Controlled synthesis of green and blue luminescent carbon nanoparticles with high yields by the carbonization of sucrose

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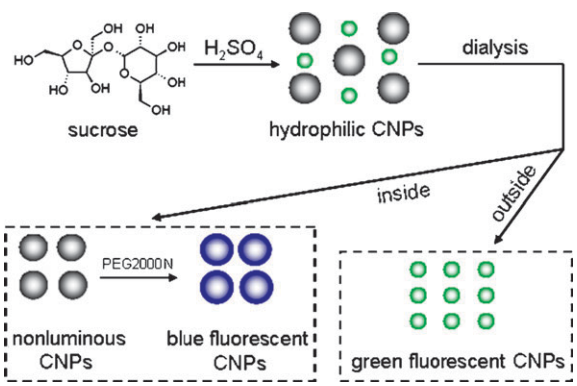
High yields of hydrophilic carbon nanoparticles (CNPs) were prepared by the controlled carbonization of sucrose. Green luminescent CNPs and non-luminous CNPs were effectively separated by dialysis. After surface functionalisation with PEG2000N, the non-luminous CNPs successfully emitted a blue fluorescence.

Recently, increased attention has been drawn to carbon-based luminescent nanomaterials, especially luminescent CNPs,[1–8] which are finding novel applications in biosensing and bioimaging.[9,10] Compared to traditional dye molecules and semiconductor quantum dots, such as CdSe, luminescent CNPs have the unique advantages in PL stability and biological non-toxicity, respectively. To date, two kinds of methods to produce luminescent CNPs have been developed. One way is primarily based on the post-treatment of large non-luminous carbon materials.[1,2,5,11–15] For example, CNPs of ~5 nm were prepared by the laser ablation of graphite, a subsequent strong acid oxidation and further surface passivation with organic moieties such as diamine-terminated PEG.[1] Other carbon precursors, such as carbon nanotubes,[11] combustion candle soot,[2] diamonds[5,12,13] and graphene,[14] have also been used to prepare luminescent CNPs *via* an electrochemical treatment or strong acid oxidization. Another effective method is the pyrolysis of carbonaceous precursors such as citric acid monohydrate and octadecyl ammonium.[7,15,16] More recently, luminescent CNPs with amorphous structures have been prepared using surfactant-modified silica spheres as carriers and resols as the carbon precursor.[4] However, these methods usually involve complex processes and severe synthetic conditions. More importantly, due to difficult separation and purification or aggregation during pyrolysis, low effective yields of CNPs are inevitable in both methods. Therefore, an effective way to prepare luminescent CNPs in high yields and in high quality is urgently needed.

We are interested in developing facile ways to obtain multicolor CNPs from environmentally friendly and biocompatible materials. Recently, Peng and Jadranka prepared luminescent CNPs using carbohydrates as starting materials.[8] During the synthesis, sulfuric acid was used to produce carbonaceous materials, though further treatment with nitric acid and amine-terminated compounds was indispensable for the synthesis of luminescent CNPs. Here, different from Peng and Jadranka's work, we have developed a more convenient way to synthesize hydrophilic CNPs in high yields (~50%) by the controlled carbonization of sucrose using only sulfuric acid. Interestingly, we successfully obtained green luminescent CNPs (~1–2 nm) by dialysis from hydrophilic CNPs without surface passivation. The majority of hydrophilic CNPs, which cannot emit fluorescence effectively, can, however, successfully emit blue fluorescence after surface functionalisation with diamine-terminated compounds (PEG2000N), as illustrated in Scheme 1.

An XRD pattern and FTIR spectrum were used to characterize the hydrophilic CNPs. After treatment with concentrated sulfuric acid, the CNPs showed excellent solubility, as shown in Fig. 1(a) (inset), caused by the formation of –C═O (1703 cm^{-1}) and –OH (3426 cm^{-1}) groups, as shown in Fig. 1(b), during the carbonization. The concentrated sulfuric acid may have three functions: (a) to form CNPs by the dehydration of sucrose, (b) to introduce oxygen-containing groups onto the surface of the CNPs and (c) to form more defects on their surface. The characteristic absorption band at 1019 cm^{-1} demonstrates the existence of sulfonic groups on the surface of the CNPs. The XRD pattern of the hydrophilic CNPs in Fig. 1(a) demonstrates that their (002) interlayer spacing is 4.2 Å, larger than that of bulk graphite (3.3 Å), indicating poor crystallization.

Ultrafine CNPs were obtained from hydrophilic CNPs by dialysis. The colour of the solution was light yellow, as shown in Fig. 3(a), inset (right). The AFM image (Fig. 2(a)) and size



Scheme 1 The synthesis procedure of green and blue luminescent CNPs.

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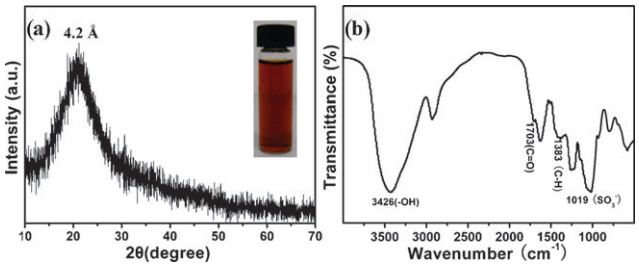

Fig. 1 The (a) XRD pattern and (b) FTIR spectrum of the hydrophilic CNPs. Inset: photograph of the hydrophilic CNP solution taken under visible light.

distribution (Fig. 2(b)) show that the product consists of symmetrical ultrafine CNPs with sizes of ~1–2 nm. It is exciting that, unlike other reported CNPs,[1,3,4,8] these ultrafine CNPs emit a bright green luminescence (Fig. 3(a), inset (left)) without further treatment, such as passivation. The optical properties of the green luminescent CNPs dispersed in water are shown in Fig. 3(a,b). No obvious absorption band was observed in the UV-vis absorption spectrum. Upon excitation at 410 nm, the maximum PL peak was observed at 500 nm (Fig. 3(a)). As shown in Fig. 3(b), the PL spectrum of the green luminescent CNPs was dependent on the excitation wavelength (the PL peak shifted from 490 to 550 nm as the excitation wavelength increased from 400 to 500 nm). It is worth mentioning that these easily obtained green luminescent CNPs are suitable for biological labelling and imaging.

Most of the hydrophilic CNPs exhibited no detectable PL signal and were cut off inside when dialysed in a dialysis bag (retained molecular weight 3500 Da). After surface passivation

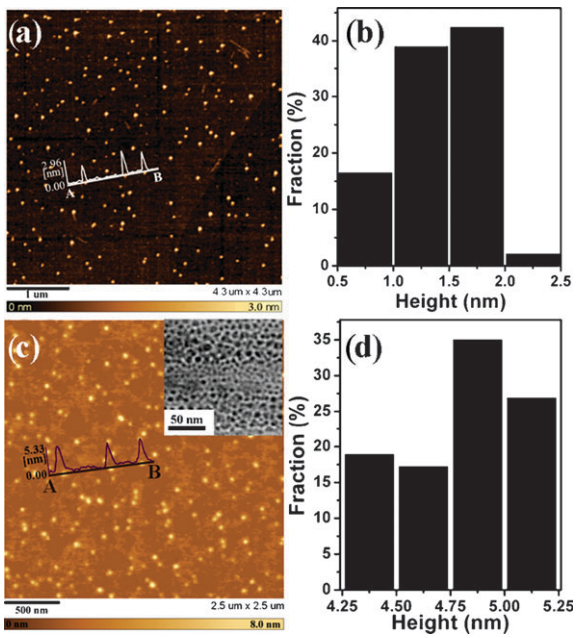

Fig. 2 AFM images and cross-section analyses of the (a) green and (c) blue luminescent CNPs deposited onto freshly cleaved mica substrates. Note that the size of the green luminescent CNPs is about 2 nm and that of the blue luminescent CNPs is ~5 nm. The height distribution of the (b) green and (d) blue luminescent CNPs. Inset: TEM image of the blue luminescent CNPs.

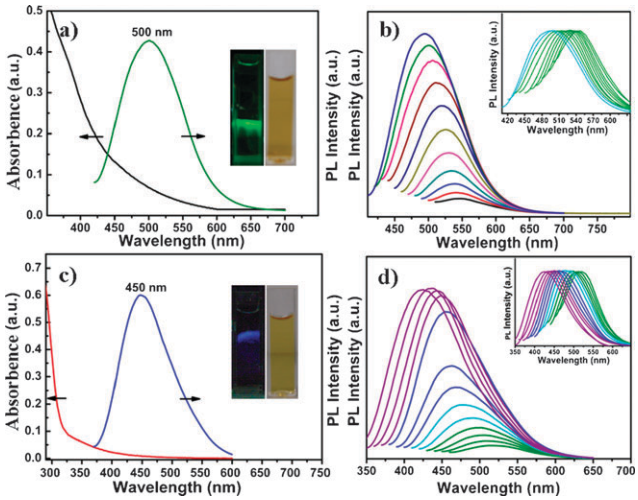

Fig. 3 Absorption and emission spectra of (a) green and (c) blue luminescent CNPs dispersed in distilled water. Inset: photographs of each kind of luminescent CNP solution taken under a UV light in a fluorescence spectrophotometer (left) and under visible light (right). (b) Emission spectra of green luminescent CNPs at excitation wavelengths progressively increasing from 400 nm in 10 nm increments. (d) Emission spectra of blue luminescent CNPs at excitation wavelengths progressively increasing from 330 nm in 10 nm increments. Inset: normalized emission spectra.

with PEG2000N, the non-luminus CNPs emitted a blue fluorescence (Fig. 3(c), inset (left)). The AFM image of the blue luminescent CNPs is shown in Fig. 2(c), the average size of the CNPs being about 4–5 nm (Fig. 2(d)), much larger than that of the green luminescent CNPs. The diameter of these CNPs, as estimated from the TEM image (Fig. 2(c), inset), is approximately 5 nm. Therefore, these CNPs are symmetrical and well-dispersed small carbon nanospheres. The absorption and PL spectra of this product in a dilute aqueous solution is shown in Fig. 3(c). There is a slight absorption shoulder at about 355 nm and the maximum emission wavelength is not significantly changed by the excitation wavelength between 330 and 360 nm. Upon 355 nm excitation, a maximum emission peak at 450 nm was observed with a Stokes shift of 95 nm. Similar to the green luminescent CNPs, the PL spectrum of the blue luminescent CNPs was dependent on excitation, and the emission could be tuned between 400 and 520 nm.

Fig. 4 shows the photostability of the green and blue luminescent CNPs. No photobleaching was observed for 600 s in a fluorescence spectrophotometer upon 410 nm (Fig. 4(a)) and 355 nm (Fig. 4(b)) excitation, indicating that these CNPs display good photostability.

The intrinsic mechanism of CNP luminescence is not yet fully understood. The luminescence has been tentatively suggested to arise from excitons of carbon,[11] emissive traps,[1] aromatic structures[5] and free zig-zag sites.[14] In this Letter, green luminescent CNPs have been shown to emit fluorescence effectively without surface passivation, possibly because of certain defects, such as edge defects or zig-zag sites, due to their much larger surface area. Besides, surface functionalisation with PEG2000N could increase such defects on the surface of non-luminous CNPs so that effective fluorescence is

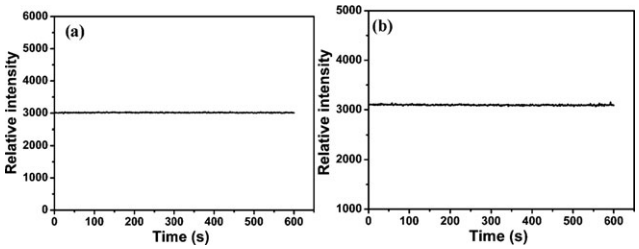

Fig. 4 Photostability tests of (a) green and (b) blue luminescent CNPs in a fluorescence spectrophotometer using 410 and 355 nm excitation, respectively.

detected. However, a widely accepted mechanism for luminescence emission from CNPs needs systematic investigation; work related to this is under way in our laboratory.

In conclusion, we have developed a facile one-step method to synthesize high yields of hydrophilic CNPs using sucrose as the starting material. Bright green luminescent CNPs were obtained by dialysis. Blue luminescent CNPs were prepared from non-luminous CNPs functionalized with PEG2000N. The origin of the luminescence may be derived from defects on the surface of these CNPs. These non-toxic and multi-colored CNPs should have a wealth of applications in biological labelling and imaging.

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Experimental section

Preparation of hydrophilic carbon nanoparticles (CNPs)

1 mL of distilled water was added to 2.04 g of sucrose. After the sucrose had completely dissolved, 2 mL of concentrated sulfuric acid was added dropwise with vigorous stirring. No solid was observed during the reaction. 40 mL of distilled water was then added. The obtained uniformly brown solution was then neutralized with 1.5 g of NaOH. The hydrophilic CNPs (~1.0 g) were obtained *via* dialysis over water in a dialysis bag (retained molecular weight 1000 Da) for 1 d to remove all salts and the remaining sucrose.

Separation of green luminescent CNPs and non-luminous CNPs

0.5 g of hydrophilic CNPs were dissolved in distilled water and dialyzed over water in a dialysis bag (retained molecular weight 3500 Da) for 1 d. The solutions outside and inside the dialysis bag were collected separately. The outside solution was evaporated to remove the water, and green luminescent CNPs were obtained. Non-luminous CNPs were obtained by evaporating the inside solution.

Preparation of blue luminescent CNPs

10 mg of non-luminous CNPs mixed with 20 mg of PEG2000N were added to 4 mL of distilled water and heated to 90 °C with vigorous stirring under a nitrogen atmosphere for 4 h. The reaction mixture was cooled to room temperature and the supernatant retained after centrifugation at 18 000 rpm. The obtained solution was dialyzed over water in a dialysis bag (retain molecular weight 3500 Da) for 1 d to remove the remaining PEG2000N.

Characterization methods

Atomic force microscopic (AFM) images were acquired using a SPM-9600 atomic force microscope. Transmission electron microscope (TEM) observations were performed using a JEOL JEM-2010F electron microscope operating at 200 kV. X-Ray powder diffraction (XRD) patterns were obtained from a Japan Regaku D/max-2500 instrument using Cu-K_α radiation. Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad FTIR spectrometer FTS 165. Absorption and fluorescence spectra were recorded at room temperature by a Hitachi 3100 spectrophotometer and a Hitachi 7000 fluorescence spectrophotometer, respectively.

References

1 Y. P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, H. F. Wang, P. G. Luo, H. Yang, M. E. Kose, B. L. Chen, L. M. Veca and S. Y. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756–7757.
2 H. P. Liu, T. Ye and C. D. Mao, *Angew. Chem., Int. Ed.*, 2007, **46**, 6473–6475.
3 S. L. Hu, K. Y. Niu, J. Sun, J. Yang, N. Q. Zhao and X. W. Du, *J. Mater. Chem.*, 2009, **19**, 484–488.
4 R. L. Liu, D. Q. Wu, S. H. Liu, K. Koynov, W. Knoll and Q. Li, *Angew. Chem., Int. Ed.*, 2009, **48**, 4598–4601.
5 V. N. Mochalin and Y. Gogotsi, *J. Am. Chem. Soc.*, 2009, **131**, 4594–4595.
6 Q. L. Zhao, Z. L. Zhang, B. H. Huang, J. Peng, M. Zhang and D. W. Pang, *Chem. Commun.*, 2008, 5116–5118.
7 A. B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, M. Karakassides and E. P. Giannelis, *Small*, 2008, **4**, 455–458.
8 H. Peng and T. S. Jadranka, *Chem. Mater.*, 2009, **21**, 5563–5565.
9 L. Cao, A. Harruff, L. M. Veca, D. Murray, S. Y. Xie and Y. P. Sun, *J. Am. Chem. Soc.*, 2007, **129**, 11318–11319.
10 S. T. Yang, L. Cao, P. G. Luo, F. S. Lu, X. Wang, H. F. Wang, M. J. Meziani, Y. F. Liu, G. Qi and Y. P. Sun, *J. Am. Chem. Soc.*, 2009, **131**, 11308–11309.
11 J. G. Zhou, C. Booker, R. R. Li, X. T. Zhou, T. K. Sham, X. L. Sun and Z. F. Ding, *J. Am. Chem. Soc.*, 2007, **129**, 744–745.
12 B. R. Smith, D. W. Inglis, B. Sandnes, J. R. Rabeau, A. V. Zvyagin, D. Gruber, C. J. Noble, R. Vogel, E. Osawa and T. Plakhotnik, *Small*, 2009, **5**, 1649–1653.
13 S. J. Yu, M. W. Kang, H. C. Chang, K. M. Chen and Y. C. Yu, *J. Am. Chem. Soc.*, 2005, **127**, 17604–17605.
14 D. Y. Pan, J. C. Zhang, Z. Li and M. H. Wu, *Adv. Mater.*, 2009, DOI: 10.1002/adma.200902825.
15 A. B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, M. Karakassides and E. P. Giannelis, *Chem. Mater.*, 2008, **20**, 4539–4541.
16 B. R. Selvi, D. Jagadeesan, B. S. Suma, G. Nagashankar, M. Arif, K. Balasubramanyam, M. Eswaramoorthy and T. K. Kundu, *Nano Lett.*, 2008, **8**, 3182–3188.