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Supporting Information

Regulating the photoluminescence of carbon dots via a

fluorine-doping derived surface-state-controlling strategy

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Experimental Section

Chemicals and materials

O-PD (o-phenylenediamine), 4-fluoro-1,2-phenylenediamine (4-fluoro-o-PD), pbenzoquinone (p-BQ), and CBL were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). Alanine (Ala), arginine (Arg), cysteine (Cys), glutamine (Gln), glycine (Gly), glutamic (Glu), glutathione (GSH), homocysteine (Hcy), lysine (Lys), phenylalanine (Phe), serine (Ser), tyrosine (Tyr), ascorbic acid (AA), leucine (Leu), VB1, VB6 and glucose were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents are of analytical grade and used as received. Deionized water (18 MΩ cm) was used for all experiments.

Instrumentations

Ultraviolet-visible (UV-Vis) spectra were collected on a Hitachi U-3900 UV-Vis spectrophotometer (Hitachi High Technologies, Japan). Photoluminescence (PL) spectra were recorded on an F-7000 spectrophotometer (Hitachi High Technologies, Japan). PL lifetime was measured using FluoroMax-4TCSPC spectrofluorometer (HORIBA Jobin Yvon, USA). Transmission electron microscopy (TEM) was performed using a JEM 2100F transmission electron microscope (JEOL, Japan). Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet-6700 FT-IR spectrophotometer (Thermo Instruments Inc., USA). The electrochemical data were measured by CHI660E electrochemical workstation (Chenhua Instrument Co., Shanghai, China). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 Xi system (Thermo Instruments Inc., USA).

Energy levels assay of CDs

To estimate their HOMO and LUMO energy levels, cyclic voltammetry (CV) assay was carried out by using a standard three electrode system with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. CV was recorded in acetonitrile containing saturated CDs and 0.1 mol/L TBAPF₆ as supporting electrolyte. The HOMO and LUMO energy levels in eV of CDs were calculated according to the following equations:

$$E_{LUMO} = -e (E_{red} + 4.4)$$
 (1)

$$E_{HOMO} = E_{LUMO} - E_g$$
 (2)

where E_{LUMO} is the energy levels of the lowest unoccupied molecular orbital, and E_{HOMO} is the energy levels of the highest occupied molecular orbital. E_{red} is the onset of reduction potential. E_g is the absorption edge in the absorption spectrum.

 E_{red} can be obtained from Figure 5A-5C, and E_{LUMO} is calculated by the formula (1). E_{HOMO} can not be obtained due to the irreversible of the oxidation behavior. Therefore, the optical band gap E_g is gained from Figure 5D-5F. Then the E_{HOMO} is calculated according to formula (2).

The limit of detection

Taking CBL detection as example, the limit of detection (LOD) is calculated as follows. The PL emission intensities of CDs samples without any CBL are measured by 11 times to obtain the standard deviation of blank measurements. Then, the PL emission intensities of CD samples with different concentrations of CBL are tested to obtain the slope of calibration curve. Finally, the LOD is derived from the equation $3\delta/S$, where δ is the standard deviation of blank measurements, and S is the slope of calibration curve.



Fig. S1 (A, B and C) High-resolution N 1s XPS profile of UCDs, FCDs1 and FCDs2;

(D, E and F) High-resolution O 1s XPS profile of UCDs, FCDs1 and FCDs2.



Fig. S2 PL emission spectra of FCDs2 with different excitation wavelengths (400-500

nm).



Fig. S3 PL spectra of FCDs1 in solid state with different excitation wavelength.



Fig. S4 (A, B and C) Photostability of UCDs, FCDs1 and FCDs2 under continuous excitation by a Xenon lamp for 3600s;



Fig. S5 (A, B and C) The recorded PL intensity of UCDs, FCDs1 and FCDs2 during 7days storage.



Fig. S6 PL images of LFPs developed stored for different time



Fig. S7 (A) The UV–Vis absorption spectrum of CBL, and the PLE spectrum of FCDs2; (B) PL lifetime decay profiles of FCDs2 in the absence and presence of CBL.

Method	Line range (µmol /L)	LOD (µmol /L)	Ref.
Photoluminescence		0.32	1
Photoluminescence	0.7–8.9	0.07	2
Photoluminescence	0.75–100	0.2	3
HPLC	1.84-9.22	0.92	4
Electrochemistry	10–60	5	5
Photoluminescence	0.5–60	0.15	This work

Table S1 Comparison of the analytical characteristics of methods for detecting CBL.

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Sample	Spiked (µmol/L)	Found ^a (µmol/L)	RSD (%)	Recovery (%)
Energy drink	0	2.60	2.9	
	5	7.47	4.5	95.0
	10	12.52	2.6	96.9
CBL tablet	0	8.63	2.1	
	5	13.49	4.2	98.4
	10	18.62	7.2	99.9

 Table S2 Results of determination of CBL in real samples.

^aMean of three measurements.