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Enrichment of Large-Diameter Single-Walled Carbon Nanotubes by Oxidative Acid Treatment**Yanlian Yang, Hongling Zou, Bin Wu, Qingwen Li, Jin Zhang,* Zhongfan Liu,* Xinyong Guo,[†] and Zuliang Du[†]***Center for Nanoscale Science and Technology, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China**Received: December 5, 2001; In Final Form: April 11, 2002*

Herein we reported a simple way to enrich the large-diameter single-walled carbon nanotubes (SWNTs) by using a mixed concentrated H₂SO₄/HNO₃ treatment. The proportion of the SWNTs with diameter larger than 2 nm measured from transmission electron microscopy was only ca. 3% in the original sample prepared by chemical vapor deposition method. It is found that this proportion becomes remarkably increased with treatment time and reached ca. 20% after 96 h of acid treatment.

Carbon nanotubes, in particular single-walled carbon nanotubes (SWNTs) have attracted attentions and interests of researchers in many fields because of their excellent physical and chemical properties. They are expected to be qualified for numerous applications, including flat panel field emission displays,^{1–3} nanoelectronic devices,^{4,5} chemical sensors,^{6,7} hydrogen storages,⁸ etc. For most of these applications, it is highly desirable to synthesize the SWNTs with defined properties and controlled structures even if the selective growth of SWNTs is still in its infancy. In view of the difficulties in controlling the diameter of SWNTs, many efforts have been made to push ahead. There are two different approaches for producing large-diameter nanotubes. The first approach is the controlled synthesis, achieved by controlling furnace temperature and choosing suitable catalysts or promoters.^{9–11} The second approach is the postsynthesis treatment either by heating treatment or by electron beam coalescing.^{12,13} For example, Nagasawa et al. reported that the SWNTs with diameters of 1.13 and 1.22 nm diameter burn more quickly than the 1.37 nm diameter tubes when heating in oxygen and that a selective oxidation occurred to the thinner SWNTs when refluxing in nitric acid.¹⁴ This suggests a possibility of using suitable chemical oxidation treatment to enrich large-diameter nanotubes. In this work, we show the experimental evidence of such an enrichment of SWNTs in mixed concentrated H₂SO₄/HNO₃, which has been used for shortening the carbon nanotubes.^{15–17}

The SWNTs were produced by the methane chemical vapor deposition (CVD) method using porous MgO supported Fe catalyst. The as-prepared carbon nanotubes were purified by 37% HCl to remove the MgO supports and Fe catalyst first and then filtrated with a 1.2 μm diameter pore membrane under vacuum after sonication in 0.2% Triton X-100 solution (pH = 10). The purified nanotubes (p-SWNTs) were oxidatively treated

in a mixture of 98% H₂SO₄ and 70% HNO₃ (v:v = 3:1) under sonication for the enrichment of the large-diameter nanotubes. Then the reaction mixture was diluted with deionized water and filtrated with 0.1 μm diameter pore membrane under vacuum. The oxidized nanotubes (o-SWNTs) were obtained by washing the remains with deionized water until the filtrate became nearly neutral.

Micro-Raman spectroscopy (Renishaw system 1000) and TEM (JEOL JEM-2010, 200KV) were employed to characterize the nanotube samples. Raman spectra were recorded in ambient atmosphere and at room temperature using a 25 mW He–Ne laser operating at 632.8 nm with CCD detector. The final spectra presented were obtained by averaging at least 10 spectra recorded at different points over the whole sample. The samples for TEM measurements were prepared as follows: dropping 0.02 g/mL farmvar solution in distilled water to form a thin membrane, transferring the membrane onto copper grids by placing copper grids onto the water surface, and then coating the membrane with a carbon film by a spray film evaporator. Dropping the water dispersion of nanotubes onto the copper grids supported farmvar membrane followed by natural drying.

Raman spectroscopy has been shown to be a powerful tool in characterizing SWNTs because of the unique Raman band around 200 cm⁻¹, which arises from the radial breathing mode (RBM).^{10,18,19} This RBM band is directly related to the tube diameter by the relation, $d = 223.75/\omega$, where d is the tube diameter in nanometer and ω the RBM in wavenumber.¹⁰ Typical Raman spectrum of the p-SWNTs is shown in Figure 1. Five RBM peaks located at 155.4, 196.5, 213.1, 253.0, and 283.5 cm⁻¹ correspond to five kinds of SWNTs with diameters of 1.44, 1.14, 1.05, 0.88, and 0.79 nm, respectively. Considering the extremely low Raman intensities of the carbon nanotubes with 0.79 and 1.44 nm diameters, the p-SWNTs samples mainly consist of the nanotubes having 0.88–1.14 nm diameters.

Figure 2a shows the typical TEM image of the p-SWNTs. Most nanotubes have diameters of 0.9 and 1.0 nm, consistent with the Raman result and corresponding to the 196.5 and 213.1

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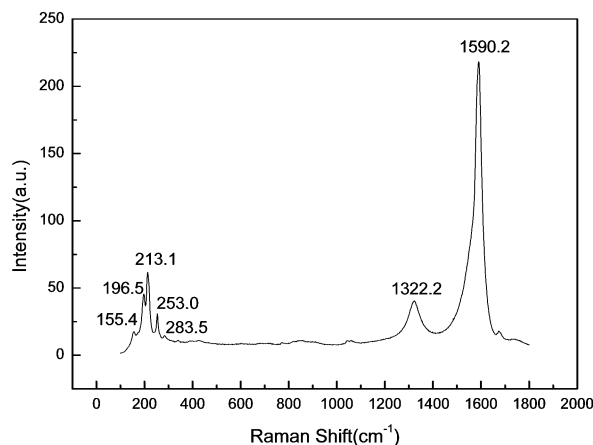


Figure 1. Raman spectrum of the purified single-walled carbon nanotubes (p-SWNTs).

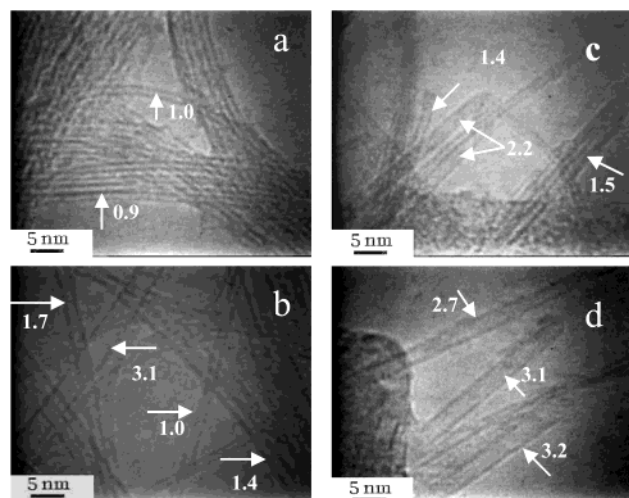


Figure 2. HRTEM images of SWNTs after mixed acid treatment for 0 (a, b), 14 (c), and 96 h (d).

cm^{-1} Raman peaks. Occasionally, we also observed larger diameter tubes, such as 1.4, 1.7, and 3.1 nm, as shown in Figure 2b. The RBM band for the nanotubes with 1.4, 1.7, and 3.1 nm diameters should be located around 159.8, 131.6, and 64 cm^{-1} in the Raman spectrum. We could not find the 159.8 and 131.6 cm^{-1} peaks in Figure 1, which may be attributed to the extremely low content of the corresponding tubes. As for the nanotubes with a 3.1 nm diameter, the corresponding RBM band in Raman spectrum is around 64 cm^{-1} , far beyond the measuring range of our Raman system. We found that its content in the sample is even low from TEM observations. The above TEM and Raman results indicate that the SWNTs synthesized by the CVD method contain large-diameter nanotubes, though the content is very low.

Figure 2 parts c and d shows the typical HRTEM images of the o-SWNTs with different treating times. It can be clearly seen that the large-diameter nanotubes were enriched gradually with increasing of the time of the mixed acid treatment. In the case of Figure 2c, the SWNTs were treated for 14 h. The tube diameters are 1.4, 1.5, and 2.2 nm, respectively. We measured hundreds of TEM images at different sample locations and found that the nanotubes with diameters of 1.4, 1.5, and 2.2 nm are more frequently observed after 14 h of acid treatment as compared with the untreated p-SWNTs samples. This tendency can be more clearly seen from the histograms of the diameter distribution. The diameter distribution of the p-SWNTs in Figure 3a illustrates a peak centered at 1.1 nm, consistent with the

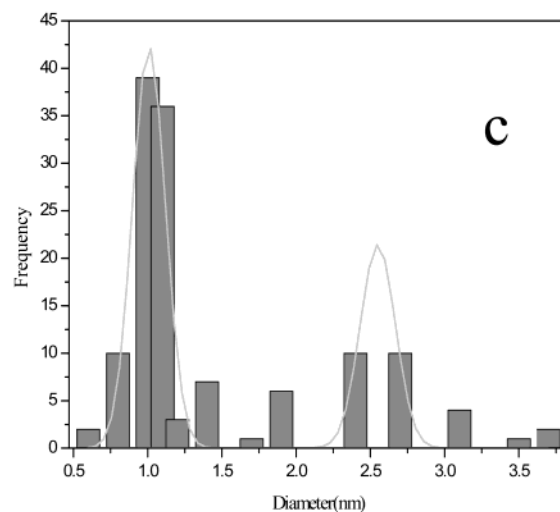
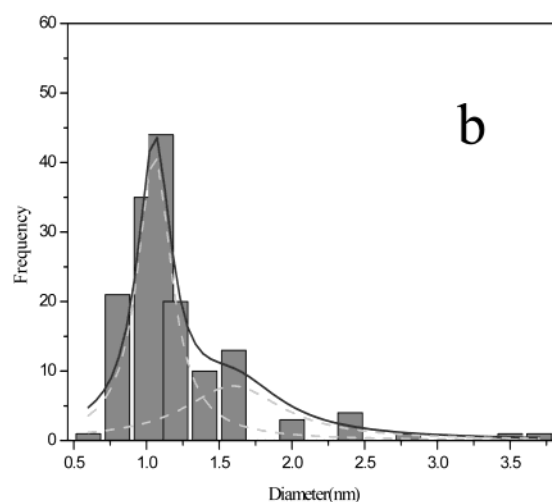
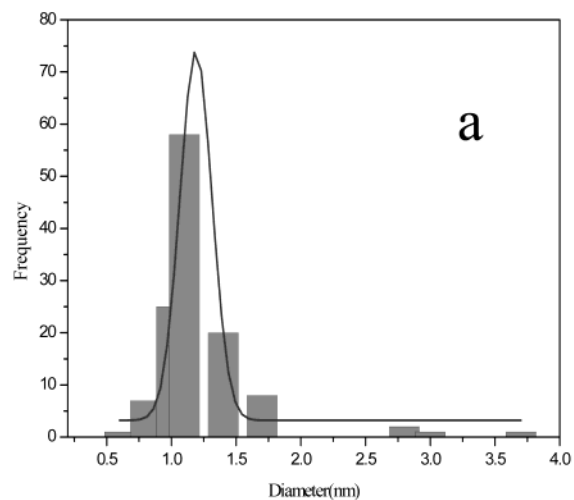


Figure 3. Histograms of the diameter distributions of single-walled carbon nanotubes after mixed acid treatment for 0 (a), 14 (b), and 96 h (c).

Raman result. In this case, the nanotubes with ≥ 2 nm diameters occupy ca. 3% p-SWNTs. After 14 h of acid treatment, a new peak centered at 1.7 nm emerged in the diameter distribution plot (Figure 3b), and the nanotubes with ≥ 2 nm diameter occupy ca. 6% of the total. In the case of 96 h of mixed acid treatment (Figures 2d and 3c), the large-diameter nanotubes were observed even more frequently. There are more nanotubes even having diameters of 2.7, 3.1, and 3.2 nm. The histogram of the diameter

distribution in this case shows a peak centered at 2.5 nm, and the proportion of the carbon nanotubes with ≥ 2 nm diameter increases to ca. 20%.

These results strongly suggest that the large-diameter carbon nanotubes have been enriched by the simple mixed acid oxidative treatment. The enrichment effect of large-diameter carbon nanotubes during the acid treatment may be explained as follows. It is known for small organic molecules that the three- or four-membered rings are energetically less stable than five- or six-membered rings because of the higher tangential strain of the smaller rings. Such a strain may also exist in carbon nanotubes, which results in less stability of thinner tubes. In fact, Nagasawa's work¹⁴ has shown the different chemical reactivity of carbon nanotubes. In this case, the thinner tubes were more quickly burnt in oxygen than the large diameter ones. We believe that the similar selective oxidization has occurred to the thinner nanotubes during the mixed acid treatment; that is, the smaller diameter tubes are more quickly oxidized into various carbon fragments leading to the enrichment of the large-diameter tubes.

The molecular dynamics simulations²⁰ based on the modified Tersoff–Brenner interatomic interaction potentials have shown that the average cohesive energy decreases with the increasing of tube diameter and levels off at a certain value. This suggests that the nanotubes having larger diameters are more stable energetically than the thinner ones. Nevertheless, for the strong temperature effect, this does not necessarily imply the large diameter nanotubes, the greater forming probability during the growth process.^{21,22} When carbon nanotubes with various diameters are treated by oxidative acids, the C=C double bonds in the thinner tubes are preferentially attacked by acids because of the higher chemical reactivity. So the nanotubes having smaller diameters are more quickly oxidized into graphene fragments.

In addition, Terrones et al.¹³ reported that the coalescence of carbon nanotubes might be induced by a high-energy electron beam during HRTEM measurement. This may not be the case because we did not find such a coalescence phenomenon in our irradiation condition.

In summary, using the mixed acid treatment, the large diameter single-walled carbon nanotubes in the original sample were increased from ca. 3% to ca. 20% after 96 h of acid treatment. At the present stage, there is no effective way to selectively synthesize large-diameter carbon nanotubes. Therefore, we believe that the enrichment of carbon nanotubes with large diameters using this simple acid treatment method would facilitate various relevant studies, such as hydrogen storage and nanotube-based electronics.

Acknowledgment. Financial support from the National Natural Science Foundation of China (NSFC, 29973001, 30000044) and the Ministry of Science and Technology (MOST, 2001CB6105) is gratefully acknowledged. We thank Dr. Liu Ying in Hebei Normal University for his helpful discussions. We also thank Ms. Zhu Mingxuan for her experimental assistance.

Supporting Information Available: Figure showing the average cohesive energy as a function of tube diameter. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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