Supporting information for

Synthesis of coal pitch-derived carbon dots with yellow emission and improved photoluminescence quantum yield through pre-surface engineering and nitrogen doping

Sha Ye,^a Qing Chang,^a* Chaorui Xue,^a Ning Li,^a Bin Liu,^a Yaling Wang,^a Jinlong Yang^{a,b} and Shengliang Hu^a*

^a Research Group of New Energy Materials and Devices, State Key Laboratory of Coal and CBM Co-Mining, North University of China, Taiyuan 030051, China

^b State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

*Corresponding authors. changneu@gmail.com (Q. Chang), hsliang@yeah.net (S.L. Hu).

Experimental section

Materials

Coal pitch was purchased from Hengshui Zehao Rubber Chemical Industry. Concentrated nitric acid (14.4 M), DL-aspartic acid (ASP), N, N-dimethylformamide (DMF), absolute ethanol (EtOH), dichloromethane (DCM), toluene (TL), ethyl acetate (EA) and polymethyl methacrylate (PMMA) were purchased from Aladdin Chemical Co., Ltd. (Shanghai, China). All reagents were used directly and without further purification.

Synthesis of the samples

2 g of coal pitch was dispersed into 80 mL of concentrated HNO₃ (14.4 M), which was stirred for 12 h at 60 °C. After the solution was centrifuged, the collected precipitates were washed with a large amount of deionized water until the pH was neutral to obtain nitro groups modified coal pitch (NO₂-coal pitch). Then 80 mg of NO₂-coal pitch and a certain amount of DL-aspartic acid (ASP) were dispersed in 20 mL of absolute ethanol. The obtained mixture was transferred to a 50 mL Teflon-lined stainless steel reactor for a solvothermal reaction at a certain temperature for 12 h and then cooled to room temperature. After the reaction solution was centrifuged, the obtained upper layer was diluted and purified using a dialysis bag of 1000 Da for 72 h. The solution in the dialysis bag was freeze-dried to obtain yellow-brown powders, which emit yellow emission and were named as y-CDs. The mass ratio of NO₂-coal pitch to ASP was set at 3:2, 1:1 and 2:3, and the sovolthermal temperature was set at 160, 180 and 200 °C, repectively. To understand the effect of ASP on the PL properties, the control CDs in the absence of ASP were synthesized using the identical method with y-CDs, which emit green emission and were named as g-CDs. The production yields of y-CDs and g-CDs after purification were calculated to be about 7.46% and 10.62% (w/w), respectively.

For comparison, a series of other control samples were also prepared. With other conditions unchanged, 80 mg of coal pitch was solvothermally treated in 20 mL of absolute ethanol and the obtained sample was named as CDs-1. Another control sample was synthesized by solvothermal reaction of coal pitch and ASP in absolute ethanol, and named as CDs-2. Moreover, pure ASP was solvothermally treated in absolute ethanol, and the obtained CDs were named as CDs-3.

Fabrication of light-emitting diode (LED)

UV-LED chips with the emission peak wavelength centered at 365 nm were used for the fabrication of LEDs. 1 g of PMMA was dissolved in 10 mL toluene solution to prepare 0.1 g mL⁻¹ PMMA solution. A certain amount of y-CDs were dispersed in PMMA solution under ultrasonic treatment. The mixed y-CDs/PMMA solution was dropped on the protective cover of the LED chip. After the film was dry under room temperature, the cover with y-CDs/PMMA was put back on the LED chip and the device was obtained. The properties of the fabricated LED devices were measured by PR655.

Characterization

The transmission electron microscopy (TEM) images of CDs were characterized using a JEOL JEM-2100F electron microscope. Phase and crystallinity were analyzed using X-ray diffraction (XRD) on a DX-2700BH diffractometer equipped with a Cu Kα X-ray source operating at 40 kV and 40 mA. Fourier transform infrared (FTIR) spectra were measured on a Thermo Fisher Scientific Nicolet iS20 spectrometer. Raman spectra were collected on a Horiba LabRAM HR Evolution spectrometer under excitation of 532 nm. X-ray photoelectron

spectroscopy (XPS) spectra were recorded using a Thermo Scientific K-Alpha equipped with a multi-channel detector. UV-Vis absorption spectra were obtained using a Shimadzu UV-2550 UV-Vis spectrophotometer. Photoluminescence (PL) spectra and absolute PL quantum yield were measured using an Edinburgh FS5 spectrofluorometer equipped with an integrating sphere. Time-resolved PL spectra were tested on the Hamamatsu C11367 fluorescence lifetime analyzer.



Figure S1. TEM and HRTEM (inset) images of the g-CDs.



Figure S2. (a) The full survey of XPS spectra and (b) O 1s high-resolution XPS spectra of y-

CDs and g-CDs.



Figure S3. (a) PL emission spectra of blank (black line) and g-CDs in TL (red line) used for measuring the photoluminescence quantum yield. (b) Time-resolved PL decay curves of g-CDs under 470 nm excitation.



Figure S4. PL emission spectra of the y-CDs in TL with different concentrations under excitation of 500 nm.



Figure S5. PL emission spectra and excitation-emission mapping of y-CDs in (a, b) DCM, (c,

d) EA, (e, f) DMF and (g, h) EtOH under excitation of different wavelengths.



Figure S6. (a) Variation of the PL intensity of y-CDs with irradiation time under 500 nm laser irradiation at 150 W. (b) Variation of the PL intensity of y-CDs with irradiation time under UV light irradiation at 60 W. (c) Variation of the PL intensity of y-CDs with heating temperatures.



Figure S7. PL emission spectra and the excitation-emission mapping of (a, b) CDs-1, (c, d)

CDs-2, and (e, f) CDs-3 under excitation of different wavelengths.



Figure S8. PL emission spectra and the excitation-emission mapping of (a, b) C-CDs, (c, d)

U-CDs, and (e, f) T-CDs under excitation of different wavelengths.



Figure S9. PLQY of (a) U-CDs and (b) T-CDs.



Figure S10. PL emission spectra of the y-CDs synthesized (a) with different mass ratios of NO₂-coal pitch to ASP, and (b) different solvothermal temperatures under 500 nm excitation.



Figure S11. PLQY of y-CDs/PMMA film.



Figure S12. (a) Variation of the PL intensity of y-CDs/PMMA film with irradiation time under UV light irradiation at 60 W. (b) Variation of the PL intensity of y-CDs/PMMA film with heating temperatures. (c) Variation of the PL intensity of y-CDs/PMMA film with storage time under ambient conditions.



Figure S13. (a) The emission spectrum of the LED with 0.25 mg mL⁻¹ of y-CDs in PMMA and (b) the corresponding CIE color coordinate. (c) The emission spectrum of the LED with 1.5 mg mL⁻¹ of y-CDs in PMMA and (d) the corresponding CIE color coordinate.



Figure S14. (a) The emission spectra of the LEDs with 1 mg mL⁻¹ of y-CDs in PMMA at different drive voltages. (b) The corresponding CIE color coordinates.

Table S1. Elemental analysis of g-CDs and y-CDs from XPS results.

Samples	C (at.%)	O (at.%)	N(at.%)	O/C (atomic ratio)
g-CDs	80.91	14.54	4.55	0.18
y-CDs	80.91	13.07	6.02	0.16

Table S2. The photoluminescence decay time (τ) and their relative amplitude (A) of the samples, which are derived from the time-resolved PL spectra in Figure 4b and Figure S3b by dual-exponential decays.

Samples	Decay t	Decay time (ns)		plitude (%)	
	τ_1	τ_2	A_1	A ₂	Average metime t (iis)
g-CDs	3.01	8.65	90%	10%	4.38
y-CDs	4.03	6.49	67%	33%	5.21

Materials	Unit price	Consumption	Price
Coal pitch	\$556.8/t	8.6 g	\$0.01
HNO ₃	\$8.35/500 mL	344 mL	\$5.74
DL-aspartic acid	\$4.3/25g	4.9 g	\$0.84
Ethanol	\$7.36/500 mL	1,820 mL	\$26.79
	\$22.20/		
CI	\$33.38/g		

Table S3. The price estimation of the obtained y-CDs.

Table S4. Properties of the LED with 1 mg mL⁻¹ of y-CDs in PMMA under different driving voltages.

Voltage (V)	CIE (x, y)	CCT (K)	CRI	PL peak (nm)
3.0	(0.56, 0.41)	1730	81	624
3.1	(0.56, 0.41)	1788	83	630
3.2	(0.56, 0.42)	1810	81	628