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RAPID COMMUNICATION

Facile route to multi-walled carbon nanotubes under ambient conditions

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Abstract−A facile and practical route is demonstrated to prepare multi-walled carbon nanotubes (MWCNTs) by a sonochemical method. By applying ultrasonic irradiation to the mixture of ferrocene and xylene with small amount of water, crystalline MWCNTs were selectively synthesized under ambient conditions, allowing MWCNTs with diameter of 25-40 nm to be obtained. A control experiment revealed that a small amount of water was essential for producing MWCNTs. The analysis of Raman spectra of MWCNTs showed that the intensity of the D-band relative to the G-band was 0.98, indicating relatively good crystallinity of these MWCNTs. This result was consistent with that of TEM observation.

Keywords: Sonochemical, Multi-walled Carbon Nanotubes, Ferrocene, Ambient Conditions, Carbon-based Nanomaterials

INTRODUCTION

The unique physical and chemical properties of carbon nanotubes (CNTs) make them valuable for numerous applications [1], including electron field emitters, quantum wires, molecular filters, and artificial muscles. Since their first discovery, various methods of producing CNTs, such as arc discharge [2], laser ablation [3], and chemical vapor deposition (CVD) [4], have been developed. Among these, CVD has the benefit of considerably lower growth temperatures than arc and laser based techniques. The common growth temperature of CVD approaches lies in the range of 450-1,000 °C. However, CNT growth at the more reduced temperature is still important, so that the growth can be compatible with other integration processes and reduce the production cost. Therefore, there have been intensive efforts to grow CNTs at the lowest possible temperature [5-7]. For example, Vohs et al. [7] synthesized CNTs at 175 °C by decomposing CCl_4 with the aid of supercritical CO_2. However, this method usually requires a long reaction time (24 hrs) and high pressure of 27.6 MPa. Previously, we also reported facile and fast sonochemical method for producing high-purity single-walled CNTs (SWCNT) in liquid solution under ambient conditions [8]. However, selective synthesis of the multi-walled CNTs (MWCNT) was not possible in this case.

In this paper, a sonochemical method is developed to prepare MWCNTs under ambient conditions. This strategy may open an opportunity for selectively synthesizing other types of carbon-based nanomaterials.

EXPERIMENTTAL

The typical process of this method for MWCNT growth is schematically shown in Fig. 1. Initially, 2 g of silica powder (average diameter of 3 mm) was added to 0.025 mol% ferrocene-dissolved p-xylene solution (50 mL). A small amount of water (1 ml) was added to the solution. Control experiments were also carried out to determine if the presence of small amount of water is essential for producing MWCNTs. The solution was then sonicated by a 1/2-in. titanium tip 200-W probe pulsed 60% for 20 min under atmospheric conditions. Finally, the resulting products were collected on filter membrane after filtration to remove the silica powder by using HF solution. The products were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4200), high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2200FS) equipped with an energy dispersive X-ray analysis system (EDX), and Raman spectroscopy (Jobin-Yvon, LabRam HR, λ=514.4 nm). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis (TA instrument SDT-Q600) were performed at a heating rate of 20 °C/min to 900 °C under air atmosphere (flow rate: 100 ml/min).

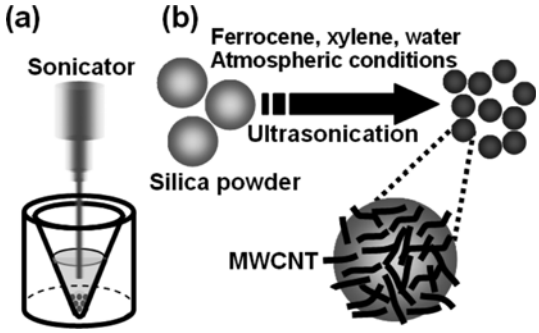

Fig. 1. Illustration of the preparation process of MWCNTs.

RESULTS AND DISCUSSION

FE-SEM image reveals that CNTs with an average length of 1.2 μm and carbonaceous deposition on the surface of silica power after ultrasonic irradiation, as depicted in Fig. 2(a). Fig. 2(b) shows

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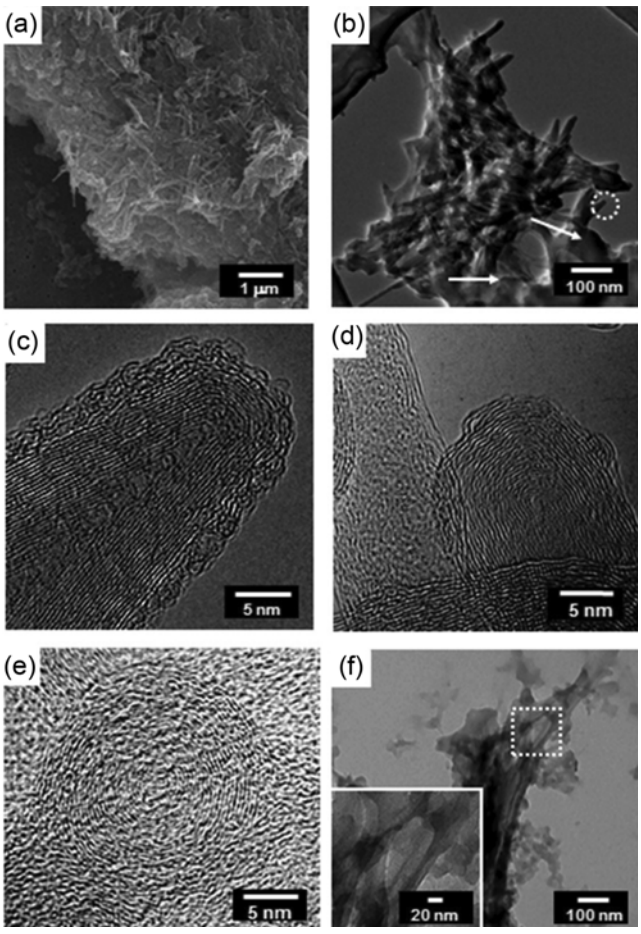

Fig. 2. (a) SEM micrographs of MWCNTs on polycarbonate filter membrane, (b) low-resolution TEM micrographs of synthesized MWCNTs, (c) high-resolution TEM micrographs of MWCNT tip, (d) high-resolution TEM micrographs of MWCNT, (d) high-resolution TEM micrographs of carbon onion, and (f) amorphous carbon synthesized without small amount of water.

a low-resolution TEM image of resulting products. The products consisted of CNTs and some amorphous carbon deposition, as indicated by the dotted and solid arrows, respectively. This fact agrees well with the observation of the SEM image. As shown in Fig. 2(c) (enlarged view of the dotted circle of Fig. 2(b)), the HR-TEM image of MWCNT confirms that the thickness of the tube wall lies in the range of 25-40 nm and consists of 10-30 graphitic walls. The inter-wall distance (d002) was 3.5 Å, slightly larger than the interlayer distance of graphite (d002=3.35 Å). As shown in Fig. 2(c) and Fig. 2(d), closed tips without any filled catalytic particles are observed. The absence of SWCNTs was also confirmed by HR-TEM observations. Interestingly, a very small amount (below 1% frequency compared to that of MWCNTs) of carbon onions was also synthesized in our experiment. Fig. 3(e) is the representative HR-TEM image of synthesized carbon onions. We believe that some modification of our experimental conditions might result in selective synthesis of carbon onions.

Fig. 3(a) shows EDX analysis, which is obtained on the center part of the product in Fig. 2(b). It reveals the signals of C, O, Si and Fe. The signal of Si is probably due to the uncompleted removal of silica powder during filtration with HF solution. Considering no Fe catalyst at the tip of CNTs in TEM images (Fig. 2(c) and Fig. 2(d)) and Fe existence by EDX, the mechanism of MWCNTs growth could be postulated as involving base growth mode [9].

Control experiments were also carried out to determine if the presence of small amount of water is essential for producing MWCNTs. For a sample sonicated without adding water, no CNTs were shown in the resulting HR-TEM images (Fig. 2(f)). Only amorphous carbon formation was observed. It indicates that small amount of water is essential for producing MWCNTs under our experimental conditions.

Once carbon sources are produced by decomposition of ferrocene, which also act as a precursor of Fe catalyst for CNT growth, and xylene during sonication [8], there would be two possible competing reactions: CNT growth by catalytic action of Fe catalyst and amorphous carbon deposition on surface of Fe catalyst and silica particles. However, it is expected that the former reaction occurs predominantly under water added conditions, considerably reducing the amorphous carbon deposition. These are probably caused by the presence of a low concentration of water in our experiment. It is well known that OH radical is produced in the sonolysis of water [10]. It was also reported that OH radical under chemical vapor deposition conditions could reduce the amorphous carbon formation by attacking the carbon atoms with a dangling bond [11,12]. Also, cavitation bubbles during sonication can instantaneously generate local spots of several thousand degrees Celsius of temperature and several thousand atmospheres of pressure [13]. Although details of MWCNT growth mechanism are still under investigation, we believe that these sonochemical treatments facilitate decomposition of ferrocene and p-xylene, and provide the required energy to synthesize MWCNTs. Unlike our previous method for producing SWCNTs via sonochemical method [8], relatively high concentration of ferrocene and presence of small amount of water was essential for producing MWCNT. It is well-known that CNT growth through carbon precipitation from the formed carbide on the surface and/or inside the catalyst particle and deactivation of catalyst by amorphous carbon deposition on active sites are competing pathways [16]. The solubility of carbon to form carbide in catalyst particles is strongly size-dependent. As Moisala et al. [17] highlighted, the solubility of carbon in catalyst particle significantly increases for metal particles with a diameter of less than approximately 10 nm. Moreover, the CNTs exhibited diameters corresponding to the catalyst particle size. Therefore, much smaller size of catalyst generated by decomposition of ferrocene from a very low concentration solution could result in the formation of SWCNTs under the ultrasound irradiation conditions, thus avoiding significant deactivation of catalyst particles. This could be the reason for SWCNT growth without adding water in our previous report [8]. On the other hand, the concentration of ferrocene in the current experiment is much higher than that of our previous report, inevitably resulting in the formation of larger size of catalyst. In this case, reducing the amorphous carbon deposition is essential for the formation of MWCNTs.

Although the growth mechanism of our carbon onion is not clear, we believe that already synthesized, some MWCNTs collapse

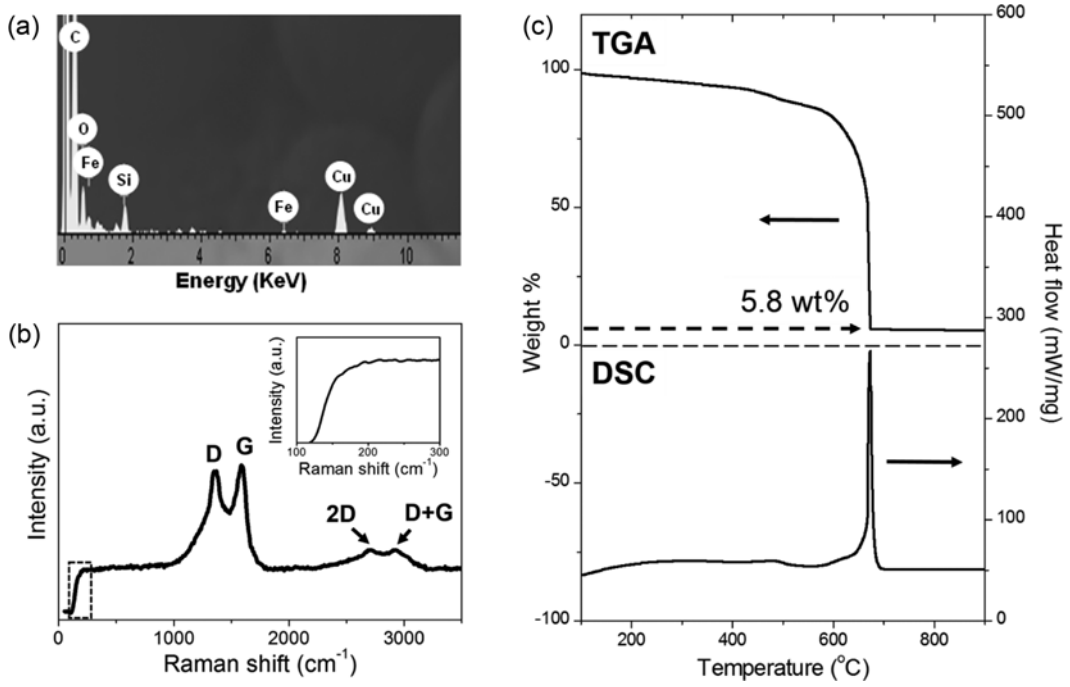

Fig. 3. (a) EDX characterization of the samples in Fig. 2(b), (b) Raman spectra of the synthesized MWCNTs, and (c) TGA/DSC curve for the collected samples.

to form carbon onion due to cavitation effect during sonication process. In fact, Sun et al. previously reported the carbon onion produced by collapsing of hydrocarbon nanotubes under the ultrasound irradiation [18].

As shown in Fig. 3(b), the Raman spectrum of MWCNTs shows a D-band peak at 1,356 cm^{-1} (related to disordered graphite or amorphous carbon) and a stronger G-band peak at 1,583 cm^{-1} (tangential mode), The intensity of the D-band relative to the G-band (intensity ratio, ID/IG=0.98) indicates that the crystallinity of these MWCNTs is relatively good [14,16]. This result is consistent with that of TEM observation. To identify the absence of SWCNT, enlarged view of Raman spectra between 100 and 300 cm^{-1} is inserted in the inset of Fig. 3(b). As confirmed in the inset of Fig. 3(b), any noticeable peaks related to radial breathing mode (RBM) could not be found. In addition, there is no shoulder peak on the G-band, which is one of the characteristic peaks of SWCNTs. In these contexts, it could be concluded that no SWCNTs were synthesized under our experimental conditions.

As shown in Fig. 3(c), further characterization of collected samples by using TGA/DSC was carried out. The significant weight loss (~80%) of the sample could be observed at the temperature range between 600 and 700 °C. A strong exothermic peak with maximum at 673 °C, accompanied by significant loss of weight, could be attributed to the oxidation of MWCNTs in air. These results are in good agreement with the previous report [19]. The weight loss at the temperature below 600 °C might mainly originate from the oxidation of amorphous carbon and residual organic solvent. On the other hand, the final weight of sample (~5.8%) could be attributed to iron catalyst and residual silica. Although a small reactor of 100 ml was used for the sonochemical synthesis of MWCNTs, the proposed method in our experiment could be easily scalable for mass production because the large-scale sonochemical processing of liquid was already demonstrated [8,13].

CONCLUSION

We have proposed a simple sonochemical method for producing MWCNTs in liquid solution under ambient conditions. The presence of a small amount of water was essential for synthesizing crystalline MWCNTs in our experiment. Further study on the generalization of this method to synthesizing other forms of carbon materials, such as fullerenes and carbon onions, is under way.

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