

Purification of Single-Wall Carbon Nanotubes by Microfiltration

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A purification procedure for single-wall carbon nanotubes (SWNTs) prepared by pulsed laser ablation is discussed, which separates coexisting carbon nanospheres (CNS), metal nanoparticles, polyaromatic carbons, and fullerenes from the SWNT fraction. The process involves the suspension of CNS, metal nanoparticles, and SWNTs in an aqueous solution using a cationic surfactant and the subsequent trapping of SWNTs on a membrane filter. No oxidative treatment is required. Scanning/transmission electron microscopy and Raman scattering were used to evaluate the purification process and the vibrational features of SWNTs. Purity of SWNTs at the final stage sample is in excess of 90% by weight, and no evidence of impurity carbon phases was revealed in the Raman spectrum of the SWNT fraction.

In 1993, 1–2% yields of single-wall carbon nanotubes (SWNTs) were discovered in soot generated in an arc struck between carbon electrodes containing a few atomic percent Fe,¹ Co,² or Ni.³ These 3d transition metals were found necessary to catalyze the formation of SWNTs that exhibited tube diameters in the range 1–2 nm and lengths greater than 1 μ m. Much higher yields of SWNTs (>70%) were demonstrated recently by Rice University using a pulsed laser vaporization of a heated carbon target⁴ containing 1–2 at. % Ni/Co. Most recently, Journet et al.⁵ reported that high yields (>70%) of SWNTs in a cathodic deposit could also be obtained from a carbon arc catalyzed with Ni/Y (4.2/1 atom %).

In both the laser vaporization and electric arc methods for SWNT production, a considerable (or even dominant) fraction of the carbon generated is in the form of sp²-bonded carbon nanospheres (CNS).⁶ In addition, carbon-coated metal and metal carbide nanoparticles are also present, as well as fullerenes and hydrocarbons. In many cases, contributions from these impurities mask the SWNT contribution to the experimental data. Therefore, it is important to separate the SWNT fraction from these impurities. In this paper, we report the details of a microfiltration technique that was found successful in separating the SWNTs from the other fractions present in the soot produced by the laser vaporization method. We have also successfully applied this technique to arc-derived carbons with low SWNT yield. However, it should be emphasized that the carbon soot containing low SWNT yield should be pretreated by centrifugation⁷ for effective purification by the microfiltration process described in Figure 1.

Details of the laser ablation method used to prepare the samples discussed in this study has been described earlier.⁴ Briefly, SWNTs were formed in a carbon plasma created by the laser ablation of Ni/Co (1–2 at. %) composite carbon rod at a temperature of 1200 °C in an Ar flow. A two-pulse sequence at 10 Hz from a Nd:YAG laser (532 nm, 250 mJ followed by a 50 ns delayed second laser pulse at 1064 nm,

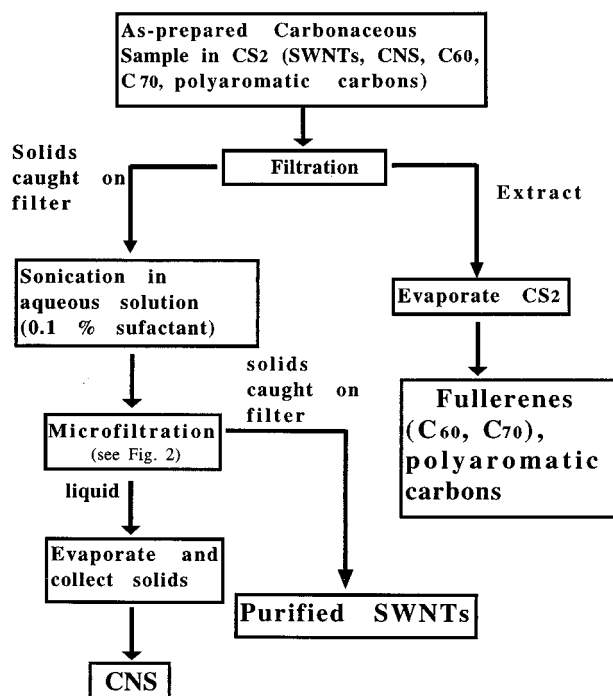


Figure 1. Schematic of the purification technique to separate coexisting carbon nanospheres (CNS), metal nanoparticles, and polyaromatic carbons or fullerenes from the laser-synthesized single-wall carbon nanotubes (SWNTs). Using this technique, ~84, 10, and 6 wt % of purified SWNTs, CNS, and CS₂ extracts, respectively, can be separated from as-prepared laser-synthesized SWNTs. Purity at the final stage sample (purified SWNTs) is in excess of 90% by weight.

300 mJ) was directed to a 6 mm spot on the carbon target. The as-prepared, carbonaceous material was observed to be a black mat in which the SWNT yield was ~70%, as determined by electron microscopy.⁴

The procedure, which results in three fractions (CNS, CS₂ solubles, SWNTs), is shown schematically in Figure 1. A typical amount of starting material was ~30 mg. Polyaromatic carbons and fullerenes were first extracted by soaking the as-prepared sample in CS₂. The CS₂ insolubles were then trapped in a filter, and the CS₂ solubles passed through the filter and were saved for later experiments. The insoluble solids caught

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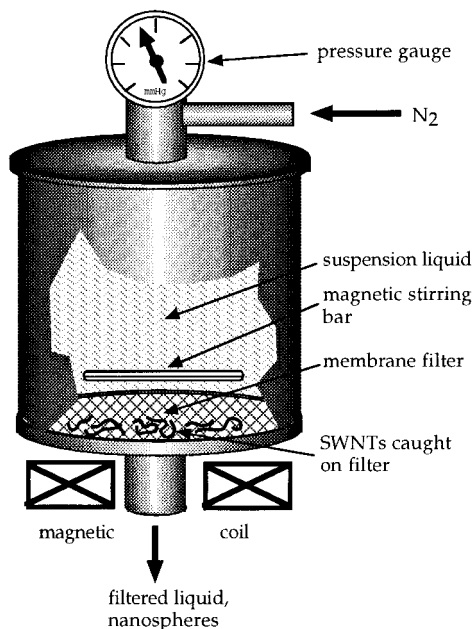


Figure 2. Schematic of the microfiltration cell. An overpressure of dry N_2 gas allows the nanoparticles to pass through the filter. SWNTs and small amounts of nanoparticles are caught on the filter.

on the filter paper were removed and dispersed in 150 cm^3 of aqueous solution of 0.1% cationic surfactant (benzalkonium

chloride, KANTO Chemical, Japan) using ultrasonic agitation (in ordinary ultrasonic bath) to separate the CNS and metal nanoparticles from the SWNTs. After sonication for 2 h, the suspension was forced through a microfiltration cell (FILTRON, $0.3\text{ }\mu\text{m}$ Omega series membrane) using an overpressure ($\sim 2\text{ atm}$) of N_2 gas. A stirring unit was used to prevent surface contamination of the membrane filter by the unfiltered components (Figure 2). Most of the CNS and metal nanoparticles were observed to pass through the filter while the SWNTs and a small amount of residual CNS and metal nanoparticles were trapped. The removal of CNS and metal nanoparticles from the as-prepared SWNTs was monitored by high-resolution scanning electron microscopy (HRSEM) and transmission electron microscopy (TEM). The microfiltration process was repeated for three cycles to minimize the amount of residual CNS and metal nanoparticles trapped between the ropes of SWNTs. The suspension that passed through the membrane filter was dried in a rotary evaporator at $60\text{ }^\circ\text{C}$, and the extract was found to be primarily CNS and metal catalyst. The solids caught on the membrane filter were similarly found to be primarily SWNTs. Both the CNS and SWNT fractions were first soaked in ethanol to wash out the surfactant. Individual weight percentages of the separated fractions were 6, 10, and 84 weight (wt) % for the CS_2 extracts, CNS and SWNTs, respectively.

Mass spectral analysis of CS_2 extracts indicated the existence of C_{60} and C_{70} together with other strong peaks in the m/e range

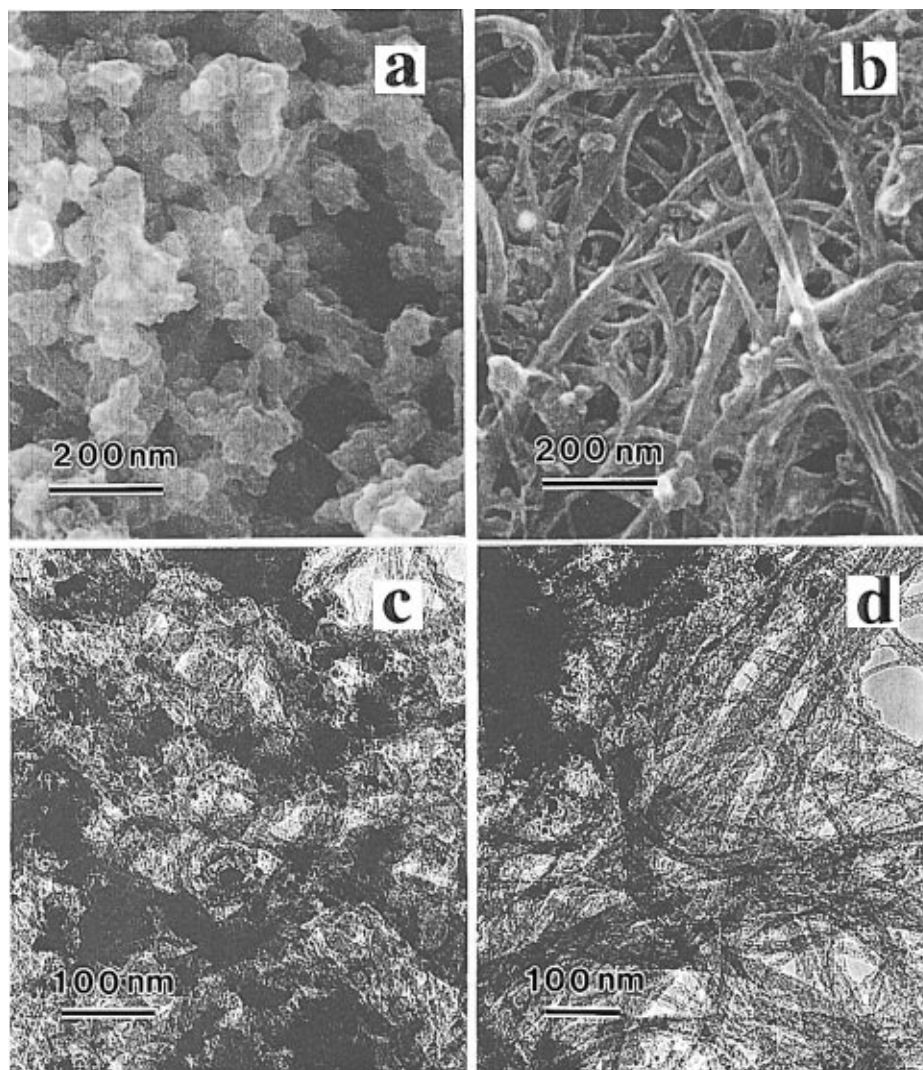


Figure 3. Electron micrographs of separated fractions shown in Figure 1. Here, panels a and b represent the scanning electron micrographs taken for CNS and SWNT fractions, respectively. Panels c and d are transmission electron micrographs of CNS and SWNT fractions, respectively.

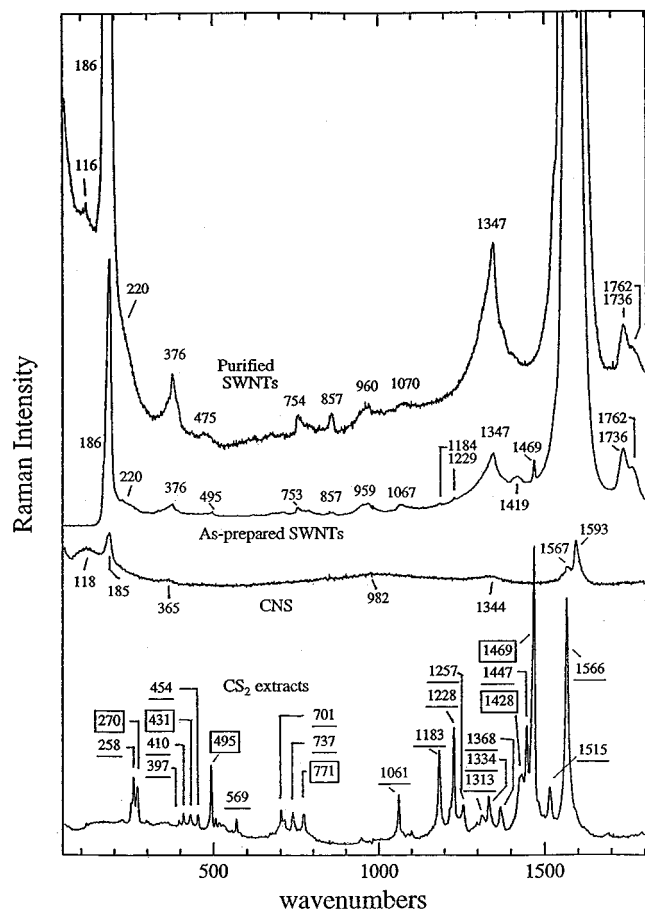


Figure 4. Raman spectra of purified SWNTs, as-prepared SWNTs, CNS, and CS₂ extracts. In the spectrum of CS₂ extracts, the boxed and underlined numbers are associated with intramolecular Raman active frequencies of C₆₀ and C₇₀, respectively.

between 300 and 700, which may be polyaromatic carbons, where m and e correspond, respectively, to the molecular mass and electron charge. The electron micrographs of the CNS and purified SWNT fractions taken by an HRSEM and TEM are shown in Figure 3. A small amount of tubules can be seen in the TEM image of the CNS fraction (Figure 3c). However, most of the carbon species that can be recognized in Figure 3c can be identified as nanoparticles and are more clearly seen in the HRSEM image of the CNS sample (Figure 3a). On the other hand, relatively few CNS can be seen in the images of purified SWNT fraction taken by HRSEM (Figure 3b) and TEM (Figure 3d). The purity of the SWNTs in the final purified fraction was in excess of 90 wt %, as estimated by counting the number of SWNT bundles and CNS in the unit area of electron micrographs. A tube diameter distribution was measured from the contrast image of TEM pictures of the purified SWNTs. A Gaussian type diameter distribution with a frequent diameter (d_0) of 1.22 nm and a standard deviation (σ) of 0.20 nm was determined. For the tubes sampled, this value of d_0 most closely corresponds to that of a (9,9) nanotube.⁸ However, this technique yields frequently diameters $\sim 10\%$ smaller than that obtained from X-ray diffraction.⁹ As mentioned earlier, the laser synthesized mats of SWNTs have been reported previously to contain predominantly (10,10) SWNTs⁴ whose d_0 is 1.36 nm.

The as-prepared SWNTs and separated fractions of purified SWNTs, CNS, and CS₂ extracts were also examined by Raman scattering. The Raman spectra were collected in an inert atmosphere on pellets prepared by mixing ~ 20 wt % of KBr with each fraction. We used an Ar ion laser (514.5 nm, 20 mW/mm²) in a backscattering configuration¹⁰ with a single

grating (f/5, 0.46 m) monochromator (Jobin-Yvon, HR460) equipped with a "supernotch" filter (Kaiser Optical) and a liquid N₂ cooled charge coupled array detector (CCD). From top to bottom in Figure 4, we display the room-temperature Raman spectra of purified SWNTs, as-prepared SWNTs, CNS, and CS₂ extracts. Most of the narrow peaks observed in the Raman spectrum of the CS₂ extract correspond to the well-known Raman peaks for crystalline C₆₀ (boxed numbers) and C₇₀ (underlined numbers). The Raman spectrum of the CNS exhibited relatively broad weak features at 118, 365, and 982 cm⁻¹. As expected for a disordered sp² carbon, a broad peak at 1344 cm⁻¹ was also observed. Since the Raman scattering from the SWNTs is resonantly enhanced,¹¹⁻¹³ both the purified and as-prepared SWNTs samples exhibit similar spectra that dominate contributions from the minority phases. Nevertheless, few weak sharp features associated with fullerenes can be easily seen in the "as-prepared" sample. For a detailed analysis of the Raman spectrum of SWNTs, the reader is referred to ref 13.

In conclusion, we have presented HRSEM, TEM, and Raman spectroscopic evidence for the separation of transition metal and carbon impurity nanophases from the laser-synthesized SWNT mats using a microfiltration technique. This technique allows us to separate the as-prepared SWNT mats into three separate fractions without the use of acid, heat, or oxidative treatment. Unlike the purification by combustion process in which high sample loss is unavoidable, the present method is very efficient. Of course, further refinements in the choice of surfactant and an increased number of filtration cycles should noticeably improve the separation. The advantage of our approach is that most of the SWNTs in the as-prepared sample are retained and captured in the final product.

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- Here, the sp²-bonded CNS refer to graphitic nanoparticles (or nanocapsules), amorphous carbon nanospheres, or onion-like nanoparticles.
- To purify SWNTs present in the arc-generated soot produced with Fe/Ni or Co/Ni catalyst (i.e., SWNTs yield < 2%), the soot must be centrifuged twice in an aqueous solution of surfactant (benzalkonium chloride, Kanto Chemical Co., Japan). First, the carbon soot is spun at 8000 rpm for 30 min. The nanotubes and nanoparticles (size < ~ 50 nm) are concentrated in the suspension, while the larger nanoparticles (size > ~ 50 nm) preferentially precipitate out during the centrifugation. Next, the suspension is decanted and centrifuged again at 15 000 rpm for 30 min. The suspension is again decanted, and the SWNT yield was found to increase to $\sim 40\%$. Further increase in the SWNT yield was obtained by the purification scheme outlined in Figure 1.

(8) The notation (n,m) defines the atomic coordinates for the 1D unit cell of the nanotube. For $n \neq m \neq 0$, the tube has chiral symmetry. Achiral tubes exist if $m = 0$ or $n = m$. The former and the latter subclasses of achiral tubes are referred to as "zigzag" $(n,0)$ and "armchair" (n,n) tubules. See, for example: Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: New York, 1996. Chapter 19.

(9) The average SWNT diameter $\langle d_i \rangle$ can be calculated from the position of the (11) X-ray diffraction peak associated with the intertubule spacing d_{11} according to the relation $\langle d_i \rangle = d_{11}/\cos 30^\circ - s$, where s is the intertubule (van der Waals) spacing taken to be 0.32 nm. The value of $s = 0.32$ nm used is midway between the interplanar spacing in graphite (0.335 nm) and the interfullerene distance in solid C_{60} (0.29 nm).

(10) In the backscattering geometry, the excitation wavelength was incident at 45° relative to the sample normal. The scattered light was collected in a cone centered about the normal.

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