

Supporting Information

Synthesis of photoluminescent carbogenic dots using mesoporous silica spheres as nanoreactors

Jie Zong, Yihua Zhu, Xiaoling Yang, Jianhua Shen and Chunzhong Li*

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

*Corresponding author: Tel.: +86-21-64252022, Fax: +86-21-64250624

E-mail address: yhzhu@ecust.edu.cn (Y. Zhu)

Experimental Part

Materials

N-hexadecylamine was purchased from Sigma-Aldrich Chemicals Co. Citric acid and all other chemicals were purchased from Shanghai Chemical Reagent Co. All chemicals were used as received without any further purification. Double distilled water was used in all experiments.

Synthesis

Firstly, MS spheres were synthesized as previously described in the literature.^{15,S1} The main procedure was as follows: 1 g of hexadecylamine was dissolved in a mixed solution including 100 mL isopropanol and 90 mL double distilled water to form a clear solution. Then 1.4 mL ammonia was added, which was followed by the addition

of 5.8 mL of tetraethoxysilane (TEOS). The mixture was homogenized and kept at room temperature overnight. The resulting white precipitate was collected by filtration of the reaction mixture, washed with ethanol three times and then with the distilled water twice, and dried at ambient temperature. The templates were removed by calcination at 600 °C for 6 h in flowing air, and then the MS spheres with a pore size of approximately 3.60 nm were obtained. Subsequently, 0.4 g of MS spheres and 0.05 g of citric acid were soaked in 1 mL of mixed solution with three ingredients including NaCl, LiCl and KNO₃ (mass ratio 20: 5: 5). The mixture was dispersed with ultrasonic vibrations and then calcined at 300 °C for 2 h in air. The resulting yellow powders were denoted as CDs/MS. To release the CDs, MS spheres were removed by etching with 2 M NaOH solution at 40 °C 24 h. The excessive NaOH was first neutralized by HNO₃ and then removed by dialyzing the supernatant against double distilled water through a dialysis membrane ((molecular weight cut off) MWCO 1000). The homogeneous yellow CDs were finally obtained.

Characterization Part

Scanning electron micrograph (SEM) was obtained using a JEOL JSM-6360LV instrument. The sample surface was coated with gold before the SEM measurements. Adsorption-desorption measurements were conducted on a Micromeritics ASAP 2010 apparatus at 77 K using nitrogen as the adsorption gas. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. And the pore diameters were calculated by the Barrett-Joyner-Halenda (BJH) method. High-resolution TEM images were taken on a JEOL JEM 2011 microscope (JEOL, Japan) at an acceleration

voltage of 200 kV. The specimen was prepared by drop casting the sample dispersion onto a carbon-coated copper grid, followed by drying under room temperature. FT-IR spectrum was recorded on a Nicolet 5700 Fourier transform infrared spectrometer. Photoluminescence spectra were measured on a Fluorolog-3-P UV-VIS-NIR fluorescence spectrophotometer (Jobin Yvon, France). UV-vis spectrum of the CDs dispersed in water was obtained using a Unico UV-2102PC spectrophotometer. All spectra were recorded with quartz cells of 10 mm path length.

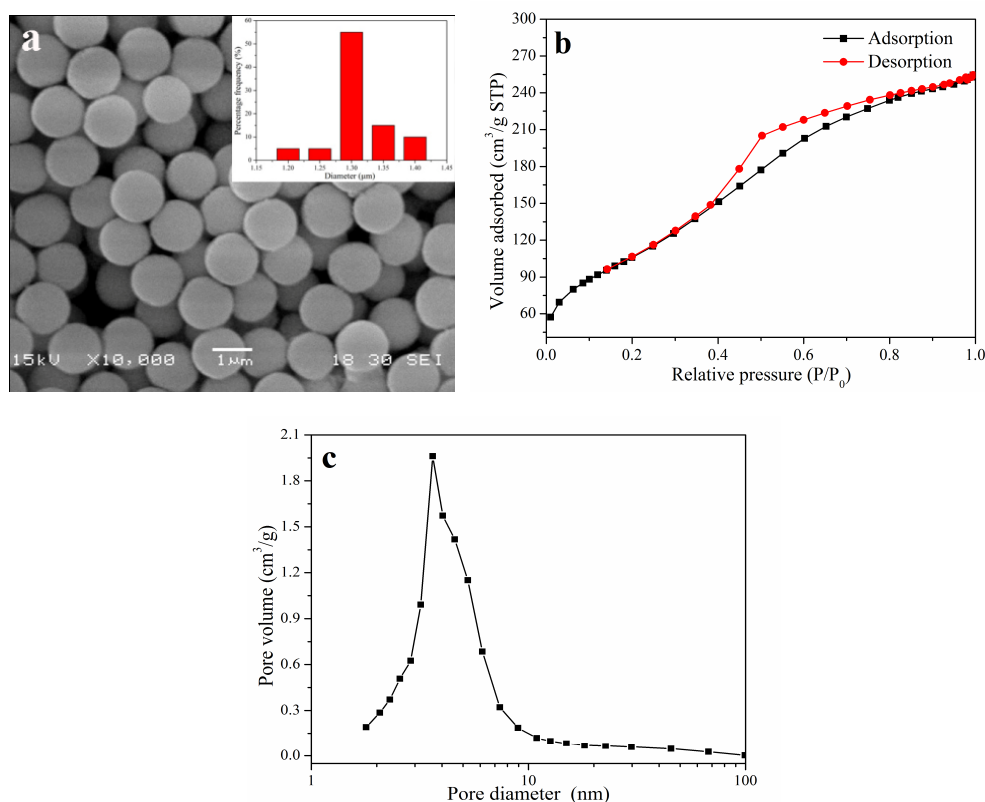


Fig. S1 (a) Scanning electron micrographs (SEM) image of MS spheres (Inset: the corresponding size distribution). The corresponding (b) Nitrogen adsorption-desorption isotherms and (c) pore size distribution.

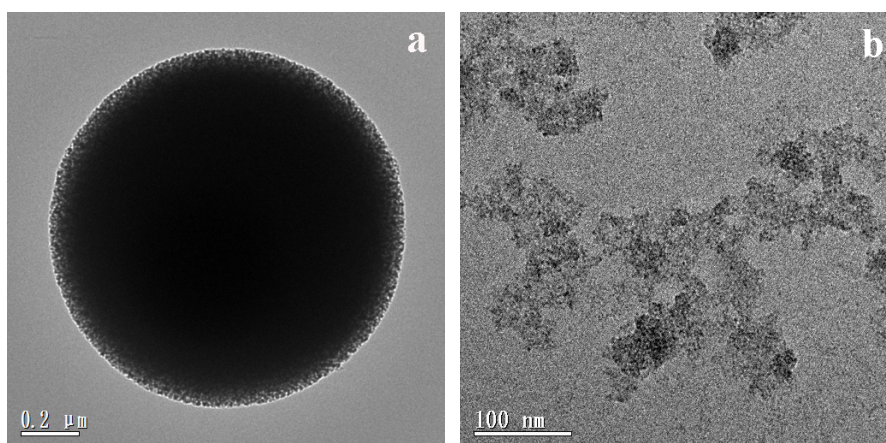


Fig. S2 TEM images of (a) a representative CDs/MS composite microsphere and (b) the photoluminescent CDs derived from CDs/MS composites etched with NaOH.

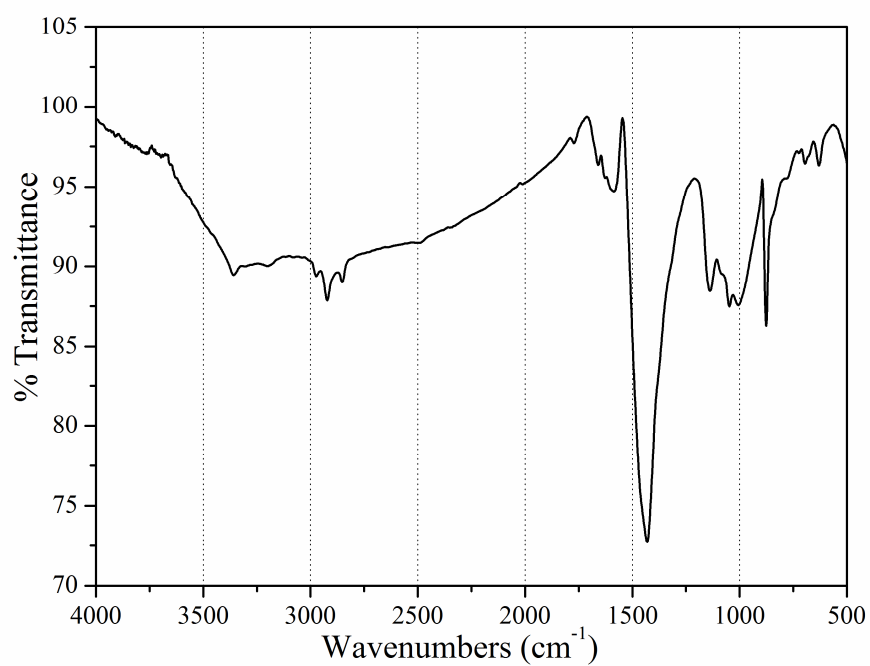


Fig. S3 FT-IR spectrum of CDs.

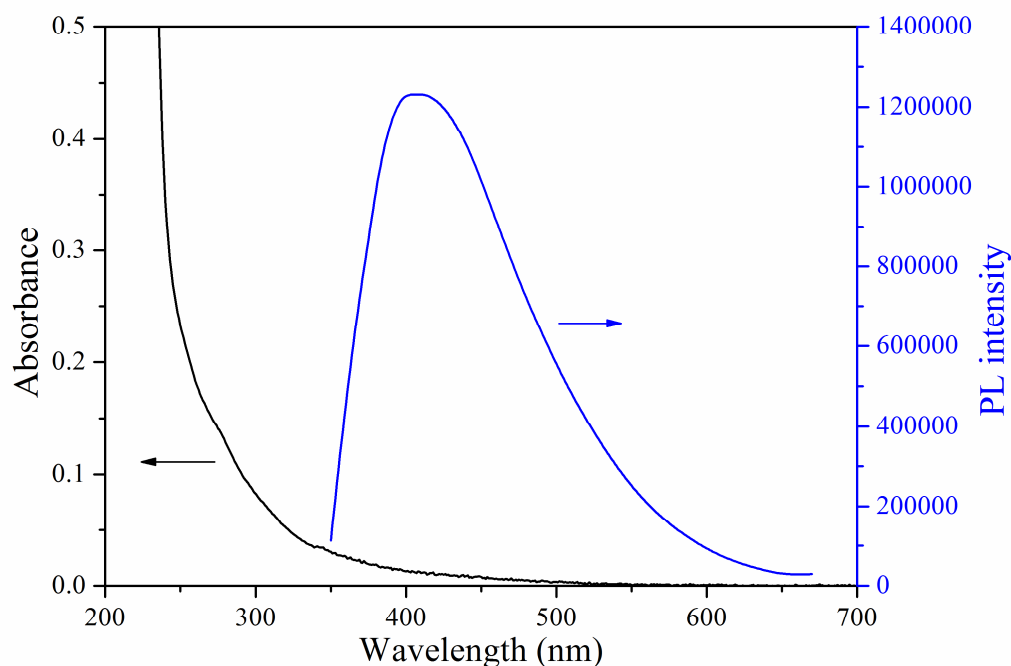


Fig. S4 UV-vis absorption and PL emission spectra of the CDs dispersed in water. The emission spectrum was obtained under excitation at 340 nm.

Quantum Yield (QY) Measurements

Rhodamine B in water (literature^{S2} quantum yield 0.31) was chosen as a standard. The quantum yield of CDs in water was calculated according to:

$$\phi = \phi_r \times \frac{A_r}{I_r} \times \frac{I}{A} \times \frac{n^2}{n_r^2}$$

Where Φ is the quantum yield, I is the measured integrated emission intensity, n is the refractive index (1.33 for water), and A is the optical density. The subscript “r” refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects, absorbencies in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength of 340 nm.

Table S1 quantum yield of the as-prepared CDs

Sample	Integrated emission intensity (I)	Abs. at 340 nm (A)	Refractive index of solvent (n)	Quantum Yield (Φ)
Rhodamine B	342156346	0.05279	1.33	0.31
CDs	168734173	0.03477	1.33	0.23

References

[S1] Y. X. Li, Y. H. Zhu, X. L. Yang and C. Z. Li, *Cryst. Growth Des.*, 2008, **8**, 4494.

[S2] D. Magde, G. E. Rojas and P. G. Seybold, *Photochem. Photobiol.*, 1999, **70**, 737.