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A Novel One-Step Approach to Synthesize Fluorescent Carbon Nanoparticles

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Fluorescent carbon nanoparticles (CNPs) were prepared directly by a simple hydrothermal method by using L-ascorbic acid as a carbon source. The synthesized CNPs with higher photoluminescence efficiencies (6.79 %) are monodisperse, and their diameter is about 2.0 nm. In contrast to previous methods, for this one-step process, neither strong acid treatment nor further surface modification is necessary. Aqueous solutions of the CNPs are stable at room temperature for at least half a year. In particular, the fluorescence of the CNPs does not change over a wide pH range and even in solvents with strong ionic strengths (e.g. 2 M NaCl).

Introduction

Fluorescent semiconductor nanomaterials (InAs, CdS, CdSe, etc.), often called quantum dots (QDs), have wide potential application in many fields such as biomedical imaging and sensing,[1–4] photovoltaic devices,[5–7] and lasers.[8] Although semiconductor quantum dots have unique properties and excellent performance, they have obvious deficiencies, such as being cytotoxic and posing environmental hazards. Many efforts have been devoted in recent years to overcome these disadvantages; however, these efforts have not resulted in significant success. Thus, to develop novel alternative materials is a very challenging goal for the next few years.

Fluorescent carbon nanoparticles (CNPs) were first produced by Sun et al.[9] They were considered as a brand-new class of fluorescent materials due to their nontoxicity, biocompatibility, and environment-friendliness, relative to semiconductor quantum dots. Recently, several methods to prepare CNPs have been reported, for example, laser ablation of graphite,[9,10] electrochemical oxidation and treatment of graphite[11,12] and mutiwalled carbon nanotubes (MWCNTs),[13] chemical oxidation of candle soot[14] and natural gas soot.[15] Nevertheless, these routes usually require not only complicated apparatus and expensive materials, but also complex post-treatment to improve the quantum yield (QY) and water solubility of the CNPs. Meanwhile, their isolation, purification, and functionalization are all complex and time-consuming. The hydrothermal method has been widely applied to prepare various materials, because of the high reactivity of the reactants, easy control of the solution, low level of air pollution, and low energy consumption under hydrothermal conditions.[16] However, there are no reports on the direct synthesis of fluorescent CNPs by the hydrothermal approach. In the present work, we established a one-step hydrothermal route to prepare fluorescent CNPs. Compared with the previous works, the process is economical and green, the prepared fluorescent CNPs have higher photoluminescence efficiencies, they are water-soluble and monodisperse. The most important feature is that the CNPs did not need further surface modification, as was usually the case with complex and poisonous amine-terminated compounds, such as diamine-terminated oligomeric poly(ethylene glycol), poly(propionylethyleneimine-co-ethyleneimine), octadecylamine, and tridecanediamine, or strong acids (sulfuric acid, nitric acid, perchloric acid). The one-step preparation process and the separation of CNPs from the mixture are simple and effective, which makes this approach very suitable for industrial production.

Results and Discussion

Field-emission transmission electron microscopy (FETEM) images of the CNPs in samples A and B are shown in Figures 1a and b, respectively. The particles are well dispersed. sample A has a highly uniform shape with a particle diameter of 2.0–2.5 nm (Figure 1a). Sample B has a wide size distribution (1.0–8.5 nm) and irregular shapes (Figure 1b). The X-ray diffraction pattern of sample A has a broad peak at about 23° (Figure S2 in the Supporting Information). In the Raman spectrum of sample A (Figure S3), there are two characteristic vibrations at 1346 and 1590 cm^{-1}, which can be related to a defect band (D band) and a graphite band (G band).[19] The G band is attributed to the vibration of sp^2-bonded carbon atoms in a 2D hexag-

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onal lattice, while the D band is associated with vibrations of carbon atoms with dangling bonds in plane terminations of the disordered graphite and related to the defects and disorders in the structures of carbon materials. The relative intensities of these two bands reflect the graphitization degree,[20] and the fact that these two broad peaks overlap strongly indicates the amorphous structure of the CNPs prepared in the present work, which is consistent with many previous studies[17,21,22] and with the results of XRD experiments.

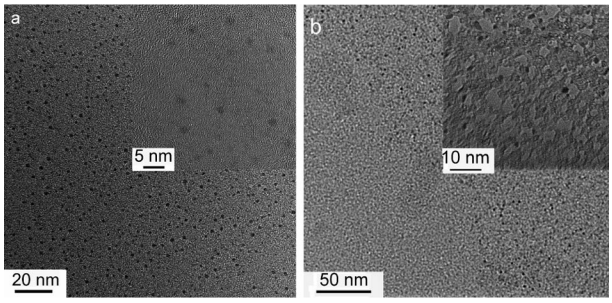

Figure 1. (a) FETEM image of sample A, (b) FETEM image of sample B.

As shown in Figure 2 and Figure S1 (Supporting Information), the absorption peaks of samples A and B appear at about 264 and 265 nm, respectively. The excitation and emission spectra with good symmetry are similar to those of semiconductor quantum dots. A very well-defined excitation peak appears at 340 nm, and an emission peak at 420 nm, with a large energy discrepancy. This small Stokes shift (80 nm) could provide a new idea for investigating the mechanism of the fluorescence of CNPs. Certainly, further investigation will be needed to confirm this. With increasing excitation wavelength, the fluorescence spectra shift to longer wavelengths (Figures 2a and S1a). These reflect not only the effects of particles of different sizes, but also a considerable distribution of emissive trap sites on each CNP.[17] Although samples A and B have the same photoluminescence emission peaks centered at 430 nm (blue), the relative intensity of sample B is much weaker than that of sample A under the same conditions. The spectrum of sample A is characterized by good symmetry and relatively narrow spectral width. The full width at half maximum (FWHM) of the emission spectrum of the sample A excited at 330 nm is only 65 nm (Figure 2a), much smaller than that previously reported,[10–15,17,18] which suggests a narrow size distribution of the product particles, in accordance with the result in Figure 1a. The fluorescence QY of sample A, measured against an aqueous solution of quinine sulfate (λ_{exc} = 340 nm), is about 6.79% (Table S1). This value is higher than those in previous reports.[14,15,17,23] Figure S6 shows that the as-synthesized CNPs yielded bright blue emission in four different solvents (water, ethanol, acetone, ethyl acetate) when illuminated under UV light (365 nm). It was observed that the water-soluble CNP solutions were very stable for at least six months at room temperature without a decrease in their fluorescence.

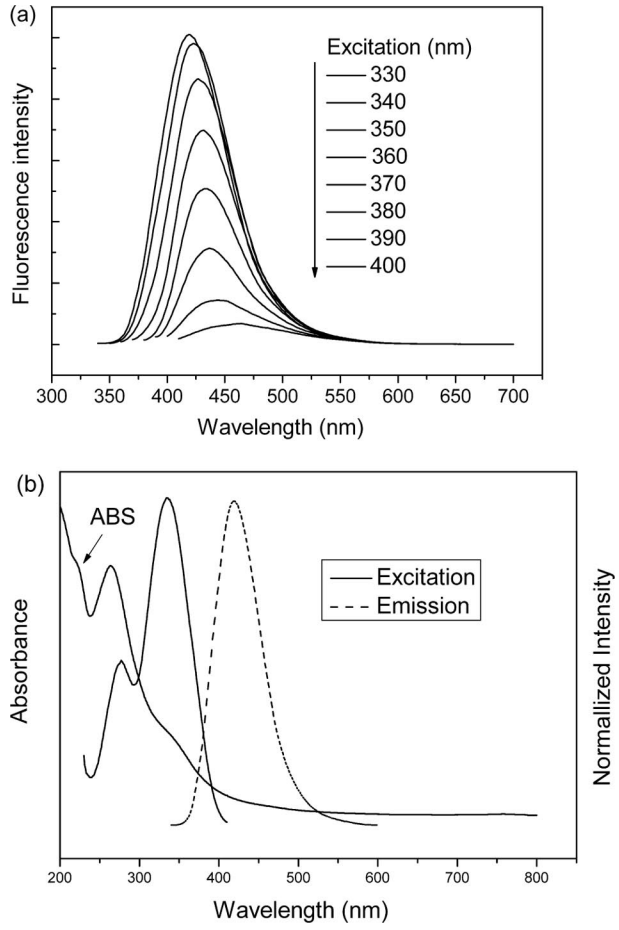

Figure 2. (a) Emission spectra of sample A at different excitation wavelengths; (b) UV/Vis absorption, excitation, and emission spectra of sample A.

The experiments showed that the QY of the CNPs varies with the hydrothermal reaction time. For example, at 180 °C, changing the reaction time from 2 h to 4 h caused an increase in the QY of the sample from 2.39% to 6.79%, and after 6–16 h, the quantum efficiency was stable at around 6% (5.55% for 6 h, 6.15% for 8 h, and 5.85% for 16 h). This change in the emission efficiency was most likely due to defects on the surface of the particles introduced during hydrothermal treatment. After a certain time, the states of the surface of particles were not changed significantly by this nonradiative pathway. In contrast, the QY of sample B measured against quinine sulfate (λ_{exc} = 340 nm) was only about 0.82% (Table S1), much lower than that of sample A.

The enhanced QY of emission of sample A with respect to that of sample B is an interesting phenomenon. The only difference between the two samples is that sample A was prepared with ethanol (see Experimental Section); all other conditions were the same. We also tried other solvents in the experiment instead of ethanol, such as 2-propanol, glycol, 1,2-propanediol, polyethylene glycol 600 (PEG_{600}), PEG_{300}. However, the quantum yield of as-synthesized CNPs were low in each case (<2%) (Table S1). It is reasonable to deduce that ethanol plays a key role in the prepara-

tion of fluorescent CNPs. The above results indicate that photoluminescence is correlated with the type of solvent, size, and shape. Up to now, the luminescence mechanism of CNPs and carbogenic dots has still not been clearly understood. Some scientists put forward the theory that the quantum confinement of the emissive energy traps on the surface of the particles is responsible for the fluorescence of CNPs,[9] some others attribute the origin of the luminescence to carboxylate ligands on the surface of the CNPs.[10] Evidently, ethanol plays a key role in obtaining the fluorescent CNPs in the present work. Firstly, CNPs could uniformly grow in a mixed solvent composed of water and ethanol; further, the ethanol may have capped the CNPs and inhibited their aggregation. Secondly, ethanol improved surface state of the CNPs to enhance the fluorescence effect. Therefore, the origin of the luminescence may be attributed to the solvent, as well as the shape and size of the CNPs.

FTIR spectra were acquired to determine the ligands on the surface of the CNPs; the results are shown in Figure 3. Spectra of samples A and B display many common characteristics. The FTIR peaks at 3425 and 1637 cm^{-1} are attributed to the stretching vibrations of O–H and C=O; the peaks at 1410 and 1100 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of C–O–C, respectively.[20] Obviously, the surfaces of the CNPs were partially oxidized, and the hydroxy groups were transformed to the carboxylate groups. However, the surface hydrophilic groups could stabilize the CNPs in aqueous solution and provide the medium for hydrophilic reaction. The as-obtained CNPs had different solubilities in various solvents. The CNPs obtained can be freely dispersed in water and in ethanol. Experiments showed that the solubility of the CNPs reached 160 mg/mL in water, approximately 80 mg/mL in ethanol, 20 mg/mL in acetone, and 12 mg/mL in ethyl acetate; they were insoluble in dichloromethane and toluene. Moreover, we investigated the influence of ionic strengths and pH on the fluorescence intensity of sample A (Figures S4 and S5). The results showed that the fluorescence intensity of the CNPs did not change even in aqueous solution with a high ionic strength (2 M NaCl). The pH value of the solution had some effects on the photoluminescence of the CNPs. The fluorescence intensity of the CNPs did not change when the solution pH varied from 4.0 to 8.0. Interestingly, the fluorescence intensity decreased significantly when the pH value was out of this range. When the pH of the system was adjusted back to the range of 4.0 to 8.0, the fluorescence intensity of the CNPs became high again. These phenomena make the fluorescent CNPs good candidates for biological applications and for use as pH sensors.

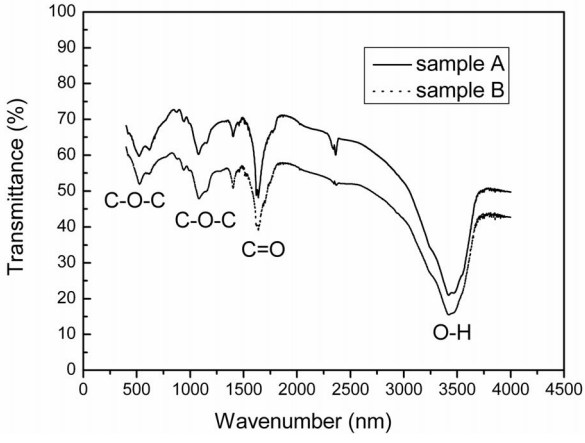

Figure 3. FTIR spectra of samples A and B.

Conclusions

In summary, we have developed a one-step route to generate fluorescent carbon nanoparticles by a hydrothermal method using L-ascorbic acid as a carbon source. The CNPs with diameters of about 2.0 nm have higher photoluminescence efficiencies and are monodisperse. No strong acid treatment or further surface modification were necessary in their preparation. This method has significant advantages such as being simple, green, and economical with regard to the carbon source. The fluorescence intensity of as-prepared CNPs show good stability in environments of high ionic strength. It can also be tuned by adjusting the pH. Excellent water solubility, good stability, low cost, and environmental friendliness make the application of these fluorescent CNPs in biological labeling, imaging, and disease diagnosis feasible.

Experimental Section

All chemicals were purchased from the Beijing Chemical Company and used without further purification. L-Ascorbic acid (1.1 g) was dissolved in deionized water (25 mL) in a 100 mL glass beaker, and then ethanol (25 mL) was added into the solution to form a homogeneous solution under magnetic stirring. Then, an aliquot (25 mL) of the mixture was transferred into a 40 mL Teflon®-lined stainless steel autoclave and heated at 180 °C for 4 h and then cooled to room temperature naturally. A dark brown solution was obtained, which implied the formation of the CNPs. After extraction with dichloromethane, the water-phase solution was dialyzed by using cellulose ester dialysis membranes (MW: 8000–14000) for two days to remove all impurity molecules. Finally, a yellow aqueous solution containing CNPs was obtained and named sample A. For control experiments, ethanol was replaced by deionized water in the system, and other conditions were kept the same, the resulting product was named sample B.

Supporting Information (see footnote on the first page of this article): UV/Vis absorption and fluorescence spectra of sample B; quantum yields; X-ray diffractogram of sample A; Raman spectrum of sample A; influence of ionic strengths on the fluorescence intensity of sample A; the effect of pH on the fluorescence intensity of sample A.

[1] M. Bruchez, M. Moronne, P. Gin, S. Weiss, A. P. Alivisatos, *Science* **1998**, *281*, 2013–2016.
[2] W. C. W. Chan, S. M. Nie, *Science* **1998**, *281*, 2016–2018.

[3] W. Jiang, A. Singhal, J. N. Zheng, C. Wang, W. C. W. Chan, *Chem. Mater.* **2006**, *18*, 4845–4854.
[4] A. M. Derfus, W. C. W. Chan, S. N. Bhatia, *Nano Lett.* **2004**, *4*, 11–18.
[5] E. Kikuchi, S. Kitada, A. Ohno, S. Aramaki, S. Maenosono, *Appl. Phys. Lett.* **2008**, *92*, 173307–173309.
[6] K. S. Leschkies, R. Divakar, J. Basu, E. Enache-Pommer, J. E. Boercker, C. B. Carter, U. R. Kortshagen, D. J. Norris, E. S. Aydil, *Nano Lett.* **2007**, *7*, 1793–1798.
[7] R. S. Aga, D. Gunther, A. Ueda, Z. Pan, W. E. Collins, R. Mu, K. D. Singer, *Nanotechnology* **2009**, *20*, 465204–465211.
[8] H. S. Djie, B. S. Ooi, X. M. Fang, Y. Wu, J. M. Fastenau, W. K. Liu, M. Hopkinson, *Opti. Lett.* **2007**, *32*, 44–46.
[9] 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. J. G. Luo, H. Yang, M. E. Kose, B. L. Chen, L. M. Veca, S. Y. Xie, *J. Am. Chem. Soc.* **2006**, *128*, 7756–7757.
[10] S. L. Hu, K. Y. Niu, J. Sun, J. Yang, N. Q. Zhao, X. W. Du, *J. Mater. Chem.* **2009**, *19*, 484–488.
[11] Q. L. Zhao, Z. L. Zhang, B. H. Huang, J. Peng, M. Zhang, D. W. Pang, *Chem. Commun.* **2008**, *41*, 5116–5118.
[12] L. Y. Zheng, Y. W. Chi, Y. Q. Dong, J. P. Lin, B. B. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 4564–4565.
[13] J. G. Zhou, C. Booker, R. Y. Li, X. T. Zhou, T. K. Sham, X. L. Sun, Z. F. Ding, *J. Am. Chem. Soc.* **2007**, *129*, 744–745.
[14] H. P. Liu, T. Ye, C. D. Mao, *Angew. Chem. Int. Ed.* **2007**, *46*, 6473–6475.
[15] L. Tian, D. Ghosh, W. Chen, S. Pradhan, X. J. Chang, S. W. Chen, *Chem. Mater.* **2009**, *21*, 2803.
[16] S. H. Feng, R. R. Xu, *Acc. Chem. Res.* **2001**, *34*, 239–247.
[17] H. Zhu, X. L. Wang, Y. L. Li, Z. J. Wang, F. Yang, X. R. Yang, *Chem. Commun.* **2009**, *34*, 5118–5120.
[18] R. L. Liu, D. Q. Wu, S. H. Liu, K. Koynov, W. Knoll, Q. Li, *Angew. Chem. Int. Ed.* **2009**, *48*, 4598–4601.
[19] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Poschl, *Carbon* **2005**, *43*, 1731–1742.
[20] F. B. Su, J. H. Zeng, X. Y. Bao, Y. S. Yu, J. Y. Lee, X. S. Zhao, *Chem. Mater.* **2005**, *17*, 3960.
[21] F. Wang, M. Kreiter, B. He, S. P. Pang, C. Y. Liu, *Chem. Commun.* **2010**, *46*, 3309–3311.
[22] A. B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, V. Georgakilas, E. P. Giannelis, *Chem. Mater.* **2008**, *20*, 4539–4541.
[23] S. C. Ray, A. Saha, N. R. Jana, R. Sarkar, *J. Phys. Chem. C* **2009**, *113*, 18546–18551.

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