Structural Evolution of Carbon Dots During Low Temperature Pyrolysis

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1. Materials Preparation

The CDs were prepared by hydrothermal carbonisation of D-(+)-glucose. Briefly, the precursor was dissolved in water (4% w/v) and placed in a Teflon-lined, stainless steel autoclave, which underwent treatment at 200 °C for 12 h. The obtained yellow solution was centrifuged at 10,000 rpm for 10 min to separate the liquid containing fluorescent CDs from the micro-spheres. The liquid phase containing CDs was then filtered using standard syringe filters and freeze-dried to obtain solid CDs, which are named HTC-CDs. These CDs are then pyrolyzed for two hours under different temperature in N_2 atmosphere, the products are named as CDs_350_N_2, CDs_550_N_2 and CDs_750_N_2, respectively.

2. Materials Characterisation

Ex situ Transmission electron microscopic (TEM) and high resolution TEM (HRTEM) images were obtained on a Jeol JEM 2010 microscope. The X-ray diffraction (XRD) patterns were performed using Panalytical Xpert Pro diffractometer with Cu-Kα radiation. Raman spectra were obtained with a Renishaw InVia Reflex Raman spectrometer with a wavelength of 633 nm. The Synchrotron X-ray total scattering experiment was carried out at BL22XU[1] at Spring-8 using the rapid acquisition pair distribution function (RA-PDF) technique.[2] CD samples were packed in polyimide capillaries with the inner diameter of 1.4 mm. X-ray wavelength was 0.17892 Å (E=69.296 keV), and the sample to detector distance was set to be 500 mm. For data

acquisition, 75 frames of 8 second data were collected for each sample to decrease signal-to-noise ratio. The signal from an empty container (a polyimide capillary) was subtracted from the raw data, and various other corrections were made.[3] The X-ray PDFs were obtained by a sine Fourier transformation of the powder diffraction data according to the equation

$$G(r) = \frac{2}{\pi}\int_{Q_{\min}}^{Q_{\max}} Q[S(Q)-1]\sin(Qr)dQ$$

where Q is the magnitude of the momentum transfer and $S(Q)$ is the total scattering structure function.[3] Because of the unfavorable signal-to-noise ratio at the high-Q regions, $Q[S(Q)-1]$ was truncated at Q_{max}=12.5 Å^{-1} before the transformation. The program PDFgetX2[4] was used for obtaining the X-ray PDFs. For PDF calculation DiffPy-CMI[5] programs was used.

The Fourier transformed infrared spectra (FTIR) of CDs were recorded with freeze-dried powders by using a Bruker Tensor 27 instrument equipped with diamond lens attenuated total reflectance (ATR) module in the range from 4000 cm^{-1} to 400 cm^{-1}. X-ray photoelectron spectroscopic (XPS) measurements on all CDs were performed using an AXIS Ultra DLD (Kratos Surface Analysis) setup equipped with an 180° hemispherical analyser, using Al $K_{\alpha 1}$ (1486.74 eV) radiation from a monochromatized X-Ray source at operating power of 300W (15 kV × 20 mA). The time-resolved *in-situ* TEM experiment was carried out on a double aberration corrected JEOL JEM 2200FS TEM/STEM *in-house* modified for Environmental *in-situ* gas experiments,[1] and operating at 200 kV in TEM mode. The microscope is equipped with an *in-column* Omega type electron energy loss filter, and with a DENS Solutions Wildfire heating holder with MEMS chips to support and heat up the materials. The MEMS chip contains a resistance to produce heat when electricity is applied. In the middle of the chips a series of small windows with silicon nitride membranes are used for imaging, with a thickness of around 100 nm. The sample was heated at 20 °C/min under N_2 atmosphere until 750 °C was reached with holding at 350 °C, 550 °C to observe the structural changes at those specific

temperatures. Pressure at the sample was fixed at 2 Pa throughout the experiment. The UV-Vis measurements were performed using Perkin Elmer Lambda LS 35 instrument. The CD samples were dispersed in DI water to obtain a dilute solution (0.1 mg/mL). The same solutions were also measured for PL using Perkin Elmer LS55 instrument with excitation of 350 nm. The solid-state PL measurement was done using two excitation lasers of 325 nm and 442 nm, respectively.

3. Supporting Figures and tables

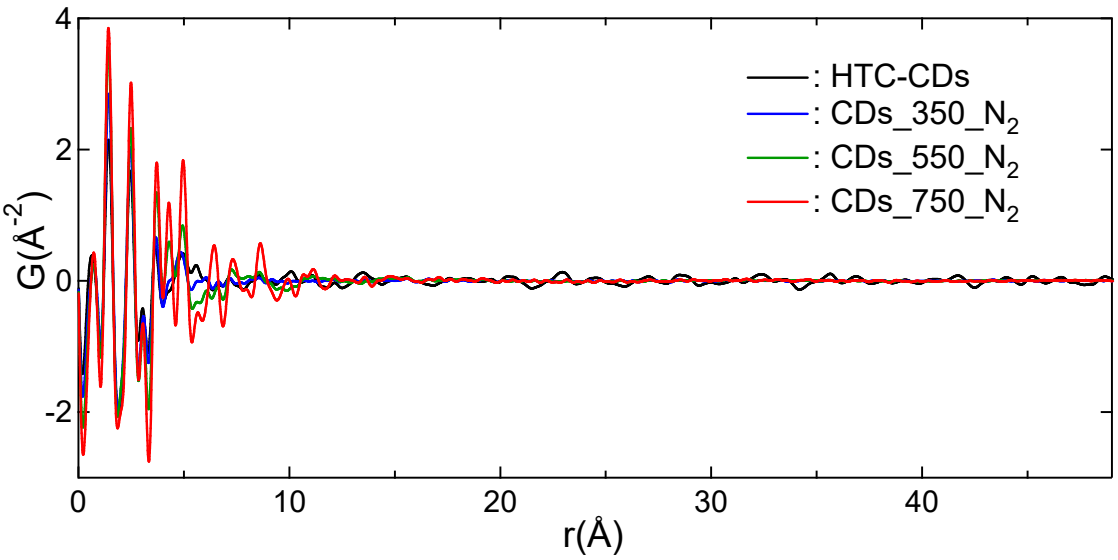

Figure S1. PDF spectra of all CD samples on a longer *r* range.

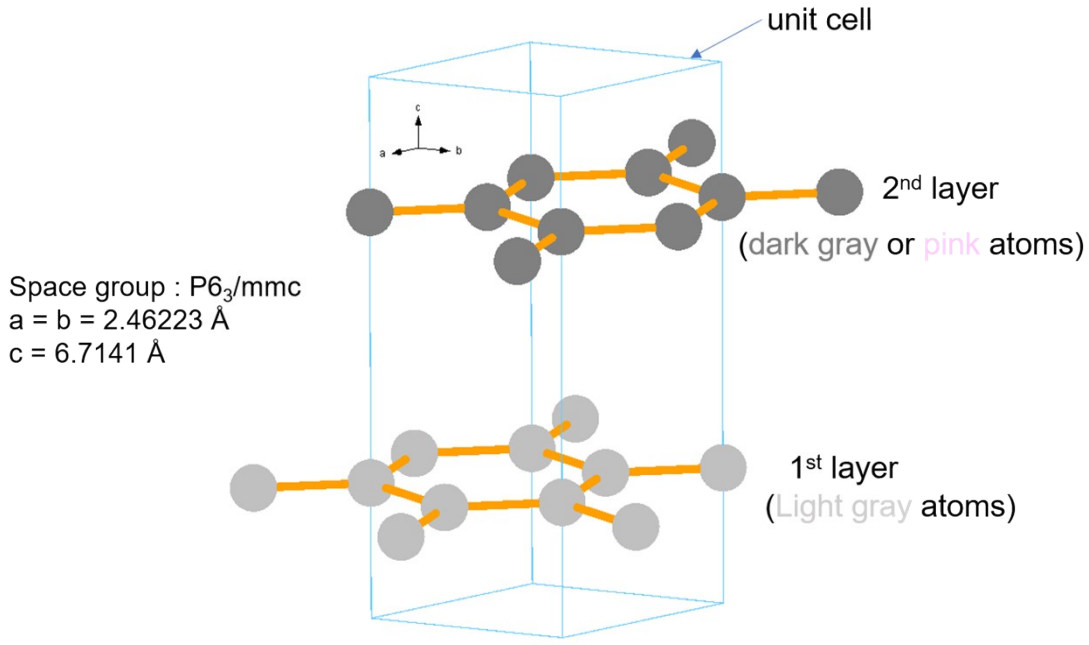

Figure S2. Graphite model based on which small aromatic cluster models shown in Figure 3 (b)-(d) were made to reproduce the experimental PDF spectra of all CD samples.

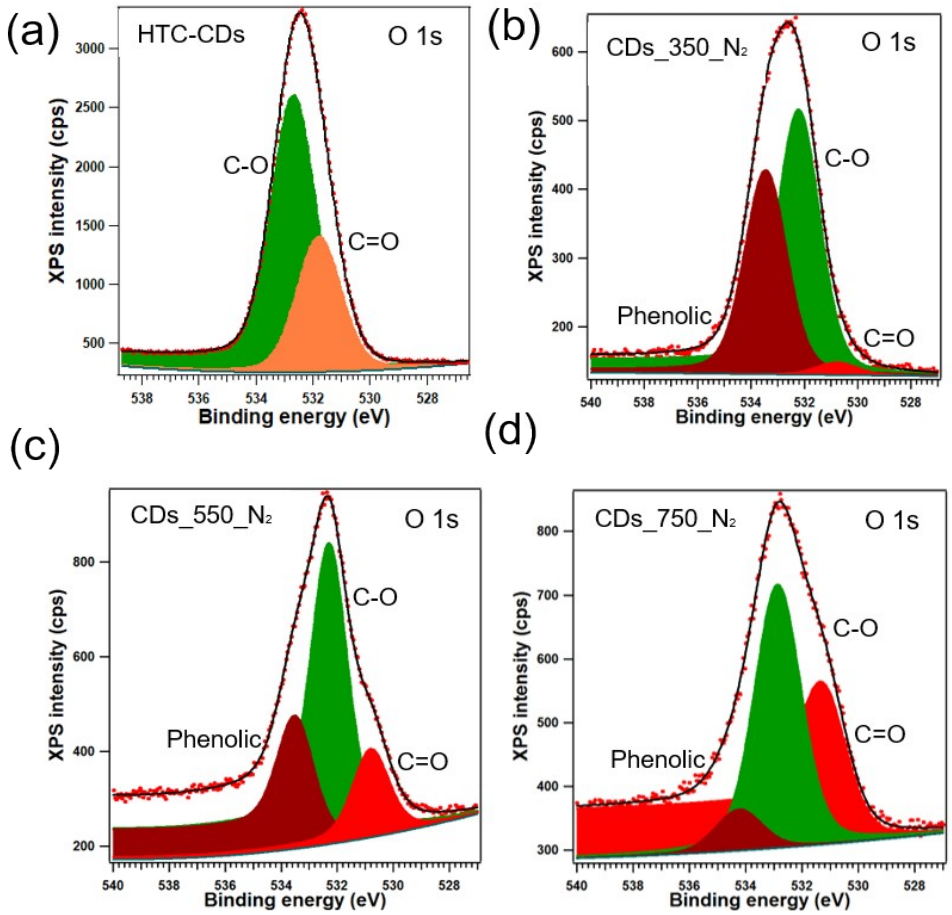

Figure S3. O 1s XPS spectra of CDs: (a) HTC-CDs, (b) CDs_350_N_2, (c) CDs_550_N_2, (d) CDs_750_N_2.

Table S1. Chemical composition and O 1s binding energy in different CDs (from XPS).

Samples	C=O/eV	C-O/eV	Phenolic/eV
CD_350_N_2	530.78	532.2	533.45
CD_550_N_2	530.82	532.29	533.5
CD_750_N_2	531.26	532.88	534.25

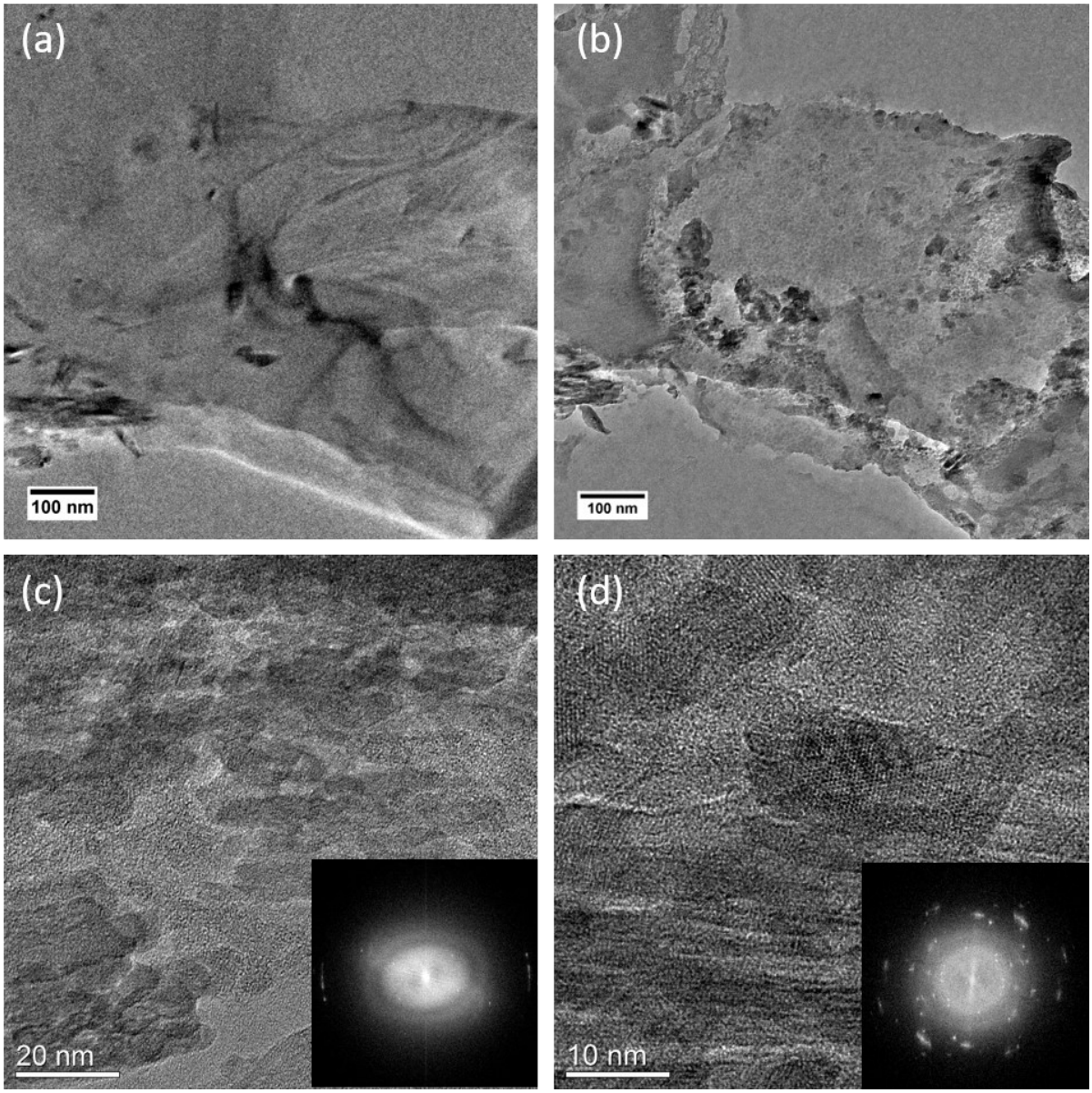

Figure S4. *in situ* TEM images of carbon matrix containing CDs at RT (a, c) and 750 °C (b, d).

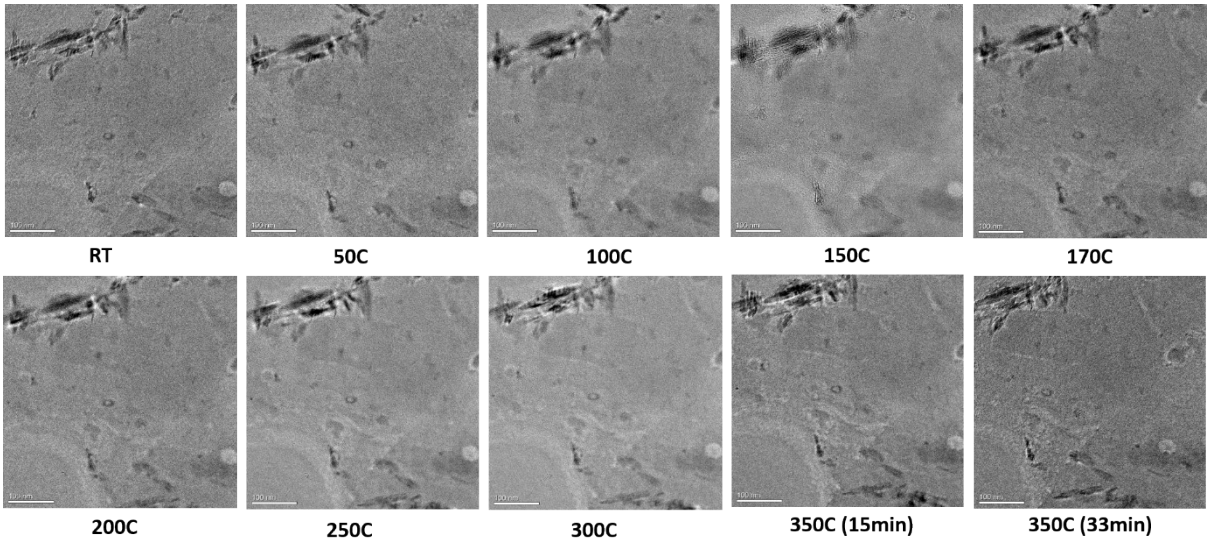

Figure S5. *in situ* TEM images of a temperature series from RT to 350 °C with a ramping rate at 20 °C/min (all scale bars are 100 nm).

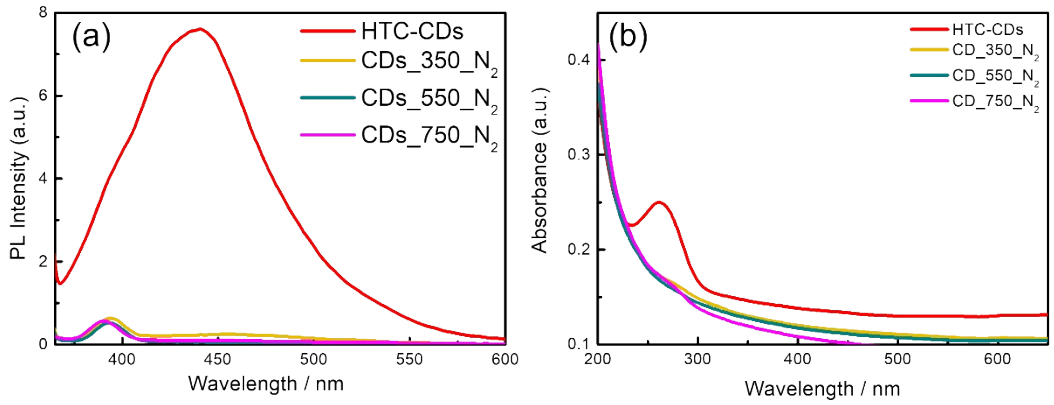

Figure S6. (a) PL and (b) UV-Vis spectra of all CD samples in diluted solution. the excitation wavelength for PL spectra are 355 nm.

References

(1) Watanuki, T.; Machida, A.; Ikeda, T.; Ohmura, A.; Kaneko, H.; Aoki, K.; Sato, T. J.; Tsai, A. P. Development of a Single-Crystal X-ray Diffraction System for Hydrostatic-Pressure and Low-Temperature Structural Measurement and Its Application to the Phase Study of Quasicrystals. *Philos. Mag.* **2007**, 87, 2905-2911.

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(3) Egami, T.; Billinge, S. J. L. *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*: Pergamon Press Elsevier: Oxford, England, 2003.

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