The infrared spectra were measured using a TENSOR 27 infrared spectrophotometer (BRUKER,

Germany). The XPS spectra were measured using a XSAM-800 X-ray photoelectron spectroscope (KRATOS, UK).

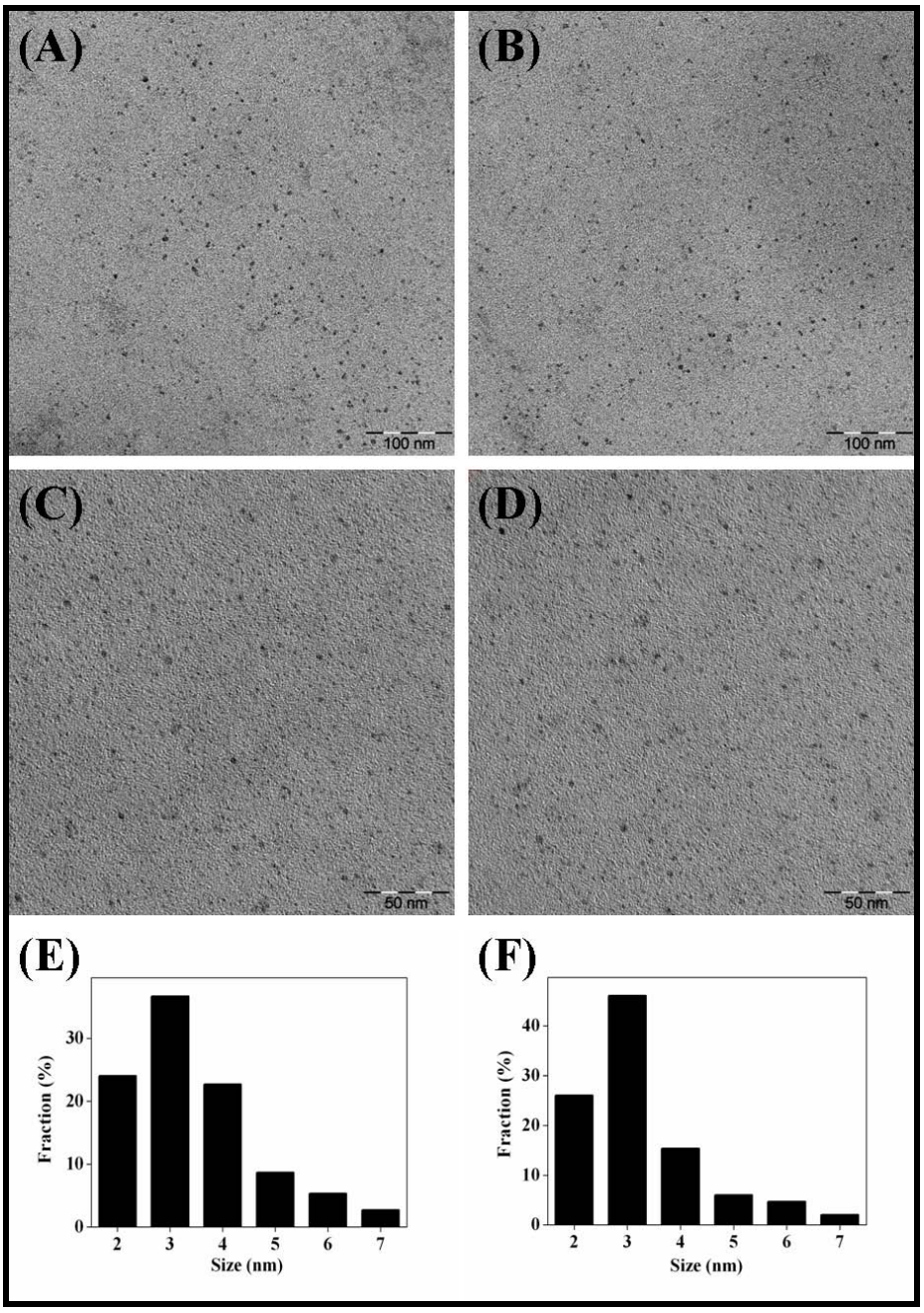

Figure S1. TEM images and particle size distributions of CDs (A, C and E) and r-CDs (B, D and F).

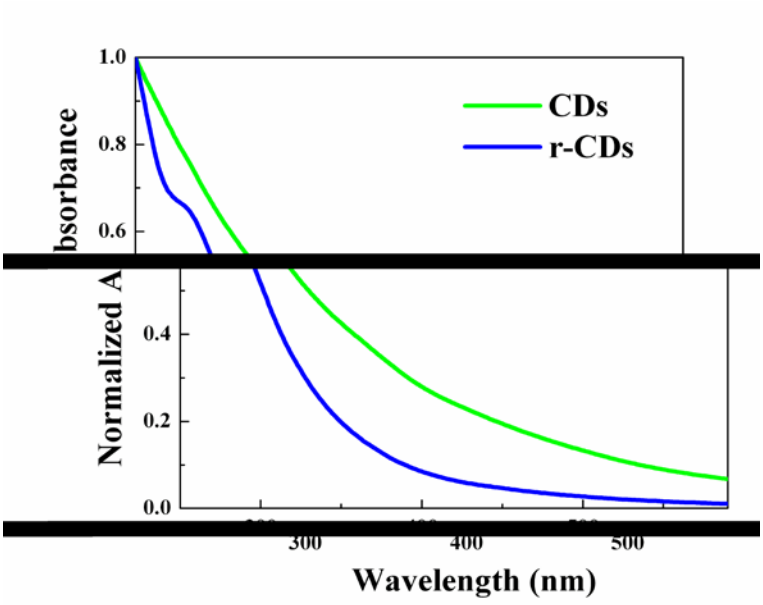

Figure S2. UV-Vis absorption spectra of the CDs and the r-CDs.

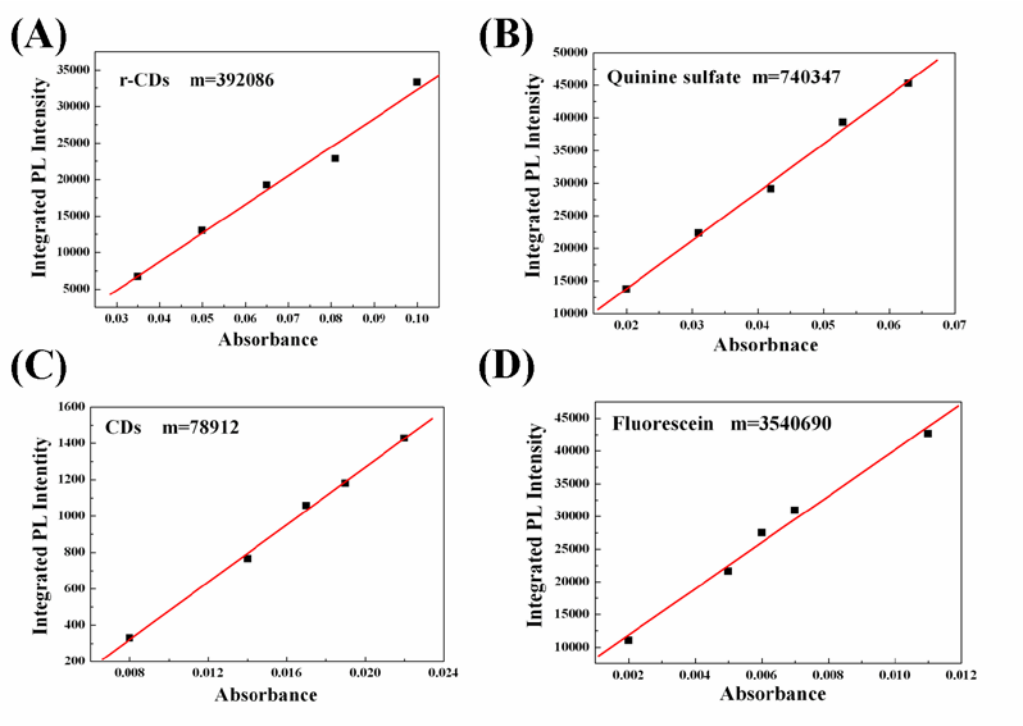

Figure S3. Photoluminescence and absorbance of the r-CDs (A), quinine sulfate (B), CDs (C) and fluorescein (D).

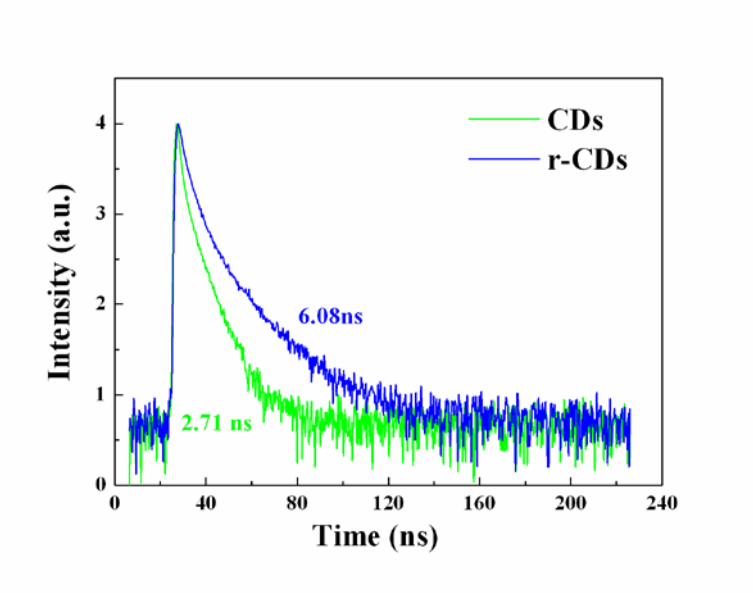

Figure S4. Luminescence lifetimes of the CDs (the excitation wavelength is 470 nm and the emission wavelength is 520 nm) and the r-CDs (the excitation wavelength is 280 nm and the emission wavelength is 440 nm).

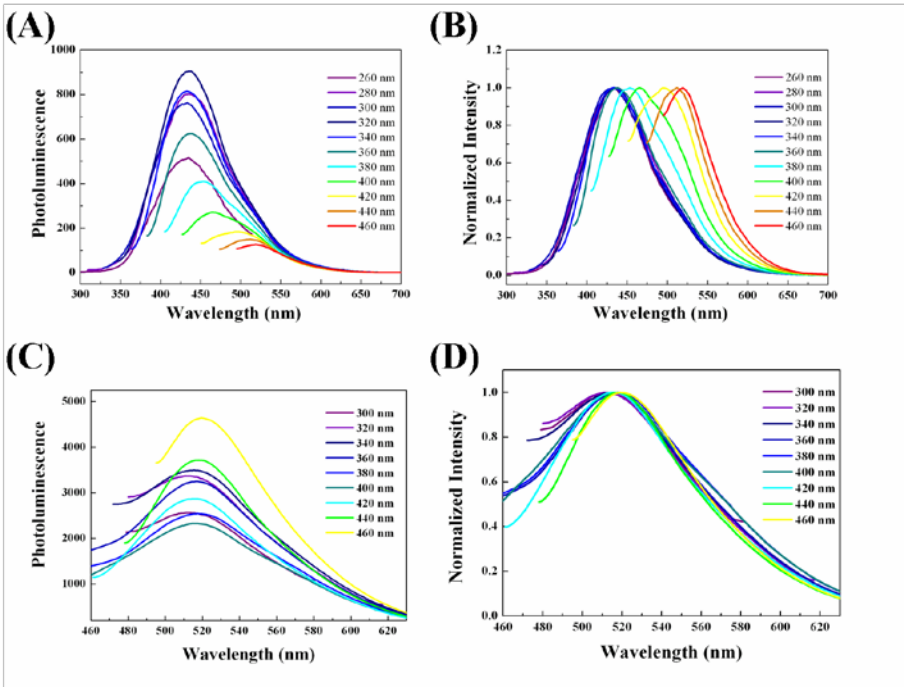

Figure S5. Photoluminescence emission spectra (A) and normalized spectra (B) of r-CDs (excitation wavelengths from 260 to 460 nm in 20 nm increments). Photoluminescence emission spectra (C) and normalized spectra (D) of CDs (excitation wavelengths from 300 to 460 nm in 20 nm increments).

The r-CDs showed excitation-independent behavior within an excitation wavelength range from 260 to 360 nm and excitation-dependent behavior within an excitation wavelength range from 380 to 460 nm. In addition, the original CDs showed excitation-independent behavior within an excitation wavelength range from 300 to 460 nm.

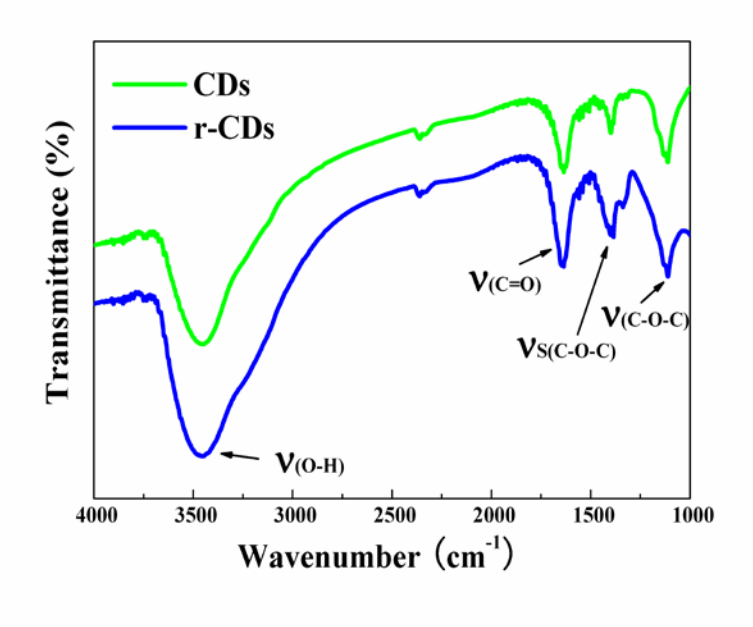

Figure S6. FT-IR spectra of the CDs and r-CDs.

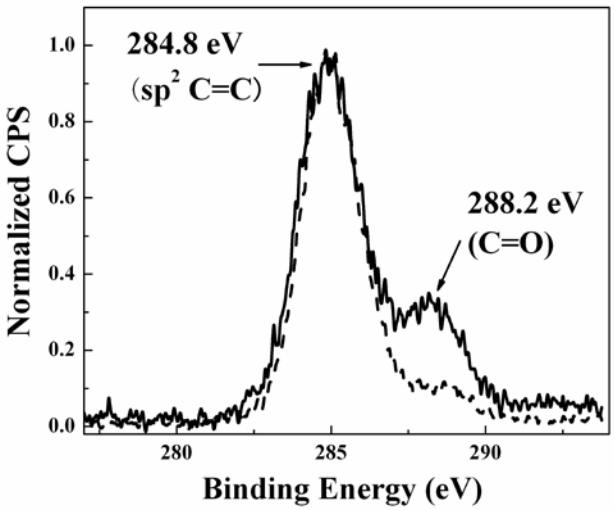

Figure S7. X-ray photoelectron spectroscopy (XPS) spectra of the C 1s of the CDs (solid line) and the r-CDs (dashed line) on the glass substrate.

Table S1. Comparison of the quantum yields of the CDs and the r-CDs prepared from different precursors.

Sample of CDs	original CDs quantum yield	r-CDs quantum yield
Candle soot	0.75%	6.3%
Lamp black	1.1%	7.3%

References

(S1) Jr W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.,* 1958, **80**, 1339.