Electronic Supplementary Information

Carbon dots in magnetic colloidal nanocrystal clusters

Ye Liu, Ye Tian and Wuli Yang*

State Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, Shanghai 200433, China.

E-mail: wlyang@fudan.edu.cn.

Experimental section

Materials: Ferric chloride hexahydrate (FeCl₃·6H₂O), sodium acetate (NaOAc), trisodium citrate dihydrate (Na₃Cit·2H₂O), ethylene glycol (EG), polyethylene imine (PEI), and dopamine hydrochloride were obtained from Aldrich. All reagents used in this synthesis were commercially available analytical grade and used as received, without further purification.

Synthesis of MCNCs

FeCl₃·6H₂O (5.41 g) was first dissolved in EG (100 mL) to form a brown solution, which was given an ultrasonic treatment (150 W, 40 kHz) for 5 min, and followed by adding Na₃Cit·2H₂O (1.2 g) and NaOAc (6 g) to the system. Then the mixture was stirred vigorously for 30 min. The obtained homogeneous brown solution was transferred to a Teflon-lined stainless-steel autoclave (200 mL capacity) and sealed to heat at 200 °C. After reacting for 10 h, the autoclave was cooled to room temperature. Finally, the black products were washed with ethanol and deionized water for several times.

Synthesis of MCNC-dopamine

The MCNCs (200 mg) and dopamine hydrochloride (20 mg) were dispersed in pH 7.4 buffer (50 mL) by ultrasonication, and the resulting solution was subject to mechanical stirring at room temperature overnight.

The etch of Fe₃O₄ in MCNCs

The MCNCs (250 mg) was dissolved in 1.2 M HCl (50 mL) uniformly with sonication and vigorous stirring overnight. After that, 2 M NaOH was added dropwise into the resulting dispersion to adjusting the pH until the Fe³⁺ ions precipitated completely. Finally, the obtained solution was centrifuged and the supernatant was collected. Besides, in order to simulate physiological environment, the MCNCs (15 mg) was dissolved in pH 4 buffer, other steps were the same as the above.

Synthesis of MCNC-PEI composites

The MCNCs (250 mg) and polyethylene imine (40 mg) were dispersed in deionized water (50 mL) by ultrasonication, and the resulting dispersion was subject to mechanical stirring at 80 °C for 3 h.

Characterization Techniques

UV/vis spectra were obtained by a Perkin-Elmer Lambda 750 spectrophotometer. Fourier transform infrared (FT-IR) analysis was conducted on a Nicolet Nexus-440 FT-IR spectroscopy. Zeta-potential was measured by a Zetasizer Nano-ZS (Malvern) at 25 °C. Thermo gravimetric analysis (TGA) was carried out on a Pyris 1 TGA thermal analyzer from 100 to 800 °C (20 °C min⁻¹) in a flow of N₂. The fluorescence spectra were measured using a QM40 spectrometer. Transmission electron microscopy (TEM) (JEM-2100F) was performed at an accelerating voltage of 200 kV. XPS analysis was performed on a Perkin-Elmer PHI-5000C ESCA system using Al Kα radiation (1486.6 eV). Raman spectra were collected on an XploRA laser Raman spectrometer (HORIBA JobinYvon) with 532 nm laser excitation. ¹H and ¹³C NMR spectra were measured on an AVANCE III HD FT-NMR spectrometer (400 MHz, Bruker) in dimethylsulfoxide-*d*6 (DMSO-*d*6), and chemical shifts were reported in ppm units with tetramethylsilane (TMS, $\delta = 0$ ppm) as an internal standard.

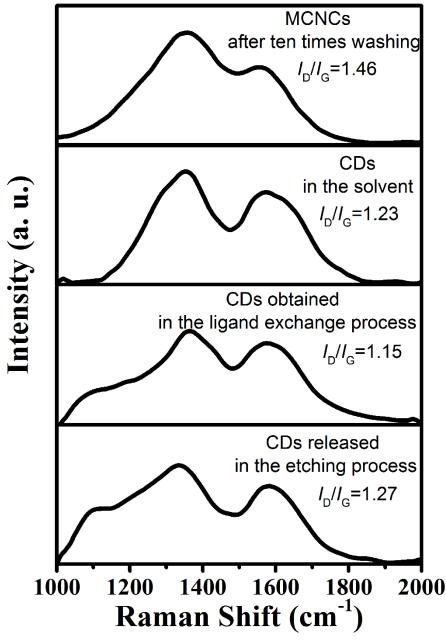


Figure S1 Raman spectra of MCNCs and the three kinds of CDs.

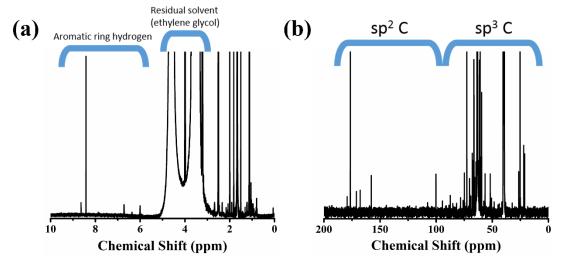


Figure S2 The ¹H-NMR (a) and ¹³C-NMR (b) spectra of CDs in the solvent.

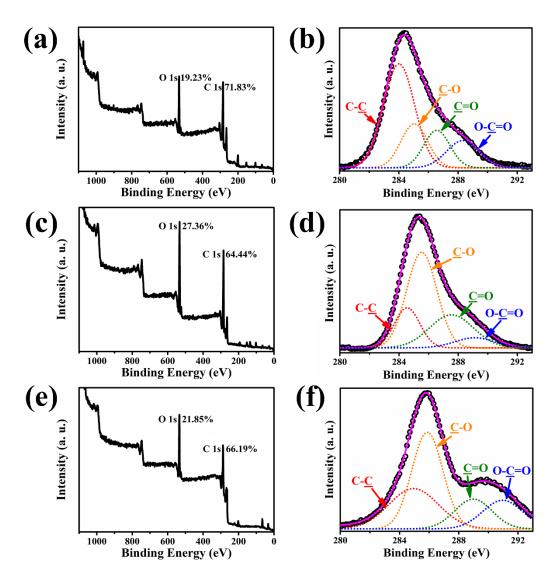


Figure S3 XPS characterization of the CDs. (a), (c), (e) are XPS wide scans of CDs obtained in the solvent, ligand exchange and etching process, respectively. (b), (d), (f) are corresponding C 1s

spectra of the CDs (the circle lines). The dotted lines are the contributions of various types of carbon atoms and the solid curves are the simulated spectra from summed peaks.

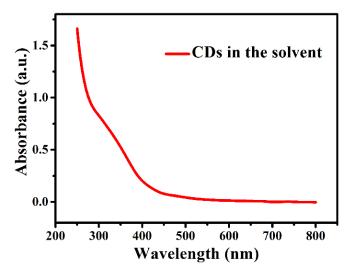


Figure S4 UV/Vis absorption spectrum of CDs in the solvent.

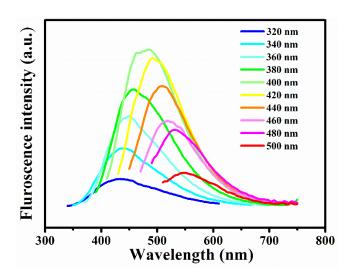


Figure S5 PL emission spectra of MCNCs at different excitation wavelengths.

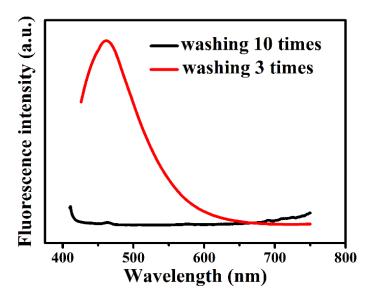


Figure S6 PL emission spectra of MCNCs washed with deionized water.

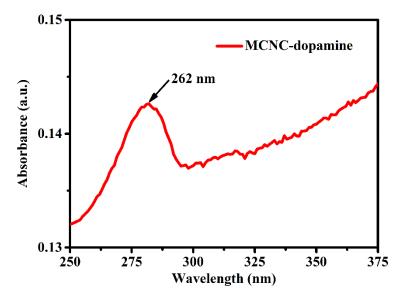


Figure S7 UV/Vis absorption spectrum of MCNC-dopamine.

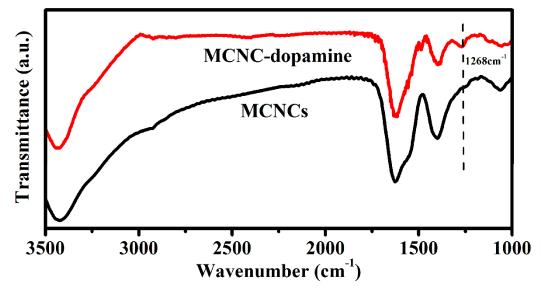


Figure S8 FTIR spectra of MCNCs and MCNC-dopamine.

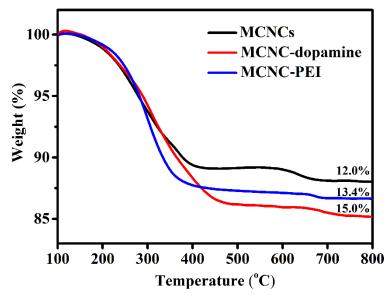


Figure S9 Thermo gravimetric (TG) curves of MCNCs, MCNC-dopamine and MCNC-PEI composites. The TG curves were obtained in N_2 with a heating rate of 20 °C min⁻¹.

Table S1 Zeta potential of MCNCs, MCNC-dopamine and MCNC-PEI composites.

Sample	Zeta Potential
	(mV)
MCNCs	-14.8
MCNC-dopamine	-0.02
MCNC-PEI	20.8