One-step synthesis of fluorescent carbon nanoparticles by laser irradiation†

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Fluorescent carbon nanoparticles (CNPs) were synthesized by laser irradiation of a suspension of carbon powders in organic solvent. The surface modification on the CNPs was fulfilled simultaneously with the formation of the CNPs, and tunable light emission could be generated by selecting appropriate solvents. The origin of the luminescence was attributed to carboxylate ligands on the surface of the CNPs.

Introduction

Fluorescent carbon nanoparticles (CNPs) show high potential in the application of biological labelling and life sciences,[1–12] as they have many advantages over the conventional quantum dots based on sulfides, selenides or tellurides of zinc and cadmium; they are biocompatible, chemically inert, and can be surface-modified.[1–8] In particular, CNPs can emit visible light *via* two-photon excitation by using near-infrared light. The two-photon excitation makes photodynamic therapy harmless to health tissue adjacent to diseased target tissue.[9–11]

One common route for obtaining luminescent CNPs is to create point defects, *e. g.* nitrogen-vacancy centres, in reasonably large nanodiamonds (over several tens of nanometres).[2,3,12] However, it is difficult to introduce a large number of point defects into ultra-fine nanodiamonds (<10 nm) for bright luminescence. Recently, fine luminescent CNPs (<6 nm) were obtained *via* surface passivation[13] with an electrochemical route,[14] or from candle soot,[15] where the luminescence was strong, and did not show any sign of blinking.[13–15] Nevertheless, these methods usually involve complex processes,[13,15] or need expensive starting materials and severe synthetic conditions[14]. On the other hand research on the luminescent mechanism of CNPs is far from sufficient,[9,13,14] with, for example, information on the microstructure and surface ligands remaining unclear, and details of the organic passivation not available to aid understanding of the surface states beneficial for light emission.

Herein, we report an effective method of synthesizing fluorescent CNPs by laser irradiation of a suspension of carbon materials in organic solvent; the synthesis and the surface modification of the luminescent CNPs were believed to occur simultaneously. Compared with previous work, such a one-step process is simple and can easily be carried out industrially. In particular, by selecting organic solvents, the surface states could be modified conveniently to achieve tuneable light emission. Based on the results of control experiments, the origin of the luminescence is proposed to be the surface states related to the ligands on the surface of the CNPs.

Experimental

All chemicals were purchased from Kewei Company and used without further purification. Graphite powders with an average size of 2 μm were purchased from Qindao Graphite Co. Ltd. A Nd:YAG pulsed laser with a wavelength of 1.064 μm and power density of 6.0×10^6 W cm^{-2} was used to irradiate graphite powders dispersed in three kinds of solvents, diamine hydrate, diethanolamine, and poly(ethylene glycol) (PEG$_{200N}$), respectively. Ultrasound was employed during the laser irradiation to expedite the movement of carbon particles. After 2 h irradiation a homogeneous black suspension was obtained which was centrifuged and separated into a black carbon precipitate and a colourful supernatant. The supernatant was used for further analysis. The supernatant from the suspension of graphite in PEG$_{200N}$ was named as sample A.

The experiments on functionalizing the CNPs were also performed to clarify the luminescent mechanism. Firstly, sample B was produced by irradiating the suspension of graphite powders in deionized water using the procedures described above, next, sample B was boiled in perchloric acid ($HClO_4$), mixed with PEG$_{200N}$, heated to 120 °C, held for 72 h, cooled to room temperature, and then centrifuged (6000 rpm) for 40 min. The resultant supernatant was separated and named as sample C.

Diluted supernatants containing CNPs were dropped onto copper grids covered with amorphous carbon film to prepare specimens for transmission electron microscopic (TEM) observation which was performed in a FEI Tecnai G2 F20 microscope with a field-emission gun operating at 200 kV. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured on a Hitachi F4500 fluorescence spectrophotometer. A Nicolet 560 Fourier transform infrared (FTIR) spectrometer and a Perkin-Elmer PHI-1600 X-ray photoelectron spectrometer (XPS) were employed to analyze chemical bonds on the surface of CNPs.

The quantum yield was measured by comparing the integrated photoluminescence intensities and the absorbency values of the samples with the reference quinine sulfate. The protocol for

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quantum yield measurements follows references16–18 and the quantum yield was calculated using the following equation:

$$Q = Q_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

where Q is the quantum yield, I is the measured integrated emission intensity, η is the refractive index, and A is the optical density. The subscript R refers to the reference fluorophore of known quantum yield. In order to minimise re-absorption effects the optical densities in the 20 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength. An excitation slit width of 2.5 nm and an emission slit width of 2.5 nm were used to excite the CNP samples and to record their photoluminescence spectra.

Results and discussion

Three samples were prepared to fabricate luminescent CNPs and investigate the luminescent mechanism. Samples A and B were produced by laser irradiation of the suspensions of graphite powders in PEG_{200N} and water, respectively; then sample B was oxidized by perchloric acid and reacted with PEG_{200N} to obtain sample C.

Transmission electron microscope (TEM) images of the CNPs in samples A and B are shown in Fig. 1a and 1b, respectively, the as-prepared CNPs are well dispersed. Both samples give the same selected area electron diffraction (SAED) pattern, as shown in the inset of Fig. 1a. The ratio of the squares of the ring radius is 3:8:11:16:19, which implies a diamond-like structure, and the rings correspond to the {111} {220} {311} {400} {331} planes of a diamond structure.[19] The direct photographs illustrate that sample A shows blue color under irradiation with a 365 nm ultraviolet (UV) lamp (right image in Fig. 1a), while sample B can not emit any visible light (right image in Fig. 1b). HRTEM images in Fig. 1c show that most of the CNPs contain defects; the lattice spacings observed vary from 0.20 to 0.23 nm. The size distribution of the CNPs in both samples are in a narrow range, 1–8 nm, a statistical result of sample A is shown in Fig. 1d as an example. The maximum values of the fitted Gaussian peak for samples A and C are 3.2 and 3.3 nm, respectively.

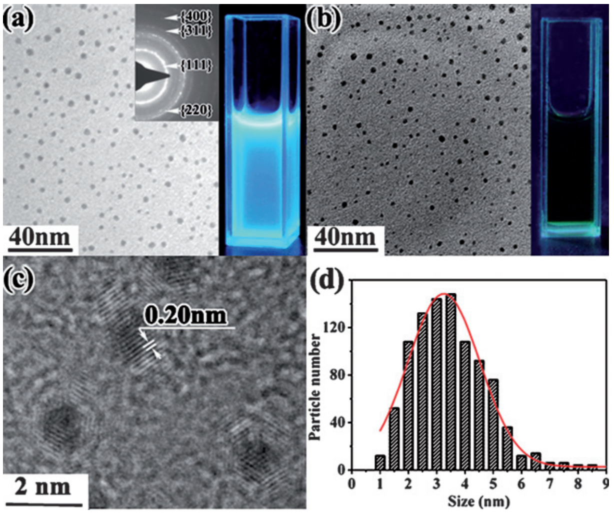

Fig. 1 Representative TEM images of the CNPs and direct photographs of suspensions under a 365 nm UV lamp. (a) TEM image of the CNPs in sample A and direct photograph of sample A under a 365 nm UV lamp, the inset is the SAED pattern of the CNPs; (b) TEM image of the CNPs in sample B and direct photograph of sample B under a 365 nm UV lamp; (c) HRTEM image of the CNPs in sample A; (d) the size distribution of the CNPs in sample A.

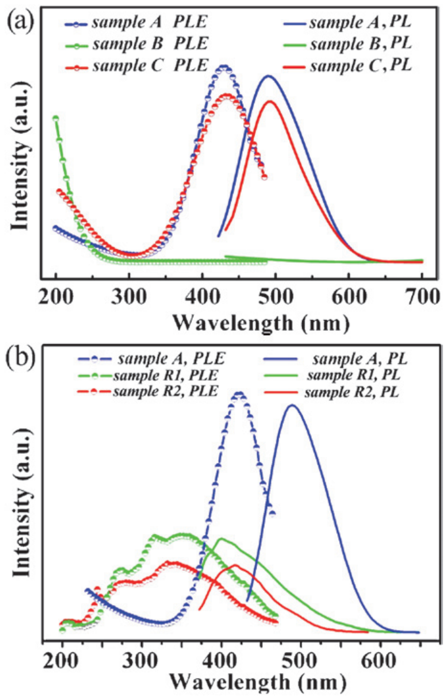

Fig. 2 (a) PL and PLE spectra of samples A, B and C. The PL spectra were recorded under 420 nm light excitation, and PLE spectra were acquired with the detection wavelength of 490 nm. (b) PL and PLE spectra of sample A, R1 and R2, PL spectra were recorded under 350 nm light excitation, while PLE spectra were acquired by exciting the samples with the strongest absorption wavelength in PLE spectra.

Fig. 2 shows the photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples A, B, and C. When excited with 420 nm incident light, sample A with CNPs in PEG_{200N} shows a strong peak around 490 nm. As a comparison, only a horizontal baseline can be found in the PL spectrum of sample B with CNPs in water, the PL spectrum does not change obviously after boiling sample B in $HClO_4$ (see ESI, Fig. S1†). However, after further heat treatment in PEG_{200N}, the product, sample C, exhibits a similar PL peak to that of sample A. The PLE spectra of the three samples have a common excitation edge at 280 nm (4.4 eV), which is somewhat lower than the band gap of diamond (about 5.5 eV), and may be ascribed to the intrinsic absorption of CNPs with defects. Moreover, samples A and C have a PLE peak centred at 430 nm, which is symmetrical with the PL peak, while sample B does not show this PLE peak. The above results indicate that the photoluminescence is correlated with the type of solvent and subsequent treatment.

In order to investigate the origin of photoluminescence, two control experiments were carried out. Firstly, pure PEG_{200N} was irradiated by laser for 2 h and the sample was named as R1; secondly, a mixture of PEG_{200N} and perchloric acid was heated to 120 °C and held for 72 h and was named as R2. PL and PLE spectra of the two samples were measured and are shown in

Fig. 2b. Weak fluorescence was found from both the samples, but the shape and peak position were completely different from sample A with CNPs. On the other hand, PL intensities of samples R1 and R2 were much weaker than that of sample A. Therefore, it is reasonable to deduce that the blue fluorescence is related to the CNPs.

PEG_{200N} and water can not give fluorescence by themselves, and both pure PEG_{200N} irradiated by laser and the reaction product of perchloric acid with PEG_{200N} hardly emit light, whereas the solvent or treatment can modify the surface ligands of CNPs, therefore we believe the surface state of the CNPs may play an important role on the photoluminescence.

Fourier transform infrared (FTIR) spectra were acquired to determine the surface ligands of CNPs, the results are shown in Fig. 3. Samples A and C with light emission display many common characteristics in their spectra (see spectra a and c in Fig. 3). Besides the vibrations of C–OH, C–O–C and C–H bonds in PEG, the stretching vibrations of C=O (1623 cm^{-1}) combined with the asymmetric and symmetric stretching vibrations of C–O–C (around 1300 cm^{-1} and 1200 cm^{-1}) in carboxylate groups are also detected.[6,20]

For sample B with CNPs in water, three peaks at 2960 cm^{-1}, 2876 cm^{-1}, 1380 cm^{-1} are assigned to $\nu_{as}(CH_3)$, $\nu_s(CH_3)$, and $\delta_s(CH_3)$, respectively, which suggests the surfaces of the CNPs are attached with methyl groups. Moreover, C=O and C–O stretching vibrations are detected, which indicates that the CNP surfaces are partially oxidized. After sample B is oxidized with perchloric acid, the peaks of the methyl groups disappear and those related to the carboxylic acid groups (–COOH, IR frequency $\nu_{C=O} = 1719$ cm^{-1} and $\delta_{OH} = 927$ cm^{-1}) emerge (see curve d in Fig. 3),[20,21] therefore, it is proposed that the methyl groups on the surface of the CNPs are oxidized into carboxylic acid groups. The carboxylic acid groups could react with PEG_{200N} during the incubation treatment, which leads to the formation of carboxylate groups in sample C.[22]

The correlation of the optical properties with surface ligands could be clarified by comparing the optical results with FTIR results. The carboxylate groups formed on the surface of the CNPs, sample A, can give visible light emission whereas on the

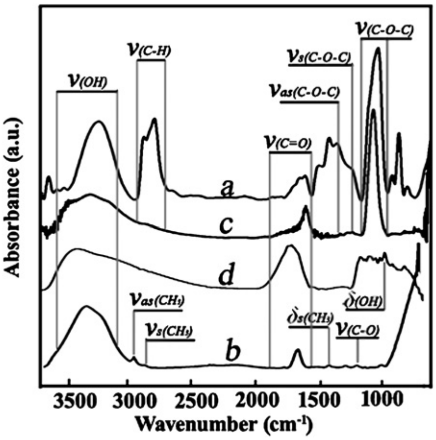

Fig. 3 FTIR spectra on different products. Curves a, b, c are from the samples A, B and C, respectively; curve d is from the the CNPs treated with $HClO_4$.

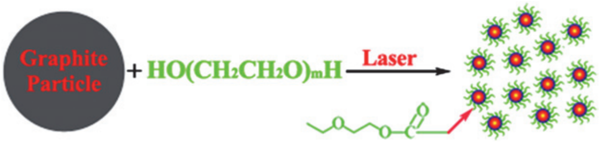

Fig. 4 Schematic map of the one-step synthesis of luminescent CNPs in PEG_{200N} solvent.

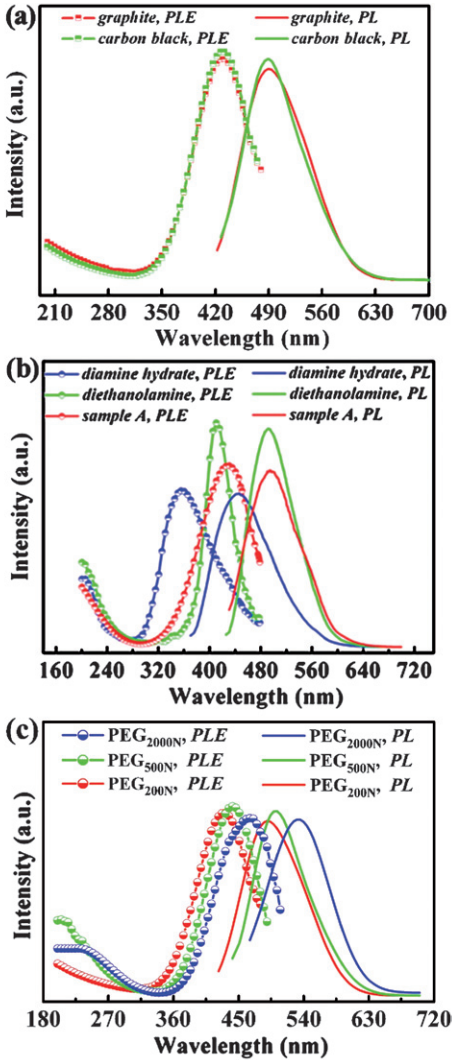

Fig. 5 PL and PLE spectra of the suspensions of the CNPs. (a) The spectra of the CNPs suspension prepared from carbon and graphite, respectively, in the same solvent (PEG). PL spectra were acquired under 420 nm excitation and PLE spectra acquired with 490 nm detection wavelength. (b) The spectra of the CNPs in three solvents, PLE spectra were acquired with the detection wavelength of 490 nm, and the corresponding PL spectra were recorded by exciting the samples with the strongest absorption wavelength in the PLE spectra. (c) The spectra of the CNPs in PEGs with different molecular weight (PEG_{200N}, PEG_{500N}, PEG_{2000N}); PLE spectra were acquired with the detection wavelength of 490 nm, and the corresponding PL spectra were recorded by exciting the samples with the strongest absorption.

contrary, CNPs with methyl groups in sample B do not show any photoluminescence. Once the methyl groups are transformed into carboxylate groups by subsequent treatments, sample C emits the same light as that of sample A. These results indicate that the carboxylate groups provide a surface state responsible for the photoluminescence from the CNPs.

As for the formation of CNPs and carboxylate groups under laser irradiation, we propose the following mechanism. The pulsed laser could generate a thermodynamic state with high temperature and high pressure in PEG_{200N} solvent, where the carbon materials were heated up to plasma state; the condensation of carbon plasma after the laser pulse induced the formation of the CNPs.[19] The surface of the CNPs could be oxidized by the residual or decomposed oxygen atoms, and further reaction with PEG_{200N} or its fragment molecules produced by the plasma may lead to the appearance of carboxylate groups on the surface of the CNPs.[23–25] The above process is schematically expressed in Fig. 4.

The influence of the starting materials on the luminescence of CNPs was also investigated. The results in Fig. 5 indicate that the carbon materials hardly affect the PL properties of CNPs, whereas the solvent can modify the color and intensity of the luminescence effectively. Fig. 5b shows the PL and PLE spectra of CNPs produced in three solvents, PEG_{200N}, diamine hydrate and diethanolamine; the absorption and emission peaks of the three samples are located in different wavelength ranges, although the size distribution of the CNPs in the three samples is almost constant (see ESI, Fig. S2†). This phenomenon suggests that different surface ligands were produced under the laser irradiation. Moreover, the molecular weight of solvent shows a distinct effect on the PL peak, which shifts to a longer wavelength (Fig. 5c) with the increase in the molecular weight of PEG. Therefore, the luminescence from the CNPs can be tuned easily by changing the organic solvents. The quantum yields of the three samples were also measured (see Tables 1–3); the values vary from 3% to 8%, and are comparable to those of the CNPs derived from carbon nanotubes and surface modification.[13–15]

Table 1 Quantum yield of sample A

Sample	Integrated emission intensity (*I*)	Abs at 430 nm (*A*)	Refractive index of solvent (*η*)	Quantum yield (*Q*)
Quinine sulfate	92.3	0.062	1.33	0.54 (known)
CNPs sample	9.17	0.069	1.36	0.050 (calculation)

Table 2 Quantum yield of CNPs in diamine hydrate

Sample	Integrated emission intensity (*I*)	Abs at 365nm (*A*)	Refractive index of solvent (*η*)	Quantum yield (*Q*)
Quinine sulfate	147.35	0.064	1.33	0.54 (known)
CNPs sample	11.62	0.072	1.33	0.037 (calculation)

Table 3 Quantum yield of CNPs in diethanolamine

Sample	Integrated emission intensity (*I*)	Abs at 410nm (*A*)	Refractive index of solvent (*η*)	Quantum yield (*Q*)
Quinine sulfate	107.4	0.067	1.33	0.54 (known)
CNPs sample	16.14	0.073	1.36	0.078 (calculation)

Conclusions

We have developed a one-step route to create fluorescent CNPs by laser irradiation of carbon powders in organic solvents. The surface modification on the CNPs occurred simultaneously with the formation of the CNPs, and effective surface states for luminescence could be generated by selecting appropriate solvents. The present method is not limited to carbon materials, the extreme conditions created by laser ablation should be conducive to obtaining semiconductor (such as Si, Ge, and GaN) nanoparticles with unusual structures. On the other hand, the surface ligands and then luminescent properties could be modified conveniently by adopting different organic solvents. Therefore, this method shows high potential for fabricating new luminescent materials.

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