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多分叉和铁填充碳纳米管的合成与表征

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摘要：以二环戊二烯和二茂铁为前驱体,通过化学气相沉积法可控地制备了多分叉的碳纳米管,在其分叉处观察到铁填充物。通过调变前驱物的比例、生长温度等条件能够有效地调变填充物Fe的含量。结果表明,前驱体中二茂铁的相对含量越高,分叉和填充现象越明显,说明铁物种在分叉形成中起重要作用。随着分叉次数的增加,支管的直径显著减小。

关键词：纳米管；化学气相沉积；分叉结构；碳；铁填充
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Synthesis and Characterization of Multi-branch and Iron-Filled Carbon Nanotubes

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Abstract: Multi-branch carbon nanotubes (CNTs) have been synthesized by a chemical vapor deposition method using dicyclopentadiene and ferrocene as precursors. Iron nanoparticles are observed inside the CNTs around the junction points. The content of the filled Fe-species could be effectively regulated by adjusting the recipe and growth temperature. The results indicate that the more ferrocene is used, the more branches will be formed and the more Fe species will be filled inside the CNTs around the junctions, suggesting the important role of the Fe species in forming the branchy CNTs. The diameter of the branches becomes significantly smaller with the increase in number of branches for the corresponding mother tubes.

Key words: nanotube; chemical vapor deposition (CVD); branching structure; carbon; Iron-filled

Since the discovery of carbon nanotubes (CNTs) by Iijima[1], the carbon nanotubes abundant shapes such as straight, bent, helical, planar spiral, toroidal, and branching have been observed experimentally[2-3]. Their structures and properties have been widely studied both by theoretical simulation and experimental measurements. The electronic structure of CNTs can be metallic or semiconducting, mainly depending on both their diameter and chirality[4]. Introduction of pentagon-heptagon pair defects into the hexagonal network of CNTs can change the helicity of the nanotube thereof its electronic structure[5]. The interconnecting of nanotubes with different diameters and chiralities can therefore generate a fascinating variety of the electronic structures. These junctions could be used as the building blocks for all-carbon nanoelectronic devices, which could provide extra terminals as nodes to control the switching mechanism, power gain, or other transistor properties [5-6]. Three-terminal Y-branching CNTs have been studied both experimentally and

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theoretically [7-8] and then their stability, electric conductibility and rectifying behavior have been confirmed[9-10]. With four or more terminal junctions of nanotubes in three dimensions, one could also envision a "network" of nanotubes based architecture where multi-terminal junctions or nodes may have multi-functional logic characteristics [6]. To date, multi-terminal CNTs have been synthesized through different approaches such as DC-arc discharge [7,11], Chemical Vapor Deposition (CVD)[12-13], aluminum oxide (AAO) template-confined CVD[14], flow fluctuation CVD [15], and introducing sulfur as a branching promoter[16].

On the other hand, CNTs filled with various substances, especially ferromagnetic materials, have potential applications in different areas, e.g., magnetic recording media and biomedicine[17]. The combination of multi-branching and filling of ferromagnetic materials might produce some novel properties for the potential applications in nanomagnetics and bioengineering. However, CNTs with both multi-branching and ferromagnetic materials-filling were seldom been reported [18]. Here we report a simple thermal CVD method to grow multi-branching and iron-filled CNTs using dicyclopentadiene and ferrocene as precursors. Higher filling ratio and more branching morphology could be achieved through increasing the ferrocene proportion in the precursors. The divergence of iron-containing fillings seems to be a critical factor in growing the branchy CNTs.

1 Experimental

In a typical pr ocess, ferrocene was placed at the inlet side with a distance of ca. 50 mm to the center of the horizontal tubular furnace. Dicyclopentadiene was put into a bubbler at room temperature and its saturated vapor can be carried into the system with Ar. After the reactor was heated to a specific temperature, e.g. 800 ℃, dicyclopentadiene precursor was then introduced into the system by 60 $cm^3 \cdot min^{-1}$ of Ar. The temperature at ferrocene is about 80 ℃ and its vapor was brought to the furnace center by a total Ar flow of 200 $cm^3 \cdot min^{-1}$. The growth of CNTs lasted for 60 min, and then the system was cooled to room temperature in Ar. Similarly, CNTs arrays were grown on the surface of silicon wafer at 850 ℃ and 200 $cm^3 \cdot min^{-1}$ flux of Ar passing through dicyclopentadiene bubbler. The as-prepared products were characterized by transmission electron microscopy (TEM, JEOL-JEM-1005), scanning electron microscopy (SEM, LEO 1530 Vp), Raman spectrum, and X-ray diffraction (XRD, Philips XPert with Cu $K_{\alpha 1}$ radiation of 0.1540 56 nm, 40 kV, 40 mA, Ni filter, Hybrid detector).

2 Results and discussion

Fig.1 display s TEM images of the products synthesized using dicyclopentadiene and ferrocene as precursors at 650 to 850 ℃ and 60 $cm^3 \cdot min^{-1}$ flux of Ar passing through dicyclopentadiene bubbler. Fig.1a presents the CNTs bundles formed at 800 ℃, and the bundles are partially filled as shown in the inset. Fig.1b shows the TEM image of multi-branching CNTs with discontinuous fillings. From the enlarged images (Fig.1c and 1d), it is clearly indicated that CNTs are multi-branched. The filled CNTs have inner diameters ranging from 6 to 40 nm and outer diameters from 16 to 100 nm, and the length up to hundreds of micrometers. The length of the fillings varies from 100 nanometers to several micrometers. More interestingly, the diameters of the CNTs are decreased with the formation of branches. At most of the junction points, iron-containing fillings are present in branch-like forms.

The effect of growth temperature on the product was also investigated, carbon particles, rather than nanotubes, are the dominative product at 750 ℃(Fig. 1i) and no nanotubes are observed in the products obtained at 650 and 700 ℃(Fig.1g and 1 h). When the growth temperature is raised to 850 ℃, the branching of CNTs decreases and the surface of CNTs is decorated with many Fe@C nanocapsules (Fig.1e and 1f). Thereby the optimal temperature for the synthesis of multi-branching and Fe-filled CNTs should be ca. 800 ℃ in this process.

To investigate the role of the precursors and improve the graphitization degree, the ratios of dicyclopentadiene and ferrocene are deliberately adjusted and the growth temperature of 850 ℃ is used.

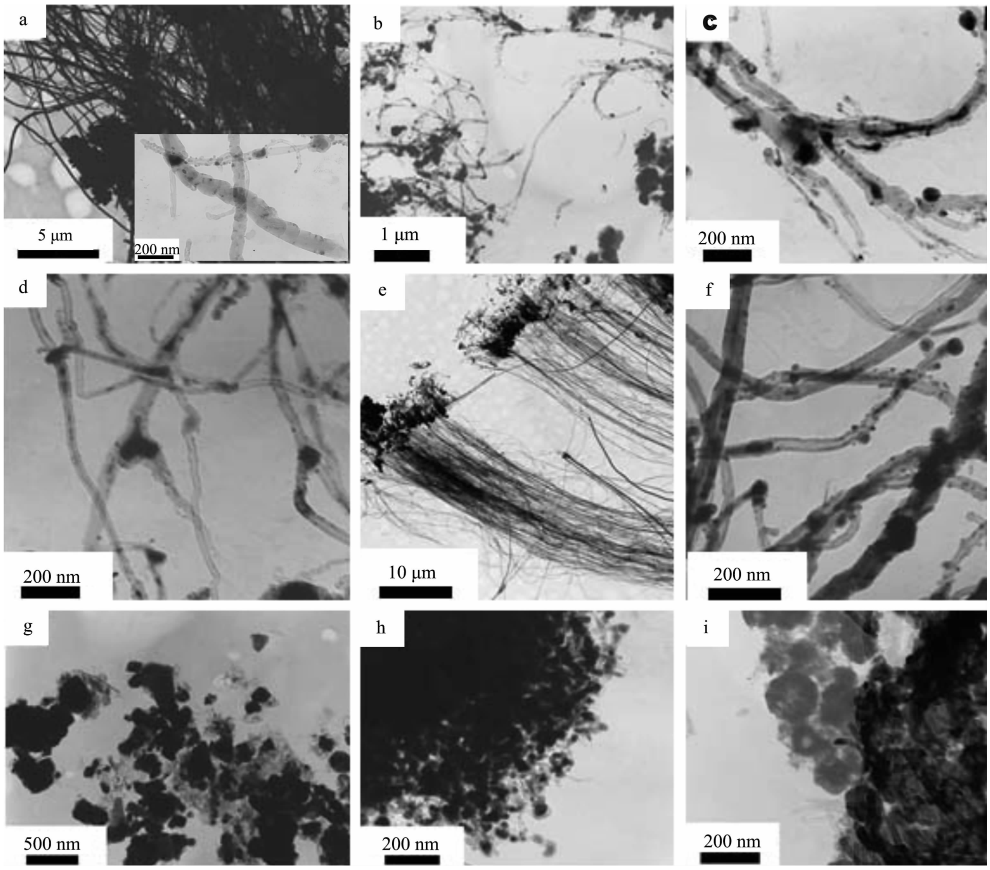

Fig.1　Typical TEM images of multi-branching and filled CNTs deposited using dicyclopentadiene and ferrocene as precursors at 800 ℃ (a~d), 850 ℃ (e~f), 650 ℃(g), 700 ℃ (h), and 750 ℃(i) while 60 $cm^3 \cdot min^{-1}$ flux of Ar passing through dicyclopentadiene bubbler

Fig.2a and 2b depict the morphologies and Raman scattering spectrum of CNTs arrays deposited on the surface of silicon wafer at 850 ℃ and 200 $cm^3 \cdot min^{-1}$ flux of Ar passing through dicyclopentadiene bubbler. Upper inset of Fig.2a shows the length of the CNT arrays is up to 100 micrometers. The branching and Fe-filled nanotubes are rarely observed (Lower inset of Fig. 2a). This implies that increasing the feeding of dicyclopentadiene, that is, decreasing the ratio of ferrocene, will result in the formation of straight and unfilled CNTs. The corresponding micro-Raman spectrum is shown in Fig.2b. The peak located at 1 574 cm^{1} (G line) is corresponding to the high-frequency E_{2g} first-order mode[19], and that at 1 353 cm^{1} (D line) could be attributed to the defects in the curved graphene sheets, tube ends, and finite size crystalline domains of the tubes[20]. From the intensity ratio of G to D lines, it is learned that the CNTs arrays have good crystallinity.

On the contrary, higher filled and multi-branching CNTs are expected to obtain if ferrocene is used as the only precursor. This is confirmed by the TEM images (Fig.2c) for the product synthesized at 850 ℃ in the absence of dicyclopentadiene. According to the XRD pattern (Fig.2d), the CNTs have good graphitized degree and the fillings are composed of cementite (Fe_3C), iron carbide (FeC), and iron.

The sole Fe source comes from ferrocene, it is found that the higher ferrocene content will lead to higher Fe-filled amounts and in the growth of CNTs. The preceding results indicate that ferrocene is the key factor for the formation of branching structures, while the dicyclopentadiene contributes little. When the precursor varies from higher flux of dicyclopentadiene to pure ferrocene, the morphology also changes from straight CNTs forest to CNTs with a few branches and to

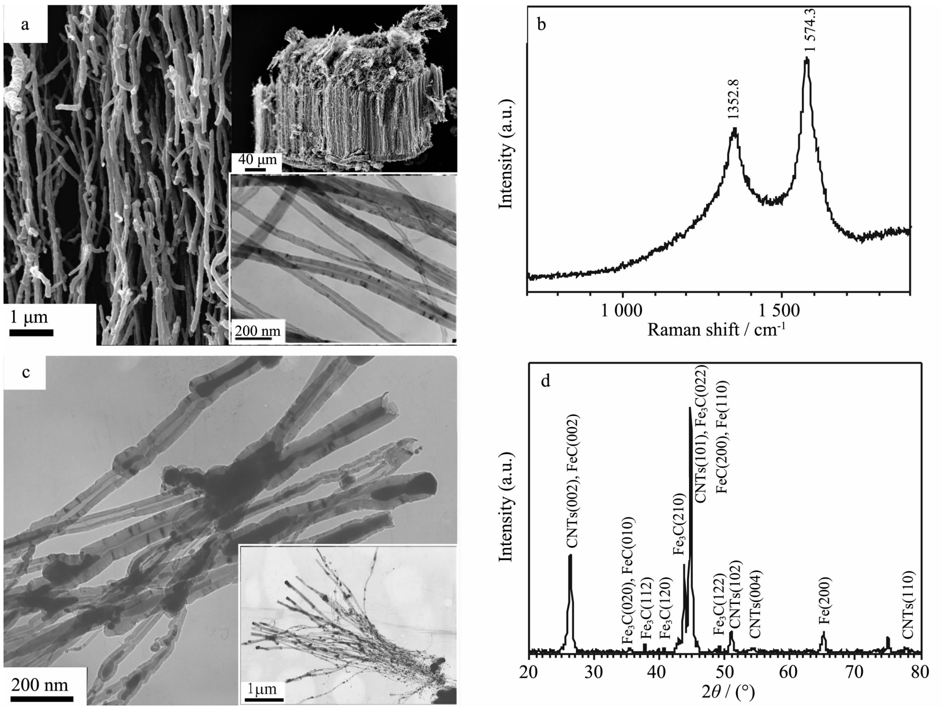

Fig.2 (a, b) SEM images and Raman scattering spectrum of CNTs array deposited on silicon wafer at 850 ℃ and 200 $cm^3 \cdot min^{-1}$ flux of Ar passing through dicyclopentadiene bubbler. (c, d) TEM images and XRD pattern of multi-branching and filled CNTs obtained using ferrocene as only precursor

the branched CNTs. The reason is that the Fe catalysts from the ferrocene could provide more nucleation centers for CNTs growth, thus inducing more branching phenomena. Also, since the diameter of CNTs are determined by the size of the catalyst nanoparticles [21], the diameter of the branches are significantly smaller. CNTs without branching are formed via the six-membered-ring growth mechanism[22] when C_6-configuration benzene is used as the precursor. The introduction of defects, e.g., pentagons and heptagons, on honeycomb-like network could change the curvature of nanotubes, leading to the generation of negative or positive curvature [13], and finally forming the branching of nanotubes. In this case, the precursors of cyclopentadiene and ferrocene are both C_5-ring molecules and the formation of highly branching CNTs is involuntary.

3 Conclusions

In summar y, we have fabricated multi-branching and iron-filled CNTs by using dicyclopentadiene and ferrocene as precursors. The growth conditions of CNTs, such as growth temperature and the proportion of precursors, could greatly affect the morphology and structure of the resulting products. With the increasing in ferrocene proportion in the precursors, the branching phenomena of CNTs becomes complicated and a large amount of tree-like branching and iron-filled CNTs are formed.

References:

[1] Iijima S. *Nature*, **1991**,**354**:56-58
[2] Wang X Z, Hu Z, Wu Q, et al. *Catal. Today*, **2002**,**72**:205-211
[3] Zhang M, Li J. *Mater. Today*, **2009**,**12**:12-8
[4] Saito R, Fujita M, Dresselhaus G, et al. *Appl. Phys. Lett.*, **1992**,**60**:2204-2206
[5] Chico L, Crespi V H, Benedict L X, et al. *Phys. Rev. Lett.*, **1996**,**76**:971-974
[6] Andriotis A N, Menon M, Srivastava D, et al. *Phys. Rev. Lett.*, **2001**,**87**:0668021-0668024
[7] Zhou D, Seraphin S. *Chem. Phys. Lett.*, **1995**,**238**:286-289
[8] Meunier V, Nardellic M B, Bernhol J, et al. *Appl. Phys. Lett.*, **2002**,**81**:5234-5236
[9] Menon M, Srivastava D. *Phys. Rev. Lett.*, **1997**,**79**:4453-

4456
[10]Papadopoulos C, Rakitin A, Li J, et al. *Phys. Rev. Lett.*, **2000**,**85**:3476-3479
[11]Wang Z Y, Zhao Z B, Qiu J S. *Carbon*, **2006**,**44**:1321-1324
[12]Ting J M, Chang C C. *Appl. Phys. Lett.*, **2002**,**80**:324-325
[13]Garcia A G, Correa M J D, Robles J F P, et al. *Diam. Relat. Mater.*, **2010**,**19**:1052-1057
[14]Meng G W, Han F M, Zhao X L, et al. *Angew. Chem. Int. Ed.*, **2009**,**48**:7166 7170
[15]Wei D C, Liu Y Q, Cao L H, et al. *Nano Lett.*, **2006**,**6**:182-192
[16]Romo-Herrera J M, Sumpter B G, Cullen D A, et al. *Angew. Chem. Int. Ed.*, **2008**,**47**:2948-2953
[17]Ray S C, Bhattacharyya S, Wu S L, et al. *Diam. Relat. Mater.*, **2010**,**19**:553-556
[18]Wei D C, Liu Y Q, Cao L H, et al. *J. Am. Chem. Soc.*, **2007**, **129**:7364-7368
[19]Nemanich R J, Solin S A. *Phys. Rev. B*, **1979**,**20**:392-401
[20]Li W Z, Zhang H, Wang C Y, et al. *Appl. Phys. Lett.*, **1997**, **70**:2684-2686
[21]Cheung C L, Kurtz A, Park H, et al. *J. Phys. Chem. B*, **2002**, **106**:2429 2433
[22]Tian Y J, Hu Z, Yang Y, et al. *J. Am. Chem. Soc.*, **2004**, **126**:1180-1183