Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Rapid in situ anti-solvent recrystallization synthesis of wide-spectrum CDs@$BaCl_2$ composite for white LEDs

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Contents

1. Experimental section

1.1 Chemicals and materials

NH_2CONH_2(A.R.) and $BaCl_2{\cdot}2H_2O$ (A.R.) were purchased from Guangzhou Chemical Reagent Co., Ltd (Guangzhou, China). Citric acid ($C_6H_8O_7{\cdot}H_2O$, 99.5%) and absolute ethanol (A.R.) were purchased from Aladdin Industrial Inc. and Tianjin Fuyu Fine Chemical Co. Ltd (Tianjin, China), respectively. All the reagents were utilized directly without any further purification.

1.2 Synthetic procedures

N-doped CDs were prepared according to the method reported by Qu etc.[S1] In a typical process, 2.000 g citric acid and 2.000 g urea were added to 20.0 ml distilled water under stirring to form a homogeneous solution. Then, the solution was heated for about 5 minutes in a domestic microwave oven with a power of 650 W. The colorless liquid gradually transformed into a brown gel and ultimately into a dark-brown solid. The obtained-precursor solid was dissolved in 10.0 mL deionized water and centrifuged at a speed of 10000 rpm to remove the aggregated particles. To further purify the CDs, the upper solution was dialyzed in deionized water using membranes (MWCO = 1.0–10.0 KD) for three times. The obtained CDs solution was freeze-dried, and some fluffy dark-brown powders were collected as the final product. The CDs@$BaCl_2$ hybrid phosphors were synthesized in an anti-solvent process in a water-alcohol phase. Firstly, CDs solutions with different concentrations (0.1, 0.5, 1.0 mg/mL) were prepared by dispersing the as-prepared CDs powders into DI water. Then, 0.5000 g, 1.0000 g, or 1.8600 g of inorganic salt $BaCl_2{\cdot}2H_2O$ was added into 5.0 mL of the CDs solution under stirring until it is completely dissolved; the value of 1.8600 is estimated by the saturated solubility of $BaCl_2{\cdot}2H_2O$ in water. Subsequently, 50.0 mL absolute ethanol was poured into the mixed solution, after which the clear solution immediately turned into a milky turbid liquid. After

washing the white sediment with absolute ethanol for 5 times and drying it at 200 °C under argon atmosphere, a fine white powder sample named CDs@$BaCl_2$ was obtained.

1.3 Characterization

The surface morphology of CDs@$BaCl_2$ composite phosphors is characterized by a confocal microscopy and field emission scanning electron microscope (FE-SEM, JEOL JSM-7001F). X-ray diffractometer PW3040/60 was applied to attain the X-ray powder diffraction (XRD) patterns of the synthesized CDs@$BaCl_2$ composite. A transmission electron microscope (TEM, JEM 2100F) was used to figure out the microstructure of the composite. The functional groups of the samples were analyzed using a Fourier transform infrared spectrometer (Vertex70, Bruker, Germany), with the scanning range setting from 4000 to 800 cm^{-1} with a resolution ratio of 8 cm^{-1}. X-ray photoelectron spectroscopy (XPS, Escalab 250Xi) was used to analyze the surface electronic structure. Raman spectrum was recorded by a laser Raman spectrometer (Thermo Scientific, USA) under a 532 nm laser. Photoluminescence (PL), photoluminescence excitation (PLE) spectra, and the photoluminescence quantum efficiency (PLQE) of the samples at RT were collected using a HITACHI F-7000 spectrometer. The temperature-dependent PL spectra and PL decay curves were measured using an Edinburgh FLS980 assembled fluorescence lifetime and steady-state spectrometer. The PL decay curves were monitored at the characteristic emission peak wavlength of the samples and a 405 nm laser was used as the excitation source. A high-power WLED prototype was fabricated by assembling the green-emitting CDs@$BaCl_2$ phosphor, commercial blue-emitting phosphor (BAM:Eu^{2+}, Shenzhen looking long technology co., LTD)**,** and commercial red-emitting phosphor (No. 0763, Grirem Advanced Materials Co., Ltd.) onto a 420 nm NUV LED chip. The electroluminescence (EL) spectra of the fabricated WLEDs were recorded on a PMS-80 LED spectrophotocolorimeter (EVERFINE, China). The commercial phosphors of BSS:Eu^{2+} and *β*-Sialon were bought from Shenzhen looking long technology co., LTD.

Reference：

S1 Zhou, Y. Zhai, S. Qu, D. Li, P. Jing, W. Ji, D. Shen and A. L. Rogach, Electrostatic assembly guided synthesis of highly luminescent carbon-nanodots@$BaSO_4$ hybrid phosphors with improved

stability, *Small*, 2017, **13**, 1602055.

2. Supplementary figures

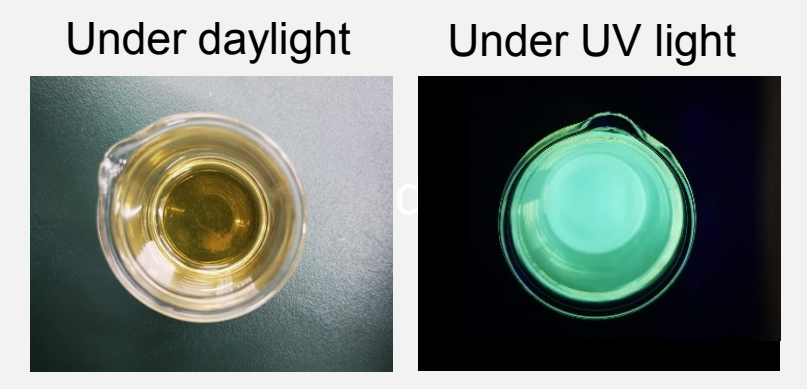

Fig. S1 Digital images of the as-prepared CDs solution (0.1 mg/mL).

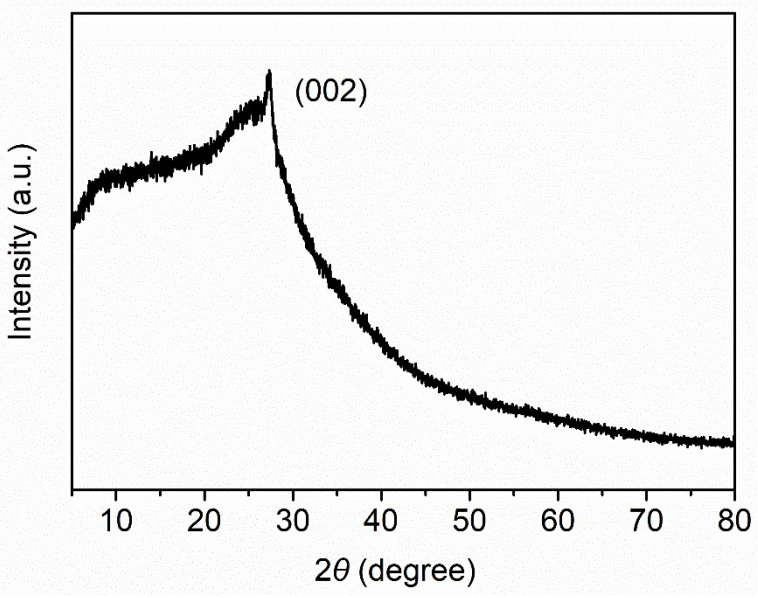

Fig. S2 XRD patterns of the prepared CDs.

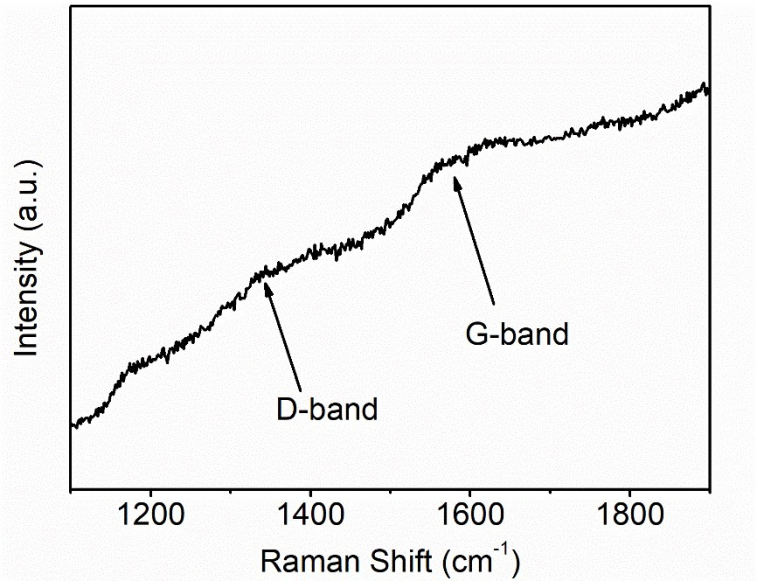

Fig. S3 Raman spectrum of the prepared CDs.

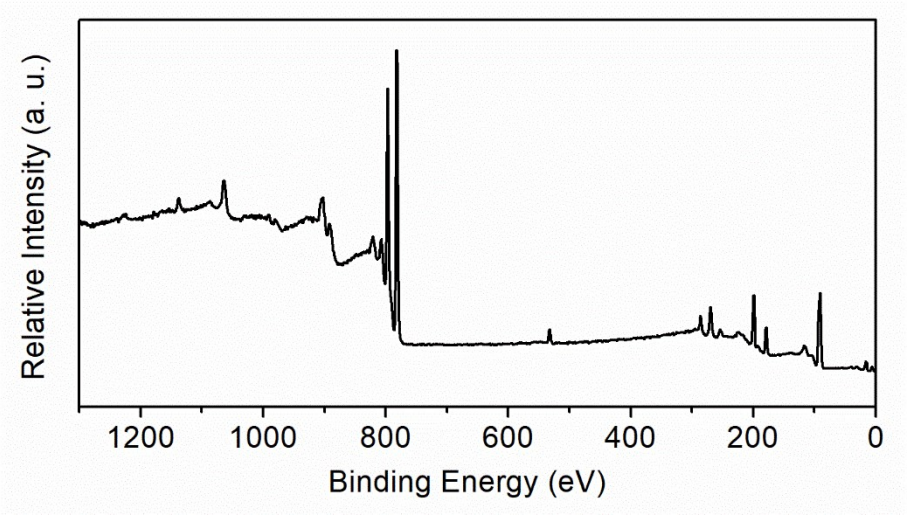

Fig. S4 XPS survey spectrum of CDs@$BaCl_2$.

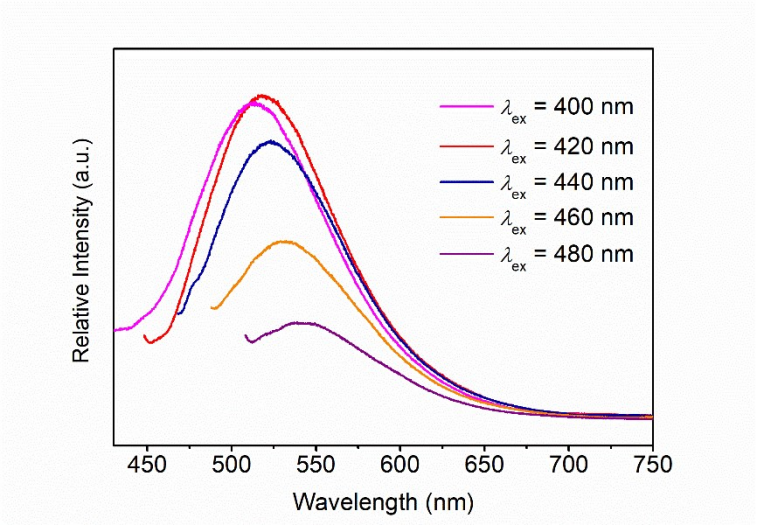

Fig. S5 PL spectra of CDs@$BaCl_2$ under different excitation wavelengths.

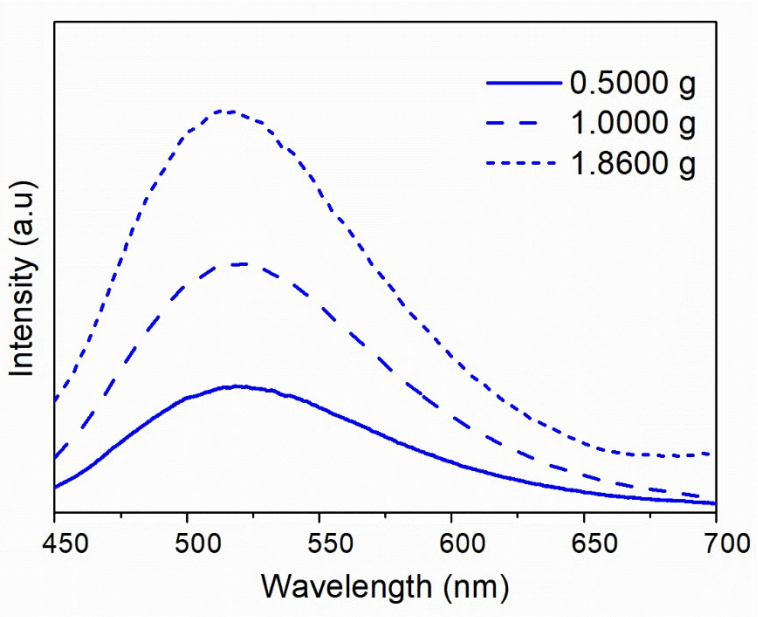

Fig. S6 PL spectra of the CDs@$BaCl_2$ phosphors made with different weights of $BaCl_2$.

3. Supplementary table

Table S1 Calculated lifetimes of CDs@$BaCl_2$ and CDs solution.

	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ_{ave} (ns)	R^2
CDs@$BaCl_2$	4.68	15.4	10.59	84.6	9.68	0.9989
CDs solution	4.65	63.1	9.18	36.9	6.32	0.9997