A Rapid and Simple Homogenizing Method for the Purification of Single-walled Carbon Nanotubes

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(Received June 10 2008, Accepted September 29 2008)

We developed a simple and effective purification method to obtain high-purity single-walled carbon nanotubes (SWCNTs) with low surface damage. The purification process consists of oxidization at 430 °C for 1 h in a furnace system of air atmosphere and homogenization in dilute hydrochloric acid solution for extremely short time. The role of homogenizer was examined during purification process in terms of purity and quality of purified SWCNTs. High-purity and low surface damage of SWCNT products was obtained using homogenizer which was operated at 8500 rpm for 10 min in the environment of 7 % HCl solution. From XRD spectra, we observed that metal catalysts were thoroughly removed. Raman spectra showed that the intensity values of crystallization (I_G/I_D) of purified SWCNTs were very similar with that of pristine SWCNTs. Moreover, the structure damage of purified SWCNTs was hard to find from electron microscopy. Consequently, homogenizing, which is a quick and simple manner, can be promising method for obtaining final SWCNTs with clearly high purity and crystallinity.

Keywords : SWCNT, Homogenizing, Electron microscopy, X-ray scattering, Raman spectroscopy

1. INTRODUCTION

Since the first report of single-walled carbon nanotubes (SWCNTs) in 1993[1], there have been many reports on basic scientific research and technological applications. SWCNT is an ideal material for various applications due to its outstanding properties such as high electric conductivity and high mechanical strength [2,3]. Recently, synthesizing large quantities of SWCNTs have been also achieved through various mass production methods[4,5]. Purifying SWCNTs, however, still remains a critical issue to puzzle out in a systematic way because as-synthesized SWCNTs produced by arc discharge method contain actually a lot of impurities such as metal catalysts, carbon particles, and amorphous carbon materials. As for removal of such contaminants, conventional purification methods generally can induce much surface damage and a lot of weight loss of SWCNTs[6-9]. Moreover, it requires complicate procedure and tedious time consumption by severe acid treatment to eliminate extensive metal catalysts[10-13]. Even though other interesting purification methods have been appeared[14-16], more simple and effective purification method should be developed to overcome these problems. In this work, we demonstrate a simple and effective purification method to obtain high-purity SWCNTs with low surface damage by homogenizer. The role of homogenizer was examined during purification process in terms of purity and quality of purified SWCNTs. The entire operation time in our purification process allows just around 90min which could be better handy and useful than conventional tedious and long-time process. This is improved purification method with shortest operation time than any others[6-13].

2. EXPERIMENTAL

SWCNTs were synthesized by arc discharge method [17] in a stainless steel chamber that was filled with hydrogen at 500 Torr. The anode was a graphite rod (6 mm in diameter) with a drilled hole (3 mm in diameter and 300 mm in length) filled with a mixture of graphite powder and Fe catalyst. The cathode was a pure graphite rod (40 mm in diameter). The purity of the graphite rod and graphite powder was 99.998 % and the purity of the Fe catalyst was more than 99 %. The discharge current was typically 60 A, and the voltage drop between electrodes was about 30 V. The duration of arc discharge process was 20 min. The purification process began with oxidization of the as-synthesized SWCNTs at 430 °C for 1 h in a furnace system of air atmosphere in order to remove amorphous carbon materials and carbon particles on the surface of SWCNTs. After oxidizing, the as-synthesized SWCNTs were soaked in a dilute hydrochloric acid solution (3-15 %) at room temperature. Simultaneously, we carried out homogenizing (homogenizer, IKA, DI-25 basic yellow line) by controlling speed and operation time to remove metallic catalyst particles. Finally the suspension was collected by membrane filtration (pore size: 0.2 μm) and washed with DI-water several times. The morphologies and microscopic structures of SWCNTs were characterized by scanning electron microscopy (SEM) (Hitachi S-4700) and high-resolution transmission electron microscopy (HRTEM) (JEOL, JEM-3011, 300 kV). X-ray diffraction (XRD)(Rigaku, DMAX2000) was used to analyze a residue of metal catalyst. Raman spectroscopy (Bruker RFS-100/S, excitation beam wavelength: 1064 nm) was operated using Nd : YAG laser excitation to observe crystallinity of SWCNT products.

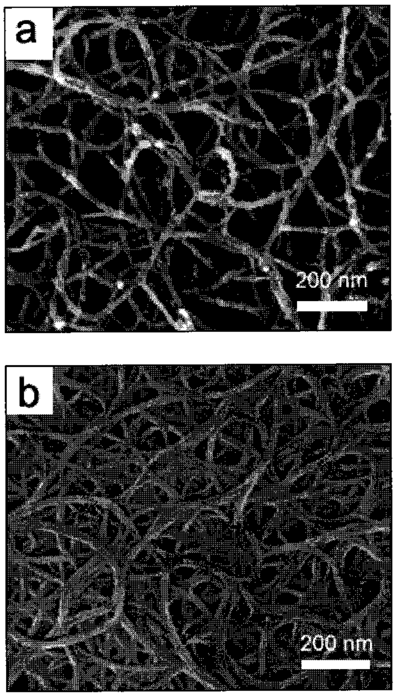

Fig. 1. SEM images of as-synthesized (a) and purified (b) SWCNTs (b: after thermal oxidizing and homogenizing for 10min in 7 % HCl).

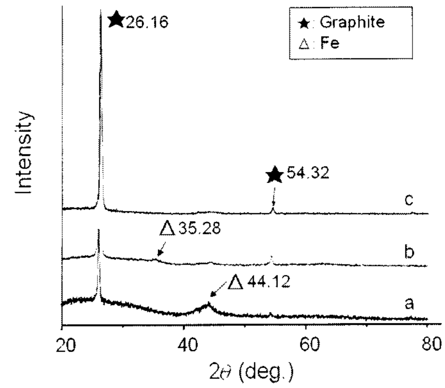

Fig. 2. XRD patterns of as-synthesized (a) and purified (b,c) SWCNTs. After oxidizing and stirring for 10min in 7 % HCl (b) and homogenizing for 10 min in 7 % HCl (c).

3. RESULTS AND DISCUSSION

Figure 1(a) shows the SEM image of as-synthesized SWCNTs. It indicates that SWCNTs are entangled with a large amount of impurities sticking to the SWCNTs bundles. Fig. 1(b) shows the SEM image of purified SWCNTs after thermal oxidizing and homogenizing for 10 min in HCl (7 %) environment. The purified SWCNTs indicate with clean and smooth morphology of high-density of bundles compared with as-synthesized SWCNTs. In addition, purified SWCNTs reveal increased bundle diameters of several tens of nanometer size and the trace of strongly entangled structure which indicates the increment of interactive van der Waals force between SWCNTs bundles after complete purification[18].

Figure 2 shows the XRD pattern of SWCNTs before and after the purification process. In Fig. 2, two peaks at 26.16 and 54.32 ° 2 θ indicate graphite, another two peaks at 35.28 and 44.12 ° 2 θ indicate Fe catalyst, respectively. While two Fe catalyst peaks appear at 35.28 and 44.12 ° 2 θ in conventional stirring method (Fig. 2(b)), only two graphite peaks emerge at 26.16 and 54.32 ° 2 θ without Fe peaks in homogenizing method (10min in 7 % HCl) as shown in Fig. 2(c). This result is well agreed with SEM observation, revealing that Fe catalysts are thoroughly removed. As compared with general stirring method, we consider that homogenizing is more effective to eliminate Fe catalyst from pristine SWCNTs. Figure 3 shows Raman spectra of as-synthesized and purified SWCNTs: as-synthesized (a), after oxidizing at 430 °C for 1 h, homogenizing for 10 min in 7 % HCl (b) and refluxing as a conventional method with 60 % HNO_3: 35 % HCl (3:1) solution for 12 h at 100 °C (c), respectively. The typical G and D band of carbon nanotubes were detected. In case of the homogenizing, the peaks of weak D-band at 1273.2 cm^{-1} and strong G-band at 1593.3 cm^{-1} indicate clearly high-crystalline SWCNTs as compared with as-synthesized SWCNTs. The intensity values of crystallization (I_G/I_D) are very similar with as-synthesized SWCNTs around 11. In Fig. 3(c), however, it shows clearly low crystallinity and high damage in conventional refluxing method compared with homogenizing method. some fluctuated because of huge damage on SWCNTs.

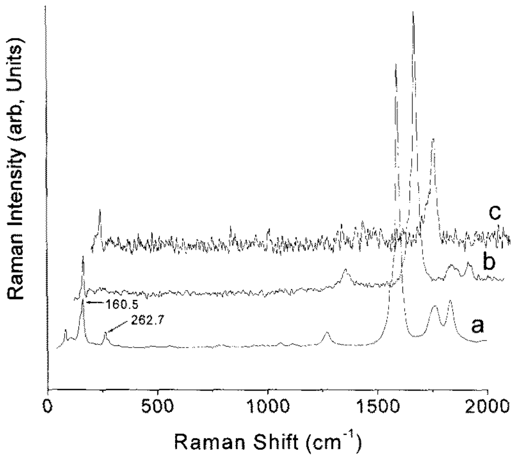

Fig. 3. Raman spectra of as-synthesized (a) and purified (b, c) SWCNTs. After oxidizing at 430 °C for 1h: homogenizing for 10 min in 7 % HCl (b) and conventional refluxing in 60 % HNO_3: 35 % HCl (3:1) solution for 12 h at 100 °C (c).

In RBM mode, it indicates that small-diameter of purified SWCNTs disappear due to chemical treatment with strong acid. As considering the role of homogenizer, the SWCNTs might be affected by two main forces. First one is the shear force occurring principally within the gap between the rotor and stator. Another one is the mechanical impingement against wall due to high fluid acceleration. Therefore, homogenizing can make SWCNTs to purify effectively in the shearing field by controlling rotational speed and operational time of homogenizer. In this work, high-purity and low surface damage of SWCNT products could be obtained in the condition of 8500 rpm in speed for 10 min in the environment of 7 % HCl solution.

Figure 4 shows HRTEM images of as-synthesized and purified SWCNTs. In Fig. 4(a), a lot of metal catalysts as well as carbon impurities are emerged in the as-synthesized SWCNTs. But after purification, the SWCNTs bundles indicate highly purified in graphene layers with low damage as shown in inset of Fig. 4(b). From HRTEM observation, exceedingly amorphous

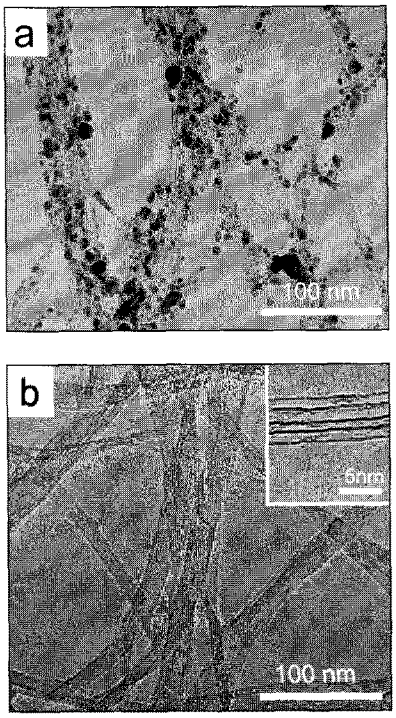

Fig. 4. HRTEM images of as-synthesized (a) and purified (b) SWCNTs (b: thermal oxidizing and homogenizing for 10min in 7 % HCl).

carbon layers appear rarely on the surface of SWCNTs and most metal catalysts are removed. It is also found that the purified bundles of SWCNTs have larger diameters than pristine samples from the TEM images before (Fig. 4(a)) and after (Fig. 4(b)) purification. This phenomenon is very consistent with another report which is explained by the surface modification of as-synthesized carbon products with acid treatments[19]. The structure damage of purified SWCNTs could hardly be found from HRTEM image which is consistent with Raman spectroscopy. So far, general metal removal process using acid treatment, HCl in particular, has been performed at high temperature[20] or long-time treatment with strong acid environment[10,11], resulting in quite serious loss and damage of SWCNTs. From above results, we suggest that using homogenizer might be an effective tool to obtain high-purity with low surface damage in the purification of SWCNTs produced by arc discharge method.

4. CONCLUSION

For removal of impurities in SWCNTs, chemical and thermal treatment should be conducted with some methods. Mostly, however, it is important to completely eliminate metal catalysts because metal occupies high percentage in the as-synthesized SWCNTs and is hard to extract perfectly from carbon products. In general, the process of metal removal has been performed at high temperature or long-time treatment by chemical treatment with strong acid environment. This procedure results in quite serious loss and damage of SWCNTs. In this work, thus, we report that the effect of homogenizing is significant to obtain high-purity with low surface damage compared with conventional method. This quick and simple purification method can promise to obtain SWCNTs with high purity and quality.

ACKNOWLEDGMENTS

This work was supported by National R&D project for Nano Science and Technology of MOST and supported by Korea Ministry of Education, Science and Technology through the Global Partnership Program for International Cooperative Research. This work was partly supported by KICOS through a grant provided by MOST in No. K20501000002-07-E0100-00210 and by the Seoul R&BD Program (10919).

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