Commercial Activated Carbons as the Sources for Produding Multicolor Photoluminescent Carbon Dots by Chemical Oxidation

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Experimental Section

Synthesis of carbon dots (CDs): In a typical preparation, 0.5 g of actived carbon (coal activated carbon, wood activated carbon or coconut activated carbon, Guangfu Fine Chemical, China) was dispersed in 50 mL of HNO_3 (1 mol/L) aqueous solution and sonicated for 10 min. The mixture was then refluxed for 12 h. When cooled down to room temperature, the brownish yellow supernatant after centrifugation was neutralized by Na_2CO_3, and then dialyzed against water through a dialysis membrane (Spectrum, MW cutoff 1000) for 1 day.

Surface passivation process of CDs: Typically, 0.5 g of 4, 7, 10-trioxa-1, 13-tridecanediamine (TTDDA) or diamine-terminated oligomeric poly (ethylene glycol) $H_2NCH_2(CH_2CH_2O)_nCH_2CH_2CH_2NH_2$ (n_{av}=35, PEG_{1500N}) was added to the CDs solution and the mixture was heated to 120 ºC for 72 h under N_2 for surface passivation. Then the optically transparent and photoluminescent CDs solution was again purified via dialysis for 1 day. Finally, a clear, light yellow aqueous solution containing surface passivated CDs was finally obtained.

Fluorescence Imaging Experiments: COS-7 cells were cultured in 2 mL Dulbecco's modified Eagle's medium (DMEM, Sigima) containing 10% fetal bovine serum (FBS, Gibco) and 1% Antibiotic-Antimycotic (Gibco) at 37 °C in a 5% CO_2/95% air incubator. 20 μL TTDDA-passivated carbon dots suspension (0.3 mg/mL) was added into the test cell culture. After an incubation of 24 h, the medium was removed and the cells were washed thoroughly twice by PBS. The emission was measured over the range of 475-575 nm, λ_{ex} = 405 nm.

Characterization: UV-Vis absorption spectra were recorded using a Perkin-Elmer Lambda 20 UV/Vis spectrometer. Photoluminescence (PL) spectra were measured on a Shimadzu RF-5301PC spectrophotometer. The morphologies and dimensions of the samples were revealed with a JEOL JEM-3010 transmission electron microscope (TEM) operating at 300 kV. The IR spectra were acquired with a recorded with a Bruker IFS 66v/S FTIR spectrometer. Dynamic light scattering (DLS) studies and ζ -potential measurements were carried out on a Malvern NanoZS zetasizer at room temperature. Fluorescence Imaging experiments were performed with a FV1000 confocal laser-scanning fluorescent microscope (Olympus, Japan) with a 10 × objective lens.

Table S1 The detail parameters of the three types of industrial activated carbons (surpported by Guangfu Fine Chemical).

Property	Coal Activated Carbon (Powder)	Wood Activated Carbon (Powder)	Coconut Activated Carbon (Powder)
Dimension	0.7-2.5 mm	0.5-2 mm	0.4-3 mm
Pore volume	0.8-1.2 cm^3/g	0.8-1.5 cm^3/g	0.7-1 cm^3/g
BET surface area	750-850 m^2/g	900-1200 m^2/g	590-1500 m^2/g
Ash	≤5%	≤6%	≤5%
Hardness	≥92%	≥90%	≥90%
Iron salt	≤0.05%	≤0.02%	≤0.05%
Zinc salt	≤0.05%	≤0.05%	≤0.02%
Sulfate	≤0.1%	≤0.1%	≤0.075%
chloride	≤0.05%	≤0.025%	≤0.05%

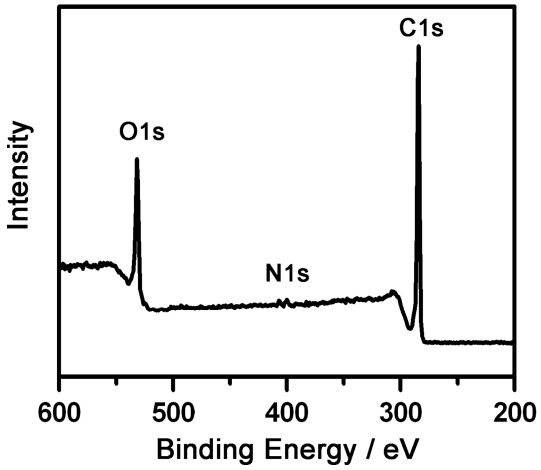

Fig. S1 XPS spectrum of the crude CDs.

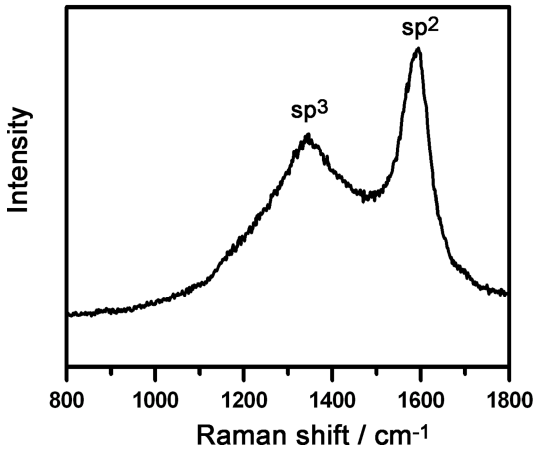

Fig. S2 Raman spectrum for the resultant crude CDs.

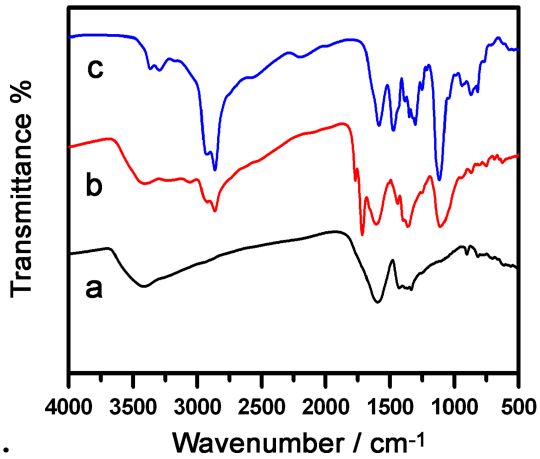

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Fig. S3 FT-IR spectra of the CDs before (a) and after (b) passivation by using TTDDA; and (c) passivation agent TTDDA alone.

The carboxyl group is clearly identified both through the broad 3423 cm^{-1} O-H stretching vibration and the 1602 cm^{-1} C=O stretching vibration, which is due to the oxidation of C–OH bonds by the residual or decomposed oxygen atoms under the nitric acid treatment. Another broadened peak with increased intensity at 1708 cm^{-1} and 1762 cm^{-1} indicates the co-existence of $\delta_{CON\text{-}HR}$ and $\nu_{C=ONR}$ vibrations, which suggests that carboxyl groups on the surface of CDs have been converted into amide groups after the passivation. The results of zeta potential measurements provide further evidence for supporting this analysis. The zeta potential of the crude CDs was -15.1 mV, suggesting the surface of CDs was negatively charged due to carboxyl groups. While the zeta potential of CDs was 13.8 mV after TTDDA passivation, indicating the surface was positively charged, due to the conversion of carboxyl groups to amide groups.

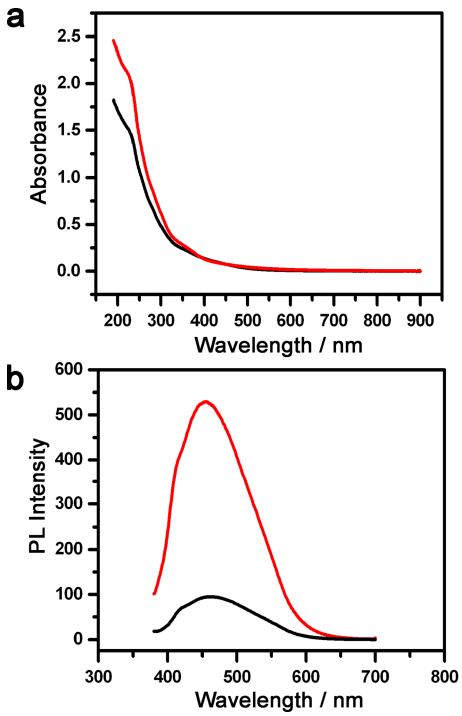

Fig. S4 UV/Vis absorption (a) and photoluminescence emission spectra (b) of the crude (black lines) and TTDDA-passivated (red lines) CDs prepared from coal activated carbon.

The CDs suspension shows a broad UV/Vis absorption and exhibits strong blue luminescence under excitation at 365 nm after surface passivation by treatment with TTDDA (see Figure 2). The absorbance increased in the range of 200 to 550 nm upon surface passivation and the maximum emission wavelength was not significantly changed. Furthermore, the passivation greatly enhanced the photoluminescence intensity, with the quantum yield improving dramatically from 0.015 to 0.126 by selecting quinine sulfate as the standard and 360 nm as the excitation wavelength.

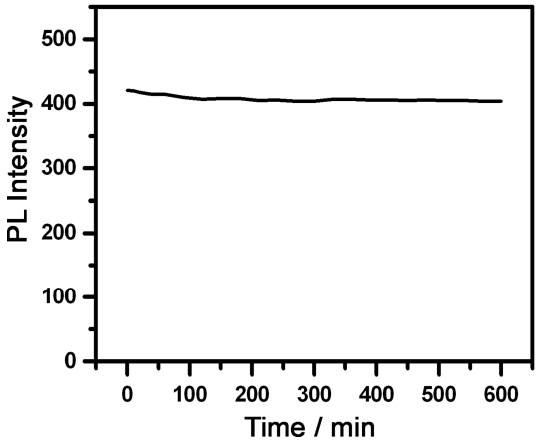

Fig. S5 Emission intensity of TTDDA passivated CDs during continuous excitation at 365 nm.

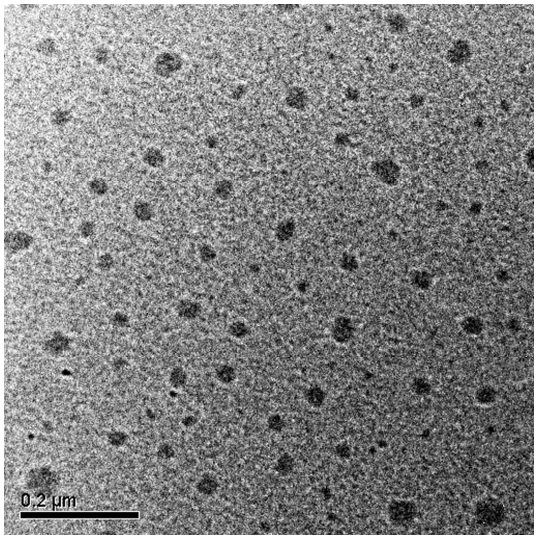

Fig. S6 TEM image of the larger carbon particles (30-50 nm in average diameter) prepared by 5 M HNO_3.

Quantum Yield Measurements.

Quantum yield was measured according to established procedure **(**Lakowicz, J. R. *rinciples of Fluorescence Spectroscopy,* 2nd Ed., **1999**, Kluwer Academic/Plenum Publishers, New York). The optical densities were measured on Perkin-Elmer Lambda 20 UV/Vis spectrometer. Quinine sulfate in 0.1 M H_2SO_4 (literature quantum yield 0.54 at 350 nm) was chose as a standard. Absolute values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value, according to the following equation:

$$\varphi_x = \varphi_{std} \frac{I_x}{A_x} \frac{A_{std}}{I_{std}} \frac{\eta^2_x}{\eta^2_{std}}$$

where φ is the quantum yield, I is the measured integrated emission intensity, and A is the optical density, and η is the refractive index. The subscript "std" 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 (360 nm).