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Carbon dot hybrids with oligomeric silsesquioxane: Solid-state luminophores with high photoluminescence quantum yield and applicability in white light emitting devices

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Materials. Octa(tetramethylammonium)-POSS was purchased from Hybrid Plastics. Other chemicals were purchased from Sigma-Aldrich. All chemicals were used without further purification.

Synthesis of CDs. N,S-co-doped CDs were synthesized according to the method reported previously.[1] Typically, 1.83 g (9.5 mmol) anhydrous citric acid and 1.0 g (8.3 mmol) L-cysteine were mixed and dissolved in 5 mL Milli-Q water under vigorous stirring, and the resulted mixture was heated at 70 ^{o}C for 12 h to form thick syrup. The syrup was placed in a 25 mL Teflon-lined stainless steel autoclave and annealed at 200 ^{o}C for 3 h with a heating rate of 10 ^{o}C/min. After reaction, the obtained black product was neutralized with 1.0 mol/L NaOH solution, dissolved in 20 mL Milli-Q water and the solution was centrifuged at 6000 rpm to remove the precipitate. The resulted supernatant was purified by filtering out large sized carbonnanoparticles using a syringe filter with pores of 0.22 μm, and CDs were recovered as powders applying the freeze-drying process.

Materials Characterization. UV-vis absorption spectra of the colloidal solutions were recorded using a Cary 50 UV-vis spectrophotometer (Varian). UV-vis diffuse reflectance absorption spectra of the powder samples were collected on a UV-3600 UV-vis-NIR spectrophotometer (Shimadzu) equipped with an integrating sphere using $BaSO_4$ as the reflectance standard. TEM images were taken on a JEOL 2010F microscope operated at 200 kV (LaB6 cathode, resolution 0.19 nm) using ultrathin carbon film coated copper grids. The XPS measurements were carried out with the PHI VersaProbe II (Physical Electronics) spectrometer using Al K_α source (15 kV, 50 W).

Photoluminescence Measurements. All photoluminescence (PL) measurements were performed at room temperature under ambient conditions. PL spectra were measured on a fluorescence spectrometer (FLS920P, Edinburgh Instruments) equipped with a calibrated photomultiplier in a Peltier (air cooled) housing (R928P, Hamamatsu), with a 450 W continuous xenon arc lamp as the excitation source for steady-state PL measurements. The PL spectra of the CDs in solution and in the powder were measured with identical instrument settings to obtain comparable values (excitation at 345 nm, 1.0/0.5 nm excitation/emission bandwidths, 1.0 nm step sizes and 0.2 s integration times).

Time-resolved PL decay curves were measured using the same spectrometer equipped with a time-correlated single-photon counting (TCSPC) lifetime spectroscopy module (TCC900, Edinburgh Instruments) with a picosecond pulsed LED (EPLED-320 nm, pulse width: 700 ps) as the single wavelength excitation light source. The PL decay curves of the CDs in solution and powder were measured with identical instrument settings to obtain comparable values (excitation at 320 nm, detection at the emission maximum, emission bandwidth of 1.0 nm, pulse period of 100 or 200 ns). An appropriate long pass filter For the PL measurements liquid samples were filled in a UV quarts cuvette with a light path of 10 mm (QS, Hellma) using a PTFE stopper to prevent solvent evaporation. The powdered samples were measured in a quartz powder sample cell mounted on a front face sample holder. The photoluminescence quantum yield (PL QY), defined as the ratio between photons emitted and absorbed by the sample, was determined by an absolute method using the same fluorescence spectrometer equipped with a 120 mm integrating sphere with BENFLEC® coated inner face (Edinburgh Instruments). For the PL QY measurements liquid samples were filled in a UV quarts cuvette with a light path of 10 mm (QS, Hellma). The same cuvette filled with a solvent was used as a blank sample for a reference measurement. The powder samples were measured in a PTFE powder sample holder. A non-fluorescent sample consisting of POSS powder having the same morphological characteristics has been used as a blank sample for a reference measurement. The spectral correction curve which takes account of the sensitivity of the monochromator, detector, sphere coating and optics to wavelength was provided by Edinburgh Instruments. The accuracy of the integrating sphere apparatus was tested against reference dyes with known quantum yield. For Rhodamine B in water (reference QY of 31%, Exciton) the PL quantum yield was measured as 31%, and for Rhodamine 101 in ethanol (reference QY of 100%, Exciton) the PL quantum yield obtained was 99%.

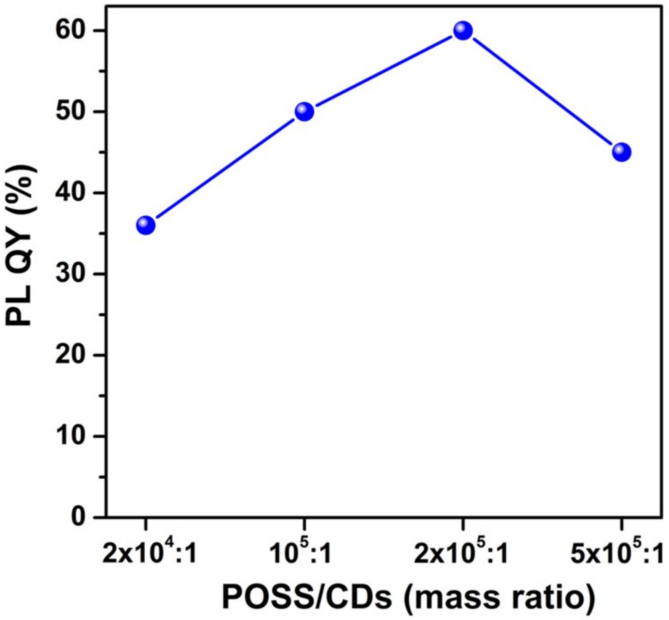

Fig. 1S PL QYs of CDs@POSS luminophores with different mass ratios of the constituents.

References

1. Y. Q. Dong, H. C. Pang, H. B. Yang, C. X. Guo, J. W. Shao, Y. W. Chi, C. M. Li and T. Yu, *Angew. Chem. Int. Ed.*, 2013, **52**, 7800-7804.