Electronic Supplementary Information

Insight into mechanism of photoluminescence of carbon nanoparticles derived from cryogenic studies

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Experimental part

Synthesis

"Violet" C-dots (VCD): 0.5 g of β-alanine was dissolved in 2 ml of distilled water and treated in MW oven (600 W, 1.5 min). The obtained material was diluted with distilled water and followed by repeated centrifugation with the collection of supernatant. The supernatant solution was filtered through a 50 nm-membrane filter and after that was deposited on the quartz substrate and dried to form the film.

Luminescence measurements

Absorption spectra were recorded using a Specord 200 spectrophotometer (Analytik Jena, Germany). Excitation and fluorescence spectra at 300 K were obtained using LUMINA fluorescence spectrometer (Thermo Scientific, USA). The photoluminescence steady-state spectra at different temperatures were excited by UV lamp through grating monochromator (λ_{ex} = 340 nm) and CW He-Cd laser (λ_{ex} = 325 nm), and registered using the high-resolution grating monochromator and the Hamamatsu R9110 PMT operated in the photon counting mode. Temperature of the sample was varied from 10 K to 300 K using closed cycle helium cryostat CS204AE-FMX-1AL (Advanced Research Systems, USA) equipped with a LakeShore 335 temperature controller (Lake Shore Cryotronics, USA). He-Cd was also used as light source for measurements of the decay of phosphorescence.

The technique of the time-correlated photon counting was used to study the lifetimes of the CDs. The photoluminescence decay curves were measured with the fluorescence lifetime spectrometer FluoTime200 (PicoQuant, Germany) as well as the setup based on the multi-photon counting system TimeHarp 260 NANO and the single photon detector PMA 182 (PicoQuant, Germany). An excitation was provided by the pulsed laser diode heads PLS-270 (λ_{ex} = 270 nm), PLS-330 (λ_{ex} = 330 nm) and PLS-360 (λ_{ex} = 360 nm) controlled by the PDL 800-D pulse generator (PicoQuant, Germany), as well as the 3-rd (λ_{ex} = 355 nm) harmonic of the YAG:Nd^{3+} pulsed laser (NL202 model, EKSPLA, Lithuania) synchronized with TimeHarp 260 NANO system.

The time-resolved emission spectra (TRES) were measured under excitation by He-Cd laser and YAG:Nd^{3+} laser. The series of the decay curves were obtained with steps of 20 nm and 10 nm at 355 nm and 325 nm excitation, respectively.

Complementary spectroscopic data

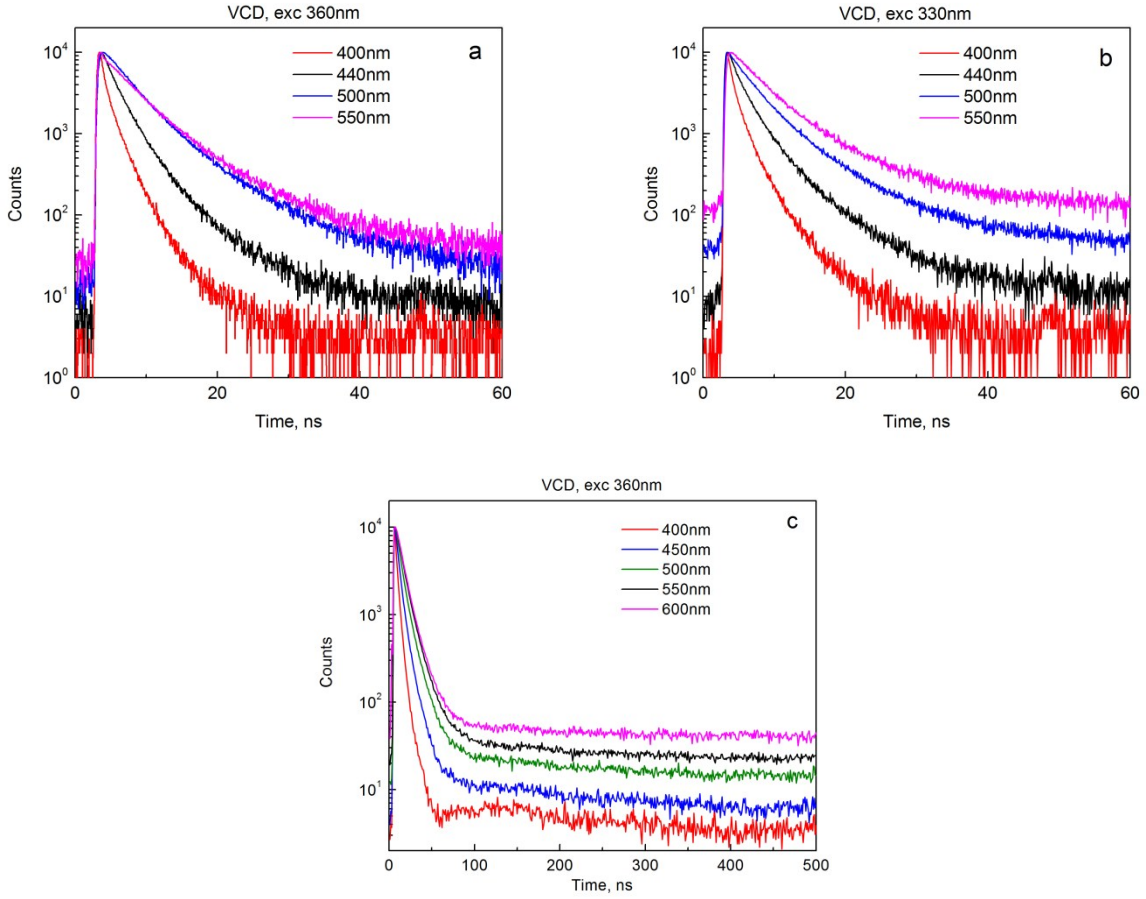

Fig. 1 SI. The luminescence decay curves at different excitation wavelengths (a,c) λ_{ex} = 360 nm, (b) λ_{ex} = 330 nm and different temperatures (a,b) 300 K and (c) 10 K measured at indicated emission wavelengths. The time scale in Fig.1c SI is specially extended to show the contribution of phosphorescence decay. The decay curves were fitted by two exponents and the corresponding decay times are presented in Tables 1 SI and 2 SI below.

Table 1 SI. Luminescence decay times at 300 K at different emission and excitation wavelengths.

Excitation wavelengths	Decay times (ns) and Weight	Emission wavelengths			
		400 nm	440 nm	500 nm	550 nm
270 nm	t_1	1.5	2.6	3.7	4.3
	A_1	0.85	0.89	0.85	0.80
	t_2	3.8	7.7	10.2	11.0
	A_2	0.15	0.11	0.15	0.2
330 nm	t_1	1.2	2.6	3.6	4.2
	A_1	0.82	0.84	0.82	0.81
	t_2	3.9	7.5	10.0	11.4
	A_2	0.18	0.16	0.18	0.19
360 nm	t_1	1.7	2.4	3.9	4.4
	A_1	0.87	0.91	0.87	0.87
	t_2	4.3	7.6	11.2	11.7
	A_2	0.13	0.09	0.13	0.13

Table 2 SI. Luminescence decay times at 10 K at different emission wavelengths.

Excitation wavelength	Decay times (ns) and Weight	Emission wavelengths				
		400 nm	450 nm	500 nm	550 nm	600 nm
360 nm	t_1	2.4	4.1	6.4	8.1	8.4
	A_1	0.83	0.84	0.91	0.96	0.98
	t_2	5.5	9.7	16.6	29.0	29.0
	A_2	0.17	0.16	0.09	0.04	0.02

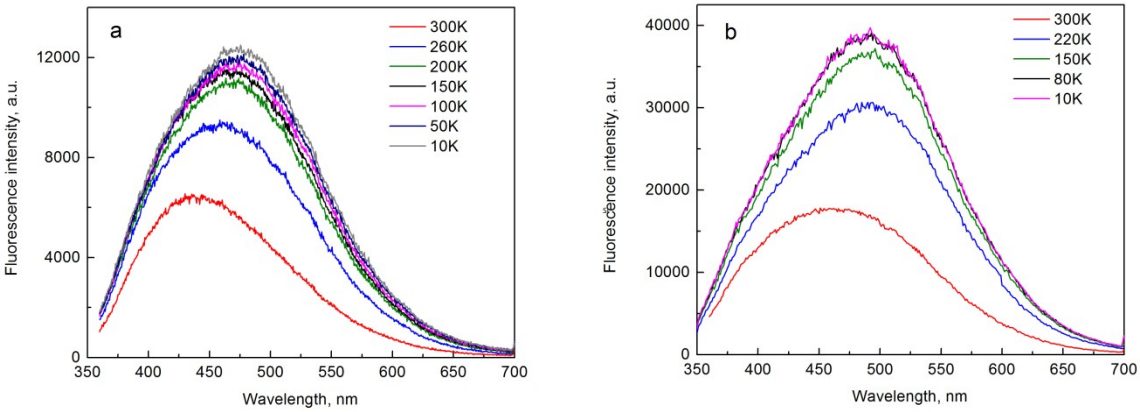

Fig. 2 SI. Photoluminescence spectra in the broad temperature range at (a) λ_{ex} = 340 nm and (b) λ_{ex} = 325 nm.

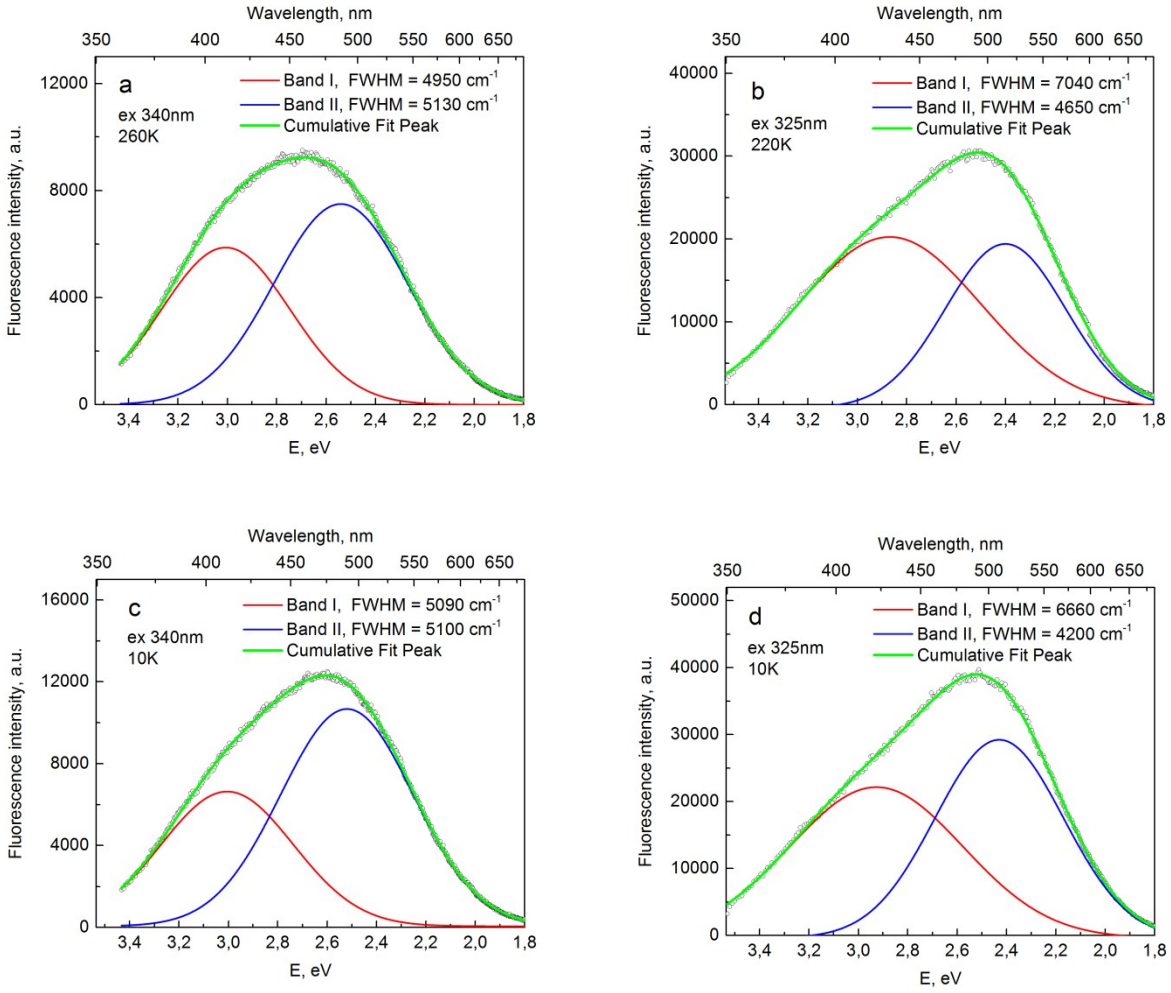

Fig. 3 SI. Examples of the deconvoluted spectra by Gaussian function at indicated excitation wavelengths and temperatures.

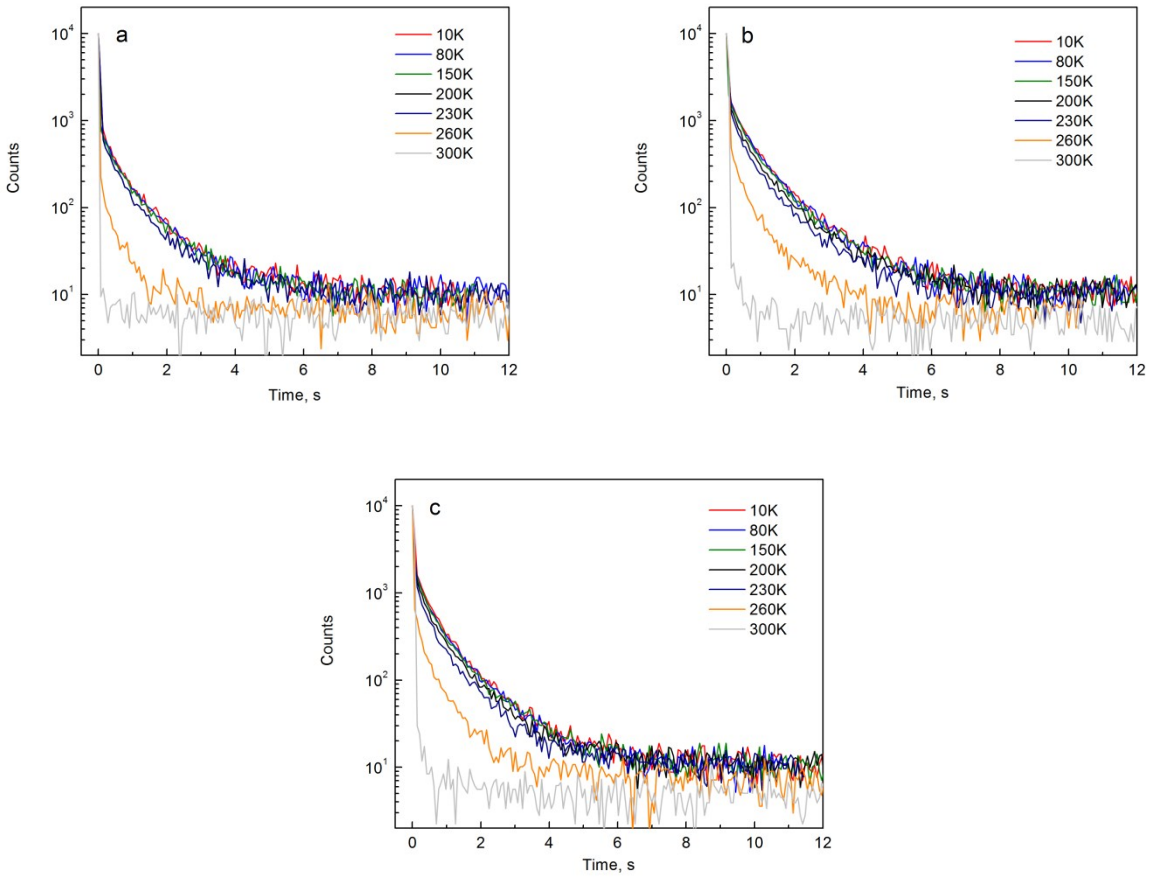

Fig. 4 SI. Temperature dependences of the phosphorescence decay curves of Band II recorded at emissions (a) 440 nm, (b) 510 nm and (c) 590 nm; λ_{ex} = 325 nm.

Table 3 SI. Average decay times, τ_{avr} (s), of the phosphorescence Band II at different temperatures and emission wavelengths.

Excitation and emission wavelengths		Temperature				
λ_{ex}	λ_{em}	10 K	80 K	150 K	220 K	290 K
325 nm	440 nm	0.62	0.63	0.57	0.56	0.2
	510 nm	0.64	0.65	0.64	0.58	0.21
	590 nm	0.61	0.58	0.55	0.54	0.18

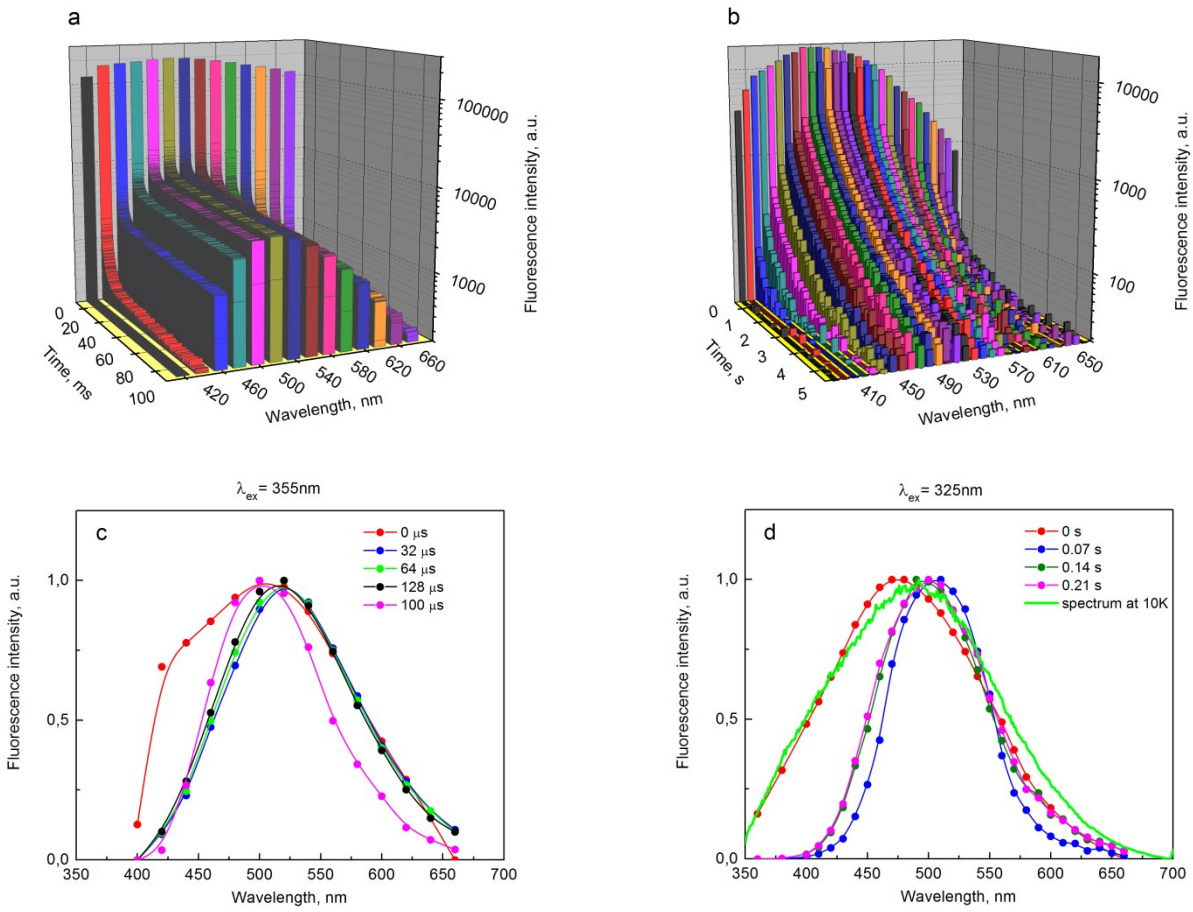

Fig. 5 SI. (a,b) 3D and (c,d) normalized TRES compared with the steady-state luminescence spectra of CDs at 10 K; (a,c) λ_{ex} = 355 nm, (b,d) λ_{ex} = 325 nm.

Table 4 SI. Spectral characteristics of the Band II extracted from the time-resolved emission spectra.

Excitation wavelengths	Time delay	λ_{max}, nm	FWHM, cm^{-1}
355 nm	32 μs	519	4560
	64 μs	517	4940
	128 μs	514	4850
	512 μs	490	5090
	100 μs	503	4240
325 nm	0.07 s	504	3400
	0.14 s	498	4050
	0.21 s	498	4250
	1.05 s	495	4200