



# Purification of single-walled carbon nanotubes synthesized by the catalytic decomposition of hydrocarbons

F. Li<sup>a</sup>, H.M. Cheng<sup>a,\*</sup>, Y.T. Xing<sup>a</sup>, P.H. Tan<sup>b</sup>, G. Su<sup>a</sup>

<sup>a</sup>*Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110015, China*

<sup>b</sup>*National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China*

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## Abstract

A procedure for purifying single-walled carbon nanotubes (SWNTs) synthesized by the catalytic decomposition of hydrocarbons has been developed. Based on the results from SEM observations, EDS analysis and Raman measurements, it was found that amorphous carbon, catalyst particles, vapor-grown carbon nanofibers and multi-walled carbon nanotubes were removed from the ropes of SWNTs without damaging the SWNT bundles, and a 40% yield of the SWNTs with a purity of about 95% was achieved after purification. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Recently, the large-scale synthesis of single-walled carbon nanotubes (SWNTs) has made great progress since the laser ablation method was reported by the Smalley group [1], and SWNTs can now be obtained in quantity by the laser ablation method [1], electrical arc method [2], and most recently the hydrocarbon catalytic decomposition method [3]. However, all the SWNT products from these methods include impurities, such as catalyst particles, amorphous carbon, and possibly multi-walled carbon nanotubes (MWNTs), carbon nanoparticles, C<sub>60</sub> and other fullerenes. In order to explore their physical and chemical properties and applications, SWNTs with higher purity are needed.

It has been reported that the purification procedures for SWNTs should be different from those for MWNTs [4] because SWNTs can be oxidized by strong oxidants. Moreover, the impurities depend strongly on the synthesis methods, reaction time, types of catalyst and carbon source employed. Tohji et al. [4,5] reported that high-purity SWNTs can be obtained through hydrothermally initiated dynamic extraction (HIDE) of the products synthesized by the electrical arc method. Shelimov et al. purified their

SWNTs obtained by the laser vaporization technique using ultrasonically assisted filtration [6]. As these methods all used some mild oxidants such as HNO<sub>3</sub> [4,5], and H<sub>2</sub>SO<sub>4</sub> [6], amorphous carbon and catalyst particles can be efficiently removed from the products, though they can cause the intercalation and partial exfoliation of SWNT bundles [7]. However, these procedures cannot efficiently get rid of the vapor-grown carbon nanofibers (VGCNFs) and MWNTs in the vapor-grown SWNT product.

In this paper, a new method to purify SWNTs synthesized by the catalytic decomposition of benzene and methane is described. It has been reported [3,8] that the impurities in our as-prepared SWNT product are mainly amorphous carbon, catalyst particles, MWNTs and VGCNFs. This purification procedure includes three steps: acid washing, and ultrasonic and freezing treatments. After purification, it is estimated that the purity of SWNTs was at least 95 wt.% and the SWNT bundles were not destroyed.

## 2. Experimental

### 2.1. Synthesis of SWNTs

The preparation of SWNTs by the catalytic decomposition of hydrocarbons has been described in detail else-

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\*Corresponding author. Fax: +86-24-2389-1320.

E-mail address: cheng@imr.ac.cn (H.M. Cheng)

where [3]. In brief, a vapor-phase catalyst precursor (ferrocene) and a SWNT growth promoter (thiophene) together with hydrocarbon gases and hydrogen were passed into a horizontal reactor to achieve semi-continuous growth of SWNTs at about 1473 K. The SWNTs were collected on a graphite plate, on the thermocouple-protecting tube or on the inside tube wall at the lower-temperature end of the reaction tube. The original products were silver-black, web-like, very light, very thin, and freestanding.

### 2.2. Purification procedure

The procedure was shown in Fig. 1. The product with the most impurities was chosen in order to test the efficiency of the procedure. At first, about 200 mg of product was suspended in benzene for about 1 week and was filtered to extract benzene-soluble materials, such as the catalyst precursor and fullerenes. After the sample was washed with de-ionized water, it was treated by ultrasound at  $1000 \text{ W cm}^{-2}$  for 1 h in 37 wt.% hydrochloric acid followed by the acid dissolution of Fe catalyst particles for 10 h under stirring. After filtering, the samples were frozen at  $-196^\circ\text{C}$  for about 10 h followed by further ultrasonic treatment for 1 h. Finally the sample was washed with de-ionized water and dried, and about 75 mg of purified SWNTs was obtained.

### 2.3. Evaluation of the purified SWNTs

In order to evaluate the effectiveness of the above procedure, samples before and after purification were characterized by energy dispersion spectrum (EDS), scanning electron microscope (SEM), and laser Raman measurement with an excitation wavelength of 514.5 nm.

## 3. Result and discussion

### 3.1. Morphology observations

Fig. 2 shows SEM images of the SWNT products before and after purification. In Fig. 2(a), the SWNT rope cannot be easily distinguished, as some amorphous carbon and catalyst particles are dispersed in the product. From Fig. 2(b), the SWNT ropes consist of a large number of SWNT bundles, similar to the bundles observed from the products produced by the laser vaporization technique [1]. These observations suggest that the purification procedure does not destroy the SWNT bundles.

### 3.2. EDS result

EDS was employed to identify the concentration of catalyst-Fe element before and after purification. Several regions about  $1 \text{ mm}^2$  were chosen to measure the element distribution and results for the products before and after purification are shown in Fig. 3. These show that the main elements in the SWNT products are C and Fe, with a small amount of S [Fig. 3(a)]. This is reasonable because Fe came from the catalyst precursor and S from the promoter. Comparing Fig. 3(a) and (b), the Fe and peaks are lowered dramatically, but the C peak became much higher after purification. From the integral calculation, the percentage of C increased from 41.3 to 96.9%, and that of Fe decreased from 54.9 to 2.5%, and S from 3.9% to 0.6%. These results imply that the purity of our SWNTs can be very high after purification.

### 3.3. Raman measurements

It is well known that SWNTs have two groups of characteristic resonant Raman peaks [9]. The one at low

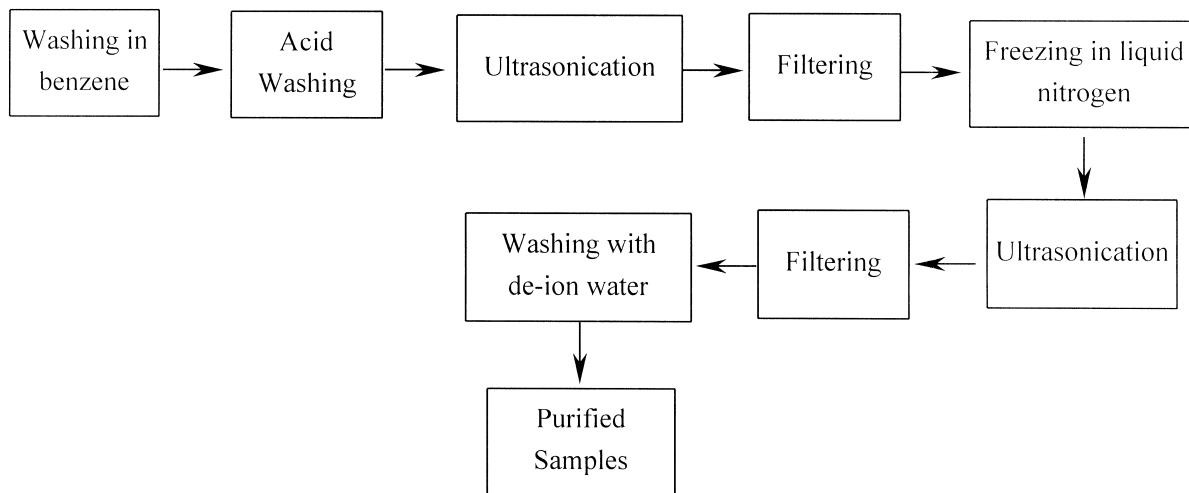


Fig. 1. The flowchart for the purification procedure of SWNTs.

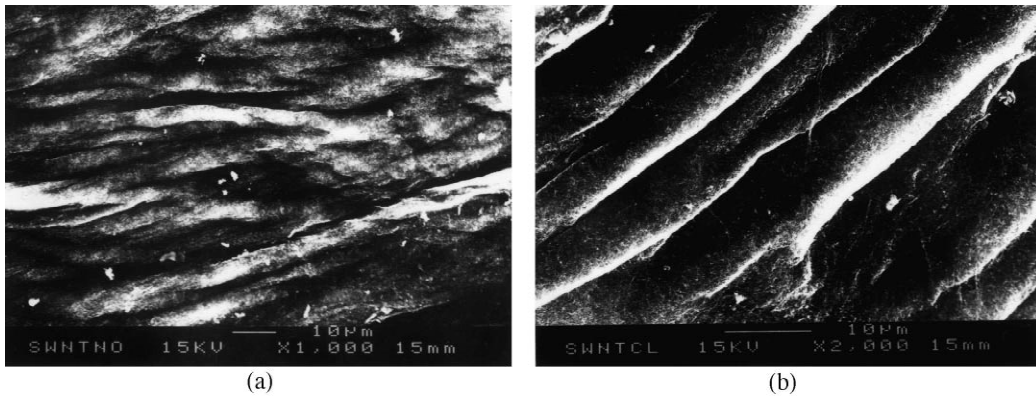


Fig. 2. SEM image of SWNTs before (a) and after (b) purification.

frequency around  $180\text{ cm}^{-1}$  is called the radial breathing mode, and the other at high frequency about  $1500\text{--}1600\text{ cm}^{-1}$ , shows a multi-split characteristic peak of crystalline graphite centered as their cylindrical symmetry [9]. Amorphous carbon or fine graphitic particles generally show a broad peak near  $1350\text{ cm}^{-1}$ .

Fig. 4 shows the Raman spectra of the SWNT from  $1200\text{ to }1600\text{ cm}^{-1}$  before and after purification with a laser wavelength of  $514.5\text{ nm}$ . The SWNTs after purification clearly show a multi-split peak at ( $1570\text{--}1590\text{ cm}^{-1}$ ) while the SWNT before purification hardly shows this

peak. From Lorentzian fitting, we can obtain two peaks at  $1573\text{ and }1590\text{ cm}^{-1}$ . At the same time, the intensity of the peak at  $1300\text{ cm}^{-1}$  became much lower after purification. This result suggests that the product consists of high-purity SWNTs.

### 3.4. The effectiveness of the procedure

The impurities of the SWNTs obtained by catalytic decomposition of hydrocarbons are different from those introduced by other methods [1,2], which are mainly

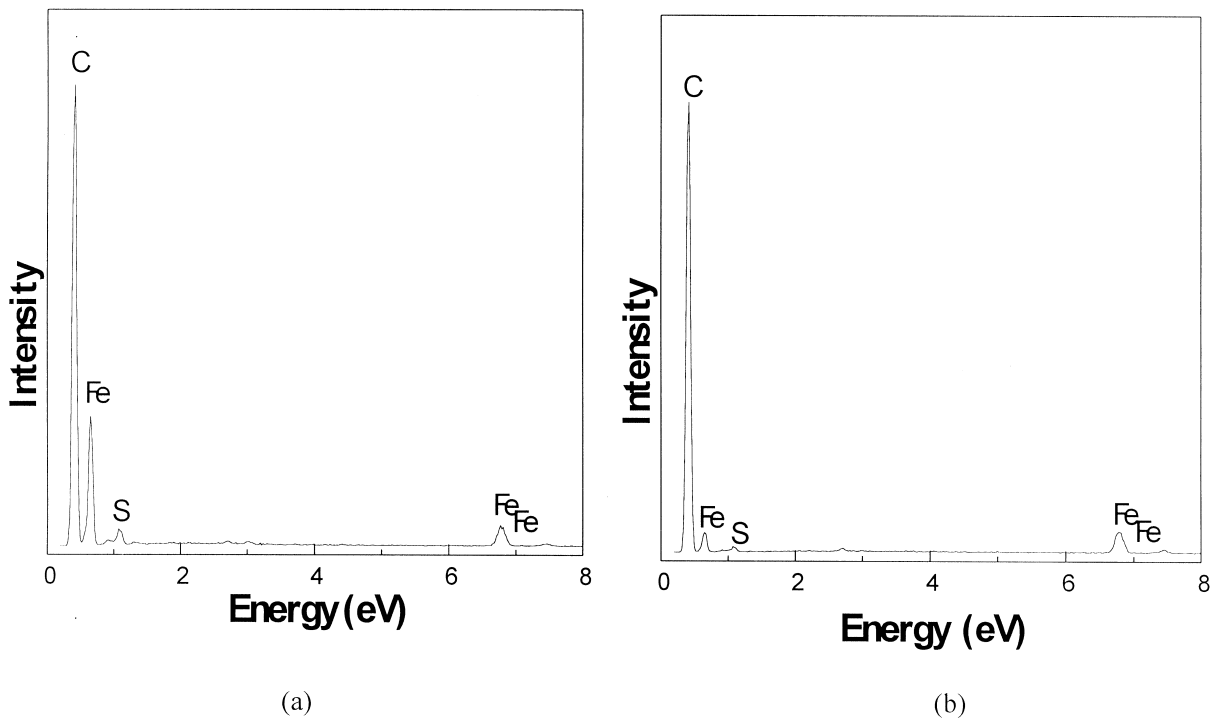


Fig. 3. EDS of SWNTs (a) before and (b) after purification.

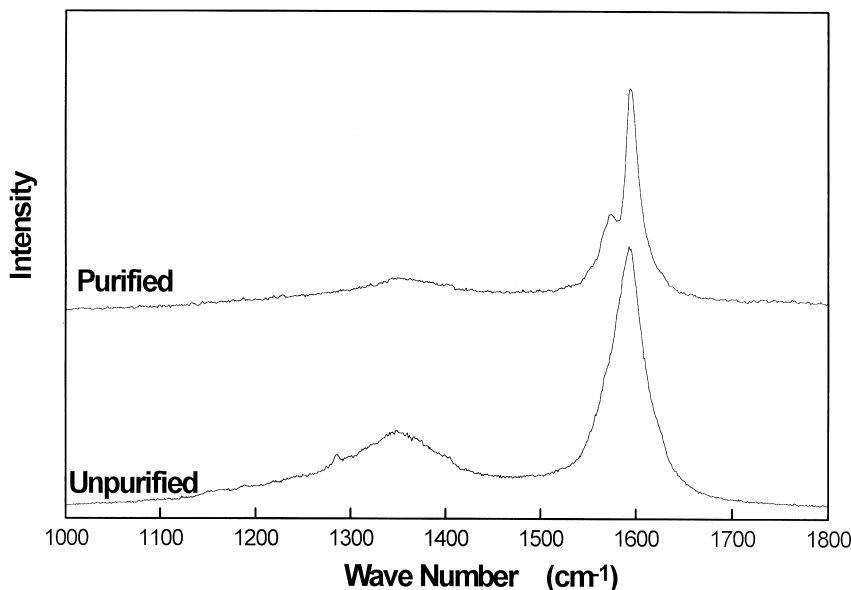


Fig. 4. Raman spectra of the purified and unpurified SWNTs with a laser wavelength of 514.5 nm.

catalyst particles, amorphous carbon, VGCNFs and some MWNTs [8]. In some regions, there are many impurities and in others purity is very high. Therefore, a suitable purification procedure should be carefully chosen.

In the first step, immersion benzene, the solution gradually became yellow–green because the catalyst precursor and some fullerenes can dissolve in the benzene solvent [4–6]. From previous observations, the nanoparticles in the products were mainly catalyst Fe,  $\text{FeC}_3$  or  $\text{Fe}_2\text{O}_3$  of 10–40 nm in diameter [3]. Thus a hydrochloric acid treatment can be effective with stirring. When the sample was treated with hydrochloric acid (37 wt.%), the color of the liquid became yellow–green quickly.

It is believed that ultrasonic treatment can remove the catalyst nanoparticles and the amorphous carbon from the SWNT bundles. After the treatment, small particles floated in the solution. Combination of the ultrasonic and hydrochloric acid treatments can effectively remove the amorphous carbon and the large particles.

Endo et al. reported that vapor-grown carbon fibers can be broken in liquid nitrogen, but the nanotube core of VGCFs can survive this low-temperature quenching [10]. Therefore, a liquid nitrogen quenching of the SWNT samples was employed to get rid of possible VGCNFs and MWNTs.

#### 4. Conclusion

The results from SEM observation, EDS analysis and resonant Raman measurements show that the purification procedure proposed in this work, in which benzene and

HCl washing, and ultrasonic and freezing treatments are employed, is effective in purifying SWNTs obtained from the catalytic decomposition of hydrocarbons. After purification, SWNTs with a purity of 95 wt.% can be obtained and the procedure does not destroy the bundles of SWNTs formed during the synthesis.

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