

Carbon nanofiber microspheres obtained from ethylene using FeCl_3 as the catalyst precursor

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Abstract

Carbon nanofiber microspheres (CNFMSs) were synthesized from ethylene using FeCl_3 as the catalyst precursor. The CNFMSs were characterized by SEM, TEM, SEAD, EDS and Raman spectra. The as-grown CNFMSs were about 5 μm in diameter. The size of CNFMS was decreased to 1.5 μm by sonication. They were consisted of CNFs with a diameter less than 70 nm. The inner core of these CNFMS was composed of highly curved CNFs, the tortuosity factors of which were about 1.75 ± 0.20 . The HRTEM image and the corresponding SAED pattern confirmed the herringbone structure of the CNFs. The ratio of I_D/I_G of the CNFs was 0.74. The EDS spectra showed the existence of Fe and Cl from the catalyst precursor in the CNFMSs. The iron catalyst was seriously poisoned for the high Cl:C ratio in the FeCl_3 as catalyst precursor in the floating catalyst process, then curved CNFs were grown. With the continuous feeding, most newly grown CNFs will interact with an already grown host CNF sphere to form a CNFMS. Then a simple strategy to prepare CNFMSs with inexpensive reagents was provided, which enhanced the potential uses of CNFs in a wide range of fields.

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1. Introduction

Research on nano- or micro-sized carbons has drawn much attention because of their potential uses in a wide range of fields [1–4]. The practical and potential applications of these nano- or micro-sized carbon materials depend mainly on their physical and chemical properties that are closely related to their geometrical micro- and nano-structures, their chemical compositions, and the physical and chemical properties of these materials as well. Ajima K. et al. reported a dahlia-flower-like aggregate with a diameter of 70 nm that consisted of hundreds of carbon nanohorns [5]. Qiu J. S. et al. reported a fluffy carbon balls with a diameter of 120 μm from coal by arc discharge methods which consisted of carbon fibers [1]. Here, we present a method to synthesize fluffy carbon

nanofiber microspheres (CNFMSs) with a size of several micrometers from ethylene with FeCl_3 as catalyst precursor by floating catalysis process. The size of sphere can be further modulated by sonication in solution.

2. Experimental

The CNFMSs were grown by the floating catalyst process using FeCl_3 as catalyst precursor and ethylene as carbon source. The reaction was carried out in a two-stage furnace system with the length of 300 and 600 mm, respectively. The evaporation and reaction stages were heated to 260 and 700 °C under a gas flow composed of 90% Ar and 10% H₂ at a rate of 200 ml/min. Then the ethylene with a flow rate of 200 ml/min was introduced into the reactor for 30 min and the product was collected on a silica substrate which was 40 mm from the end of the furnace. The morphology of the product was characterized

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with a high resolution scanning electron microscope (HRSEM, JSM 7401F, at 5.0 kV) and a high resolution transmission electron microscope (HRTEM, JEM 2010, at 120.0 kV). Scattering Raman characterization of the CNFMS was obtained by a Raman Microscope (Renishaw, RM2000, He–Ne laser excitation line at 633.0 nm).

3. Results and discussion

After reaction, a thin soft film was uniformly coated on the silica plate. Fig. 1a shows the morphology of the film which is a single layer of the carbon microspheres. These carbon microspheres were with a narrow size distribution of diameters ranging from 4.5 to 5.6 μm. An individual microsphere (Fig. 1b) was composed of CNFs. Numerous curly CNFs entangled with each other that randomly stretch out along various directions, the morphology of which resembles a dahlia flower. Meanwhile, the CNFMSs have a perfect centrosymmetric structure. Qiu J.S. et al. reported a fluffy carbon ball with a diameter of 120 μm which consisted of short curly carbon fibers [1]. The carbon fibers had a diameter of about 1 μm [1]. In our case, the CNFs are with a diameter less than 70 nm. Meanwhile, the size of CNFMS can be modulated by

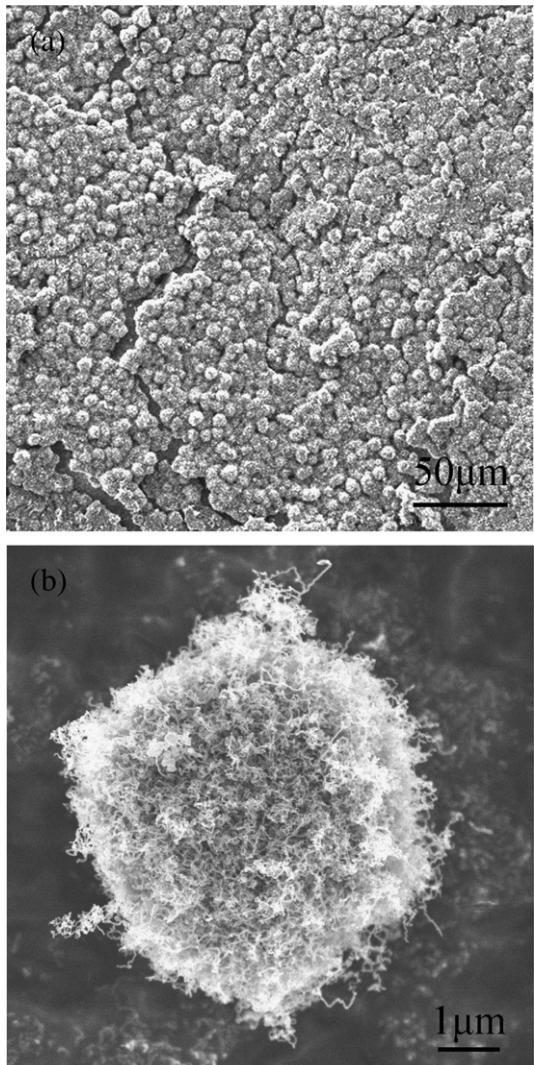


Fig. 1. (a) Morphology of the as-grown CNFMS film; (b) Detailed morphology of the CNFMS.

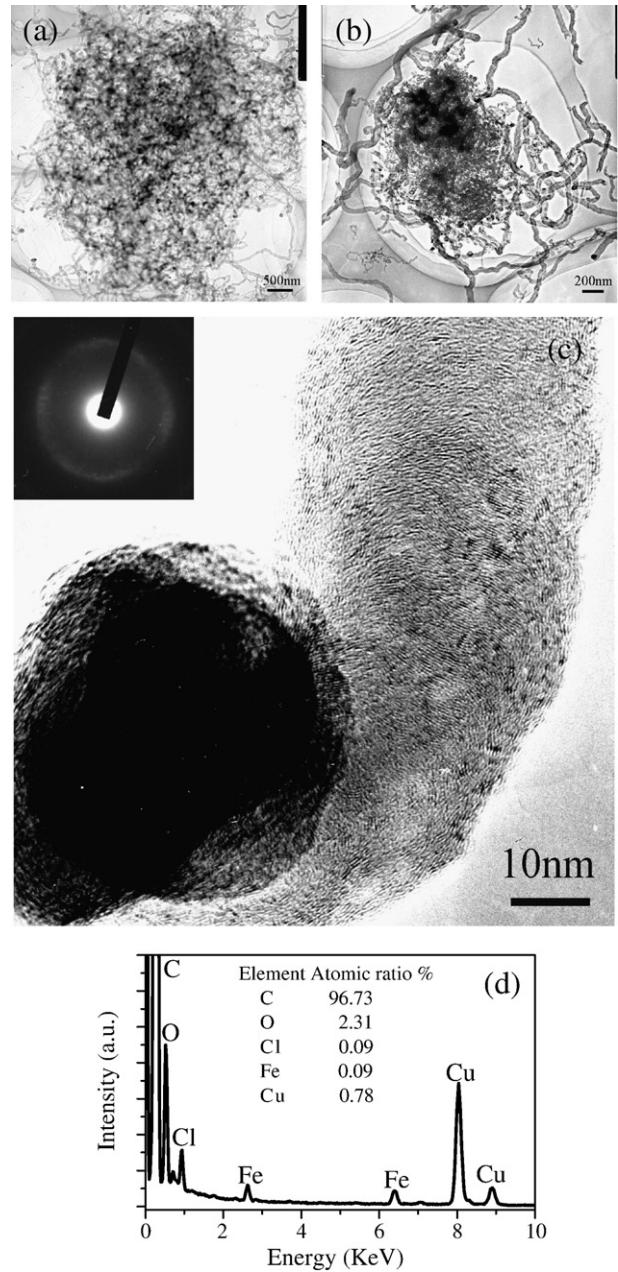


Fig. 2. (a–c) Typical TEM images and (d) EDS analysis of the CNFMSs after (a) 5 min and (b) 1 h sonication. The HRTEM image and SAED pattern of a CNF on the surface of the microsphere in (a) are shown in (c).

sonication. Fig. 2a and b shows the TEM images of agglomerated CNFMS after different sonication times. After sonication for 5 min (Fig. 2a), the CNFMS was with a diameter of 5 μm. After a 1 h sonication, some CNFs retained their sphere-like agglomerate state. The size decreased to 1.5 μm, as shown in Fig. 2b. The physical degradation of the microsphere allowed the examination of the CNF profiles inside the CNFMS. The CNFs on the outer surfaces of the microspheres were mainly with the diameters of 40–70 nm. The inner core of these microspheres was composed of highly curved CNFs with diameters of 20–30 nm, the tortuosity factors of which were about 1.75 ± 0.20 with a calculating scale of 1 μm [6].

The HRTEM image showed the typical herringbone graphite sheets of CNF (Fig. 2c). The corresponding selective area electron diffraction (SAED) pattern, inset in Fig. 2c, showed four (002) diffraction

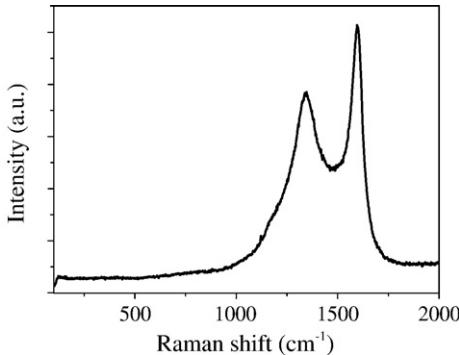


Fig. 3. Raman spectrum of the CNFMS.

elongated spots, which confirmed the herringbone structure of the CNFs [7]. As shown in Fig. 2a–c, most of the CNFs had a catalyst particle at the external free ends, which suggested the tip growth mode for the CNFs. The EDS spectra confirmed the existence of Fe and Cl from the catalyst precursor in the CNFMSs.

The Raman spectrum of the CNFMS is shown in Fig. 3. A typical D and G peaks of carbon nanofibers in the Raman spectrum were shown. In our case, the ratio of I_D/I_G of the CNFs was 0.74, which showed similar value as that of herringbone carbon nanotubes (CNTs) [8] and it was larger than that of CNTs with cylindrical graphite layer [8,9]. Thus, a macroscopically evidence of the defect density of the herringbone CNFs, which was coincided with defects densities in HRTEM images, was provided.

The formation mechanism of the proposed structure is suggested to be as follows. First, FeCl_3 sublimated, decomposed and formed iron catalyst particles. CNFs grew on the iron catalyst from decomposed ethylene. Distinct from an iron catalyst produced by the decomposition of ferrocene, the iron catalyst from the FeCl_3 precursor was poisoned by the presence of a large amount of Cl. The Cl can bond with the dangling bonds of carbon [10] or hydrogen [11]. These factors are all unfavorable for the normal dissolution of carbon in the iron phase and its precipitation at the carbon–metal interface [12] to form CNTs. Similar to most previous results, bamboo-like carbon sheets were formed in the presence of Cl [13]. Since Cl in the chlorine-containing precursor can decompose more easily into Cl radicals that combined with hydrogen radicals [11], the ratio of Cl to C will be the determining factor on whether the formation is CNFs or CNTs [14]. Catalyst-filled thin walled CNTs were formed when the Cl:C ratio were 0.0013 [13] and 0.16 [12,14]. In comparison, in the present work, the ratio of Cl to C was as high as 0.23. It can be suggested that part of the iron catalyst was seriously poisoned. Then the yield of CNFMS was just 0.01%, which was extremely low. Since the FeCl_3 supply was continuous, there would be a Cl balance between the supply and a loss by evaporation and form a steady Cl concentration. The poisoning of the catalyst can be viewed as irreversible. Helical CNTs/CNFs will be formed, as indicated in the previous result [12]. Thus, CNFs would tend to agglomerate to form a quasi-sphere-like product. Moreover, due to the continuous supply of carbon source and FeCl_3 , the newly formed entangled CNFs would add to an already grown CNF sphere. It is probable that a newly formed iron particle will deposit on the outer

surface of an already grown CNF due to the high aspect ratio of the CNFs. Thus, most newly grown CNFs will interact with an already grown host CNF sphere to form a CNFMS. Interestingly, this will imply that the controllable production of CNFMSs with different structures is possible. Further investigation is needed on this.

4. Conclusion

In summary, we have successfully fabricated CNFMSs from ethylene using FeCl_3 as the catalyst. This is a simple but effective strategy to prepare CNFMSs with inexpensive reagents. Compared with conventional carbon microsphere with a solid core, the newly formed CNFMSs were consisted of CNFs. Since the herringbone structured CNF is favorable for the certain metals loading [3], such CNFMSs would be expected to be used in the battery and catalysis. Further investigation is needed to determine its electrical conductivity and applications in lithium cells, biosensors, and catalysts.

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References

- [1] J.S. Qiu, Y.F. Li, Y.P. Wang, Carbon 42 (2004) 2359–2361.
- [2] M.M. Hasan, Y.X. Zhou, S. Jeelani, Mater. Lett. 61 (2007) 1134–1136.
- [3] X.B. Fu, H. Yu, F. Peng, H.J. Wang, Y. Qian, Appl. Catal., A Gen. 321 (2007) 190–197.
- [4] H.L. Zhang, Y. Zhang, X.G. Zhang, F. Li, C. Liu, J. Tan, et al., Carbon 44 (2006) 2778–2784.
- [5] K. Ajima, M. Yudasaka, K. Suenaga, D. Kasuya, T. Azami, S. Iijima, Adv. Mater. 16 (2004) 397–401.
- [6] W.P. Zhou, Y.L. Wu, F. Wei, G.H. Luo, W.Z. Qian, Polymer 46 (2005) 12689–12695.
- [7] A.D. Lueking, H.R. Gutierrez, D.A. Fonseca, E. Dickey, Carbon 45 (2007) 751–759.
- [8] W.Z. Qian, T. Liu, Z.W. Wang, H. Yu, Z.F. Li, F. Wei, et al., Carbon 41 (2003) 2487–2493.
- [9] Q. Zhang, W.Z. Qian, Q. Wen, Y. Liu, D.Z. Wang, F. Wei, Carbon 45 (2007) 1645–1650.
- [10] S.Y. Xie, F. Gao, X. Lu, R.B. Huang, C.R. Wang, X. Zhang, et al., Science 304 (2004) 699.
- [11] R.T. Lv, F.Y. Kang, W.X. Wang, J.Q. Wei, J.L. Gu, K.L. Wang, et al., Carbon 45 (2007) 1433–1438.
- [12] W.Z. Qian, F. Wei, T. Liu, Z.W. Wang, Y.D. Li, J. Chem. Phys. 118 (2003) 878–882.
- [13] H. Hou, A.K. Schaper, Z. Jun, F. Weller, A. Greiner, Chem. Mater. 15 (2003) 580–585.
- [14] W.X. Wang, K.L. Wang, R.T. Lv, J.Q. Wei, X.F. Zhang, F.Y. Kang, et al., Carbon 45 (2007) 1127–1129.