An Effective Process for Cutting Carbon Nanotubes via Fenton Reaction

Qiu Liao, Jing Sun,* and Lian Gao*
State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics,
Chinese Academy of Sciences, Shanghai 200050, P. R. China

(Received August 27, 2007; CL-070918; E-mail: jingsun@mail.sic.ac.cn, liangaoc@online.sh.cn)

An effective process via Fenton reaction combined with acid treatment was firstly used to cut carbon nanotubes (CNTs) into shorter ones.

Since the discovery of carbon nanotubes (CNTs), they have attracted much attention because of their unique electronic and mechanical properties. However, cutting process is a big challenge before these properties can be applied to materials science and engineering because they are in micrometer lengths and bound into macroscopic entangled ropes.[1]

Mechanical,[2–4] physical,[5] and chemical[1,6–10] methods have been developed to cut CNTs. Lithographical cutting employed by Lustig et al.[5] was controllable, and chemical functional groups were produced at the ends of single-walled carbon nanotubes (SWCNTs). However, its special equipments are not available to all. Chen et al.[4] reported that multiwalled carbon nanotubes (MWCNTs) could be cut short efficiently by a two-roll ball milling with addition of poly(methyl methacrylate). Being oxidized in strong oxidant solutions such as the mixture of H_2SO_4 and H_2O_2,[1] the mixture of HNO_3, H_2SO_4,[11] and $KMnO_4$,[12] CNTs could be easliy tailored by the reaction time. Although the equipments for ball milling and wet-chemical oxidizing are much easier to get, the processes consume much energy. Therefore, an economical as well as effecive process is necessary to be developed to cut CNTs.

Fenton and Fenton-like reactions based on the formation of reactive oxidizing species, hydroxyl radicals (HO•), are known to be very effective in the destruction of many aromatic pollutants in water owing to the high oxidizing potential (2.80 eV) of HO•.[13] Wang et al.[14] developed a novel purification method for SWCNTs assisted with Fenton reaction. Their results inspire the idea that HO• generated from Fenton reaction attacks the defects on the CNTs and makes CNTs broken. In this paper, we firstly applied Fenton-like reaction in cutting CNTs, which is effective and economical.

The experimental procedure is described as following. Pristine MWCNTs (CVD method, 95 wt % purity) ultrasonicated in a mixed acid (98 wt % H_2SO_4:63 wt % HNO_3 = 3:1 v/v) at 30 °C for 5 h were noted as acid-MWCNTs. SWCNTs (CVD method, 40 wt % purity) refluxed in 2.6 M HNO_3 and 63 wt % HNO_3 at 140 °C for 24 h were noted as SWCNTs-A and SWCNTs-B, respectively. SWCNTs ultrasonicated in the mixed acid at 30 °C for 5 h were noted as SWCNTs-C. The acid-treated CNTs were ultrasonicated in $Fe(NO)_3$ solution for 5–10 min, and the mixture was left still in a water bath at 50 °C for 36 h. Then, they were filtered, dried, and calcinated in the air at 200 °C for 4 h to get Fe_2O_3/CNTs nanocomposites. Fenton reaction was carried out with 10 mg of Fe_2O_3/CNTs and 100 mL of 0.1 g/L phenol solution. As the overall reaction efficiency is determined by the concentration of Fe^{3+}, H_2O_2, and contaminant together in the Fenton reaction, phenol solution rather than pure water is used to control the balance of HO• production and consumption. The temperature was kept at 80 °C and pH value was adjusted to about 3.5. 0.5 mL of 30 wt % H_2O_2 was added into the mixture while stirring. The sample was collected through filtering after 6 h.

The morphologies of the samples from each step were observed by a transmission electron microscope (TEM, Model 200CX, JEOL Tokyo, Japan) equipped with an energy Dispersive spectrometer (EDS). X-ray diffraction (XRD) was used to characterize the sample by using a Rigaku D/max 2550V diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å).

XRD patterns of Fe_2O_3/CNTs nanocomposites are shown in Figure 1a. From the diffractive peaks, It was concluded that Fe_2O_3 formed after calcination. EDS data shown in Figure 1b indicates the presence of Fe and O in the nanocomposites.

Figures 2a and 2b show that the length of both pristine MWCNTs and acid-MWCNTs ranges from several to ten micrometers. Most MWCNTs are coated with Fe_2O_3 nanoparticles with size less than 10 nm as displayed in Figure 2c. After Fenton reaction, we find that MWCNTs are homogeneously cut to 100–500-nm long with a narrow length distribution, which is verified from the TEM image shown in Figure 2d. From Figures 2e and 2f of higher magnification, it can be seen that shortened MWCNTs have open ends; several nearly broken sites indicated by arrows could be observed which are supposed to be broken with the prolongation of reaction.

For SWCNTs-A shown in Figure 3a, they are very long and most of them are curved and entangled. Impurities are still present after 2.6 M HNO_3 refluxing. Fenton reaction is not very effective in cutting SWCNTs-A displayed in Figure 3b. They are in the same length scale as the pristine ones. By reflux in concentrated HNO_3, the impurities such as amorphous carbon and metal catalyst are removed in SWCNTs-B as shown in Figure 3c, which is consistent with the previous result[15] that SWCNTs can be purified by concentrated HNO_3. Figure 3d shows that SWCNTs-B have been cut into 0.5–2 µm effectively after Fenton reaction; they are straight and some are in very thin bundles. Sample SWCNTs-C (Figure 3e) can be cut into length scale of 0.2–1.5 µm as shown in Figure 3f. Compared

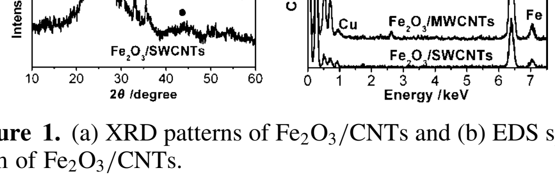

Figure 1. (a) XRD patterns of Fe_2O_3/CNTs and (b) EDS spectrum of Fe_2O_3/CNTs.

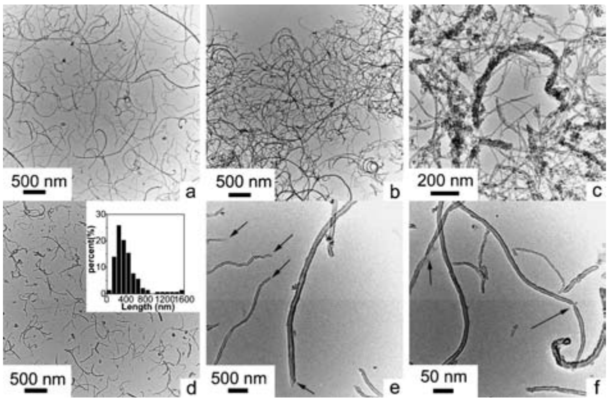

Figure 2. TEM images of (a) pristine MWCNTs, (b) acid-MWCNTs, (c) Fe_2O_3/MWCNTs, and (d)–(f) acid-MWCNTs after Fenton reaction. Inset of (d) is the length distribution diagram of (d).

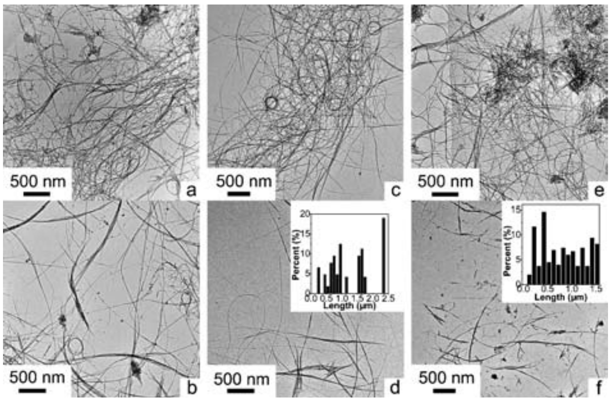

Figure 3. TEM images of (a) SWCNTs-A, (b) SWCNTs-A after Fenton reaction, (c) SWCNTs-B, (d) SWCNTs-B after Fenton reaction, (e) SWCNTs-C, and (f) SWCNTs-C after Fenton reaction. Insets of (d) and (f) are the length distribution diagrams of (d) and (f), respectively.

to Figure 3d, more shortened ones less than 0.5 μm exist in SWCNTs-C. Since the distribution of Fe_2O_3 on SWCNTs is not uniform, length distributions of cut SWCNTs are broad and random. Raman data confirm that no further defects are caused by Fenton reaction.[16]

The possible mechanism has been proposed to explain the cutting process via Fenton reaction. The carboxyl groups produced by acid refluxing act as functional groups as well as defect sites. Fe^{3+} will adsorb onto these negatively charged groups owing to the electrostatic attractions. By calcination, Fe_2O_3 will form and attach on the sidewall of CNTs. HO• will generate when Fe^{3+} reacts with H_2O_2 in the Fenton reaction as shown in eqs 1–4. These radicals are capable of attacking the defects on the CNTs because of their high oxidizing potential and thus cutting CNTs into shorter ones.

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \quad (1)$$

$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + HO_2\cdot \quad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO\cdot \quad (3)$$

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + H^+ + O_2 \quad (4)$$

In the whole process, the defects on CNTs play a critical role in shortening. Sample SWCNTs-A refluxed in dilute HNO_3 do not possess enough defects on the sidewalls. As a result, almost no cutting occurs. For Sample SWCNTs-B and SWCNTs-C, both concentrated HNO_3 and mixed acid treatments cause damage and produce a number of defects on the nanotubes where HO• attacks, and consequently CNTs are broken at these sites.

In conclusion, by combining acid-treated process and Fenton reaction, CNTs can be cut into short length effectively. For MWCNTs, they are homogeneously cut to 100–500-nm long with a narrow length distribution. SWCNTs refluxed in 63 wt % HNO_3 can be cut into 0.5–2 μm. The population of defects on the CNTs is supposed to be the decisive factor to the final length.

Financial support from NSFC (Nos. 50572114 and 50602049), Shanghai Committee of Science and Technology (Nos. 05QMH1415 and 0652nm022), Hundred Talents Program of Chinese Academy of Sciences are greatly acknowledged.

References and Notes

1 K. J. Ziegler, Z. Gu, H. Peng, E. L. Flor, R. H. Hauge, R. E. Smalley, *J. Am. Chem. Soc.* **2005**, *127*, 1541.
2 J. W. Jang, C. E. Lee, C. J. Lee, *Solid State Commun.* **2005**, *135*, 683.
3 K. Niesz, A. Siska, I. Vesselényi, K. Hernadi, D. Mehn, G. Galbács, Z. Konya, I. Kiricsi, *Cataly. Today* **2002**, *76*, 3.
4 L. Chen, X. Pang, Q. Zhang, Z. Yu, *Mater. Lett.* **2006**, *60*, 241.
5 S. R. Lustig, E. D. Boyes, R. H. French, T. D. Gierke, M. A. Harmer, P. B. Hietpas, A. Jagota, R. S. McLean, G. P. Mitchell, G. B. Onoa, K. D. Sams, *Nano Lett.* **2003**, *3*, 1007.
6 J. Li, Y. Zhang, *Appl. Surf. Sci.* **2006**, *252*, 2944.
7 Y. Wang, L. Gao, J. Sun, Y. Liu, S. Zheng, H. Kajiura, Y. Li, K. Noda, *Chem. Phys. Lett.* **2006**, *432*, 205.
8 Z. Chen, K. J. Ziegler, J. Shaver, R. H. Hauge, R. E. Smalley, *J. Phys. Chem. B* **2006**, *110*, 11624.
9 Z. Gu, H. Peng, R. H. Hauge, R. E. Smalley, J. L. Margrave, *Nano Lett.* **2002**, *2*, 1009.
10 Z. Kang, E. Wang, B. Mao, Z. Su, C. Tian, L. Xu, *Mater. Lett.* **2006**, *60*, 2266.
11 J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **1998**, *280*, 1253.
12 T. J. Aitchison, M. Ginic-Markovic, J. G. Matisons, G. P. Simon, P. M. Fredericks, *J. Phys. Chem. C* **2007**, *111*, 2440.
13 E. Neyens, J. Baeyens, *J. Hazard. Mater.* **2003**, *98*, 33.
14 Y. Wang, H. Shan, R. H. Hauge, M. Pasquali, R. E. Smalley, *J. Phys. Chem. B* **2007**, *111*, 1249.
15 E. Dujardin, T. W. Ebbesen, A. Krishnan, M. M. J. Treacy, *Adv. Mater.* **1998**, *10*, 611.
16 Supportiong Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.