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Observation of pH-, solvent-, spin-, and excitation-dependent blue photoluminescence from carbon nanoparticles†

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Highly blue luminescent carbon nanoparticles with photoluminescence quantum yields of 31.6%–40.6% were prepared by a one-step pyrolytic route from ethylenediamine-tetraacetic acid salts and a unique emission that is strongly dependent on pH, solvent, spin, and excitation wavelength was observed.

An emerging luminescent material—fluorescent carbon nanoparticles (CNPs)—has drawn increasing attention owing to their attractive applications in biomedical imaging and optoelectronic devices.[1–11] As compared with fluorescent dye molecules and semiconductor quantum dots, fluorescent CNPs show such advantages as stable photoluminescence (PL), low cytotoxicity and excellent biocompatibility.[1–5] A variety of methods have been developed to prepare fluorescent CNPs. Sun *et al.* reported the preparation of luminescent carbon dots based on a multi-step process involving the acidic oxidization of laser ablated graphite and the subsequent surface passivation with NH_2-containing long-chain molecules as a stabilizer.[1] A similar multi-step procedure was used to treat CNPs that were pre-prepared by pyrolyzing and etching polymer/F127/silica composites.[5] Such multi-step procedures are considerably time-consuming and complicated, though they are relatively effective for deriving strong green luminescence from carbon materials. Some relatively simple but less effective preparative methods have also been developed, including directly oxidizing combustion soot of candles into fluorescent CNPs,[7] hydrothermally cutting non-luminescent graphene sheets into blue fluorescent graphene quantum dots (GQD),[9] electrochemical shocking of multiwalled carbon nanotubes into fluorescent carbon nanocrystals,[4] and incomplete thermal decomposition of pre-synthesized citrate salts into fluorescent carbogenic quantum dots.[8] Thus far, one-step and fairly effective routes to fluorescent CNPs have not been reported. Here, we describe such a truly one-step synthetic method for highly fluorescent CNPs by pyrolysis of ethylenediamine-tetraacetic acid (EDTA) salts at low temperature. The CNPs are highly blue fluorescent, with a PL quantum yield (QY) as high as 40.6%, much higher than those of the CNPs reported so far (QYs $<$ 15%).[1–11] Moreover, the CNPs were found to exhibit interesting PL behaviors: the emission is strongly dependent on pH, solvent, spin, and excitation wavelength.

EDTA-2Na·$2H_2O$ was chosen as the precursor mainly because it contains relatively stable carboxylate anions (COO^-), which can remain during the low-temperature pyrolysis and thus render the CNPs soluble in water and organic polar solvents. Typically, EDTA-2Na (0.5 g) was calcined in a tube furnace at 400 °C for 2 h at a heating rate of 10 °C min^{-1} in a N_2 atmosphere. The product was purified to remove less fluorescent and less soluble CNPs as well as Na_2CO_3 by dispersing the CNPs in acetone followed by centrifugation. The resultant homogeneous supernatant contained strongly fluorescent CNPs.

Because of the incomplete pyrolysis of the precursor, H, N, O and Na are incorporated into the CNPs (The C : N : H mole ratio is 1.13 : 0.46 : 1). O and Na in the form of $-COO^-Na^+$ are present in the CNPs, as confirmed by the Fourier transform infrared (FTIR) absorption bands of COO^- at 1638 and 1438 cm^{-1} (Fig. S1a in the ESI†). The CNPs are *in situ* hydrogenated, oxidized and N incorporated. The X-ray powder diffraction (XRD) pattern of the CNPs shows a wide (002) peak at 3.46 Å, close to that of graphite (3.34 Å) (Fig. S1b). Their Raman spectrum (Fig. S1c) shows a strong D band at 1345 cm^{-1} and a weak G band at 1557 cm^{-1}, ascribed to disordered carbon and sp^2 clusters, respectively. The Raman spectrum is extremely similar to that of GO sheets that consist of small sp^2 clusters embedded in a disordered sp^3 carbon matrix.[12,13] The average size of the sp^2 clusters in the CNPs can be determined to be $\sim$3.8 nm using the empirical Tuinstra–Koenig relation,[14] which relates the intensity ratio of the D to G (1.13) to the cluster size. The average size of the CNPs ($\sim$7.5 nm) determined by the transmission electron microscopy (TEM) observation (Fig. 1a and b) is larger than that of the sp^2 clusters, which suggests that the CNPs are composed of small sp^2 clusters embedded in a disordered sp^3 carbon matrix.

The optical properties of the CNPs were investigated in their aqueous solutions. The CNPs show a strong absorption feature centered at 320 nm (3.87 eV) in the UV-vis absorption spectrum (Fig. 2a). When the CNPs were excited at the absorption feature, a strong and narrow PL peak centered at $\sim$400 nm (3.10 eV) as well as a corresponding bright blue light

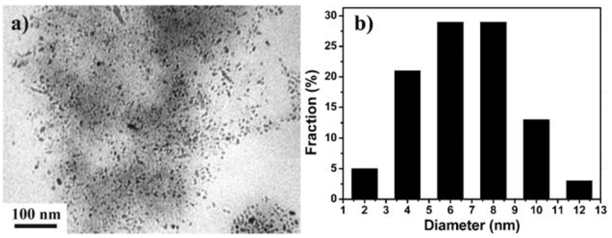

Fig. 1 (a) TEM image of the fluorescent CNPs. (b) Diameter distribution of the CNPs.

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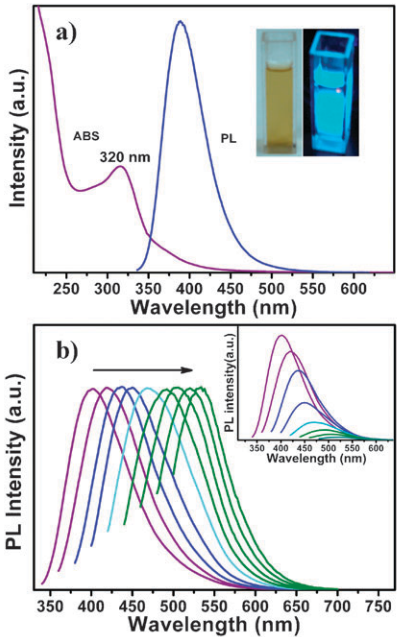

Fig. 2 (a) UV-vis absorption (ABS) and PL (320 nm excitation) spectra for the CNPs dispersed in DI water. Insert: photographs of the CNP aqueous solution taken under a visible light (left) and a UV light (right) in a fluorescence spectrophotometer. (b) Normalized PL spectra at excitation wavelengths from 320 nm to 500 nm.

from the brown solution was observed (Fig. 2a). The full width at half maximum (FWHM) of the PL peak is as small as 60 nm, and the QY is determined to be 31.6% with quinine sulfate as a reference (Fig. S2). The QY of the CNPs can be further increased to 36.2% and 40.6% upon annealing in N_2 and in air, respectively (Fig. S2). In contrast, for the emission from the CNPs reported so far, the FWHMs are always more than 100 nm, and the QYs are smaller than 15%.[1–11] When the CNPs are excited at wavelengths from 330 to 490 nm, the PL peak shifts from 400 to 530 nm and the PL intensity decreases remarkably (Fig. 2b). This excitation dependent PL behavior was extensively reported in fluorescent CNPs.[1–10] The PLE spectrum of the CNPs (Fig. S3) shows two transitions centered at 230 and 320 nm. The 320 nm transition is also shown in the absorption spectrum while the 230 nm transition can not be clearly identified due to the strong deep UV absorption background (<250 nm) from the $\pi \rightarrow \pi^*$ transition of the CNPs. These results indicate that the blue fluorescent species in the CNPs should have a considerably large LUMO–HOMO gap (3.10–3.87 eV).

Apart from the excitation-dependent PL behavior, we also note that the fluorescence is very sensitive to pH (Fig. 3). The PL intensity of the CNPs is nearly constant in the neutral range (pH = 5.5–8.0), but changes pronouncedly and inversely in the acidic and basic regions: the PL is gradually enhanced with pH increasing from 8 to 13, but decays gradually with pH decreasing from 5.5 to 1 (insert in Fig. 3). When pH is tuned from 13 to 1, the PL peak and the corresponding absorption feature consistently redshift slightly. Meanwhile, the absorption in the whole spectrum range becomes weak. After the pH value is restored to 13, both the absorption and PL spectra are also restored, which indicates that the pH-dependent PL behavior is reversible, similar to the observation with blue fluorescent GQDs.[9] This pH effect indicates that the fluorescent species in the CNPs should have basic sites relevant to the blue emission because the fluorescence is quenched in the acidic media but restored in the basic media.

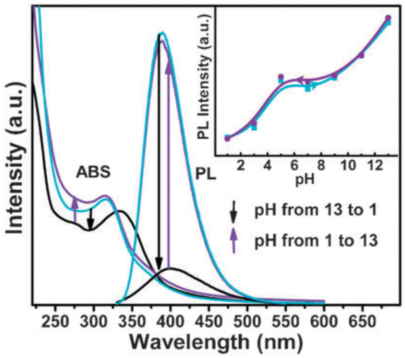

Fig. 3 (a) pH-dependent UV-vis absorption and PL spectra when pH is switched between 13 and 1. Insert: dependence of PL intensity on pH (changed from 13 to 1 and then from 1 to 13).

The optical properties of the CNPs were further investigated in polar organic solvents. All the UV-vis absorption and PL spectra observed in ethanol (Fig. 4a), methanol and glycol (Fig. S4) are nearly the same as those observed in water. In acetone, however, these spectra change remarkably (Fig. 4b): the absorption from 230 to 300 nm disappears and the 320 nm absorption feature shifts to 340 nm, while the PL peak shifts from 400 nm to 430 nm and becomes broader. These results show that the optical properties of the CNPs are greatly influenced by acetone rather than by solvents with hydroxyl (OH). This solvent effect, like the pH effect, can be related to the basic nature of the luminescent species in the CNPs because carbonyl (C=O) in acetone is a typical Lewis acid whereas hydroxyl in methanol, ethanol and glycol is a typical Lewis base.

The ground-state properties of the unknown luminescent species in the CNPs can be probed by electron paramagnetic resonance (EPR) spectroscopy. To do that, a series of fluorescent CNP samples with blue emission at ~400 nm by 320 nm excitation (Fig. S5) were prepared at different temperatures (250–400 °C). These samples show the same derivative EPR signal with a Lorentzian shape at $g = 2.004$ (Fig. 5a). A linear correlation between the intensities of the PL peak and the EPR signal is well established, as shown in Fig. 5b. This spin-dependent PL behavior reveals that the luminescent species should have such a ground state with one or more singly occupied orbitals.

Based on the above detailed spectroscopic studies, it is concluded that the unknown blue luminescent species in the CNPs should have a large LUMO–HOMO gap (3.10–3.87 eV), Lewis basic sites, and singly occupied orbitals. Evidently, the emission from carboxylate anions can be ruled out because the precursor containing such groups is not luminescent. The emission from the relatively large sp^2 clusters (~3.8 nm in size) embedded in the CNPs should also be ruled out because sp^2 clusters with a diameter of ~3 nm (more than 100 aromatic rings involved) were predicted to have an energy gap of 0.5 eV,[15] much smaller than that of the blue luminescent species.

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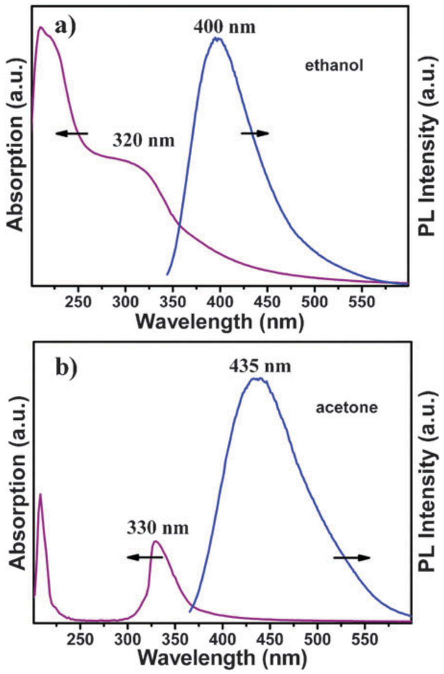

Fig. 4 UV-vis absorption and PL spectra of the CNPs dispersed in ethanol (a) and acetone (b).

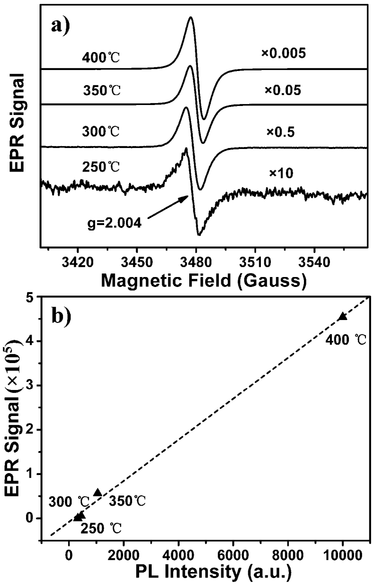

Fig. 5 (a) EPR spectra of the CNP samples prepared at different temperatures. (b) Linear correlation between the EPR and PL intensities.

Recently, Chen *etc.* have proposed that smaller clusters of few aromatic rings with large enough gaps are responsible for the blue luminescence observed in graphene oxide.[15] Radovic and Bockrath have calculated the electronic structures of graphene sheets containing 1–9 aromatic rings and one free edge site.[16] They found that free zigzag sites in graphene sheets are carbine-like with a stable triplet ground state whereas free armchair sites are carbyne-like with a stable singlet ground state. For the triplet state in zigzag graphene sheets, the two frontier orbitals σ and π are singly occupied and LUMO–HOMO gaps are within 0.9–5.8 eV. Free zigzag sites with a lone pair of electrons are Lewis basic sites, which can be protonated.[9,16] Because small clusters with zigzag edges and few aromatic rings have been predicted to have large LUMO–HOMO gaps, Lewis basal sites, and singly occupied orbitals, which are consistent with our detailed spectroscopic observations, we propose that these graphene molecules embedded in the CNPs likely account for the blue luminescence from the CNPs.

In conclusion, we have developed a one-step route to highly efficient blue luminescent CNPs with high QYs and narrow FWHMs from EDTA salts. The CNPs have interesting PL properties, which are strongly dependent on pH, solvent, spin, and excitation wavelength. The blue luminescent species are likely small sp^2 clusters embedded in the CNPs, which should have a large LUMO–HOMO gap (3.10–3.87 eV), Lewis basal sites, and singly occupied orbitals. The luminescent CNPs may hold applications in biomedical imaging and blue luminescent optoelectronic devices.

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