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Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence

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Fluorescent semiconductor quantum dots have generated much excitement for a wide variety of promising applications, especially those in biology and medicine.¹ For both in vitro and in vivo uses, however, the known toxicity and potential environmental hazard associated with many of these materials may represent serious limitations.^{1,2} Therefore, the search for benign nanomaterials of similar optical properties continues.^{3,4} For quantum-sized silicon, the discovery of Brus and co-workers4 on the strong luminescence in surface-oxidized nanocrystals has attracted extensive investigations of silicon nanoparticles and nanowires.⁵⁻⁷ For example, silicon nanoparticles capped with water-soluble polymers, thus compatible with physiological media, have been studied for the luminescence labeling of cells.⁷ Here we report a new finding on the quantumsized carbon analogues,8 namely, that nanoscale carbon particles ("carbon dots") upon simple surface passivation are also strongly photoluminescent in both solution and the solid state with spectral features and properties comparable to those of surface-oxidized silicon nanocrystals. These strongly emissive carbon dots may find applications similar to or beyond those of their widely pursued silicon counterparts.

The carbon dots were produced via laser ablation of a carbon target in the presence of water vapor with argon as carrier gas.9 The carbon target was prepared by hot-pressing a mixture of graphite powder and cement, followed by stepwise baking, curing, and annealing in argon flow. A Q-switched Nd:YAG laser (1064 nm, 10 Hz) was used for the ablation, during which the carbon target was in a flow of argon gas carrying water vapor (through a water bubbler) at 900 °C and 75 kPa. The as-produced sample, according to electron microscopy analyses, was dominated by nanoscale carbon particles in aggregates of various sizes. There was no detectable photoluminescence from the sample and its aqueous suspension. The sample was treated in an aqueous nitric acid solution (up to 2.6 M) with refluxing for up to 12 h. The treated sample still exhibited no detectable photoluminescence. However, upon the surface passivation by attaching simple organic species to the acid-treated carbon particles (Scheme 1), bright luminescence emissions were observed (Figure 1).

Many organic molecules could serve as the purpose of surface passivation. For example, diamine-terminated oligomeric poly-(ethylene glycol) H₂NCH₂(CH₂CH₂O)_nCH₂CH₂CH₂NH₂ (average $n \sim 35$, PEG_{1500N}) was used to react with the carbon nanoparticles (Scheme 1).¹⁰ In a typical reaction, PEG_{1500N} (200 mg, 0.13 mmol) was mixed with an acid-treated particle sample, and the mixture was heated to 120 °C for 72 h. After the reaction, the mixture was cooled to room temperature and dispersed in water, followed by centrifuging (~1400g) for 30 min. The colored but homogeneous

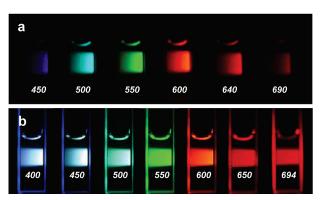


Figure 1. Aqueous solution of the PEG_{1500N} -attached carbon dots (a) excited at 400 nm and photographed through band-pass filters of different wavelengths as indicated, and (b) excited at the indicated wavelengths and photographed directly.

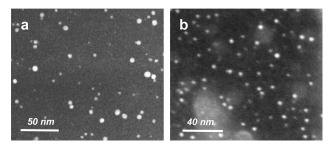
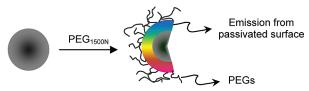


Figure 2. Representative STEM images of carbon dots surface-passivated with (a) PEG_{1500N} and (b) PPEI-EI.

Scheme 1



supernatant contained the carbon dots with PEG_{1500N} species attached to the surface (Scheme 1).¹¹ A small fraction of the supernatant was diluted for the preparation of microscopy specimens, deposited on a carbon-coated copper grid for scanning transmission electron microscopy (STEM) and on a mica surface for atomic force microscopy (AFM). The results suggest that these carbon dots are around 5 nm in diameter (Figure 2).

Other molecules or polymers, such as poly(propionylethyleneimine-*co*-ethyleneimine) (PPEI-EI), could also be used in largely the same reaction procedure for surface passivation to achieve similar results (Figure 2).

The passivated carbon dots with organic moieties attached to the surface are strongly photoluminescent both in the solution-like

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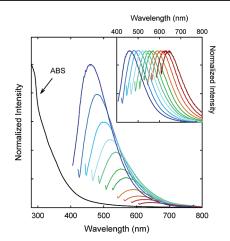


Figure 3. The absorption (ABS) and luminescence emission spectra (with progressively longer excitation wavelengths from 400 nm on the left in 20 nm increment) of PPEI-EI carbon dots in an aqueous solution. The emission spectral intensities are normalized to quantum yields (normalized to spectral peaks in the inset).

suspension and in the solid state, and the emissions cover the visible wavelength range and extend into the near-infrared (Figure 1). It should be pointed out that the organic and polymeric passivation agents (PEG_{1500N} and PPEI-EI) contain no visible or near-UV chromophores and therefore are obviously nonemissive at visible wavelengths. The observed bright and colorful luminescence emissions must be due to the surface-passivated carbon dots. As shown in Figure 3, the photoluminescence spectra of the carbon dots are generally broad and dependent on excitation wavelengths (Figure 1), which as in their silicon counterparts⁴ may reflect not only effects from particles of different sizes in the sample but also a distribution of different emissive sites on each passivated carbon dot.

The brightness of the photoluminescence is reflected in the high emission quantum yields. At 400 nm excitation, the observed quantum yields were from about 4% to more than 10%, where the variation probably depended on the effectiveness of the reaction for surface passivation. For example, when a sample of PEG_{1500N}or PPEI-EI-attached carbon dots was found to have the emission quantum yield at the lower end of the range, the sample could be reacted again with PEG_{1500N} or PPEI-EI under the same reaction conditions (thus improved surface passivation) to become more emissive with a higher quantum yield. Further effort is required to understand and better control the parameters dominating the particle surface passivation and resulting properties for carbon dots of brighter photoluminescence. Generally speaking, however, the presently observed luminescence emission yields of the carbon dots are comparable with those of traditionally prepared and passivated silicon nanocrystals.4

The photoluminescence of the carbon dots is stable with respect to photoirradiation, exhibiting no meaningful reduction in the observed intensities in the experiment of continuously repeating excitations for several hours. Unlike many other fluorescent nanoparticles,¹² there is no blinking in the luminescence emissions of the carbon dots according to laser scanning confocal microscopy analyses (commercially available gold nanocrystals as control under the same measurement conditions).

Mechanistically, the photoluminescence from carbon dots may be attributed to the presence of surface energy traps that become emissive upon stabilization as a result of the surface passivation. The requirement for surface passivation to become photoluminescent is apparently shared by the carbon dots and the silicon nanocrystals, for which a widely accepted mechanism for luminescence emission is the radiative recombination of excitons.⁴ For the photoluminescent carbon dots reported here, however, there must be a quantum confinement of emissive energy traps to the particle surface, namely, that a large surface-to-volume ratio in a particle is necessary in order for the particle upon surface passivation to exhibit strong photoluminescence. There has already been experimental evidence supporting such a mechanistic argument. Larger carbon particles (30–50 nm in average diameter, for example) with the same surface passivation were found to be much less luminescent. Conversely, it might be expected that even higher photoluminescence quantum yields be achieved in smaller carbon dots with the same or similar surface morphology and passivation.

As in their silicon counterparts,^{4,6} the carbon dots may, in principle, be separated or manipulated such that some of the inhomogeneity in photoluminescence is removed. On the other hand, the inhomogeneity may be exploited in the use of the surface-passivated carbon dots for optical labeling to allow the selection of different emission colors with different excitation wavelengths (in confocal microscopy, for example). The versatile surface functionalities as required for passivation will also be very useful for the carbon dots in bioimaging applications. The tethers, such as PEG_{1500N}, are not only aqueous compatible but also readily conjugated with antibodies or other bioactive molecules. Preliminary results on the optical imaging of biological species with the emissive carbon dots are provided in the Supporting Information.

Supporting Information Available: Additional characterization results, and preliminary results on the optical imaging of biological species. This material is available free of charge via the Internet at http://pubs.acs.org.

References

- Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. Science 2005, 307, 538–544.
- (2) (a) Derfus, A. M.; Chan, W. C. W.; Bhatia, S. N. Nano Lett. 2004, 4, 11–18. (b) Kirchner, C.; Liedl, T.; Kudera, S.; Pellegrino, T.; Javier, A. M.; Gaub, H. E.; Stolzle, S.; Fertig, N.; Parak, W. J. Nano Lett. 2005, 5, 331–338. (c) Lovric, J.; Cho, S. J.; Winnik, F. M.; Maysinger, D. Chem. Biol. 2005, 12, 1227–1234.
- (3) (a) Bharali, D. J.; Lucey, D. W.; Jayakumar, H.; Pudavar, H. E.; Prasad, P. N. J. Am. Chem. Soc. 2005, 127, 11364–11371. (b) Seydack, M. Biosens. Bioelectron. 2005, 20, 2454–2469.
- (4) Wilson, W. L.; Szajowski, P. F.; Brus, L. E. Science 1993, 262, 1242– 1244.
- (5) (a) Huisken, F.; Ledoux, G.; Guillos, O.; Reynaud, C. Adv. Mater. 2002, 14, 1861–1865. (b) Holmes, J. D.; Johnston, K. P.; Doty, C.; Korgel, B. A. Science 2000, 287, 1471–1473.
- (6) (a) Belomoin, G.; Therrien, J.; Smith, A.; Rao, S.; Twesten, R.; Chaieb, S.; Nayfeh, M. H.; Wagner, L.; Mitas, L. *Appl. Phys. Lett.* **2002**, *80*, 841–843. (b) Hua, F.; Swihart, M. T.; Ruckenstein, E. *Langmuir* **2005**, *21*, 6054–6062.
- (7) Li, Z. F.; Ruckenstein, E. Nano Lett. 2004, 4, 1463-1467.
- (8) Other recent studies on luminescence from carbon materials: (a) Xu, X.; Ray, R.; Gu, Y.; Ploehn, H. J.; Gearheart, L.; Raker, K.; Scrivens, W. A. *J. Am. Chem. Soc.* 2004, *126*, 12736–12737. (b) Yu, S.-J.; Kang, M.-W.; Chang, H.-C.; Chen, K.-M.; Yu, Y.-C. *J. Am. Chem. Soc.* 2005, *127*, 17604–17605. (c) Bottini, M.; Balasubramanian, C.; Dawson, M. I.; Bergamaschi, A.; Belluci, S.; Mustelin, T. *J. Phys. Chem. B* 2006, *110*, 831–836.
- (9) Suda, Y.; Ono, T.; Akazawa, M.; Sakai, Y.; Tsujino, J.; Homma, N. *Thin Solid Films* **2002**, 415, 15–20.
- (10) Huang, W.; Fernando, S.; Allard, L. F.; Sun, Y.-P. Nano Lett. 2003, 3, 565-568.
- (11) The linkages for the attachment might be similar to those found in the functionalization of carbon nanotubes at surface defect sites (see ref 10, for example).
- (12) (a) Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. *Nature* **1996**, *383*, 802–804. (b) Krug, J. T.; Wang, G. D.; Emory, S. R.; Nie, S. J. Am. Chem. Soc. **1999**, *121*, 9208–9214. (c) English, D. S.; Pell, L. E.; Yu, Z.; Barbara, P. F.; Korgel, K. A. Nano Lett. **2002**, *2*, 681–685.

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