

Supporting information for:

Preparation of carbon quantum dots by non-focusing pulsed laser irradiation in toluene and the formation mechanism

Experimental details:

Typically, pure commercial toluene(5ml) was sealed in a reaction cell and irradiated by an unfocused pulse laser beam (Nd:YAG laser, 10Hz, 8ns, 1064nm, 200mJ pulse-1 cm⁻²) for 30 min, during which the clear liquid changed to dark brown (marked I).

Separation-processes:

1. The resultant (I) (1ml) was first mixed with 3ml ethanol and shaken using ultrasonic.
2. Then the result of 1 was further mixed with 2 ml ultrapure water (keeping V Ethanol : V Water around 6:4) and shaken using ultrasonic.
3. The result of 2 was let sit for 5 minutes at room temperature. The mixture of 2 formed emulsion at the beginning, then the emulsion was divided into three layers automatically (about 2-3 min), upper layer is a little opacitas (dark brown), the middle layer is light brown, and the lower layer is much clear.
4. Extracted the middle layer for further analysis.

Characterization:

One droplet suspensions of pure toluene and the solution after laser irradiation for 10 mins (S-10) were put onto a KBr-disk and then covered with another KBr-disk. The IR Spectra were measured by a fourier transform infrared spectrometer (VERTEX 70). Raman spectra were recorded with a LabRAM HR800 spectrometer. A Nd:YAG laser operating at 532 nm and a power of 5 mW (10% of the original power) was used as the radiation source. TEM measurements were performed on FEI Tecnai G2 20 at operating voltage of 200 kV. Fluorescence spectra were recorded on a fluorescence spectrophotometer (FP-6500).

Fluorescence Quantum Yield

The quantum yield was measured based on reference [S3], comparing the integrated photoluminescence intensities and the absorbency values of the samples with the reference quinine sulfate (FQYs 0.54), and then the quantum yield was calculated using the following equation:

$$Q = Q_R \frac{I \cdot A_R \cdot \eta^2}{I_R \cdot A \cdot \eta_R^2} \quad (1)$$

where Q is the quantum yield, I is the measured integrated emission intensity, η is the refractive index, and A is the optical density. The subscript R refers to the reference fluorophore of known quantum yield. To minimize re-absorption effects the optical densities in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength. An excitation slit width of 5 nm and an emission slit width of 5 nm were used to excite the samples of CQDs and to record their photoluminescence spectra. The FQYs of the samples prepared under 200 mJ/pulse were 0.18.

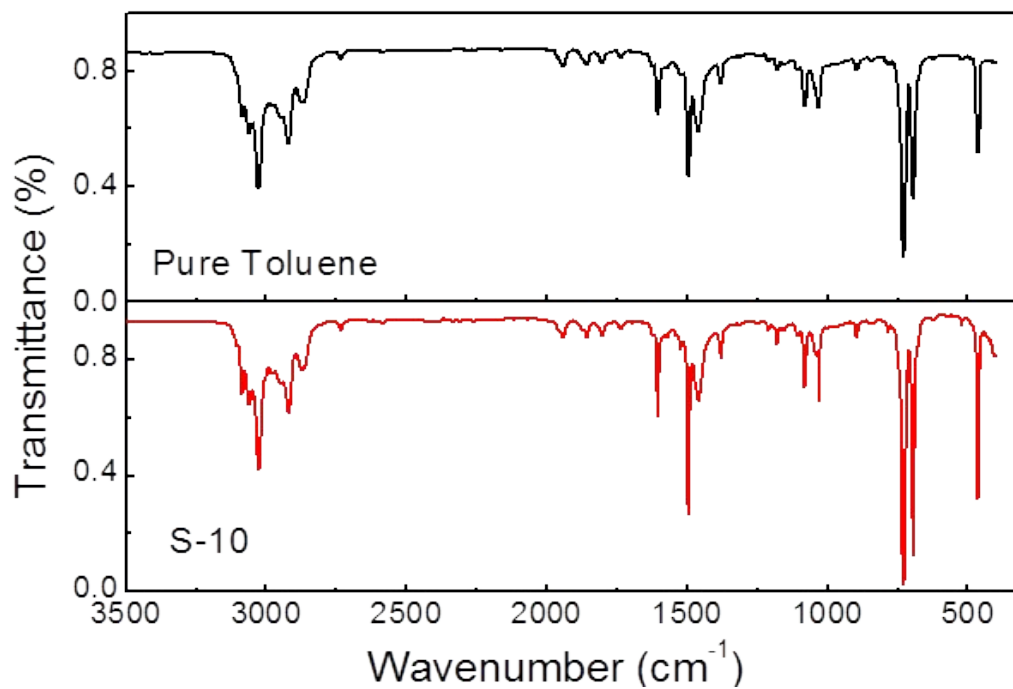


Fig. S1 FT-IR spectrum of pure toluene (black line) and the solution after laser irradiation for 10 min (red line). They displayed common characteristics and confirmed that the solvent after laser irradiation was still toluene.

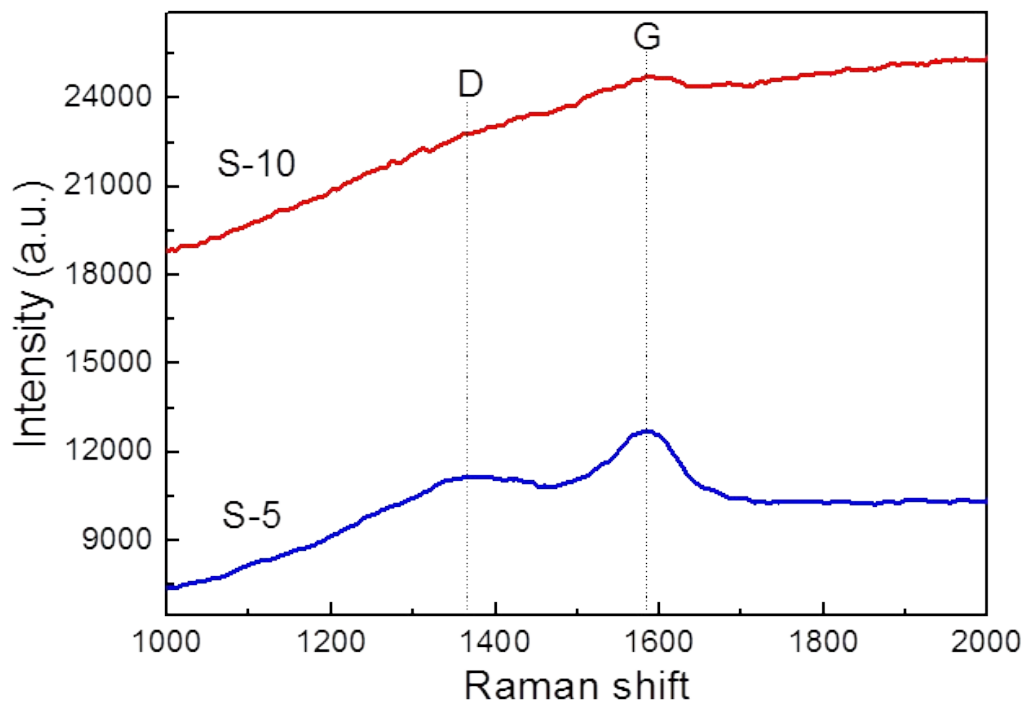


Fig. S2 Raman spectra of S-5 (blue line) and S-10 (red line). The Raman spectrum of S-5 is dominated by two peaks centered at approximately 1364 and 1583 cm^{-1} that can be identified as a defect band (D band) and a graphite band (G band), respectively (Figure S2 blue). However, the strong Photoluminescence of the CQDs masks the Raman spectra for the S-10 (Figure S2 red) [S1]. The G band is attributed to the vibration of sp^2 -bonded carbon atoms in a 2D hexagonal lattice, while the D band is associated with vibrations of carbon atoms with dangling bonds in plane terminations of the disordered graphite and related to the defects and disorders in the structures of carbon materials [S2].

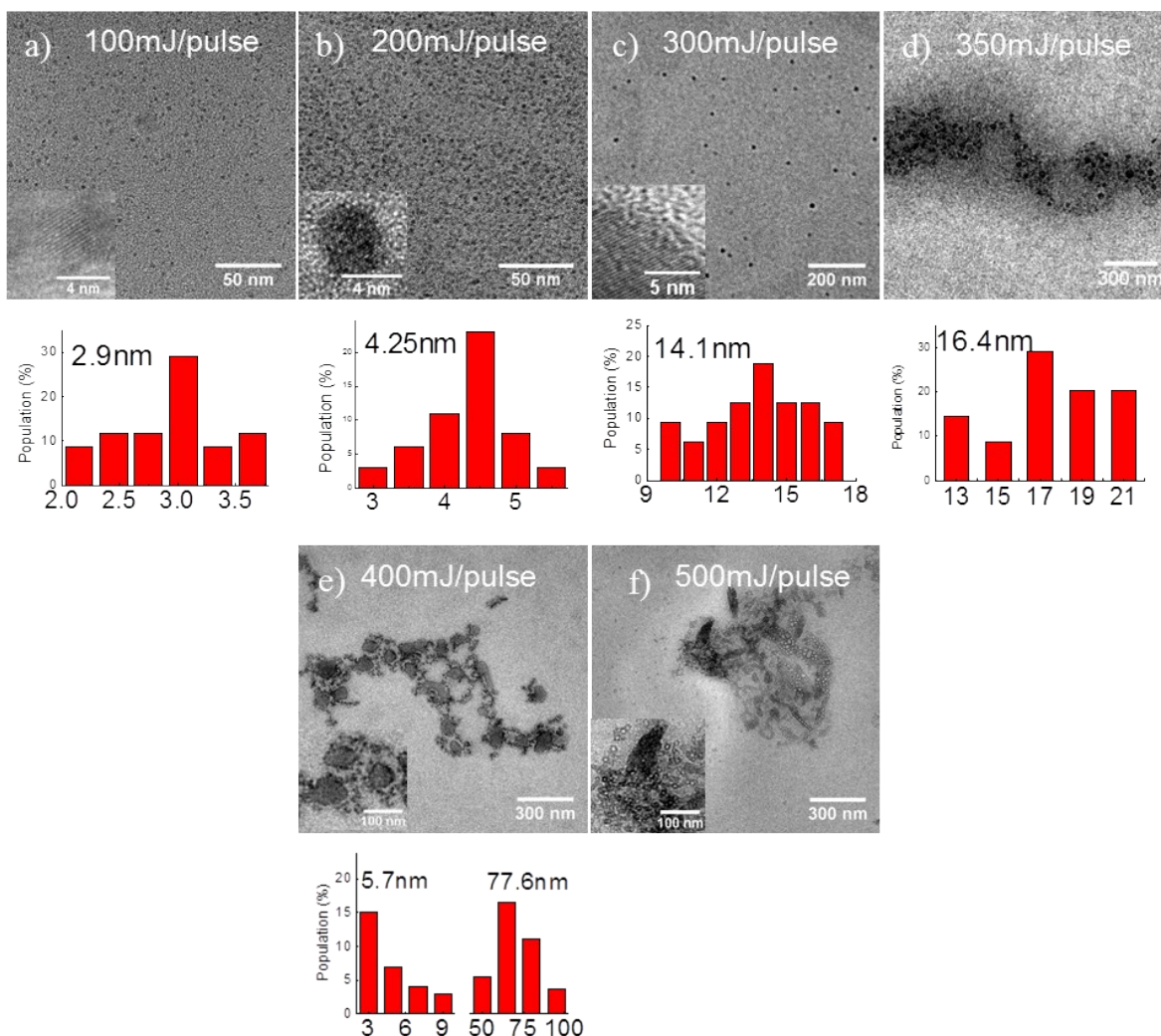


Fig. S3 TEM images and size histograms of CQDs under different laser energies. Insets are the HR-TEM images. Figures S3a, S3b, S3c and S3d show that the sizes of the CQDs prepared under 100, 200, 300 and 350 mJ/pulse were 2.9 nm, 4.25 nm, 14.1 nm and 16.4 nm, respectively. If the laser fluence is further increased up to 400 mJ/pulse, two different size distributions (5.7 nm and 77.6 nm) were found (Figure S3e). And products prepared at 500 mJ/pulse are even diversified, include large unshaped products and hollow sphere (Figure S3f)

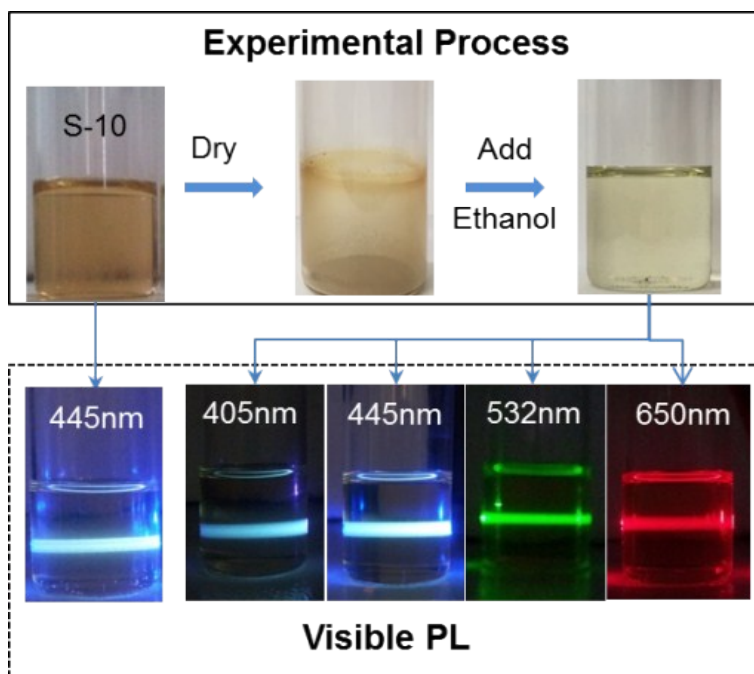


Fig. S4 The optical images under different periods. In order to confirm whether the PL was emitted from the CQDs, the suspension was dried naturally, and then the ethanol was refilled to form another suspension. The reappearance of PL proved that the PL was emitted from the CQDs and not from the liquid solvent.

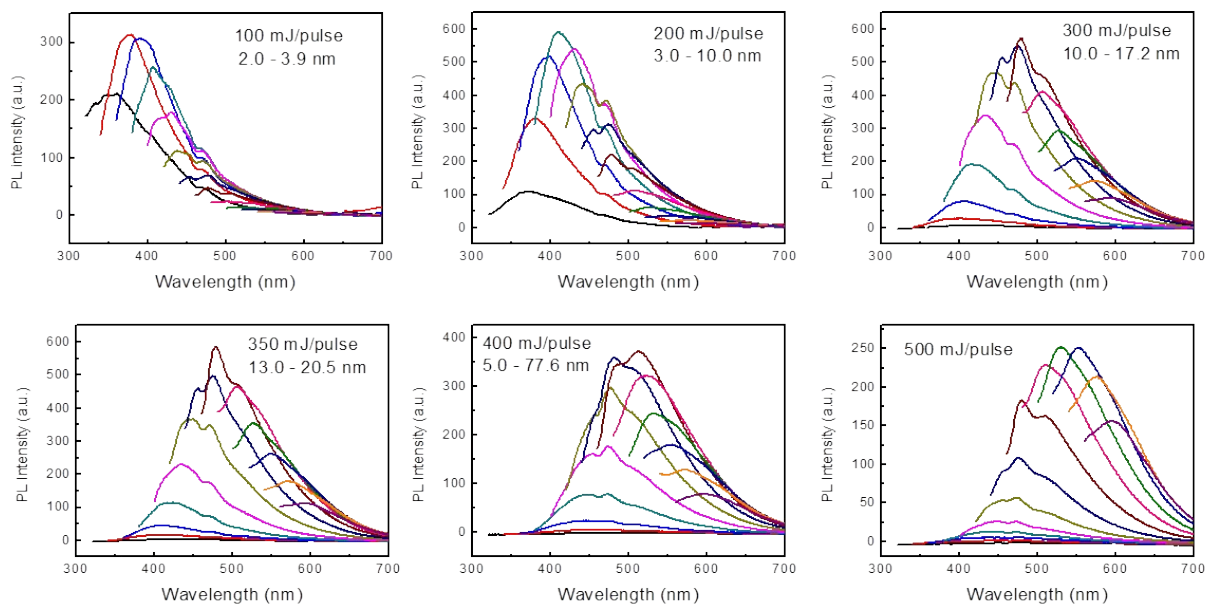


Fig. S5 PL spectrum of the products, excite at 300-540nm, space 20nm. The PL spectrums of the samples gradually shift with progressively longer excitation wavelengths from 360nm to 500nm in 20nm increment, which corroborate that the emission wavelength can be tuned by varying the excitation wavelength.

Notes and references

S1 M. J. Krysmann, A. Kellarakis, P. Dallas, and E. P. Giannelis, *J. Am. Chem. Soc.*, 2012, 134, 747–750.

S2 S. Niyogi, E. Bekyarova, M. E. Itkis, H. Zhang, K. Shepperd, J. Hicks, M. Sprinkle, C. Berger, C. N. Lau, W. A. de Heer, E. H. Conrad, R. C. Haddon, *Nano Lett.*, 2010, 10, 4061.

S3 Shengliang Hu, Jun Liu, Jinlong Yang, Yanzhong Wang, Shirui Cao, J. Laser synthesis and size tailor of carbon quantum dots. *Nanopart Res.* 2011; 13: 7247-7252.