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One-Step Cutting of Multi-Walled Carbon Nanotubes Using Nanoscissors

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Abstract: A novel, simple, and effective one-step method has been developed to cut the conventional long and entangled multi-walled carbon nanotubes (MWCNTs) with nanoscissors. The cutting process was carried out by the interactive collision of CNTs with the silicon carbide particles adhered on the abrasive papers. The final cut nanotubes have an average length of 200∼300 nm. The statistical length distribution result indicates that cutting by this method achieves high cutting efficiency for short duration of 2 min. Shortened nanotubes are found to be easily dispersed into aqueous and ethanol solutions. The cut MWCNTs/copper composite thin film fabricated by combined electrophoresis and electroplating techniques reveals that MWCNTs after cutting are well distributed and adhered to the Cu matrix. This method is not only fast and efficient but also no chemical waste, which will expand many potential applications of CNTs.

Keywords: Cutting; MWCNTs; Nanoscissors; Dispersion

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Introduction

Carbon nanotubes (CNTs) have attracted enormous interest in nanoscience and nanotechnology over the past decade owing to their unique chemical, mechanical, and electronic properties [1-4]. The length of CNTs is of great importance for a variety of applications. Shortened CNTs are expected to have shorter dimension, richer chemistry, and to be more easily dispersed. They are promising in the application of future nanoscale structures and devices [5-8]. For example, Kalita et al. [5] demonstrated that short nanotubes performed much more properties in solar cell than that of a device with pristine and long MWCNTs. In addition, shortened CNTs also have potential applications in the field of field emission display, composite materials and hydrogen storage [6-8]. Besides, shortened CNTs can also be useful in controlled growth of CNTs with specific (n, m) type. Orgin et al. [9] cut a specific single-walled carbon nanotubes (SWCNTs) into several shorter segments and then the shorter SWCNTs could grown to longer lengths with the same (n, m) chirality.

Cutting methods of CNTs can be basically classified into three categories, namely mechanical, chemical, and a combination of both. Mechanical approaches for cutting nanotubes have focused on the use of ultrasonic treatment [10-12], ball-milling [13, 14], high-speed agitation [15], lithographic techniques [16], cryogenic crushing [17], and electron beam irradiation [18, 19]. However, it is almost inevitable that these processes are usually very energy consuming or involve expensive instruments. Chemical methods cut CNTs based on the idea of selective oxidation, wherein the higher reactivity of the defect sites along the length of nanotubes is more easily oxidized, for example, oxidation in oxidative acids [20], thermal oxidation [21], ozonolysis [22],

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and fluorination [23]. However, the chemical methods always influence the structure of CNTs because of oxidation involved during violent processes and they are sometimes hard to be controlled. The third kind of cutting CNTs combines mechanical and chemical methods such as sonication induced cutting in oxide media [2], or chemically driven nanoparticles cut CNTs via catalytic hydrogenation [24], but it always quite complicated and time-consuming.

In this paper, an efficient and reliable one-step method using nanoscissors is applied to cut MWCNTs. The cutting is promoted by interactive collision of CNTs with the silicon carbide particles adhered on the abrasive papers, which broke intramolecular C-C bonds by external force. This process requires short operation time of only several minutes for cutting CNTs. It's more important that the cutting effect is limited to the collision points, so cutting of CNTs can be achieved without severe damage of the CNTs which is different from above-mentioned mechanical and chemical processes. Furthermore, the cut MWCNTs/Cu composite thin films are fabricated by combined electrophoresis and electroplating techniques. The present study provides a simple and effective method to cut MWCNTs which will broad CNTs practical applications.

Experimental

MWCNTs fabricated by a chemical vapor deposition (CVD) method were purchased from Shenzhen Nanotech Port Co. Ltd., China. The samples were annealed as purified products. Annealing process was carried out by placing the pristine MWCNTs in a graphite-tube resistance furnace at 2000℃ for 1 h under a high-purity argon gas atmosphere.

Experiments for the cutting of MWCNTs were conducted using a superfine SiC abrasive paper (antistatic abrasive paper, 5000 mesh size, Suisun Co. Ltd., Korea) as nanoscissors. A portion of nanotubes was uniformly placed between two pieces of abrasive papers. A constant pressure (25 MPa) was performed on the abrasive papers and maintained for 2 min. After that, the abrasive papers were removed and shortened MWCNTs were obtained.

After cutting, shortened MWCNTs/Cu composite thin films were prepared by combined electrophoresis and electroplating methods [25]. The additive of $Mg(NO_3)_2$ (10^{-4} mol/l) was added to CNT suspension of ethanol. A DC 10 V/cm was applied to electrophoresis for 1 min. The composition of the composite plating bath was 65 g/l $CuSO_4{\cdot}5H_2O$+196 g/l H_2SO_4 +50 mg/l HCl. Electroplating was performed at 5 mA/cm^{-2} for 2 min.

Morphologies and structures of MWCNTs before and after cutting were characterized by field-emission scanning electron microscopy (SEM, Ultra 55, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). Dispersion in aqueous solution of MWCNTs before and after cutting was investigated by measuring zeta potential using a zeta potential/particle sizer instrument (NICOMP 380 ZLS, PSS.NICOMP, USA) at room temperature.

Results and discussion

Figure 1 shows a schematic of the cutting process of MWCNTs using SiC abrasive papers as nanoscissors under 25 MPa pressure. When the pressure is invariably applied on abrasive papers, it will produce a strong squeezing force which causes the interactive collision between CNTs, and shear force in radial direction will exert on CNTs, like pairs of scissors. As a result, the length of CNTs will be shortened. In brief, MWCNTs are squeezed and sequentially sheared by nanoscissors constituted of superfine SiC particles, and finally sheared off into short nanotubes.

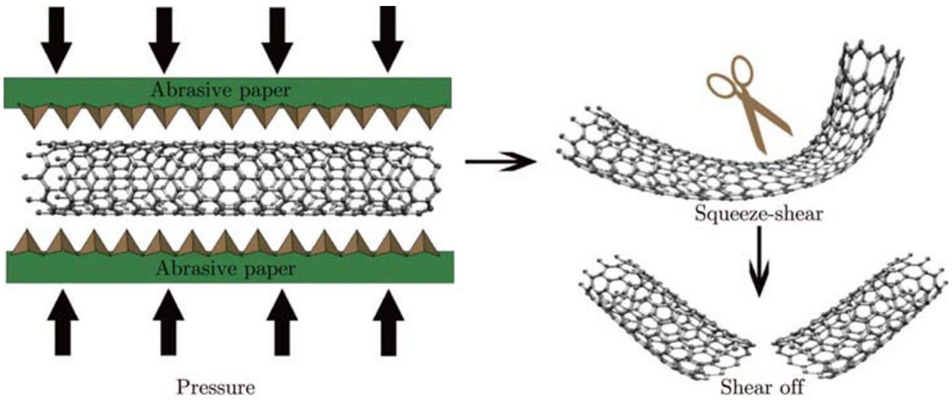

Fig. 1 Schematic of the cutting process using abrasive papers as nanoscissors.

To understand the cutting process of MWCNTs with nanoscissors, it is firstly analyzed the results obtained from TEM images illustrated in Fig. 2. Figure 2(a) reveals that the diameter and length of the annealed MWCNTs before cutting are about 20∼30 nm and 30 µm, respectively. In Fig. 2(b), a MWCNT is not yet sheared off by the SiC nanoscissors. The nanotube has distinctly twisted because of strong squeezing force. The inset to Fig. 2(b) shows a high resolution TEM image of the cut region. It can be clearly seen that there is a convex fold on the surface of the MWCNT, and the surface of the nanotubes creates part cuts on the outer graphitic layers due to the interactive collision of CNTs. The cross-section structure of a MWCNT after cutting is shown in Fig. 2(c). It is obviously observed that one end of CNT has been entirely sheared off as though it is torn by external force.

Figure 3(a) and 3(b) show SEM images of the same MWCNTs after cutting. These images illustrate remarkable changes in the lengths of MWCNTs after cutting. It is also observed that the long MWCNTs have been cut into different segments. Figure 3(b) shows a typical shortened CNT with a length of about 200∼300 nm.

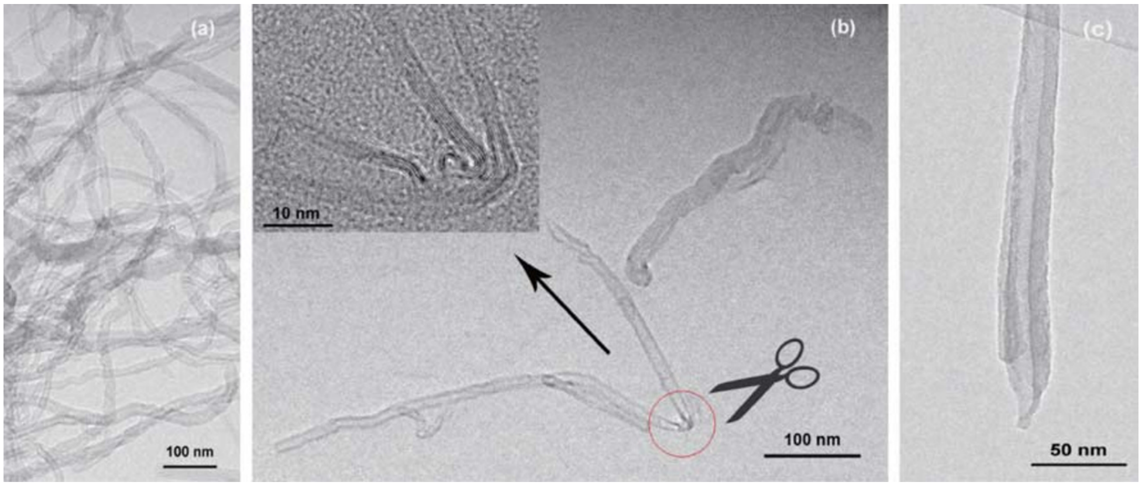

Fig. 2 TEM images of cutting nanotubes with nanoscissors: (a) TEM image of MWCNTs before cutting; (b) A MWCNT is not yet sheared off by nanoscissors. The inset shows the magnified section of the cut region; (c) A high resolution TEM image showing the structure of a MWCNT after cutting.

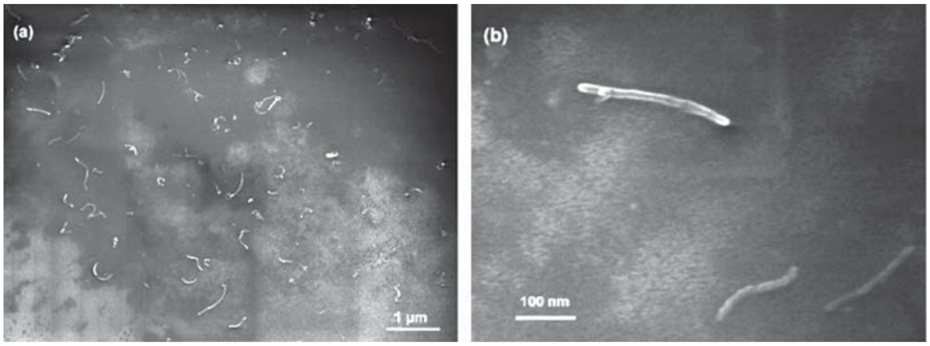

Fig. 3 SEM images of the shortened MWCNTs after cutting: (a) a low magnification image of shortened CNTs; and (b) a typical shortened CNT.

A statistical evaluation of the length distribution is performed using the MWCNTs lengths determined from SEM image (Fig. 3(a)). Histogram for shortened MWCNTs is shown in Fig. 4. The results clearly reveal significant shifts in the MWCNT population. After cutting, the most CNTs have lengths from 100 to 700 nm with an average length of 200∼300 nm.

The quality of MWCNTs dispersion can be characterized by measuring their zeta potentials. It is well-known that untreated CNTs tend to have a potential very close to zero in neutral solutions (pH=7) [26]. As shown in Fig. 5, zeta potential results of MWCNTs before and after cutting are presented. Here, the mean values of MWCNTs' zeta potential before and after cutting are about −2.33 and −16.82 mV, respectively. The more negative zeta potential values of short MWCNTs strongly support the fact that cutting MWCNTs is propitious to their dispersion in aqueous solution.

The increase of absolute value of zeta potential may be attributed to the contraction in length because long CNTs are even more tangled and aggregated compared with short CNTs. In order to intuitively investigate the dispersion of CNTs, MWCNTs before and after cutting dispersed in the ethanol solution are shown in the insert photographs of Fig. 5. MWCNTs after cutting are observed to have better dispersion than those before cutting. The MWCNTs before cutting agglomerate and precipitate at the bottom (insert photograph (a)). However, the MWCNTs after cutting are stable without aggregation for more than 2 weeks (insert photograph (b)). It can be due to the reduction of their lengths.

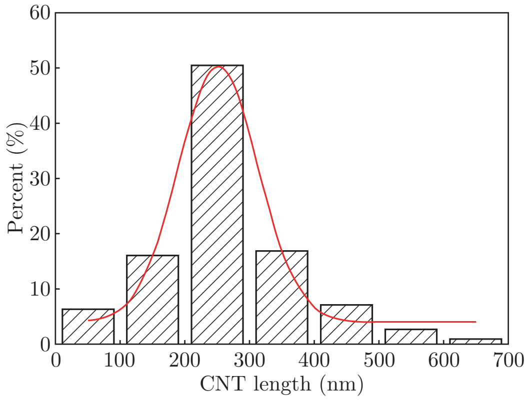

Fig. 4 Histogram of the length distribution of MWCNTs after cutting.

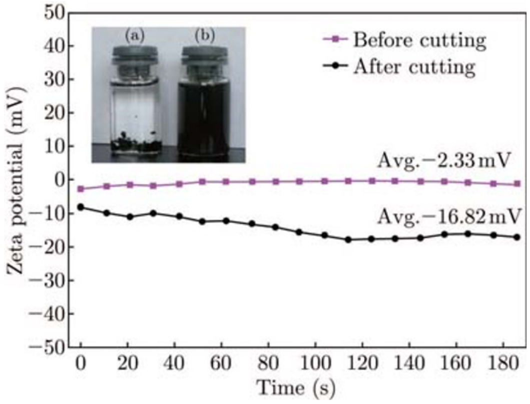

Fig. 5 Zeta potential curves of MWCNTs before and after cutting. The insert shows photographs of dispersibility of MWCNTs before cutting (a); and after cutting (b).

Figure 6 shows surface morphology of cut MWCNTs/Cu composite thin film produced by combined electrophoresis and electroplating techniques. The cut MWCNTs are well distributed and adhered to the Cu matrix because of fine dispersibility and short scale. This may avoid the agglomeration of CNTs and poor interfacial bonding between long CNTs and Cu matrix.

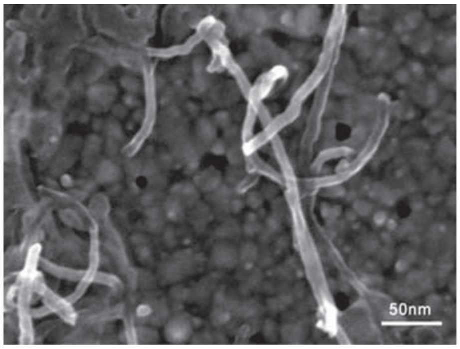

Fig. 6 Surface SEM images of shorten MWCNTs/Cu composite thin film prepared by combined electrophoresis and electroplating techniques.

Conclusions

In this paper, we have developed a simple and effective one-step method to cut MWCNTs into short lengths with nanoscissors. After cutting, MWCNTs are homogeneously cut to short length of about 200∼300 nm with a narrow length distribution. Due to without introduction of other functional groups into short CNTs during cutting process, the shortened CNTs are easily dispersible in water and ethanol without aggregation for several weeks. The cut MWCNTs/Cu composite thin films fabricated by combined electrophoresis and electroplating approaches reveal that MWCNTs after cutting are well distributed and adhered to the Cu matrix. Such cut CNTs with shorter lengths and easier dispersions will have many potential applications in many fields for CNTs.

Acknowledgements

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