Investigation on the Best Conditions for Purification of Multiwall Carbon Nanotubes

AZAM MARJANI[*], YASER SHIRAZI and SAEED SHIRAZIAN

Department of Chemistry, Islamic Azad University, Arak Branch, Arak, Iran

*Corresponding author: E-mail: a-marjani@iau-arak.ac.ir

Multiwall carbon nanotubes (MWCNTs) were synthesized using cyclohexanol, ferrocene and nitrogen as carbon source, catalyst and carrier gas, respectively. Carbon nanotubes purification was performed by oxidation and acid treatment. Characterization of carbon nanotubes before and after purification was carried out using SEM, TEM and Raman spectroscopy and show that purification can reduce amorphous carbon and metal particles significantly. Furthermore, different acid treatment [HNO_3/H_2SO_4 (1/3), (c) HNO_3/H_2SO_4 (1/1), (d) 8M HCl and (e) 8M HNO_3] demonstrated that 8M HNO_3 can decrease impurities without destroying the structure of carbon nanotubes.

Key Words: Mutiwall carbon nanotubes, Chemical vapour deposition, Amorphous carbon, Carbon precursor.

INTRODUCTION

Carbon nanotubes (CNTs) are novel materials well known for their extraordinary aspect ratio and exotic properties[1-3]. The carbon nanotubes have been synthesized by various methods *e.g.*, electric arc discharge, laser evaporation and chemical vapour deposition[4-6]. Chemical vapour deposition (CVD) appears to be a promising method to synthesis of carbon nanotubes because of its low cost, simple configuration and flexibility in adjustable parameters for controlling the carbon nanotubes structures[7]. All the raw materials produced by chemical vapour deposition method contain impurities of amorphous carbon particles, graphite, nanoparticles and metal catalysts.

In this work, multiwall carbon nanotube (MWCNTs) was synthesized by chemical vapour deposition method and the purification by different acids and different concentration were used to obtain the best method for purification of multiwall carbon nanotube. SEM, TEM and Raman spectroscopy were used to characterization of as-prepared and purified multiwall carbon nanotubes.

EXPERIMENTAL

Synthesis of carbon nanotubes: The chemical vapour deposition system consisted of a horizontal reactor housed in a one stage cylindrical furnace. Ferrocene, nitrogen and cyclohexanol was used as catalyst, carrier gas and carbon precursor, respectively. The reactor was preheated to preset temperature (at 750 ºC); subsequently the flask containing the reagents was placed in the oil bath (at 300 ºC) for immediate

vaporization process. The obtained vapour was carried by nitrogen with flow rate of 400 cm^3 min^{-1} towards the high temperature zone of the reactor. Pyrolysis of the vapours took place and carbon nanotubes was deposited on the high temperature zone of the reactor. After the chemical vapour deposition reaction, the furnace was switched off and the reactor was cooled down to room temperature under nitrogen atmosphere. Finally, the as-grown carbon nanotubes were removed from the reactor for purification and characterization.

Purification of carbon nanotubes: The as-grown carbon nanotubes were placed in the reactor. Air with flow rate of 250 cc/min was injected inside the reactor. The reactor was heated to 470 ºC and maintained at that temperature for 0.5 h. Afterwards the reactor was switched off and cooled to room temperature then carbon nanotubes was removed from the reactor for characterization and further processing. Then the oxidized carbon nanotubes was soaked in acid solution and refluxed at 120 ºC for 3 h and then carbon nanotubes was centrifuged and washed with distilled water for many times until pH of *ca.* 7 was obtained.

RESULTS AND DISCUSSION

Purification of carbon nanotubes is very important in its structural modification. Oxidation and acid treatment are the most common methods for purification of carbon nanotubes.

Fig. 1(a) presents the SEM image of as-prepared carbon nanotubes synthesized in the chemical vapour deposition reactor. Amorphous carbons and deactivated catalyst particles can be also observed in Fig. 1 (a).
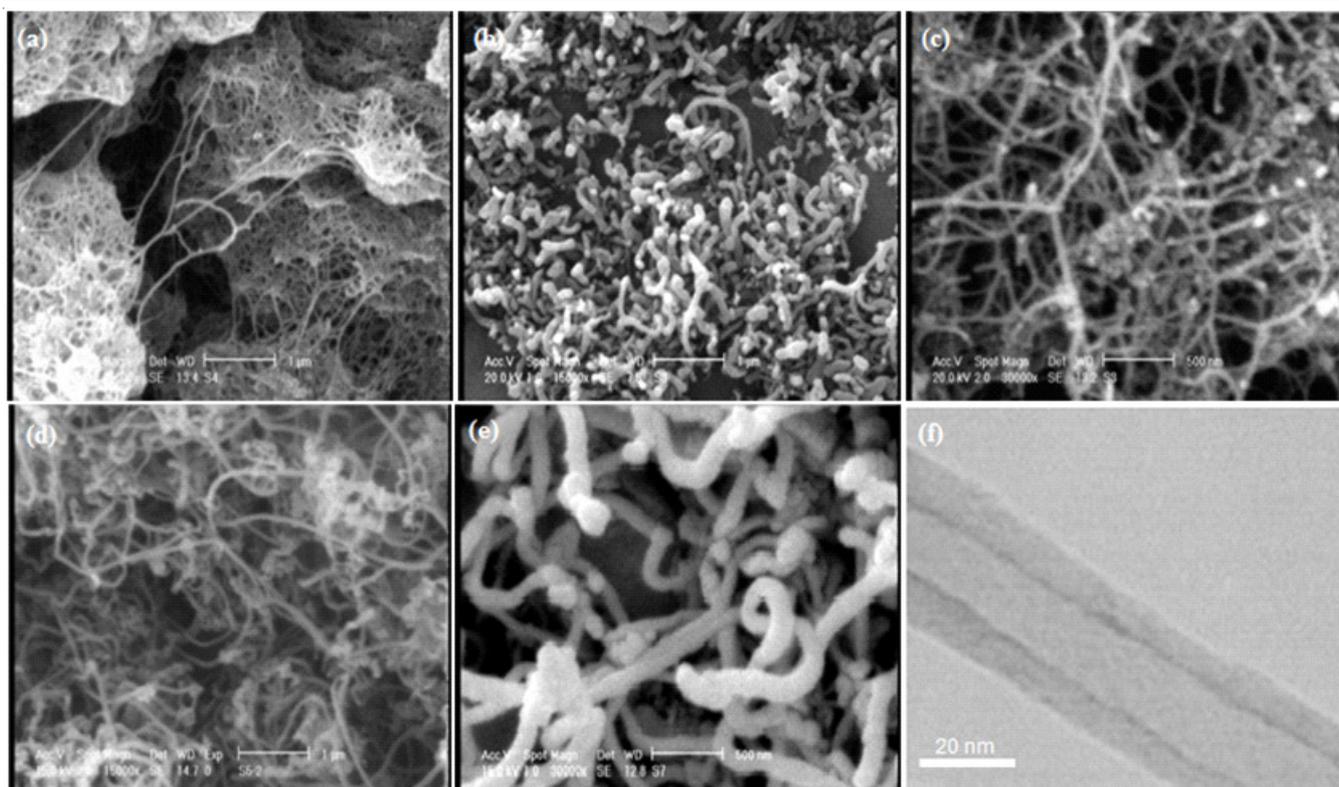
Fig. 1. SEM images of (a) as-prepared multiwall carbon nanotubes, (b) carbon nanotubes treated with HNO_3/H_2SO_4 (1/3), (c) HNO_3/H_2SO_4 (1/1), (d) 8M HCl and (e) 8M HNO_3 (f) TEM image of 8M HNO_3 treated a multiwall carbon nanotube

Oxidation can just remove amorphous carbons and is not effective for omitting deactivated catalyst particles. Acid treatment is an effective method for purification and tips opening of the carbon nanotubes. HNO_3 , H_2SO_4 and HCl are the most common acids which are used for acid treatment. At the same conditions, the carbon nanotubes were purified by 8M HNO_3, 8M HCl and HNO_3/H_2SO_4 (1/1, 1/3). Fig. 1(b-e) presents the SEM images of each acid treatment.

It must be mentioned that acid treatment can destroy the structure of carbon nanotube's array. It means that the long array of carbon nanotubes is being shorter after acid treatment. Sulphuric acid as a strong acid makes the carbon nanotubes more brittle. As can be observed in Fig. 1(b), HNO_3/H_2SO_4 (1/3) treatment causes the carbon nanotubes to be broken into smaller portions and as a result become shorter. As seen in Fig. 1(c), acid treatment with HNO_3/H_2SO_4 (1/1) have less destroying effect on the carbon nanotubes than HNO_3/H_2SO_4 (1/3). Fig. 1(d) presents the SEM image of carbon nanotubes treated with 8M HCl treatment of carbon nanotubes. It can be observed that density and compaction of carbon nanotube's bundles treated with hydrochloric acid are better than those treated with HNO_3/H_2SO_4 (1/3) and HNO_3/H_2SO_4 (1/1). The best result of acid treatment is for 8M HNO_3, as can be observed in Fig. 1(e). By using this treatment method, high pure carbon nanotubes with dense aggregation can be obtained.

TEM image of the purified multiwall carbon nanotubes is presented in Fig. 1(f). The internal and external diameters of carbon nanotubes are about 15 and 30 nm, respectively. According to the TEM image, it can be concluded that the mentioned purification method (8M HNO_3) can remove the amorphous and catalyst particles completely.

Raman spectra of the carbon nanotubes before and after acid treatment are illustrated in Fig. 2. The Raman spectra shows D and G bands at *ca.* 1360 and 1580 cm^{-1}, respectively. D and G bands originate from defect and graphite, respectively. Parameter of I_D/I_G presents ratio of defect band to the graphite bond. For the as-prepared carbon nanotubes the value of I_D/I_G is 0.22. The Raman spectra also show that after purification of the carbon nanotubes with 8M HNO_3 the value of I_D/I_G decreases to 0.17. This presents that purification have significant effect on structural properties of carbon nanotubes and results removing amorphous carbon. On the other hands, by purification D bands reduce significantly which attributed to decrease of amorphous carbon in purified carbon nanotubes sample.
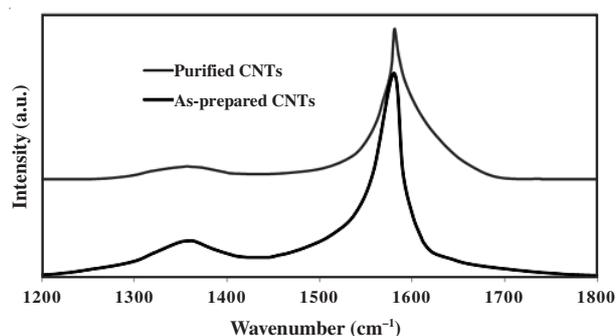

Fig. 2. Raman spectra of as-prepared and purified carbon nanotubes by 8M HNO_3

Conclusion

Entangled structure of multiwall carbon nanotubes was synthesized *via* a simple chemical vapour deposition method using cyclohexanol as carbon precursor. Carbon nanotubes purification was performed by oxidation and acid treatment. Characterization of carbon nanotubes before and after of purification was carried out using SEM, TEM and Raman spectroscopy. According to the SEM and TEM results, oxidation and acid treatment with 8M HNO_3 can remove impurities such as amorphous carbons and deactivated catalyst particles from the carbon nanotubes with less destroying effect. As confirmed by Raman spectroscopy, after purification, the value of I_D/I_G decreases from 0.22 to 0.17.

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