Supporting Information

Industrializable synthesis of narrow-dispersed carbon dots achieved by microwave-assisted selective carbonization of surfactants and their applications as fluorescent nano-additives

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1. Experimental

1.1 Materials

Octadecyl sucrose (CP, Chenxing Biology Technique Co.), Span 40 (CP, Fuchen Chemical Co.), Soybean lecithin (CP, Chenxing Biology Technique Co.), Dodecyl betaine (CP, Nanjia Chemical Co.), Polypropylene (CP, Suda Plastic Material Co.) and Silica gel (National Drug Group) were used as received. Methyl methacrylate (99%, stabilized with 30 ppm MEHQ, Aladdin) was distilled over CaH₂ before use. The general precursors of A (difunctional epoxy compound) and B (cross-linker) solutions with commercially protected formula for epoxy resin (Zhitian Glue Co.) were purchased and used as received. Azobisisobutyronitrile (AIBN) (98%, Macklin) was used as received. The solvents of petroleum ether (AR), ethyl acetate (AR) and methanol (AR) were distilled before use.

1.2 Synthesis of C-dots

50.0 g Span 40 (SP) were transferred into a 250 mL beaker and was heated by using a general commercial microwave oven (1000W, 100% power) for a certain time. After cooled down to room temperature, the mixture was washed with methanol or ethanol and was filtered to afford the final C-dots. By using this strategy, 1.0 kg of C-dots from Span 40 were successfully synthesized with a yield of 75% (Scheme 1). The other three industrial surfactants of octadecyl sucrose (OS), soybean lecithin (SL) and dodecyl betaine (DB) were also chosen as carbon sources to synthesize C-dots in the same method.

1.3 Preparation of fluorescent PMMA

i) Preparation of PMMA sheet by mixing PMMA and C-dots

0.20 g of AIBN was dissolved in 25.00 mL of PMMA. The mixed solution was heated at 75 °C for 1.0 h followed by at 45 °C for 2.0 h. The highly viscous solution was kept overnight at 30 °C to afford a rigid PMMA. 1.50 g of the resultant PMMA and 0.075 g of CD_{SP} -18 min were disolved in 30 mL of CH_2Cl_2 and afforded a fluorescent PMMA sheet after the solvent was naturally evaparized. A pure PMMA sheet were prepared in the same way for blank control.

ii) Preparation of PMMA rod through free radical polymerization of MMA in the presence of C-dots

0.12 g of AIBN and 0.14 g of CD_{SP}-18min were dissolved in 15.00 mL of MMA, resulting in a transparent solution with light brown color. The solution was heated at 75 °C for 1.0 h followed by at 45 °C for 2.0 h. The highly viscous solution was kept overnight at 30 °C to afford a rigid and transparent PMMA rod with light brown color. The pure PMMA rod was prepared in the same way for blank control.

1.4 Preparation of fluorescent epoxy resin

The epoxy resins were prepared by using commercial A and B components. 15.00 g of A solution was mixed with 5.00 g of B solution followed by addition of 0.10 g of CD_{SP} -18min. After gently stiring, a transparent viscous solution was obtained and was transfered into the mould after being degased in vacuum for 1.0 h. After 24 h, a rigid and transparent fluorescent epoxy resin was obtained. The pure epoxy resin were prepared in the same way for blank control.

1.5 Preparation of fluorescent PE

To the 20.00 g of PE melte at 180 °C, 0.20 g of CD_{SP} -18 min was added and blended by using a glass rod. After cooling down to room temperature, the brown product was cut into small pieces for comparison with the pure PE.

1.6 Characterization

The thermogravimetry (TG) measurement were performed on a Q50 thermogravimetric analyzer in nitrogen atmosphere. A heating rate of 5.0 °C/min and a temperature range from room temperature to 600 °C were applied. The C-dots were filtered by passing through a 2 cm silica gel column before fluorescence characterization. Fluorescence spectra were recorded on a Hitachi F-7000 fluorescence spectrometer with a scanning rate was 300 nm min⁻¹. The scanning voltage of the Xe lamp was set at 700 V. Quantum yields (QYs) were measured with the F-3018 Integrating Sphere on Nanolog FL3-2iHR fluorescence spectrometer. Fourier transform infrared (FT-IR) spectra of the C-dots (in the form of KBr pellets) were recorded on a Thermo Nicolet IR200 FT-IR spectrometer. The spectra were collected from 4000 to 500 cm⁻¹ with 16 scanning times with transmission mode. Transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) images were captured on FEI Tecnai F20. Atomic force microscope (AFM) images were recorded in a Nanoscope scanning probe microscope (Bruker, Dimension Icon) with ScanAsyst mode under ambient condition. X-ray photoelectron spectroscopy (XPS) data were obtained by using Thermo Fisher Scientific, ESCALAB 250XI, equipped with an Al ka X-ray source. Proton nuclear magnetic resonance (¹H NMR) and ¹³C NMR spectra were acquired on Bruker Avance III 500 MHz NMR with 512 scanning times. Deuterated chloroform (CDCl₃) was used as solvent. Raman spectroscopy was measured by using a LabRAM

ARAMIS[™] Smart Raman spectrometer (Thermofisher) with a He Ne laser. The blending of polymers with C-dots were carried out on an extruder (Ruiya TSE-35) with working temperature at 220 °C. The melt index of the polymers after blend with C-dots were measured on a melting indexer (RL-Z1B1) at 230 °C with a 2.16 kg load. The polymer samples with size of 80×10×4 mm was prepared by using an injection molding machine (Haitian SA2500) at 220 °C and their mechanical properties were measured on a universal testing machine (Zwick Z010) with a tensile rate of 5.0 mm/min.

2. Results and Discussion

2.1 Solubility of the C-dots

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Table S1. The solubility of CD_{SP} -18min in different solvents (c = 2.5 mg/mL)

Solvents	Polarity	Solubility	
Petroleum ether	0.01	soluble	
Cyclohexane	0.1	soluble	
Toluene	2.4	soluble	
Dichloromethane	3.4	soluble	
Tetrahydrofuran	4.2	soluble	
Ethyl acetate	4.3	soluble	
Trichloromethane	4.4	soluble	
Acetone	5.4	soluble	
Acetonitrile	6.2	insoluble	
Acetic acid	6.2	insoluble	
Methanol	6.6	insoluble	
Water	10.2	insoluble	

2.2 Fluorescence characteristics of CD_{SP}s with different carbonization times

Samples	CIEx ^a	CIEy ^a	$\lambda_{\mathrm{ex}} (\mathrm{nm})^b$	$\lambda_{\rm em} ({\rm nm})^c$	QY _{sol.} d
CD _{SP} -3min	0.1994	0.2101	360	432	2.6%
CD _{SP} -6min	0.2105	0.2547	380	457	1.4%
CD _{SP} -9min	0.2091	0.2479	380	453	2.9%
CD _{SP} -12min	0.212	0.2541	380	458	1.2%
CD _{SP} -15min	0.223	0.2975	400	471	0.9%
CD _{SP} -18min	0.2225	0.2996	400	473	0.8%
CD _{SP} -21min	0.2177	0.2797	380	466	1.1%
CD _{SP} -24min	0.222	0.2966	400	471	0.9%
CD _{SP} -27min	0.2246	0.3018	400	473	0.8%
CD _{SP} -30min	0.2249	0.3023	400	474	1.1%

Table S2. The coordinates in a CIE diagram and fluorescence characteristics of CD_{SP}s prepared

 with different carbonization times

^{a.} The coordinate system position of different CD_{SP} in EA solutions in CIE diagram (c = 10 mg/mL); ^{b.} Optimal excitation wavelength (c = 10 mg/mL); ^{c.} Maximum fluorescence emission wavelength and intensity (c = 10 mg/mL); ^{d.} The solution quantum yields were determined by using spectrofluorometer with an integrating sphere detector at a concentration of 5.0 mg/mL.

2.3 Quantum yields of fluorescent polymers doped CD_{SP}-18min

Table S3. The Quantum yields of fluorescent polymers doped CD_{SP}-18min

Samples	QYa
PMMA sheet (0.5 w% C-dots)	1.3%
PMMA rod (1.0 w% C-dots)	2.7%
Epoxy resin cube (0.5 w% C-dots)	3.3%
Epoxy resin sphere (0.5 w% C-dots)	3.3%
Epoxy resin diamond (0.5 w% C-dots)	2.4%
PE (1.0 w% C-dots)	3.1%

^{a.} The solid-state QYs were determined by the polymers without doping CDs as reference.



2.4 Structure and fluorescence characteristics of C-dots (Figure S1-S9)

Figure S1. The TEM images (left) and size distribution (right) of C-dots: A) CD_{SP}-3min; B) CD_{SP}-12min; C) CD_{SP}-21min; D) CD_{SP}-40min.



Figure S2. The Raman spectra of Span 40 and CD_{SP}s.



Figure S3. The fluorescence spectra of Span 40 and C-dots in EA solutions (c = 10 mg/mL): (A) Span 40; (B) CD_{SP}-3 min; (C) CD_{SP}-6 min; (D) CD_{SP}-9 min; (E) CD_{SP}-12 min; (F) CD_{SP}-15 min;



(G) CD_{SP}-21 min; (H) CD_{SP}-24 min; (I) CD_{SP}-27 min; (J) CD_{SP}-30 min; (K) CD_{SP}-40 min

Figure S4. A) Overlap of the emission spectra ($\lambda_{em} = 437 \text{ nm}$) excited by short wavelength ($\lambda_{ex} = 360 \text{ nm}$) and excitation spectra of emission at long emission wavelength ($\lambda_{em} = 473 \text{ nm}$); B) Overlap of the emission spectra ($\lambda_{em} = 458 \text{ nm}$) excited by short wavelength ($\lambda_{ex} = 380 \text{ nm}$) and excitation spectra of emission at long emission wavelength ($\lambda_{em} = 487 \text{ nm}$);



Figure S5. The UV-Visible spectra of CD_{SP}-18min, CD_{SL}-10min, CD_{DB}-12min and CD_{OS}-3min.



Figure S6. The TEM images (left) and size distribution (right) of C-dots: A) CD_{DB-1-HC}; B) CD_{DB-2-LC}; C) CD_{OS-1-HC}; D) CD_{OS-2-LC}.



Figure S7. The FT-IR spectra of C-dots: A) CD_{OS}; B) CD_{SP}; C) CD_{SL}



Figure S8. The fluorescence spectra of C-dots in EA solutions (c = 2.5 mg/mL): (A) CD_{SL-1-} _{HC}; (B) CD_{SL-2-LC}; (C) CD_{SP-1-HC}; (D) CD_{SP-2-LC}.



 $CD_{SL\text{-}1\text{-}HC} \text{ and } CD_{SL\text{-}2\text{-}LC} \quad CD_{OS\text{-}1\text{-}HC} \text{ and } CD_{OS\text{-}2\text{-}LC} \quad CD_{SP\text{-}1\text{-}HC} \text{ and } CD_{SP\text{-}2\text{-}LC}$

Figure S9. Fluorescence of different fractions of C-dots under day light (left in each image) and 365 nm UV light (right in each image) (c = 2.5 mg/mL in ethyl acetate solutions)

2.5 Some fluorescent polymeric materials prepared by using C-dots as nano-additives

PMMA:

Figure S10. CD_{SP}-18min served as nano-additive for preparation of fluorescent polymeric materials (left in each image) in contrast to a blank control (right in each image): Fluorescent PMMA sheet (0.5 w% C-dots) under day light (A) and 365 nm UV light (B); Fluorescent PMMA rod (1.0 w% C-dots) under day light (C), 365 nm UV light (D), a 405 nm blue laser (E) and a 532 nm green laser (F); Fluorescent AB resin cube (0.5 w% C-dots) under day light (G), 365 nm UV light (H), a 405 nm blue laser (I), a 532 nm green laser (J); Fluorescent AB resin diamond (0.5 w% C-dots) under day light (K) and 365 nm UV light (L); Fluorescent AB resin sphere (0.5 w% C-dots) under day light (M) and 365 nm UV light (N); Fluorescent PE (1.0 w% C-dots) under day light (O) and 365 nm UV light (P).



2.6 The melting points of CD_{SP}s with different carbonization time

Figure S11. The DSC curves of CD_{SP} s with different carbonization time: A) CD_{SP} -3min; B) CD_{SP} -9min; C) CD_{SP} -15min; D) CD_{SP} -18min; E) CD_{SP} -27min; F) CD_{SP} -30min; G) CD_{SP} -40min; H) The melting point change curve of CD_{SP} s with increasing carbonization time.