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Fluorescent Nanoparticles

Fluorescent Carbon Nanoparticles Derived from Candle Soot**

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Herein, we report on the preparation, purification, and preliminary characterization of multicolor fluorescent carbon nanoparticles (CNPs) obtained from the combustion soot of candles. The CNPs are small (< 2 nm) and water soluble. Different CNPs fluoresce with different colors under a single-wavelength UV excitation.

Carbon-based nanomaterials, which include carbon nanotubes, fullerenes, and nanofibers, have promising applications in nanotechnology, biosensing, and drug delivery.[1–3] Recently, CNPs—a new class of carbon-based nanomaterials with interesting photoluminescence properties—were isolated.[4–10] These nanoparticles are either nanodiamonds or materials derived from carbon nanotubes and the laser ablation of graphite. Unlike fluorescent semiconductor nanocrystals (so-called quantum dots or Qdots), the fluorescent CNPs have only been poorly studied up to now because of the lack of preparative methods and separation techniques. Herein, we report a method for efficiently preparing and isolating fluorescent CNPs from a common carbon source, namely, candle soot.

Our approach includes: 1) The preparation of fluorescent CNPs from the combustion soot of candles by means of an oxidative acid treatment and 2) the purification of the fluorescent CNPs by using polyacrylamide gel electrophoresis (PAGE). Incomplete combustion produces CNPs with diameters of 20–800 nm.[11,12] These particles strongly interact with each other to form agglomerates of several micrometers. To break down such inherent interactions and produce well-dispersed, individual CNPs, we adopted an oxidative acid treatment, which is commonly used for the purification of carbon nanotubes.[13] This method is known to introduce OH and CO_2H groups to the CNP surfaces,[14] thus making the particles become negatively charged and hydrophilic.

The candle soot was collected by sitting a glass plate on top of smoldering candles. The soot contained mainly elemental carbon (elemental analysis: C 91.69%, H 1.75%, N 0.12%, O (calculated) 4.36%) and was hydrophobic and insoluble in common solvents. After refluxing the candle soot with 5 M HNO_3, it turned into a homogeneous, black aqueous suspension. Upon centrifugation, the suspension separated into a black carbon precipitate and a light-brown supernatant, which exhibited yellow fluorescence when irradiated with UV light (312 nm). The black precipitate also contained fluorescent material (even after washing it several times). For maximum recovery of this fluorescent material, both the supernatant and the precipitate were neutralized and then extensively dialyzed against water. The neutralized candle soot exhibited an excellent dispersibility in water, which lasted several months.

The same procedure failed to generate visible fluorescence if an oxidant, such as HNO_3, was not present (this happened both in the presence and in the absence of surfactants, SDS). Another oxidant (30% H_2O_2/AcOH = 2:1) resulted in blue fluorescence. The oxidative acid treatment might have three functions: 1) to break down the carbon aggregates into small nanosized particles, 2) to solubilize the carbon nanoparticles, and 3) to influence the fluorescence properties.

We separated the pure fluorescent CNPs from the neutralized candle-soot dispersion by using denaturing PAGE. The soot mixtures were resolved into three classes of species (Figure 1): 1) nine fast-moving fluorescent bands, 2) slow-moving, nonfluorescent bands, and 3) agglomerates that did not penetrate the gel. Multicolor fluorescent bands were well resolved into discrete bands (Figure 1c). The mobility decreased in the order: violet-blue particles > green-yellow particles > orange-red particles. The electrophoresis data exhibited a simple relationship between the mobility and the color of the fluorescent CNPs, namely, that the fast-moving nanoparticles fluoresce at short wavelengths while the slow-moving ones do so at long wavelengths. It is

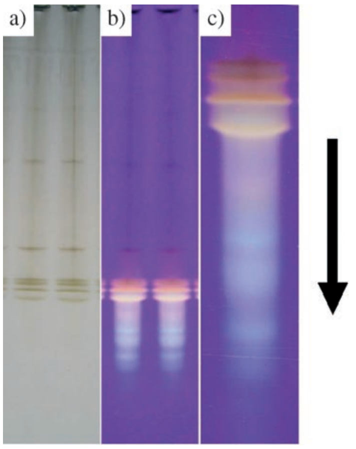

Figure 1. Electrophoretic separation of fluorescent CNPs illuminated by a) white and b) UV light (312 nm). c) Close-up view of the fluorescent bands in (b). The arrow on the right-hand side indicates the migration direction.

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known that a particle moves faster if it has either a higher negative charge or a smaller size. However, it is not clear which property (charge or diameter) determines the mobility and the fluorescence color of the particles in this case.

To recover the particles, the nine fluorescent bands were excised under UV illumination. The CNPs were eluted from the gels and extensively dialyzed against distilled water. Purified fluorescent CNPs (5–10 mg) were obtained from 100 mg of candle soot. The purified CNPs had excellent solubilities (namely, $\approx 30\ \mathrm{mg\,mL^{-1}}$ in water, $\approx 18\ \mathrm{mg\,mL^{-1}}$ in methanol, $\approx 20\ \mathrm{mg\,mL^{-1}}$ in dimethyl formamide, DMF, and $\approx 41\ \mathrm{mg\,mL^{-1}}$ in dimethyl sulfoxide, DMSO). Aqueous solutions of the CNPs were stable at room temperature for at least two months.

The purified CNPs had a quite different chemical composition from that of the raw candle soot, with a high oxygen content (elemental analysis: C 36.79 %, H 5.91 %, N 9.59 %, O (calculated) 44.66 %) and the presence of carbonyl groups, as was shown by means of Fourier-transform infrared (FTIR) spectroscopy ($\nu_{C=O} = 1721\ \mathrm{cm^{-1}}$; see Figure S2 in the Supporting Information). Solid-state ^{13}C NMR measurements (see Figure S3 in the Supporting Information) showed three kinds of carbon peaks at 114 (terminal C=C bonds), 138 (internal C=C bonds), and 174 ppm (C=O bonds).[15] No saturated sp^3 carbon atoms were observed.

Different CNPs have different optical properties (Figure 2). Their excitation spectra are similar (see Figure S4 in the Supporting Information), but their emission spectra are very different (Figure 2 and Table 1 in the Supporting Information). This behavior is akin to that of Qdots (and is also an important feature for multicolor imaging applications). The CNP photoluminescence spectra have a broad color range, with the emission-peak wavelengths ranging from 415 (violet) to 615 nm (orange-red). The photoluminescence spectra are narrow for the violet CNPs and they broaden when approaching the orange-red particles (see Figure 2 and Table 1 in the Supporting Information). The cause for this is, presumably, an incomplete separation, as suggested by the PAGE gel (see Figure 1, the lower bands are well separated, but the upper bands are close to each other). The excitation spectra of all CNPs show multiple peaks and extend from the ultraviolet to the visible regions. The quantum yields of the CNPs are relatively low, with values of 0.008, 0.019, and 0.008 (at 366 nm) for fractions 1, 4, and 7, respectively; these values are comparable to those of the CNPs derived from carbon nanotubes.[4]

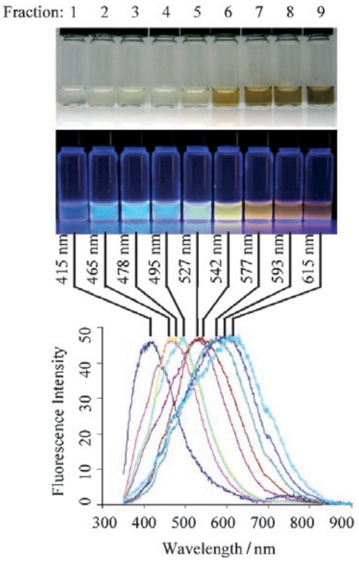

Figure 2. Optical characterization of the purified CNPs. Optical images illuminated under white (top) and UV light (312 nm; center). Bottom: Fluorescence emission spectra (excitation at 315 nm) of the corresponding CNP solutions. The maximum emission wavelengths are indicated above the spectra.

The pH value of the solution affects the photoluminescence of the CNPs (see Figure S5 in the Supporting Information). The fluorescence intensity of the nanoparticles decreases significantly (by 40–89 %) upon changing from a neutral to either an acidic or a basic solution. Additionally, the wavelength of the fluorescence peak shifts to shorter values. This is an interesting phenomenon, and even though its mechanism is not understood, this environment-sensitive property could be exploited for molecular sensing.[16]

All CNPs have similar sizes (that is, ≈ 1 nm high), as is shown by using atomic force microscopy (AFM, see Figure 3 and Figure S6 in the Supporting Information). The observed CNP heights distribute narrowly, with an average value of 1 nm (this value is significantly smaller than that of most Qdots). Note that although the absolute value of the size difference between all CNPs is small, the percentage value could still be quite large because of the small size of the nanoparticles.

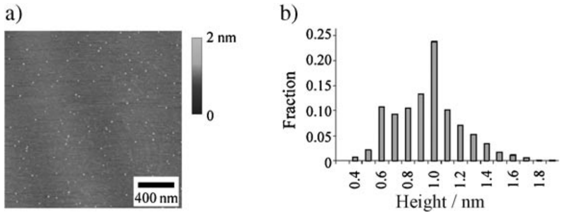

Figure 3. AFM analysis of the CNPs. a) A representative AFM image. b) Height distribution of the CNPs in fraction number 9 (other fractions show similar size distributions in terms of position and width).

What is the chemical identity of the fluorescence species? This is still an open question. One possibility is that such species are polycyclic aromatic compounds. However, this is unlikely for the following reasons: 1) The preparation includes a long, harsh, oxidative acid treatment at an elevated temperature, and it is very unlikely for ordinary organic compounds to overcome such conditions. 2) Solution NMR experiments did not give any signal—not even at a high concentration, such as $30\ \mathrm{mg\,mL^{-1}}$—which suggests that the species involved are particles (that is, a condensed phase) and not dispersed molecules. 3) The height of the species—determined by means of AFM—is ≈ 1 nm, that is, they are much higher than normal polycyclic aromatic hydrocarbons.

In summary, we synthesized and purified water-soluble fluorescent CNPs from candle soot. The nanoparticles are stable for several months under ambient conditions and can be excited by a single-wavelength light, thereby emitting multiple colors. The CNPs contain carboxylic acid groups on their surface, which allows functionalization with biomacromolecules through *N*-hydroxysuccinimide (NHS) chemistry. The method reported herein provides a convenient way to prepare CNPs by using a common carbon resource. The most immediate questions we would like to address now are: What are the exact chemical identities of the CNPs? What is the luminescence mechanism? Can we use the fluorescent CNPs for biosensing? As potential fluorescence labels, the small CNPs are expected to interfere to a much lesser extent with the biomacromolecules, or with the biological processes under study, than other bulky Qdots (and this is one of the major concerns about applying Qdots in biophysical studies).

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