Supporting Information

Surface Related Intrinsic Luminescence from Carbon Nanodots: Solvent Dependent Piezochromism

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Experimental Section

Synthesis: Citric acid ($C_6H_8O_7$, 99.5%) and urea (CH_4N_2O, 99%) were purchased from Beijing Chemical Corp. All chemicals were used as received without further purification. The water used in all experiments was purified with a Millipore system. The microwave synthesis of carbon nanodots (CDs) followed procedures given in our previous work. Citric acid (3 g) and urea (6 g) were added to water (10 mL) to form a transparent solution. The solution was then heated in a domestic 650 W microwave oven for 4–5 mins, during which the solution changed from colorless liquid to brown and finally dark-brown clustered solid, indicating the formation of CDs. This solid was then transferred to a vacuum oven and heated at 60 °C for 1 h. Then, the as-prepared CDs were processed in water, followed by centrifugation (10000 r min^{-1}, 20 minutes) to remove large or agglomerated particles. The products were freeze-dried to give the powder of CDs. The powder of CDs was redispersed in water, and the concentration of the resulting CDs solution was 3 mg/mL. Furthermore, the solution was hydrothermally treated at 160 ˚C for 6 hours, and then cooled to room temperature. The hydrothermally treated products were freeze-dried to give the powder of h-CDs for following characterizations.

Characterizations: Transmission electron microscopy (TEM) images were observed on a FEI Tecnai-G2-F20 TEM at 200 kV. Photoluminescence (PL) and UV-vis absorption spectra were collected using a Hitachi F-7000 spectrophotometer and a Shimadzu UV-3101PC spectrophotometer. Fluorescence lifetimes were measured using Edinburgh Instruments FLS920 time-corrected single photon counting system. XPS analyzes were measured on an ESCALAB MK II X-ray photoelectron spectrometer using Mg as the exciting source.

Diamond anvil cell experiment: All of the *in situ* high-pressure experiments shown in this study were carried out with a symmetric DAC apparatus, as seen in Fig. S3. IIa-type ultralow fluorescence diamonds with a culet size of 300 μm were used. A T301 stainless steel gasket was preindented by the diamonds and was drilled to generate a 100-μm-diameter cavity for loading the samples. The samples (1 mg/mL) in water, DMF, and ethanol were measured at room temperature. The sample in water as PTM was thermal treated in oven at 80 ˚C (353 K). The high-pressure evolution of steady-state PL spectra was collected utilizing a modified spectrophotometer (Ocean Optics, QE65000). A semiconductor laser with an excitation wavelength of 355 nm was employed for all fluorescence experiments. Note that all the parameters are fixed completely over each high-pressure PL experiment to avoid the effects of different excitation laser intensities and luminous fluxes on the resulting PL intensity of intrinsic CDs. Meanwhile, the *in situ* high-pressure absorption spectra of CDs were recorded with an optical fiber spectrometer (Ocean Optics, QE65000) using a deuterium-halogen light source.

Calculation details: The *ab initio* calculations based on the density-functional theory (DFT) as implemented in VASP code were carried out. Projector augmented wave basis and local density approximation for the exchange correlation term were employed. The cutoff energy for plane-wave basis and Monkhorst-Pack k-point mesh grid were set to 480 eV and Γ point, respectively. The single-layered graphene-like plate contains 54 carbon atoms and 18 hydrogen atoms, which is built in the center of 25 Å × 15 Å × 25 Å periodic cell for avoiding unphysical interactions. All of atoms were relaxed until the Hellman-Feynman force is less than 0.014 eV/Å. Because the DFT-LDA calculation underestimates the energy gap, we shift the energy gap of CD models by the scale factor of 2.00, which is determined by comparing the experimental HOMO-LOMO energy gap of Benzene molecule.

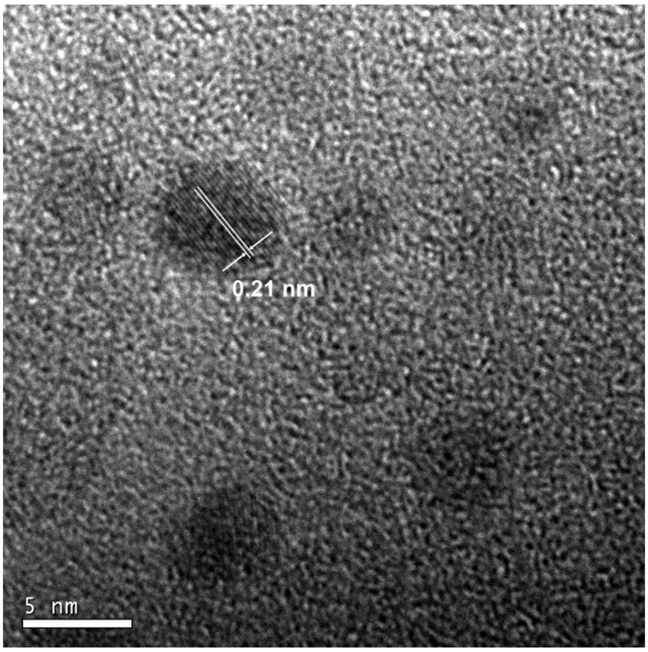

Figure S1. TEM image of CDs.

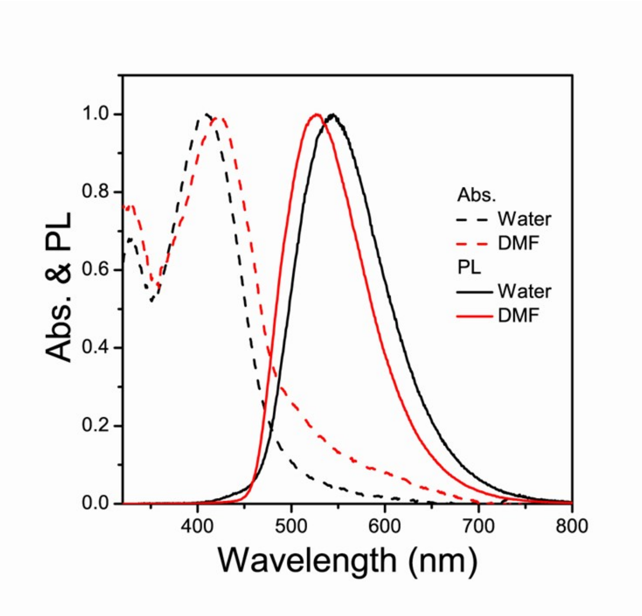

Fig. S2. Absorption (dashed lines) and PL (solid lines) spectra of CDs in water (black) and DMF (red) under atmospheric pressure. The CDs concentration in water or DMF is 0.1 mg/mL.

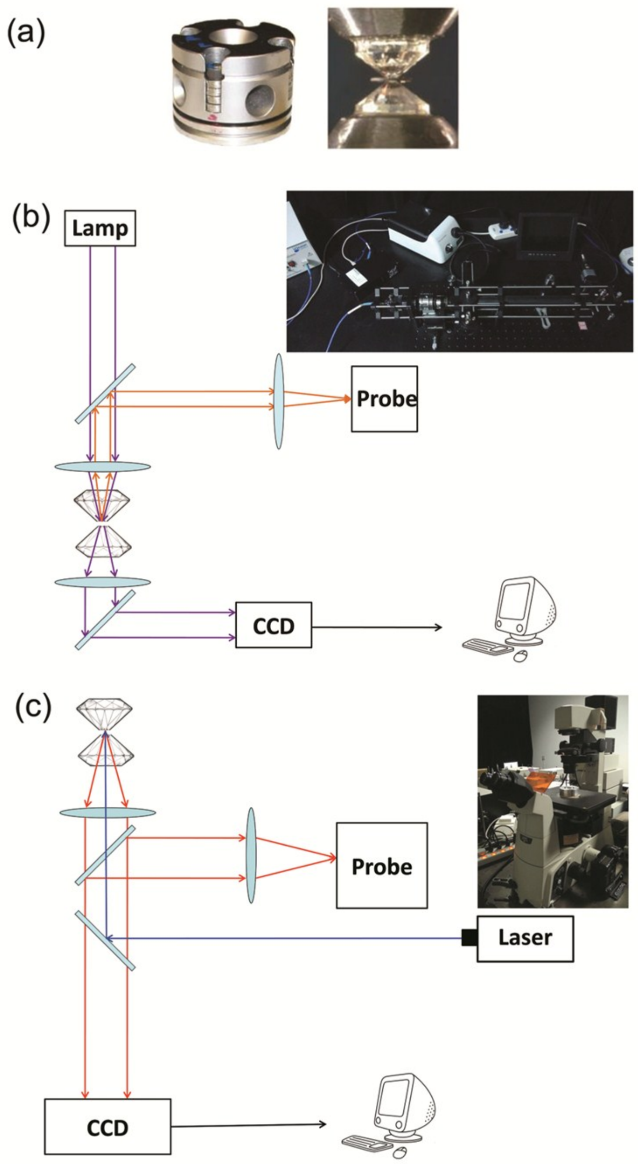

Fig. S3. (a) Image of DAC. Schematic drawing of *in situ* (b) absorption and (c) PL spectroscopy experiment setup based on DAC.

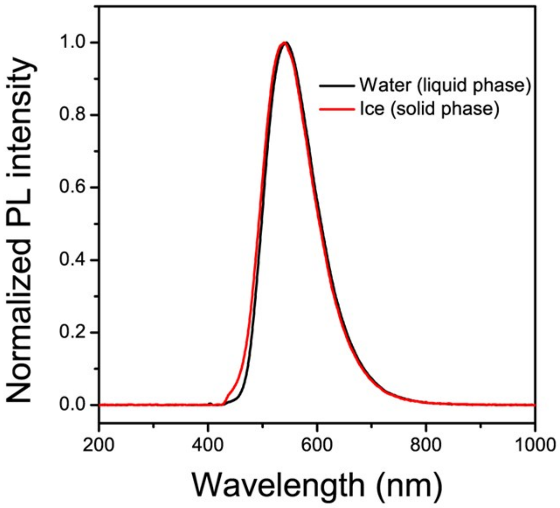

Fig. S4. PL spectra of CDs in water at room temperature (black line) and in ice at 0 ℃ (red line).

The CDs concentration in water is 0.1 mg/mL.

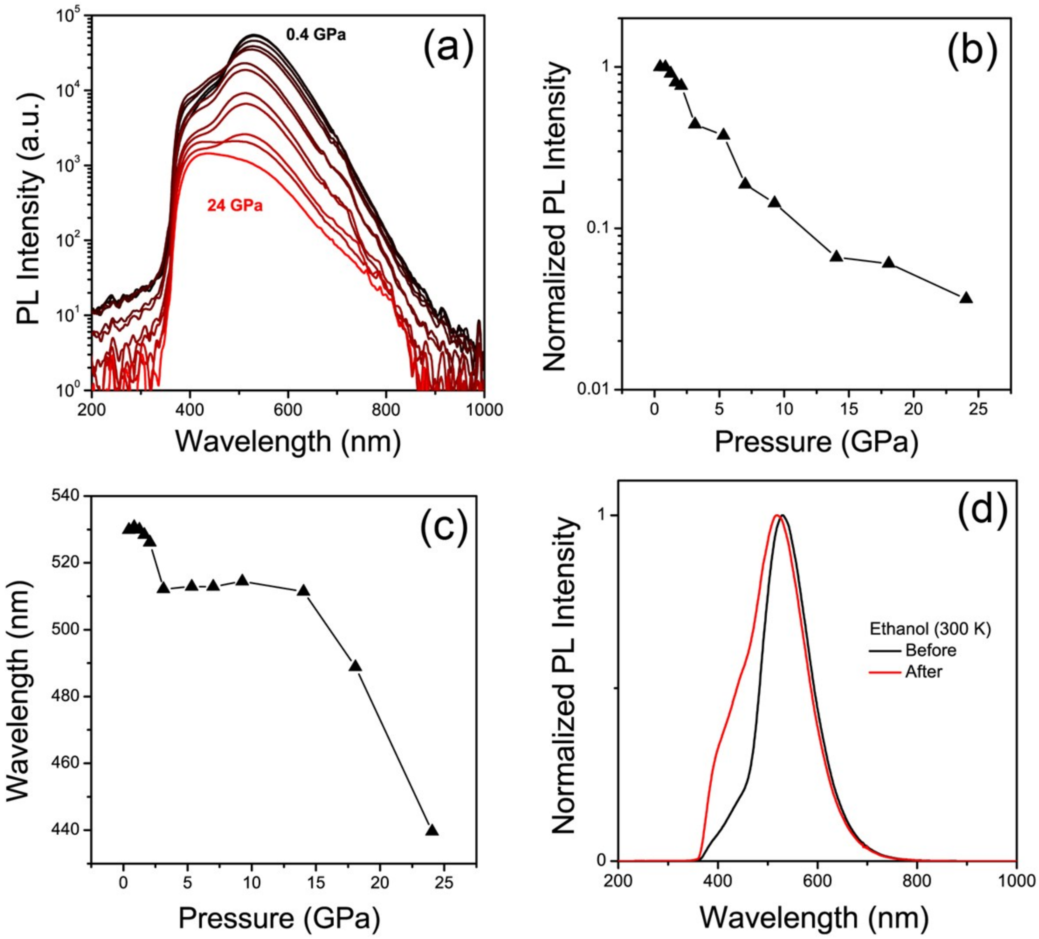

Fig. S5. (a) PL spectra evolution of CDs in ethanol with increasing pressure from atmospheric pressure to 24 GPa at room temperature (300 K). (b) PL peak and (c) integrated intensity of CDs in PTM as ethanol *vs.* pressure. (d) PL spectra before (black) and after (red) high pressure experiment in PTMs as ethanol at room temperature.

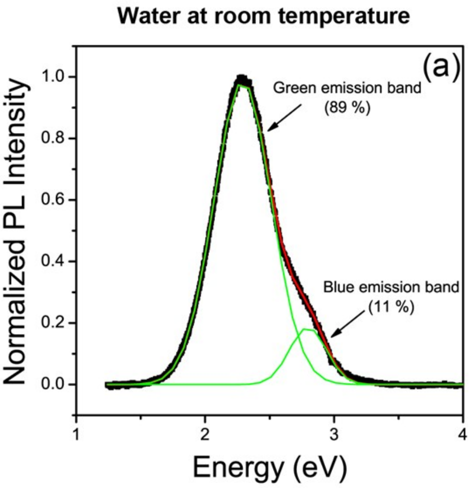

Fig. S6. Multi-peaks fitting (green lines) of PL spectrum of CDs after high pressure relaxation (black line). (a) The blue and green emission bands are 11% and 89% of the total PL band, respectively.

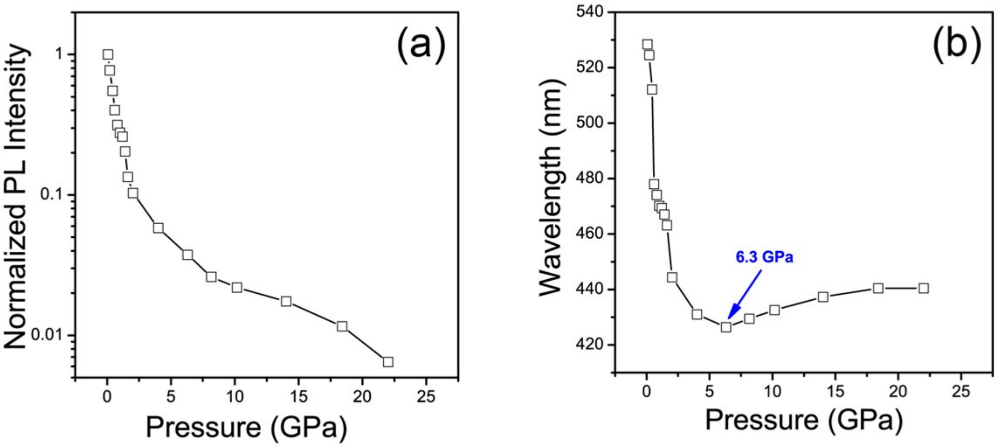

Fig. S7. (a) The normalized PL intensity and (b) PL peak wavelength of CDs in water *vs.* pressure, under high temperature treatment (353 K).

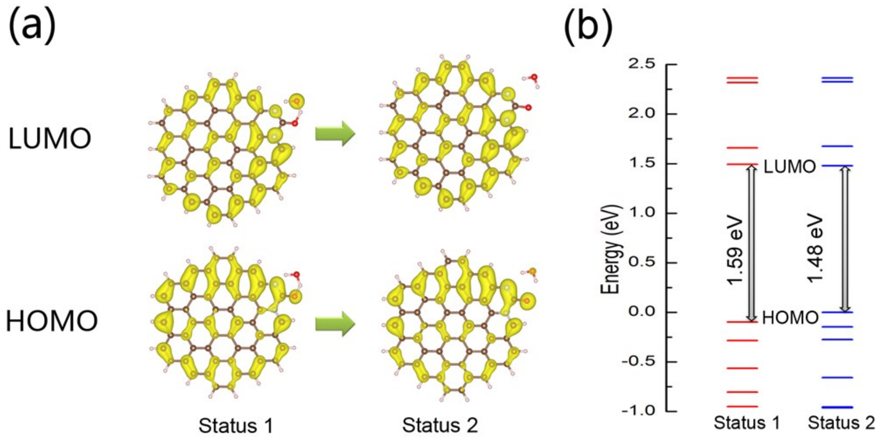

Fig. S8. Calculated structures of CD's model with one water molecule before (Status 1) and after (Status 2) structure relaxation. The charge distributions of LUMO and HOMO. The colored isosurface of charge density is 0.001 eV/Å^3. (b) Energy levels of CD's model with one water molecule before (Status 1) and after (Status 2) structure relaxation.

Table S1. Optical properties of CDs and h-CDs in dilute aqueous solutions (0.1 mg/mL).

	λ_{abs} [nm]	$\lambda_{em, max}$ [nm]	τ [ns]	τ_{av} [ns]	Φ_F [%]
CDs	410	525	4.5 (64%) 10.0 (36%）	6.5	16%
h-CDs	332	453	2.7 (33%) 10.3 (67%)	7.8	34%