New Method of Purification of Carbon Nanotubes Based on Hydrogen Treatment

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A novel method for the purification of single-walled and multiwalled carbon nanotubes is described. The method involves acid washing followed by hydrogen treatment in the 700−1000 °C range. While acid washing dissolves the metal particles, the hydrogen treatment removes amorphous carbon as well as the carbon coating on the metal nanoparticles. The high quality of the nanotubes obtained after purification has been checked by electron microscopy, X-ray diffraction, and spectroscopic methods.

Multiwalled carbon nanotubes (MWNTs) as well as single-walled carbon nanotubes (SWNTs) are produced by arc evaporation or laser ablation of graphite and by the pyrolysis of hydrocarbons and organometallic precursors.[1−5] The as-synthesized nanotubes usually contain impurities such as amorphous carbon and metal nanoparticles, the latter being prominent when metal catalysts are employed. Purification of carbon nanotubes, therefore, is an important problem in carbon nanotube research. Acid treatment and gas-phase oxidation have been employed to purify SWNTs.[6,7] Micro-filtration and hydrothermal treatment also help in eliminating amorphous carbon and catalyst particles.[8,9] Fullerenes are also removed by solvent extraction. Martinez et al.[10] have used a combination of air oxidation and microwave acid digestion, which is also employed to purify arc-discharge SWNTs. The effect of oxidation conditions on the sample purity on SWNTs prepared by the arc-discharge method has been examined.[11] Due to the importance of purification in nanotube research, we have been exploring an alternative method involving high-temperature hydrogen treatment. The method has been most effective in purifying both SWNTs and MWNTs.

Arc discharge SWNTs (arc SWNTs)[4] were heated in air at 300 °C for 12 h and then stirred in concentrated HNO_3 at 60 °C for 24 h in order to dissolve the metal nanoparticles. The product was washed with distilled water, dried, dispersed in ethanol under sonication, and filtered using Millipore (0.3 μm) filter paper. The filtered product was dried in an oven at 100 °C for 2 h and heated to 1000 °C in a furnace at a rate of 3° per minute, in flowing hydrogen at 100 sccm (standard cubic centimeter per minute) and held at that temperature for 2 h. The resulting sample was again stirred in concentrated HNO_3 at 60 °C for 3 h and heated in a furnace at 1000 °C for 2 h in flowing hydrogen (100 sccm). A similar procedure was employed for the purification of SWNTs obtained by laser ablation (laser SWNTs)[3] as well as HiPCO SWNTs. A CS_2 extraction was carried out on the laser SWNTs followed by washing with 8 N HCl and hydrogen treatment, the last steps being similar to those employed for arc SWNTs. Suspensions of SWNTs for recording visible-NIR spectroscopy were prepared following O'Connell et al.[12] Arc-discharge MWNTs were refluxed in a 2:1 mixture of concentrated HNO_3 and concentrated H_2SO_4 (acid treated MWNTs) for 20 h, followed by hydrogen treatment at 1100 °C for 2 h. Aligned MWNT bundles obtained by ferrocene pyrolysis[5] were subjected to acid treatment before they were heated in hydrogen at 1100 °C. The nanotubes were characterized at each stage by powder X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy.

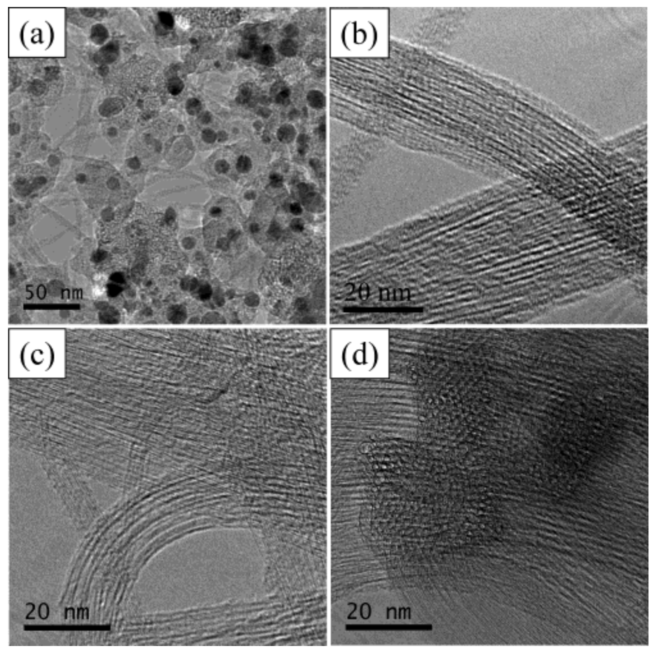

Figure 1. TEM images of (a) as-synthesized SWNTs obtained by the arc-discharge method, (b) after acid treatment, (c) after first hydrogen treatment, and (d) after the second hydrogen treatment.

Figure 1a shows a TEM image of the as-synthesized arc SWNTs containing amorphous carbon and metal nanoparticles apart from the SWNT bundles. The image reveals that the SWNT bundles have a diameter of ∼10 nm. Most of the metal nanoparticles get dissolved on acid washing, but the nanotubes are covered with amorphous carbon as seen in the TEM image in Figure 1b. The amorphous carbon is removed by high-temperature hydrogen treatment and the remaining small metal nanoparticles agglomerate into larger particles. We generally find that at this stage of purification the nanotubes have open ends. The absence of amorphous carbon is clearly evident from

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the TEM image in Figure 1c. TEM images also reveal that the bundles grow in size and have diameters in the range of 20−50 nm after the hydrogen treatment. The metal nanoparticles agglomeration occurs in the 750−850 °C range and is removed in the second acid treatment carried out for a short duration. The second acid treatment is followed by the high-temperature hydrogen treatment at 1000 °C to obtain pure SWNTs. A TEM image of such purified SWNTs is shown in Figure 1d. We do not see hollow onion-like structures often found in SWNTs purified by other methods,[9] indicating thereby that the carbon covering on the metal particles is etched away by hydrogen.

SWNTs form a triangular lattice and give a distinctive low angle reflection in the XRD pattern.[3] In Figure 2A, we show the low-angle XRD patterns of the as-synthesized and acid-treated SWNTs along with those finally obtained after the second hydrogen treatment. The (1,0) diffraction line is not observed clearly in the case of as-synthesized SWNTs and appears as a small hump in the acid treated SWNTs. We however see an intense peak in the sample after the second hydrogen treatment. The mean diameter of the purified SWNTs is estimated to be 1.52 nm from the (1,0) diffraction line.[13] The visible-NIR spectra of the arc SWNTs at various stages of purification is shown in Figure 2B. Due to their one-dimensional nature, carbon nanotubes exhibit van Hove singularities in the electronic density of states,[14] visible-NIR spectroscopy providing evidence for the one-dimensional nature. The peak centered at 1100 nm is due to the second van Hove singularity transition and the second set of peaks near 700 nm due to the first van Hove singularity transition of metallic nanotubes. The intensities of the two bands increase markedly on hydrogen treatment. The G-band and the radial-breathing modes of SWNTs in the Raman spectra are strong in intensity, whereas the other Raman modes are weak.[15] The Raman spectra of the as-synthesized and purified arc SWNTs are shown in Figure 2C. The as-synthesized sample (curve a) shows a G-band, which is split into bands at 1562 and 1586 cm^{-1}. The D-band appears as a broad peak centered at 1343 cm^{-1} indicating that the sample contains amorphous carbon. The second-order Raman bands appear as weak peaks centered at 941 and 1075 cm^{-1}. The purified sample shows an intense split G-band (1563 and 1585 cm^{-1}) and strong radial-breathing modes. The D-band becomes very weak on hydrogen treatment. The radial breathing modes show the diameters to be in the range of 1.32−1.89 nm,[15] in agreement with the diameter distribution estimated from TEM images and low-angle X-ray diffraction.

The TEM images in Figure 3 show laser SWNTs at various stages of purification. Fullerenes, metal nanoparticles, amorphous carbon, and SWNT bundles are present in the as-synthesized laser SWNTs (Figure 3a). The fullerenes were removed by CS_2 extraction and the metal nanoparticles partly dissolved on acid washing. After acid washing, amorphous carbon continues to cover the SWNTs (Figure 3b). This amorphous carbon is effectively removed by the hydrogen treatment at 1000 °C as can be seen in Figure 3c. Similar to the arc SWNTs, we observe an agglomeration of the undissolved metal nanoparticles, which could be removed by the subsequent acid treatment. The nanotubes heated again in hydrogen at 1000 °C were indeed of high purity (Figure 3d). The purity of the nanotubes was also established by the Raman and UV−visible−NIR spectra. SWNTs prepared by the HiPCO could be purified satisfactorily by this method at a relatively lower temperature of 700 °C.

We have examined the efficacy of the high-temperature hydrogen treatment procedure for MWNTs. Acid treated

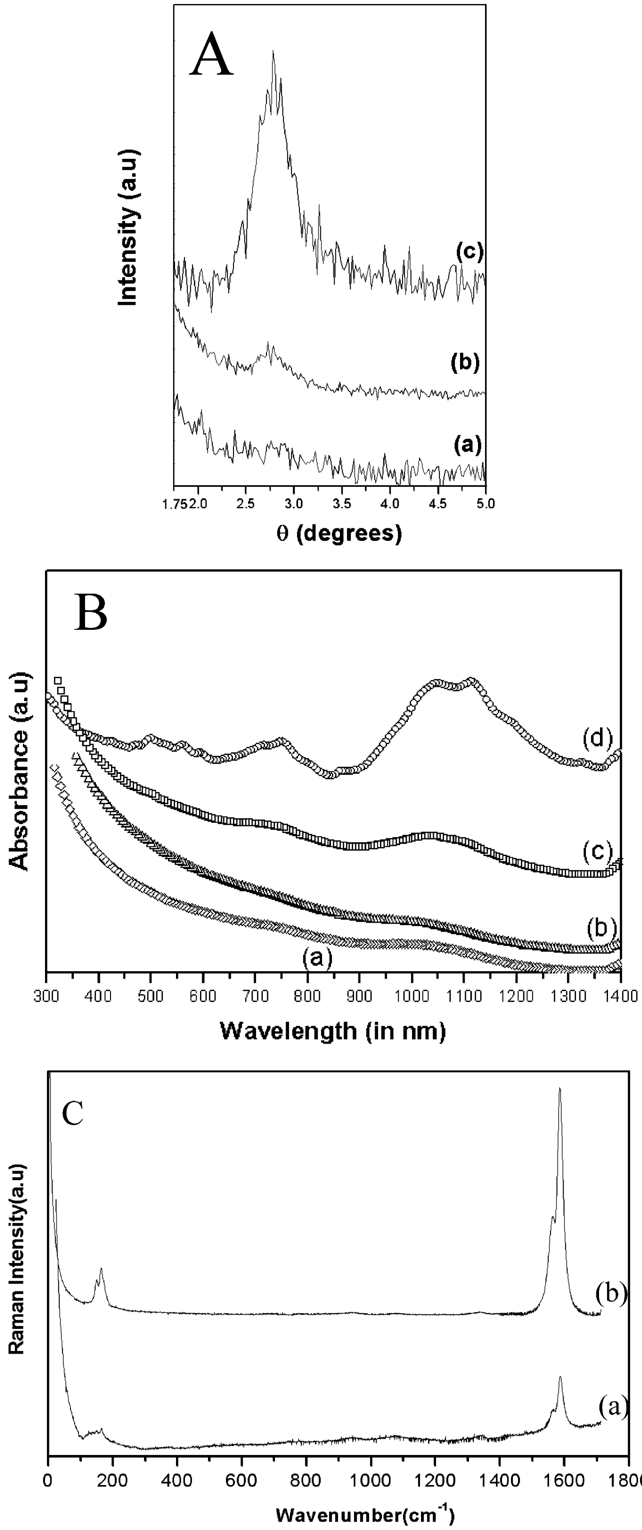

Figure 2. (A) Low-angle X-ray diffraction patterns of (a) as-synthesized arc-discharge SWNTs, (b) after first acid washing, and (c) after second hydrogen treatment. (B) Visible−NIR spectra of (a) as-synthesized arc-SWNTs, (b) after first acid washing, (c) after first hydrogen treatment, and (d) after final purification. (C) Raman spectra of (a) as-synthesized arc-discharge SWNTs and (b) after second hydrogen treatment.

MWNTs contain a large amount of amorphous carbon. A TEM image of the acid treated MWNTs is shown in Figure 4a. The amorphous carbon is removed by the high-temperature hydrogen treatment as can be seen from Figure 4b. The high-resolution electron microscope (HREM) image shown as an inset in Figure

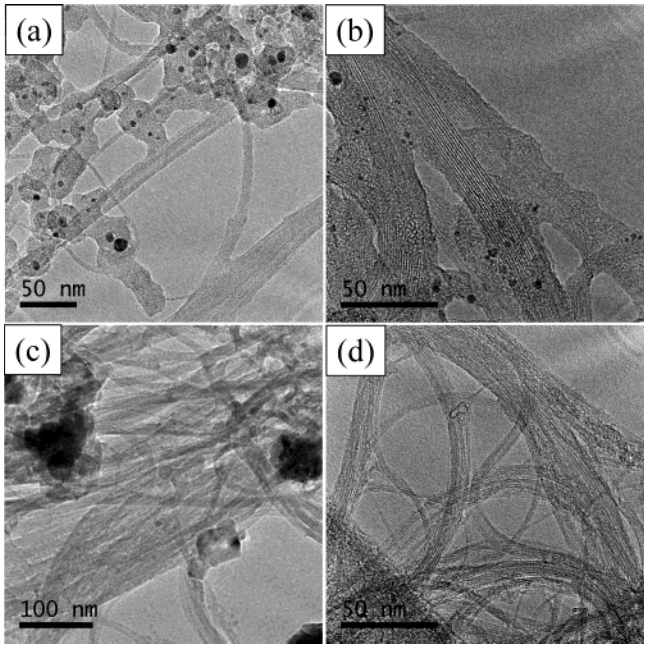

Figure 3. TEM images of SWNTs obtained by laser ablation: (a) as-synthesized, (b) after acid treatment, (c) after first hydrogen treatment, and (d) after final purification.

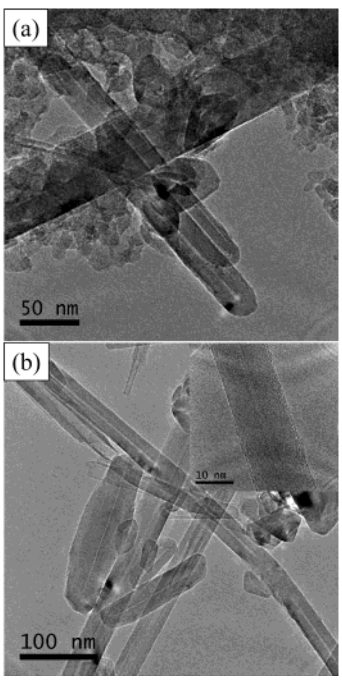

Figure 4. TEM images of arc-discharge MWNTs (a) after acid treatment and (b) after hydrogen treatment at 1100 °C for 2 h. Inset in (b) shows a HREM image of a MWNT after hydrogen treatment.

4b indicates that the crystalline nature of the MWNTs is preserved after the acid and hydrogen treatments. Raman and X-ray diffraction measurements confirmed the high purity of the MWNTs subjected to these treatments. We have found that aligned carbon nanotubes are also effectively purified by high-temperature hydrogen treatment.

It would be in order to compare the present work with the other procedures reported in the literature. All of the methods make use of acid washing to remove the metal particles where present. In the procedures involving air oxidation, SWNTs are subjected to heat treatment in the 350−500 °C range depending on the method of synthesis. The present method however employs hydrogen treatment around 1000 °C for all SWNTs and MWNTs, except for HiPCO SWNTs which require a lower temperature. Whereas in air oxidation the amorphous carbon is converted into CO_2, it is converted to CH_4 on hydrogen treatment.

In conclusion, we have developed a new and effective method for the purification of SWNTs and MWNTs. The method involves acid washing followed by the high-temperature hydrogen treatment repeated twice. Excellent SWNTs containing little or no amorphous carbon and metal particles are obtained by this means, as verified by microscopy, XRD, and spectroscopic techniques. Equally importantly, thermogravimetric measurements of MWNTs and SWNTs show that the low-temperature weight loss due to amorphous carbon is eliminated after hydrogen treatment. In the case of laser SWNTs, the oxidation temperature is substantially increased after purification.

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