Preparation of Carbon Nanoparticles from Candle Soot

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Carbon nanoparticles (CNPs) were prepared by simply mixing candle soot into ethanolic Nafion solution under ultrasonic radiation for 90 min. Well-defined CNPs could be obtained after centrifugation and washing. The products were characterized with transmission electron microscopy (TEM), X-ray diffractometry (XRD), and scanning electron microscopy (SEM). A possible formation mechanism is proposed. Electrochemical measurements show that they may be useful as biosensors.

Carbonaceous nanomaterials, including carbon nanotubes (CNTs), fullerenes (C_{60}), carbon onions (hyperfullerenes), and carbon nanofibers, are particularly attractive owing to their excellent electronic, physical, and chemical properties. These materials have many potential applications in energy and gas storage materials, templates, nanoprobes, and sensors.[1,2] Recently, carbon nanoparticles (CNPs), a new class of carbon-based nanomaterials with interesting properties were isolated.[3] Template method and chemical vapor deposition (CVD) are two main strategies for the preparation of carbonaceous materials. For the first method, the use of environmentally unfriendly reagents is required to remove silica templates.[4] And the other method requires of complex equipment.[5] Therefore, development of new efficient methods for the preparation of CNPs is very necessary.

Candle soot is a source of polydisperse and ultrafine particles that can seriously damage paintings and artifacts in historic churches and cause respiratory and cardiovascular problems. Recent studies have shown that not all particles produced from candle soot are bad; indeed, some may prove to be useful.[3] Liu et al. discovered an inexpensive reliable method to make luminescent CNPs, in which soot generated from a burning candle was used as starting material. This indicates that candle soot can be used as starting materials in the preparation of CNPs.[6] Previous studies indicated that CNTs could be well dispersed in phosphate buffer solution (PBS) or alcohol stably in the presence of Nafion with stability and biocompatibility for polar side chain, which meant that Nafion would be a good media for the dispersion of carbonaceous nanomaterials.[7] In the present letter, encouraged by the technique mentioned above, we report a simple approach for preparation of well-defined CNPs with an average diameter of 60 nm.

In a typical process, 0.5 mg of candle soot was added into 10 mL of ethanolic Nafion solution (5 wt % Nafion). The mixture was then sonicated for 90 min. After that, a homogeneous, well-dispersed suspension was observed. However, the candle soot would aggregate seriously in the ethanol without Nafion. The homogeneous suspension can be stable for about 10 days, and then a little aggregation can be observed. Sedimentation and centrifugation (at 5000 rpm for 10 min) were used to remove the big particles (diameter over 500 nm) from the solution. The remainding solution was centrifuged at 10000 rpm for 30 min, from which fine CNPs were obtained. Finally, the resulting CNPs were rinsed with ethanol three times and stored at ambient conditions for use.

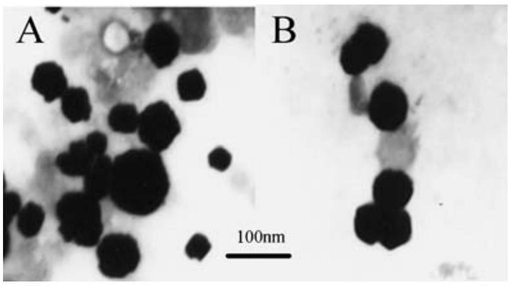

Figure 1. TEM images of the resulting CNPs.

The size of the resulting CNPs was determined by transmission electron microscopy (TEM, Hitachi, Hitachi-600). Figure 1 shows the typical TEM images of CNPs, from which it can be found that the CNPs have an average diameter of 60 nm. And good dispersibility can be also observed from the images. The wide-angle region of the X-ray diffraction (XRD, Shimadzu, XRD-6000) patterns exhibit a high-intensity diffraction peak at $2\theta = 24.3^\circ$ and two additional peaks at $2\theta = 43.8$ and 54.2° that are ascribed to (002), (101), and (004) diffractions of graphitic carbon, respectively (not shown here).

The morphologies of the resulting CNPs were observed via scanning electron microscopy (SEM, Hitachi, S-4800). As shown in Figures 2A and 2B, CNPs were encapsulated in a layer of Nafion film before rinsing, in this case the morphologies of CNPs could not clearly observed, while well-defined CNPs can be observed after rinsing with ethanol (Figures 2C and 2D). The average diameter of the CNPs is 60 nm, which was in agreement with TEM images.

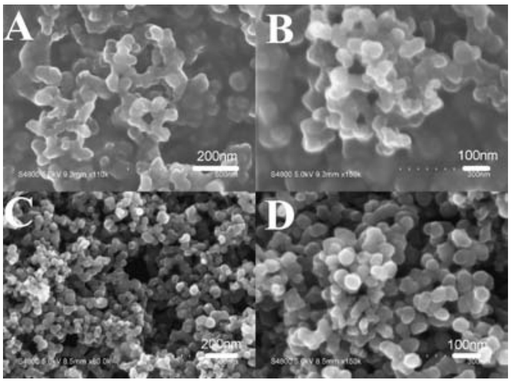

Figure 2. SEM images of the resulting CNPs before (A, B) and after (C, D) rinsing with ethanol.

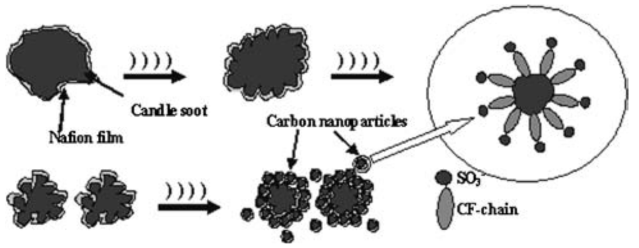

Figure 3. Proposed mechanism for the formation of CNPs in the presence of Nafion under sonication condition.

Time-dependent experiments were performed to investigate the growth of CNPs. A relatively short (5 min) sonication time led to particles with a characteristic size around 1 µm in diameter. After 10 min the particle size decreased to 500 nm in diameter and further to 150 nm after treatment for 30 min. The final products with an average diameter of 60 nm could be obtained when sonicated for 90 min. Obviously, the size of CNPs decreased with the increasing time of sonication. The TEM images showed that CNPs were encapsulated in a layer of Nafion film, indicating that Nafion not only played an important role in the dispersion of candle soot but also prohibited CNPs from forming aggregation. From the above information, we proposed the mechanism for the formation of CNPs in Figure 3. The hydrophilic polar group in Nafion dissolves well in ethanol. On the other hand, the hydrophobic backbone in Nafion interacts with the candle soot. Then a relatively (90 min) sonication time led to CNPs.

Electrochemical measurements of the resulting CNPs were performed in PBS with a CHI 660C electrochemical workstation (CH Instruments, Shanghai, China). Figure 4A displays cyclic voltammograms (CV) for 10 mM H_2O_2 at the bare (curve a) and Nafion/CNPs-modified (curve b) glassy carbon (GC) electrodes. Compared with that at the bare electrode, the oxidation and reduction currents of H_2O_2 at the Nafion/CNPs-modified electrode obviously increase, and the overpotential is significantly lowered. Based on the high electrocatalytic activity of Nafion/CNPs to H_2O_2, we further developed a glucose biosensor. Such electrochemical biosensing is illustrated in Figure 4B. From the CV, no redox peaks were observed at the glucose oxidase (GOx)-modified GC electrode (curve a), and the redox peaks at the Nafion/GOx-modified GC electrode (curve b) were very small. In contrast, there was a pair of well-defined redox peaks at the Nafion/CNPs/GOx-modified GC electrode (curve c). This indicates that CNPs played an important role in promoting the electron transfer between the proteins and underlying electrode.[8]

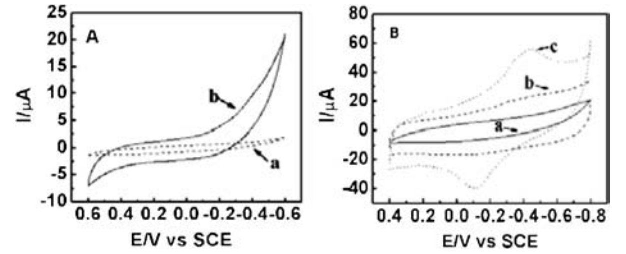

Figure 4. (A) Cyclic voltammograms of bare (a) and Nafion/CNPs-modified (b) GC electrode in 0.05 mol/L PBS solution under pH 7.4 condition with 10 mM H_2O_2 vs. saturated calomel electrode (SCE). Scan rate 50 mV/s. (B) Cyclic voltammograms of (a) bare/GOx-, (b) Nafion/GOx-, and (c) Nafion/CNPs/GOx-modified GC electrodes in 0.05 M PBS of pH 7.4 with N_2-saturated at a scan rate of 50 mV/s vs. SCE.

In conclusion, we have demonstrated a so far unexplored low-cost route for the preparation of CNPs. The strategy discussed here not only can derive CNPs from candle soot with advantages such as simple process, high speed, high quality, good reproducible ability, and low cost but also is environmentally friendly. Electrochemical studies have shown that CNPs obtained from our route have wide potential applications for development of new biosensors and biocatalysis.

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