SELECTIVE SYNTHESIS OF FISH-BONE AND BAMBOO-SHAPED CARBON NANOTUBES IN LARGE SCALE

Li. Mao, School of Chemical Engineering, Dalian University of Technology, Dalian, China 116012
Jie S. Qiu, School of Chemical Engineering, Dalian University of Technology, Dalian, China 116012
Zhi Y. Wang, School of Chemical Engineering, Dalian University of Technology, Dalian, China 116012
Li. Xing, School of Chemical Engineering, Dalian University of Technology, Dalian, China 116012

Abstract

Bamboo-shape and fishbone-like carbon nanotubes (CNTs) were selectively synthesized by simple catalytic decomposition of acetylene over Fe-based catalysts that were prepared by sodium dodecylbenezenesulfonate stabilized colloid chemical method. The morphological and chemical feature of the products was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). XRD analyses and TEM studies indicate that Fe catalysts result in the formation and growth of bamboo-shape CNTs, while Fe_3O_4 catalysts lead to fishbone-like CNTs. The mechanisms involved in the formation and morphological evolution of CNTs are discussed in term of the structural nature of Fe-based catalysts and the experimental conditions.

Introduction

The discovery of carbon nanotubes (CNTs) opened up an avalanche of research on novel carbon materials owing to their unique properties and outstanding characteristics that are greatly dependent on the tube's geometrical chirality and morphologies. It is believed that altering these properties may bring about significant breakthroughs in science and technology related to CNTs. In the past decade, the study on heteromorphic CNTs such as bamboo-shaped nanotubes, octopus nanotubes and fish-bone nanotubes has attracted great interests around the world because of their significance both in fundamental researches and in potential applications. For example, the fish-bone carbon nanotubes (FCNTs) are believed to be the good candidate for catalyst support or gas storage materials in comparison with normal ones because of the reactive outer surface induced by the presence of abundant exposed edges of graphitic layers. The bamboo-shaped carbon nanotubes (BCNTs), on the other hand, show better electrochemical performance, which was rationalized by the presence of end-caps located at regular intervals along the walls of BCNTs. In this letter, we present the selectively production of CNTs by catalytic decomposition of acetylene over Fe-containing catalysts. It has been found that the CNTs with bamboo and fishbone structures can be synthesized while the Fe-containing catalysts with different structural nature and chemical compositions were used.

Experimental

Catalysts preparation

Catalysts were prepared by a sodium dodecylbenezenesulfonate stabilized colloid chemical method. In a typical run, 4 g of $FeCl_3 \cdot 6H_2O$ was dissolved into 100 ml water, and sodium hydroxide solution (1 M) was injected under vigorous stirring. The resulting ferric hydroxide precipitate was filtered, washed several times with deioned water to remove the residual Na^+ and Cl^-, and then was peptized by 0.2 M of ferric chloride solution (100 mL). The positively charged hydrosol was coagulated by the addition of 100 mL of sodium dodecylbenezenesulfonate (SDBS) solution with the weight percent of 1%. After centrifugation, the resulting coagulated colloid particles were dried at 323 K for one night, and were calcined under different atmosphere. For one of the calcination processes, reduction was performed by 80 mL/min of H_2, at a growing temperature from 293 K to 773 K (5 K min^{-1}), then at 773 K during 2 h. The as-made catalyst was named as Cat_H. For the other calcination step, the same procedure was used except the flowing hydrogen was replaced by nitrogen. The resulting catalyst was noted as Cat_N.

Acetylene decomposition

For the production of BCNTs, 0.5 g of Cat_H was placed on a quarts boat inside a horizontal quartz tube reactor (30 mm I.D.; 70 cm in length) in an electric furnace. Nitrogen (flow rate: 100 mL/min) is firstly flowed through the reactor from top to bottom during which the temperature was increased form room value to 973 K. Then acetylene (60 % in N_2) is passed through the catalyst bed for 30 min under the same temperature. After each run, the reaction is stopped by flushing the reactor with nitrogen before cooling to the room temperature. For the preparation of FCNTs, Cat_N and a flowing mixture gas of H_2/C_2H_2 (v/v=20/80, flow rate: 75 ml/min) was adopted under identical conditions. The catalysts and the products deposit were characterized by X-ray diffraction (XRD Rigaku D/MAX 2400), scanning electron microscopy (SEM, JEOL JSM-5600LV) and transmission electron microscopy (TEM, Philips Tecnai G^2 20).

Results and discussion

The XRD patterns (Figures 1a and 1b) reveal the domination of Fe and Fe_3O_4 in Cat_H and Cat_N, respectively, which lead to the formation of the CNTs with well-developed graphitic structures after catalytic decomposition of acetylene. As detected by XRD analysis in Figures 1c and 1d, the strong reflection from graphite (002) plane can be seen clearly.

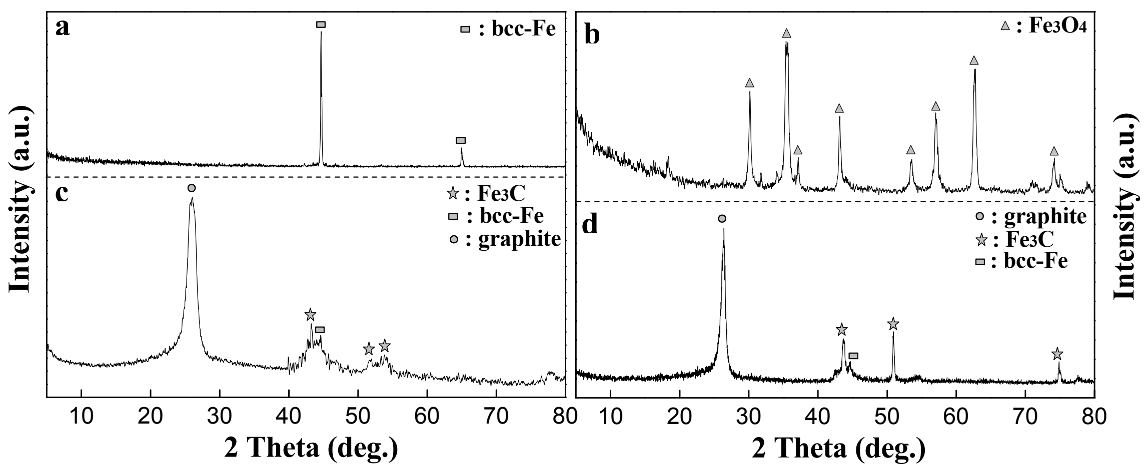

Figure 1. XRD patterns of the catalysts calcined under (a) H_2 and (b) N_2. (c) and (d): XRD patterns of the carbon samples deposited over Cat_H and Cat_N.

The SEM images of the sample made over Fe catalyst are shown in Figures 2a and 2b, revealing the presence of a film composed of high-density CNT bundles. The TEM examination (Figure 2c) shows that, the nanotubes have a periodic bamboo-like structure with the inner cavities. The catalyst particles can be observed both within the inner cavities and at the end of the tubes (as indicated by white arrows). Figure 2d is the HRTEM image of the BCNTs. The well-developed graphitic layers can be detected clearly, being in good agreement with the XRD analysis. Extensive studies indicate that the purity of the BCNTs is quite high although the uniformity of each compartment cavity is not as good as expected, which may offer more opportunity for their practicality in specific fields.

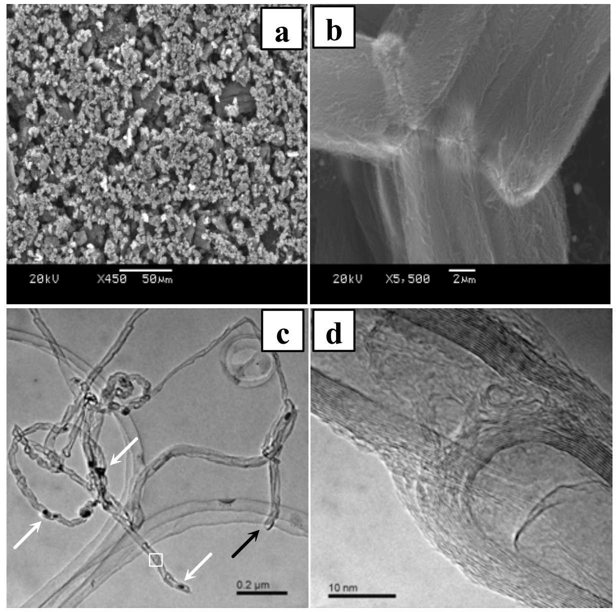

Figure 2. SEM images (a and b) and TEM results (c and d) of the bamboo-shape CNTs.

It has been found that no BCNTs were formed when Cat_N replaced Cat_H as the catalyst under other conditions unchanged. This implies that the formation of these bamboo-like carbons is catalyst sensitive. As evidenced by metal particles at the tips of the carbon nanotubes, we interpret that the growth of the BCNTs bundles favors the tip growth model. Although the CNT tip free of catalyst particles can also be observed (as indicated by the black arrow), the presence of Fe_3C diffraction peak in XRD pattern suggests quite amount of iron-containing species existed in BCNTs. Therefore, the tip growth mode predominates in the BCNTs growth.

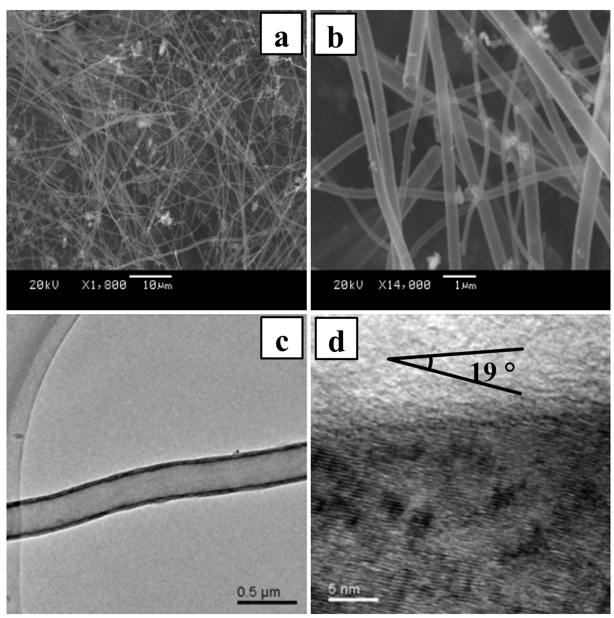

Figure 3. SEM images (a and b) and TEM results (c and d) of the fishbone-type CNTs

Figures 3a and 3b are the typical SEM images of the sample deposited on Fe_3O_4 catalyst. It reveals the domination of large quantities of fibre-like carbon in the product with a diameter of 0.2-0.8 μm. The TEM investigation (Figure 3c) indicates that the fibre products are CNTs with large hollow inner cavities. The HRTEM study demonstrates that the wall of the nanotubes is made of fishbone-like graphitic layers that inclined relative to the tube axis in orientation angle of about 19°. This structure offers the nanotubes a high surface energy due to the abundant graphitic plane exposed on the tube's outer surface, which may make the adsorption of catalyst particles or gas molecules more easily and effectively. It was reported that, hydrogen is commonly adopted to cap the surface bonding sites of FCNTs, which is critical in the formation of fish-bone like carbons. While in our case, the compared test with Cat_H as the catalyst shows no FCNT prepared. Therefore, the structural and composition nature of the catalyst do play an important roles in the formation of FCNTs.

Conclusions

Bamboo-shape and fishbone-like carbon nanotubes (CNTs) were selectively prepared by catalytic decomposition of acetylene over Fe-based catalysts that were prepared via colloid chemical method coupled with calcination treatment. XRD analyses and TEM studies indicate that Fe catalyst favors the formation and growth of bamboo-shape CNTs, while Fe_3O_4 catalyst leads to fishbone-like ones. Achieving morphologically pure bamboo-shape or fishbone-like tubes make it possible to give insights into the chemical and physical properties of these special-structured CNTs and to develop possible practical applications.

Acknowledgements

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References

Avdeeva, L. B, Goncharova, O. V, Kochubey, D. I., Zaikovskii, V. I., Plyasova, L. M., Novgorodov, B. N. and Shaikhutdinov, S. K. 1996. Coprecipitated Ni-alumina and Ni-Cu-alumina catalysts of methane decomposition and carbon deposition . II. Evolution of the catalysts in reaction. *Applied Catalysis a-General* 141(1-2):117-129.

Charlier, J. C., DeVita, A., Blasé, X. and Car, R. 1997. Microscopic growth mechanisms for carbon nanotubes. *Science* 275(5300):646-649.

Kiselev, N. A., Sloan, J., Zakharov, D. N., Kukovitskii, E. F., Hutchison, J. L., Hammer, J. and Kotosonov, A. S. 1998. Carbon nanotubes from polyethylene precursors: Structure and structural changes caused by thermal and chemical treatment revealed by HREM. *Carbon* 36(7-8):1149-1157.

Pinheiro, P., Schouler, M. C., Gadelle, P., Mermoux, M. and Dooryhee, E. 2000. Effect of hydrogen on the orientation of carbon layers in deposits from the carbon monoxide disproportionation reaction over Co/Al_2O_3 catalysts. *Carbon* 38(10):1469-1479.

Ros, T. G., van Dillen, A. J., Geus, J. W. and Koningsberger, D. C. 2002. Surface structure of untreated parallel and fishbone carbon nanofibres: An infrared study. *Chemphyschem* 3(2):209-214.

Saito, Y. and Yoshikawa, T. 1993. Bamboo-shaped carbon tube filled partially with nickel. *Journal of Crystal Growth* 134(1-2):154-156.