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Mechanical Purification of Single-Walled Carbon Nanotube Bundles from Catalytic Particles

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ABSTRACT

Ferromagnetic particles used for the catalytic growth of single-walled carbon nanotubes (SWNTs), which are embedded in a graphitic shell, represent a major obstacle in studying the bulk material. We have explored a purification method that is based on a mixing of the SWNT suspension with inorganic nanoparticles in an ultrasonic bath, which causes ferromagnetic particles to be mechanically removed from their graphitic shells. By trapping these magnetic particles with permanent magnetic poles and with a subsequent chemical treatment, a high purity SWNT material was obtained.

It is well-known that multiwall carbon nanotubes (MWNTs) can be produced without metal catalyst, while for the synthesis of single-walled carbon nanotubes (SWNTs) a small addition (the order of a percent) of transition metal (Co, Ni, Fe, or their mixture) to the carbon electrode/target is needed.[1−3] The final product consists not only of 50−90% of SWNTs mixed with polyhedral particles in the 100 nm range or above but also of small (10−20 nm) metal particles embedded in a capsule of several graphene sheets. These capsules generally cluster in aggregates and stick to the nanotube bundles, or appear as roots for the SWNTs.

The presence of these ferromagnetic materials overwhelms the magnetic response and inhibits the measurement of the intrinsic magnetic properties of SWNTs. For example, in electron spin resonance (ESR) measurements,[4] only the huge ferromagnetic resonance signal coming from the catalytic particles is recorded. Even in transport measurements, such as the measurement of the Seebeck coefficient, the passage of charge carriers through these magnetic islands gives a Kondo-like contribution.[5]

Therefore, there is a great interest to purify the raw SWNT material. The magnetic particles with their graphitic shells cannot be easily separated by dispersion because they adhere to the bundles strongly. Unfortunately, the usual acid treatment of the SWNT soot cannot open the graphitic shell without attacking the nanotubes themselves and, as a consequence, it cannot eliminate these metallic clusters.[6] This fact suggests that direct chemical purification is not achievable. Another possibility would be to heat the soot above the melting point of the metals (above 1500 °C and 1600 °C in the case of Co and Ni, respectively); after opening the graphitic shells by the vapor pressure, the metal would evaporate out into the vacuum space. However, at such high temperatures, SWNTs start to collapse and to change diameter; in other words, the original materials are degraded.[7] We found a tricky "roundabout process" to avoid these inextricable difficulties. This paper demonstrates an efficient purification method that is based on mixing the SWNT suspension with inorganic nanoparticles (mainly ZrO_2 or $CaCO_3$) in an ultrasonic bath, which mechanically removes the ferromagnetic particles from their graphitic shells. Then, the magnetic particles are trapped with permanent magnetic poles, and with a subsequent chemical treatment, a high purity SWNT material is obtained.

The sample used in this study is a commercial SWNT soot purchased from different sources. Figures 1a and 1b show transmission electron micrographs at low and higher magnification of the as-received material. It is indeed clear that, whereas, in the raw soot, the larger polyhedral particles have been eliminated, one can still very well see by transmission electron microscopy that the commercial product always contains a fair amount of the smaller particles with their characteristic graphite shell, Figure 1b. A detailed image is

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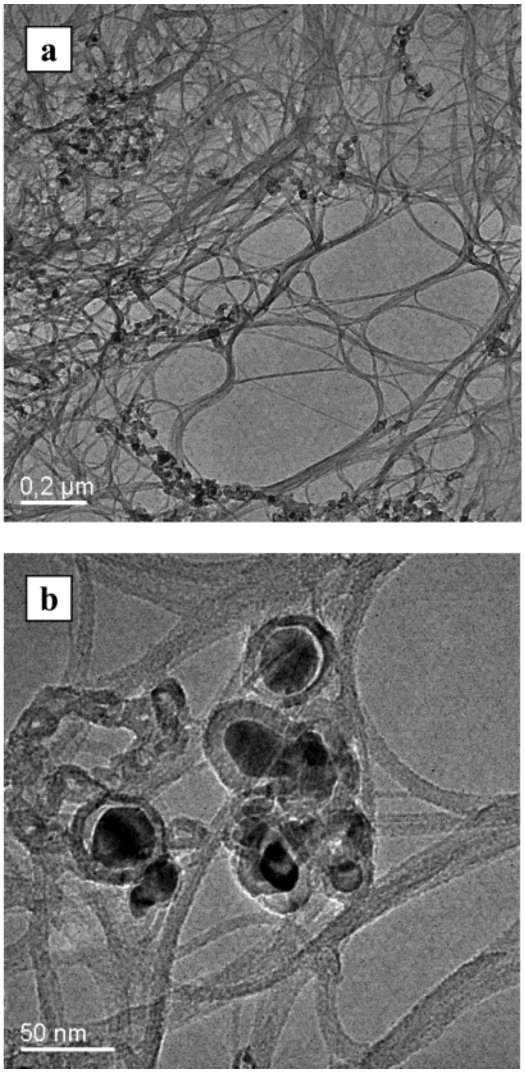

Figure 1. Transmission electron micrographs of the as-received SWNT soot at low (1a) and higher (1b) magnification. The aggregates of catalytic particles are clearly seen.

shown in Figure 2 of a large magnetic particle covered with graphitic layers, and the cross section of a rope of ordered SWNTs.

The basic principle of the purification method is like a snooker game, where we use the energy of elastic impact between encapsulated catalysts and small hard inorganic particles to eject the metal kernels and trap them by a strong magnet (Figures 3a and 3b). SWNTs (manufacturing by Tubes@Rice) were first suspended either in soap solution or in toluene and then were dispersed in various solvents such as toluene, *N*,*N*-dimethyl formamide or 30% nitric acid. A powder of nanoparticles (zirconium oxide, diamond, ammonium chloride, or calcium carbonate), that are not soluble in the given medium, was then added to the suspension. This slurry was sonicated (with a horn tip and adjustable power) for a time period, depending on the type of nanoparticles, but typically for 24 h.

TEM examination of the filtered soot after treatment shows that a large amount of the metallic particles have disappeared and numerous empty graphite shells exist (Figure 4a), which were not observed initially in the sample. On the other hand

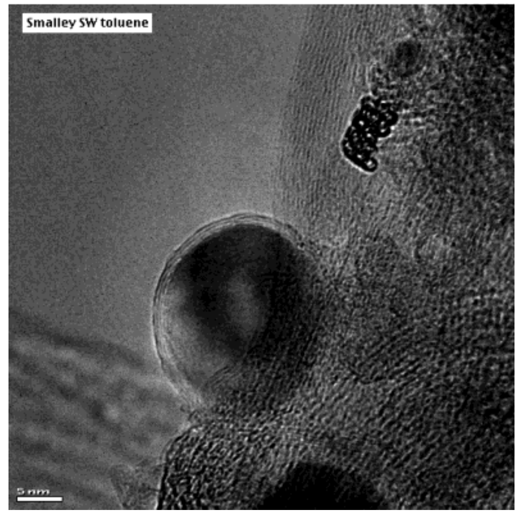

Figure 2. Transmission electron micrograph showing a characteristic feature of the sample in detail: a large catalytic particle covered with graphitic layers and a cross-sectional view of a small rope of ordered SWNTs.

the deposit covering the walls of the container in Figure 3b has a high density of metallic particles, as revealed by TEM examination (Figure 4b). We believe therefore that metallic particles are either detached with their graphite shell from the bundles, or that the graphite shell is strongly bonded to the nanotube rope, when metallic particles are knocked out of their shells and then trapped by the magnet. Control measurements of TEM and ESR were performed on pristine, sonicated, and sonicated with zirconia particles. The efficiency of the snooker procedure has been unambiguously demonstrated.

A careful examination of the deposit of the ejected catalytic particles shows that completely uncoated metallic particles were not found (Figure 4b). Nevertheless, it seems that the metal particles are covered by a small number of graphene layers (a layer of ∼1 nm thickness), whereas the majority of the initial particles in the as-received material have a much thicker shell (∼5 nm, see Figure 1b). It is likely that bonding between the metal and the first graphitic layer is stronger than between the graphene layers and that decohesion occurs between the graphene sheets and not between the metal and the first carbon layer. The magnetic field cannot extract the particles from their graphitic shells. If that were the case, there would be no concern for contamination in this field.

A comparison of the various nanoparticles used in this mechanical purification concludes that ZrO_2 and $CaCO_3$ powders yield the best results. We had the highest number of eliminated catalytic particles, and with additional acid treatment, the ZrO_2 and $CaCO_3$ was dissolved. Unfortunately, powders such as NH_4Cl, which can be suspended in toluene (or other organic solvent) and easily dissolved in water, are not hard enough to detach or knock the particles out of their shells. On the other hand, the standard diamond powder is too coarse and consists of platelets, making it a less suitable sharp for this "snooker process".

The snooker procedure may produce defects on the SWNTs although their signal in the form of localized defects

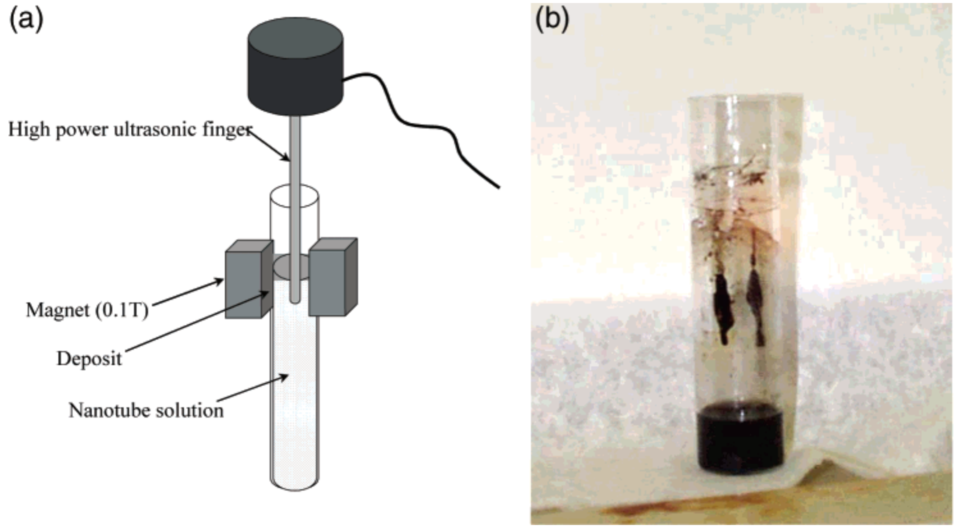

Figure 3. (a) Schematic view of the purification of SWNTs. The SWNT suspension in DMF was sonicated with ZrO_2 particles of 100 nm in size. The direct head-on collision of ZrO_2 with graphitic shells ejects the magnetic particles, which are trapped on the side of the container with a permanent magnet of 0.1 T. The black deposit of the magnetic particles is shown in Figure 3b.

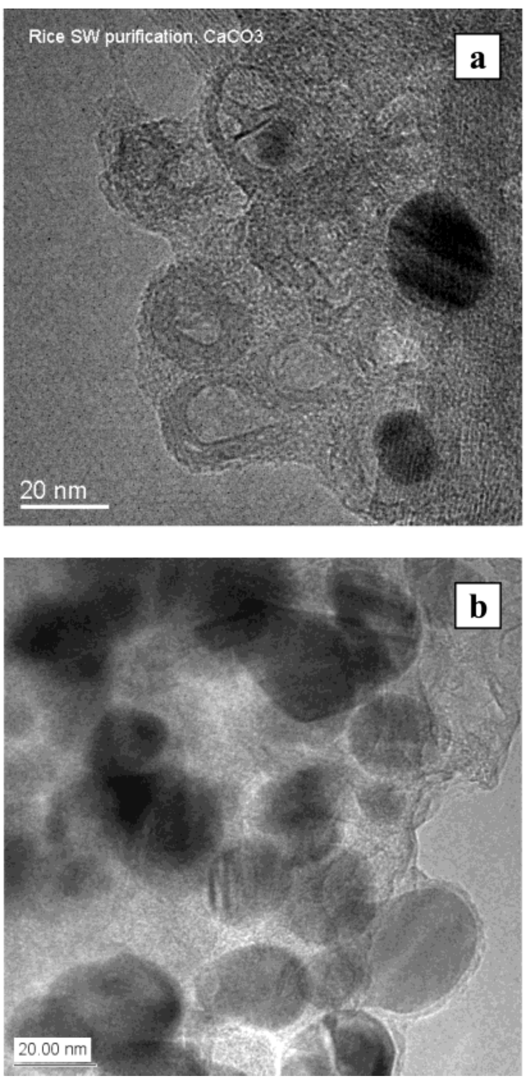

Figure 4. (a) TEM image of the empty graphitic shells after the mechanical purification procedure. (b) High-resolution TEM study of the magnetic particles trapped on the wall of the glassware by a permanent magnet shows that these particles leave the graphitic shells dressed with few graphene layers.

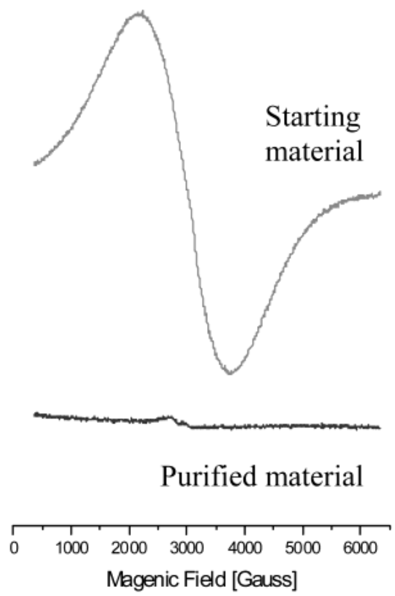

Figure 5. Electron spin resonance signal recorded at 9 GHz and at 300 K of the starting material and of the purified sample as a function of the static magnetic field. The former shows the huge ferromagnetic resonance line coming from the catalytic particles, while this signal is almost absent on the latter.

has not been detected by ESR. Even if they were there as ESR silent defects, one could heal them by high-temperature treatment. This treatment cannot work in the presence of magnetic particles, because during their evaporation they act as catalytic projectiles and transform the SWNT soot into a spiderweb-like structure. In other words, the elimination of these particles by our method is still beneficial, even if it creates some defects in the nanotubes.

In conclusion, this process does not require large equipment and enables the production of laboratory-sized quantities of SWNTs containing no magnetic impurities. This was remarkable as illustrated with the highly sensitive ESR measurement. In Figure 5, the signal of the raw material shows the huge ferromagnetic resonance signal coming from the catalytic particles. After purification, on the same quantity of SWNT material, the ferromagnetic impurity was hardly detectable.

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