

Electronic Supplementary Information

Purification, organophilicity and transparent fluorescent film fabrication derived from hydrophilic carbon dots

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1. Experimental details

Materials

Methyl Methacrylate (MMA) and benzoyl peroxide (BPO) were purchased from Aladdin-reagent Ltd (Shanghai, China) and used as received without further treatment. Reagent-grade ammonium bicarbonate, trisodium citrate dehydrate, ethanol, hexamethylene, and toluene were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). High-purity water with the resistivity of greater than $18 \text{ M} \cdot \text{cm}^{-1}$ was used in the experiments.

Synthesis

Synthesis of hydrophilic CDs (first process in Scheme S1): The prepared route is similar to the previous report¹ with a modification. Typically, 0.4 g ammonium bicarbonate, 3.0 g NH_4HCO_3 and 20 ml high-purity water were sealed into a 100 ml Teflon equipped stainless steel autoclave followed by hydrothermal reaction at $180 \text{ }^\circ\text{C}$ for 4 h. The resultant showed a transparent yellow color, which can be assigned to the ultra-small size of CDs with little light scattering.

Procedures of CDs purification (second process in Scheme S1): In a typical process, 3 ml hexamethylene was added to the CDs solution (10 ml) with magnetic stirring for about 10 min. Then 1 ml ethanol was added dropwise as an inducer to the interface at a low rate via syringe², and the CDs in water were trapped at the interface. As a result, the highly enriched CDs in the interface was obtained.

Synthesis of organophilic ODA-CDs (third process in Scheme S1): 5 ml as-purified hydrophilic CDs was dispersed in 15 ml distilled water and the pH was tuned to 5~7 with acetic acid. 20 ml toluene and 0.1 g octadecylamine (as surfactant) were added to the solution. The mixed suspension was then transferred to a 100 ml Teflon-lined autoclave and heated at $160 \text{ }^\circ\text{C}$ for 4 h. After cooling, upper solution was removed and then centrifuged 3 times with distilled water.

Fabrication of PMMA/ODA-CDs transparent fluorescent bulk (last process in Scheme S1): 1.5 ml organophilic ODA-CDs was dried in oven for about 10 min, then 10 ml methyl methacrylate monomer (MMA) and 0.01 g benzoyl peroxide were added. The as-fabricated samples was processed into 2D self-supporting films.

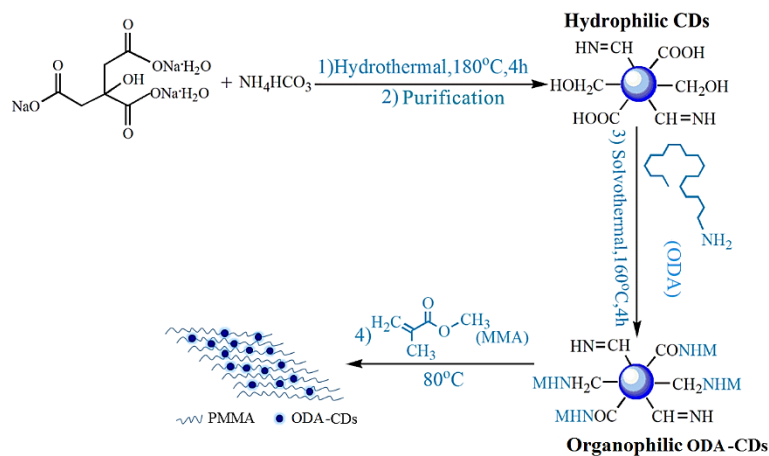
Characterization

Transmission electron microscopy (TEM): The particle diameter was examined with a JEOL JEM-2100 transmission electron microscope with 200 kV. A drop of corresponding carbon dot aqueous solution was placed on a copper grid that was left to dry before transferring into the TEM sample chamber.

Spectroscopy: The absorption spectra were measured with a Hitachi U-3010 spectrophotometer in the wavelength region of 200-800 nm. UV excitation and emission spectra were carried out at Hitachi F-4600 spectrometer. The scan speed was fixed at 240 nm/min, the voltage was 700 V and the slits were fixed at 2.5 nm. The room temperature

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PL QYs of CDs were calculated by the integrated emission of the CDs samples in solution compared with that of rhodamine 6G with a PL QY of 95% in ethanol with identical optical density³. XPS spectra of the samples on a Si (100) substrate were measured on EscaLab 250Xi X-ray Photoelectron Spectroscopy. The transient decays were recorded on an Edinburgh Instruments (FLS 980) spectrofluorimeter equipped with both continuous (450 W) and pulsed xenon lamps.



Scheme S1 Schematic procedures of (1) synthesis, (2) purification, (3) hydrophobization, (4) solification, namely fabrication of PMMA/ODA-CDs hybrid composite.

2. Results section

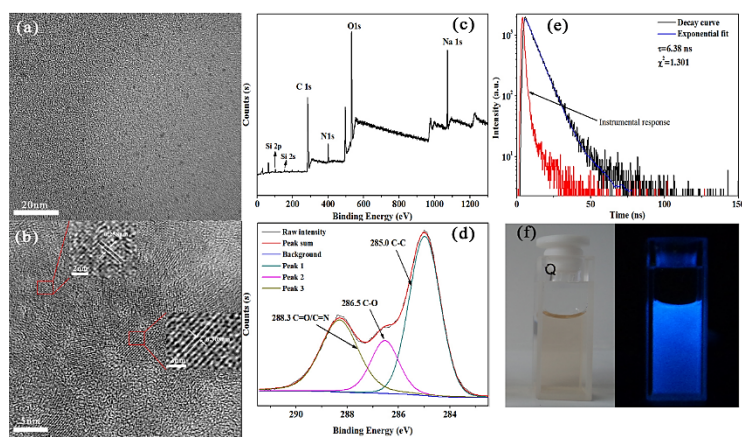


Fig. S1 (a) TEM and (b) HRTEM images of as-prepared hydrothermal-derived CDs, (c) XPS spectra of the CDs and (d) the corresponding high-resolution spectra of the C 1s peak, (e) fluorescence decay curve and (f) digital photos of the CDs under ambient and 365 nm UV light.

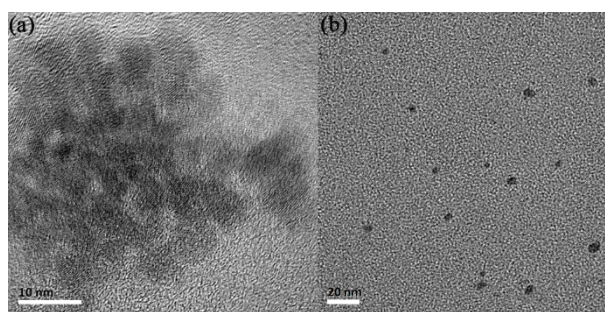


Fig. S2 TEM images of CDs: the enriched ones in the interface through oil/water interfacial self-assembly strategy (a), and then diluted by water (b).

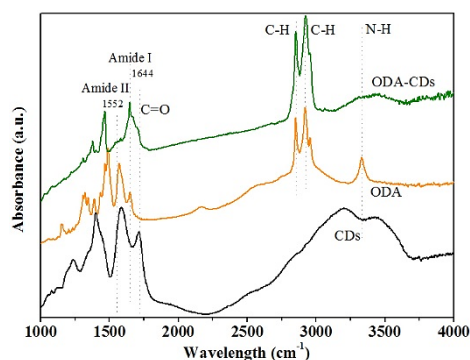


Fig. S3 FTIR spectra of CDs, octadecylamine (ODA), and octadecylamine-CDs (ODA-CDs)

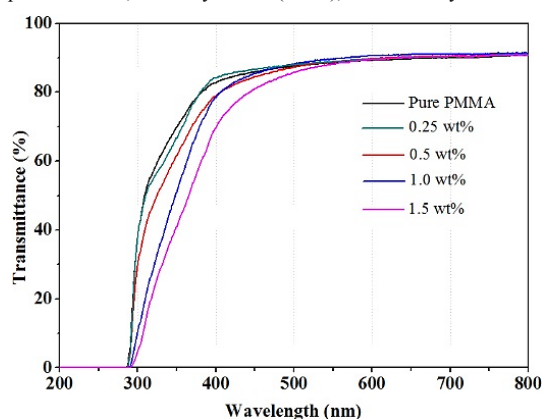


Fig. S4 The transparence of the as-prepared fluorescent bulks from CDs purified by dialysis method.

Table S1 Element contents of original, interfacial and dialytic CDs.

	C1s (mol%)	O1s	N1s	Na1s	Si2p
stoste	49.49	32.46	3.06	14.27	0.71
interface	66.98	25.08	1.82	5.94	0.18
dialysis	58.04	27.27	5.91	7.02	1.75

Table S2 Bonding variation of C element at different stages.

	Integral Area (C-C) (a. u.)	Integral Area (C-O)	Integral Area (C=O/C=N)	Integral Area (CO ₃ ²⁻)
stoste	22512 (42.3%)	10523 (19.8%)	14386 (27.1%)	5742 (10.8%)
interface	56679 (57.3%)	20534 (20.8%)	21732 (22.0%)	-
dialysis	34012 (51.6%)	11154 (16.9%)	20810 (31.5%)	-

3. Reference

- 1 Y. M. Guo, Z. Wang, H. W. Shao and X. Y. Jiang, *Carbon*, 2013, **52**, 583-589.
- 2 Y. Ren, M. Chen, L. F. Hu, X. S. Fang and L. M. Wu, *J. Mater. Chem.*, 2012, **22**, 944-950.

