Communication

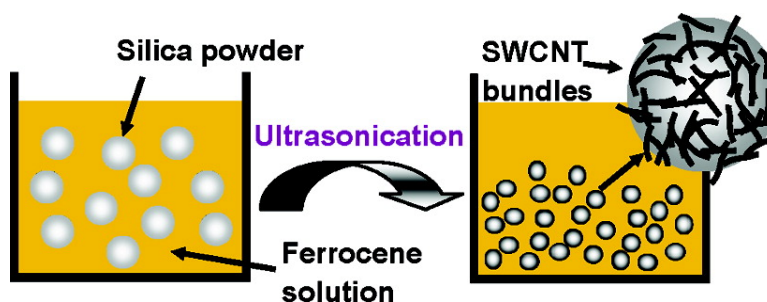# A Sonochemical Route to Single-Walled Carbon Nanotubes under Ambient Conditions

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A Sonochemical Route to Single-Walled Carbon Nanotubes under Ambient Conditions

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The unique physical and chemical properties of single-walled carbon nanotubes (SWCNTs) make them valuable for numerous applications.[1] Their potential applications include electron field emitters,[2] quantum wires,[3] molecular filters,[4] artificial muscles,[5] etc.

Although various methods of producing SWCNTs, such as arc discharge,[6] laser ablation,[7] and chemical vapor deposition,[8] have been developed, until now synthesizing SWCNTs under ambient conditions remained a great challenge. Inspired by the chemical effects of ultrasound,[9] we have developed a sonochemical route to SWCNTs of high purity in a liquid solution at atmospheric pressure and room temperature. In addition, our method offers a facile route to high-purity SWCNTs without specialized equipment and does not require a multistep purification process to eliminate the amorphous carbon and multiwalled carbon nanotubes.

The typical process of this method for SWCNT growth is depicted in Figure 1. Our strategy begins with the preparation of a mixture solution of ferrocene and *p*-xylene. Silica powder was then added in this solution. Ferrocene was chosen as a precursor of Fe catalyst for nanotube growth. The carbon source for SWCNT growth was provided by *p*-xylene as well as by ferrocene,[10] while silica powder acted as a nucleation site for SWCNT growth. Ultrasonication was performed under ambient conditions to grow SWCNTs. Finally, the resulting powder was collected on filter membrane. The products were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4500, operated at 20 kV), high-resolution transmission electron microscope (HR-TEM, Philips Tecnai ST-G2, operated at 200 keV), and Raman spectroscopy (Reinshaw, RM1000, $\lambda = 514.4$ nm, operated at room temperature).

Initially, 2 g of silica powder (diameters of 2−5 mm) was added to 0.01 mol % ferrocene−dissolved *p*-xylene solution (50 mL). The solution was then sonicated by a 1/2-in. titanium tip 200-W probe pulsed 65% at atmospheric pressure and room temperature for 20 min. During this period, the color of silica powder turned into gray, indicating a carbon deposition on its surface. It was also found that silica powder broke into small pieces below several hundreds of micrometers. This could be attributed to interparticular collisions of silica powder triggered by ultrasound irradiation.[11] The resulting powder was collected on a filter membrane. FE-SEM images reveal that fiberlike structures exist on the surfaces of silica powder, and HR-TEM energy-dispersive X-ray (EDX) spectra of our samples gave direct evidence for the formation of Fe catalyst on silica powder (see Supporting Information).

After filtration to remove the silica powder by using HF solution, fiberlike structures remained on the filter membrane as shown in Figure 2a. This morphology is similar to purified SWCNT bundles produced by the laser ablation method.[12]
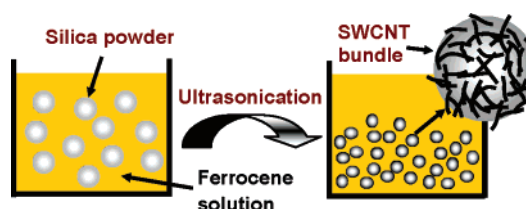

Figure 1. Schematic of sonochemical route to SWCNTs. Silica powder is immersed in the solution (ferrocene−xylene mixture). Ultrasonication then was done for 20 min at room temperature and atmospheric pressure. Sonication produces high-purity SWCNTs on the surface of silica powder.
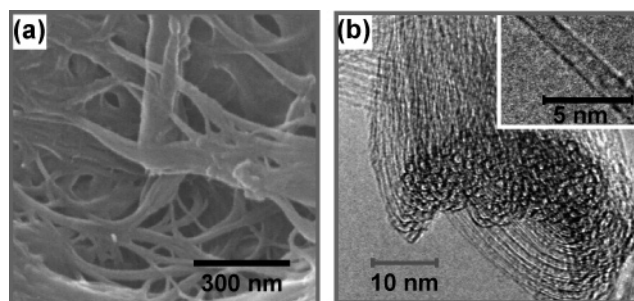

Figure 2. (a) SEM image of SWCNT bundles on polycarbonate filter membrane. (b) HR-TEM images of SWCNTs. Most SWCNTs exist in bundles. For the measurements of diameters of SWCNTs, individual SWCNTs (inset) are also imaged by HR-TEM.

HR-TEM confirmed that these structures mainly consisted of SWCNT bundles as shown in Figure 2b. The absence of multi-walled carbon nanotubes was also confirmed by HR-TEM observations. To determine the diameter of SWCNTs by HR-TEM, we also obtained images of individual SWCNTs (inset in Figure 2b). The average diameter of SWCNTs based on TEM data was 1.5 ± 0.1 nm.

Control experiments were carried out to determine if the presence of silica powder is essential for producing SWCNTs. For a sample sonicated without silica powder, no SWCNTs were shown in the resulting HR-TEM images.

Concentration effect of ferrocene in *p*-xylene solution was also studied to achieve the best conditions for the SWCNT growth. It was found that high-purity SWCNTs were obtained at relatively low concentration of ferrocene (0.01 mol %), showing no noticeable evidence for the existence of multiwalled carbon nanotubes and amorphous carbon. Once Fe nanoparticles are produced by decomposition of ferrocene during sonication, there would be two possible competing reactions: SWCNT growth by catalytic action of fine Fe catalyst and Fe particle growth by agglomeration of fine Fe catalyst. However, it is expected that the former reaction occurs dominantly under our experimental conditions, reducing the chance to form the larger Fe particles, which may result in multiwalled

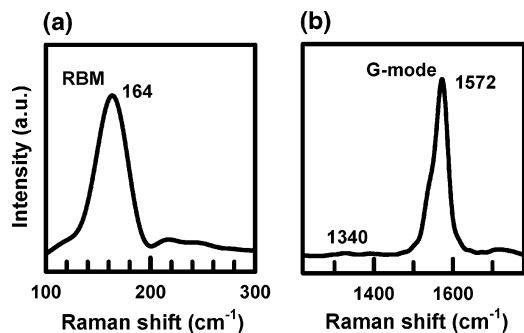[†] U-team.
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(a)   **(b)**

Figure 3. Raman spectra (Ar$^+$ laser: $\lambda = 514.5$ nm) of synthesized SWCNTs. (a) RBM and (b) G-line mode are presented for the average of 10 spectra recorded at random points.

carbon nanotube growth. These are probably caused by very low concentration of ferrocene in our experiment.

Raman spectroscopy has also confirmed sample homogeneity as shown in Figure 3. Spectra were recorded at 10 randomly selected positions and averaged. Figure 3 shows the typical spectral characteristics of SWCNT structure, as characterized by the strong G band (tangential mode) and the presence of the sharp radial breathing mode (RBM) in the lower wavenumber region $(100-300 \text{ cm}^{-1})$. RBM spectra were further analyzed to give the diameter distribution of SWCNTs. According to the equation, $\omega_{\text{RBM}} = 235/d + 9$ for bundled SWCNTs,[13] where d (nm) is the diameter and ω (cm^{-1}) is the Raman shift of a SWCNT, the RBM region in Figure 3a yields SWCNT diameters of $1.1-2.1$ nm with an average diameter of 1.55 nm (see Supporting Information). The diameters of most SWCNTs (>90%) were in the range of $1.3-1.8$ nm. These estimates agree well with the measured values from HR-TEM images. A weak peak at 1340 cm^{-1} of D-band (related to disordered graphite or amorphous carbon) and strong peak at 1572 cm^{-1} of G-band (tangential mode) are shown in Figure 3b. The relatively low intensity of D band relative to the G-band (intensity ratio, $I_D/I_G = 0.01$) indicates that only a small amount of amorphous carbon or few defects exist in these SWCNTs.[14]

It is well-known that cavitation bubbles produced in liquid solution during sonication can instantaneously generate local spots of several thousand degrees Celsius of temperature and several thousand atmospheres of pressure.[9] Although details of SWCNT growth mechanism are still under investigation, we believe that these sonochemical treatments both facilitate decomposition of ferrocene and p-xylene and provide the required energy to synthesize SWCNTs. Unlike previous methods for producing SWCNTs,[6−8] which require severe conditions such as high temperature, high vacuum, or high voltage arc discharge, our method

provides a facile route to high-purity SWCNTs under ambient conditions. Considering that methods for large-scale processing of liquids with ultrasound (for example, coal benefaction at 20 tons/h) are known,[9] this process is expected to be easily scaleable for mass production.

The process also could be readily generalized in seeking to synthesize other forms of carbon-based materials, such as fullerenes, multiwalled nanotubes, carbon onions, and diamond, in liquid solution under ambient conditions.

In summary, we have presented a simple method for producing high-purity SWCNTs in liquid solution under ambient conditions. Silica powder was immersed in a mixture solution of ferrocene and p-xylene. After sonication at atmospheric pressure and room temperature, we obtained high-purity SWCNTs. This method also presents a facile route to high-purity SWCNTs without complex purification processes.

Supporting Information Available: SEM, EDX, and TEM data for produced samples without removing the silica powder. Figure showing diameter distribution of grown SWCNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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