基于六元环生长机理高产制备碳纳米管

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摘要:基于六元环生长机理,以苯为前驱物高产率地制备了多壁碳纳米管。通过调变及优化催化剂的组成和用量、苯通量、生长温度等参量,碳纳米管的最高产率可达 859wt%。高分辨透射电子显微镜、扫描电子显微镜、热重–差热分析仪、X 射线衍射等分析结果表明,本方法制得的碳纳米管产物的直径约 20 nm,纯度高,具有良好的石墨化程度。

关键词:材料物理与化学;合成;化学气相沉积;碳纳米管
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High-Yield Production of Carbon Nanotubes Based on Six-Membered-Ring Growth Mechanism

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Abstract: A further study on the catalytic synthesis of multi-walled carbon nanotubes (MWCNTs) with benzene precursor is reported based on the six-membered-ring-based growth mechanism. Several influence factors were examined and optimized, including the chemical component of catalysts, catalyst dosage, flux of benzene vapor, and growth temperature. The maximum yield of CNTs was up to 859wt%. Transmission electron microscopy, scanning electron microscopy, thermogravimetry-differential thermal analysis, and X-ray diffraction results show that the products obtained at the optimized condition are the quasi-aligned and well-graphitized CNTs of high purity with a diameter about 20 nm.

Key words: materials science; synthetic methods; chemical vapor deposition; carbon nanotubes

Since the discovery by Iijima in 1991 [1], carbon nanotubes (CNTs) have become one of the most fascinating nanostructures due to their outstanding chemical and physical properties and extensively potential applications [2-5]. From practical point of view, the high-yield production of CNTs at low cost is an important issue. Among the developed methods [6], the thermal chemical vapor deposition (thermal CVD) is the promising one to get high-yield and with the benefits of low investment, mild preparation conditions and the availability of many inexpensive volatile carbon-containing precursors. In our previous works, based on the structural similarity between benzene ring and the building unit of CNTs, the six-membered-ring-based (h-C_6) growth mechanism was proposed through the in-situ thermal analysis-mass spectroscopic coupling measurement [7], which is further supported by DFT calculation [8]. Following the h-C_6 growth mechanism, it is expected that CNTs could be synthesized with rather high yield and quality. In this mechanism, the C-H but

not C-C bonds of the precursor are required to be selectively broken, which is critically related to the catalysts and growth conditions. Thus, to explore the dependence of chemical component of catalysts, catalyst dosage, flux of benzene vapor, and growth temperature on the yield and quality of CNTs, is certainly an interesting topic.

Here, we report a simple thermal CVD method to grow multi-walled CNTs (MWCNTs) using benzene as the precursor and iron-cobalt binary component compounds as the active catalysts. The quasi-aligned and well-graphitized MWCNTs of high purity could be achieved. The maximum yield of CNTs is up to 859wt% through modifying chemical component of catalysts, catalyst dosage, flux of benzene vapor, and growth temperature.

1　Experimental

Iron-cobalt binary-component catalysts supported on γ-Al$_2$O$_3$ were prepared by impregnation method as described in our previous work[9]. The synthesis of CNTs was carried out in a fixed-bed reactor consisting of a furnace with a quartz tube with an inner diameter of about 4 cm. The furnace was first heated to a specific temperature (e.g., 660 ℃) at a heating rate of 15 ℃·min^{-1} in flowing nitrogen of 75 sccm (standard cubic centimeter per minute). The saturated benzene vapor was then introduced into the reactor for 1 h using nitrogen gas of 75 sccm as carrier gas, passed through a triplet saturator of benzene at a designed temperature. The flux of the carrier gas was monitored by a digital mass flow controller. Subsequently, the reactor was cooled down to room temperature in argon flow. After reaction, the yield of carbon deposit in each synthesis was evaluated as follows:

$$\text{Yield(wt\%)} = (m_{tot.} - m_{cat.})/m_{cat.} \times 100\ \%$$

Where $m_{cat.}$ is the initial weight of the catalyst and $m_{tot.}$ is the total weight of the resulting product.

The products were purified by condensed hydrochloride acid at 140 ℃ for 240 min and characterized by thermogravimetry-differential thermal analysis (TG-DTA, STA-499F3, NETZSCH), transmission electron microscopy (TEM, JEOL-JEM-1005, operating at 80 kV), high resolution TEM (HRTEM, JEOL-JEM-2010, operating at 200 kV), X-Ray energy dispersive spectroscopy (EDS, VANTAGE DS (EDS)NORON, equipped in HRTEM), scanning electron microscopy (SEM, JEOL-JSM-6300 SEM, operating at 10 kV), and X-ray diffraction (XRD, Philips Xpert Pro X-ray diffractometer, Cu $K\alpha$1 radiation of 0.154 06 nm, 40 kV, 40 mA, Ni filter, Hybrid detector).

2　Results and discussion

Fig.1 shows the typical TEM, SEM, HRTEM images and EDS spectrum of the products. The quasi-
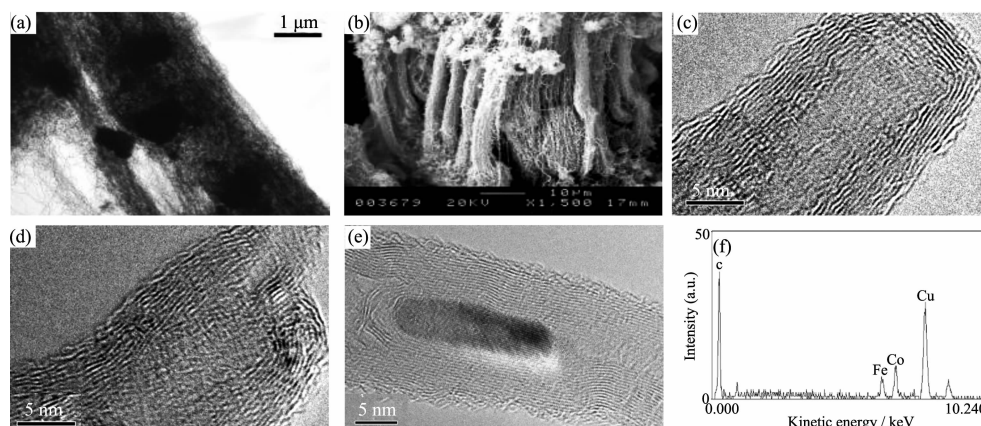

Fig.1　Typical TEM, SEM, HRTEM images and EDS spectrum of the as-prepared products. (a) TEM of the CNTs synthesized over the 1.51 mmol·g^{-1} Fe-1.51 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst with a yield of 721wt%; (b) SEM of the CNTs synthesized over the 1.00 mmol·g^{-1} Fe-2.00 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst with a yield of 857wt%; (c), (d), and (e) Typical HRTEM images of the CNTs associated with the sample in Fig.1a; (f) EDS spectrum for the as-prepared products in Fig.1e

aligned CNT bundles are formed in the case of high yields (usually higher than 300wt%) as shown in Fig.1b. The length varies in the range of a few microns to several hundreds of microns with a diameter around 20 nm. From Fig.1a and 1b, it is observed that the as-prepared quasi-aligned CNT products are composed of highly pure straight-like nanotubes, and the other kind of morphologies or species, even the used catalysts, are hardly seen due to their very small portion in the whole product. The quasi-aligned growth manner might directly result from the high productivity or overcrowding growth[10-11]. It is understandable that steric hindrance[12] is one of the important factors dominating the morphology of the product. The influence of this factor becomes remarkable, especially for high-yield production.

In order to learn the microstructures of the as-prepared products, HRTEM were employed to further characterize the samples. Typical HRTEM images of the CNTs are shown in Fig.1c~e. It is clearly seen that the CNTs are well graphitized with the interlayer space of approximately 0.34 nm. The closed end in Fig.1c and partially open end in Fig.1d are the representative ends of the CNTs. In Fig.1e, the catalyst particle, a Fe-Co alloy, is positioned in the middle of the CNT, which is confirmed by the corresponding EDS spectrum as shown in Fig.1f. The Cu signal comes from the copper grid in the HRTEM experiment.

Fig.2 displays the typical XRD patterns taken from the raw catalyst, the as-prepared and purified products for 6 and 60 min growth with a weight gain of 90 and 721wt%, respectively. XRD patterns of the two as-prepared samples are obviously different. The diffraction peaks of the catalyst can be clearly observed for the low weight-gain sample (6 mins growth, Fig.2b), while hardly identified for the high weight-gain sample (60 mins growth, Fig.2c). This is reasonably understood since the volume percentage of the catalyst is estimated to be about 8 and 1% for the two as-prepared samples, respectively. It is seen that XRD patterns for the two corresponding purified samples are highly similar with each other, with all the diffraction peaks close to the corresponding ones for hexagonal graphite. The
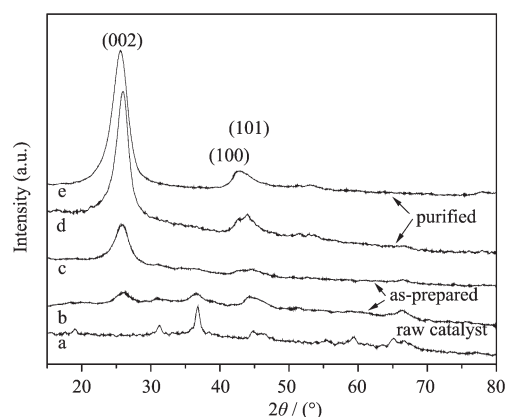

Fig.2　Typical XRD patterns for the raw catalyst, as-prepared and purified products (a) the raw catalyst; (b) and (c) the as-prepared products for 6 and 60 min growth with a weight gain of 90 and 721wt% over the 1.51 mmol·g^{-1} Fe-1.51 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst respectively; (d) and (e) the purified samples corresponding to (b) and (c)

interlayer spacing c value is deduced to be ca. 0.345 nm, slightly higher than 0.334 nm for graphite[12-13], in good agreement with the HRTEM results for CNTs. The sharp (002) peak, rather than the broad hump[14], indicates the very high graphitization degree of the CNTs synthesized by this methods. Moreover, the results also indicate that our treatment for the removal of catalyst, both metallic species and γ-Al$_2$O$_3$ support, is rather effective, which is very useful for practical applications.

The information about the purity and graphitization degree of quasi-aligned CNTs are also reflected in the TG (DTG)-DTA curves as typically shown in Fig.3, corresponding to the sample in Fig.1a after removing the catalyst by concentrated hydrochloride acid. It is learned that the initial burning temperature is about 490 ℃, and only one intense exothermic peak appears around 579 ℃. These results further indicate the high purity of the CNTs, otherwise there would exist signals much lower than 450 ℃ associated with amorphous carbon[15-16]. And, the graphitization degree of the products is rather good though it is not as high as that of CNTs derived from high temperature synthesis[17-18]. The narrow temperature ranges for the weight loss in TG (or the single peak in
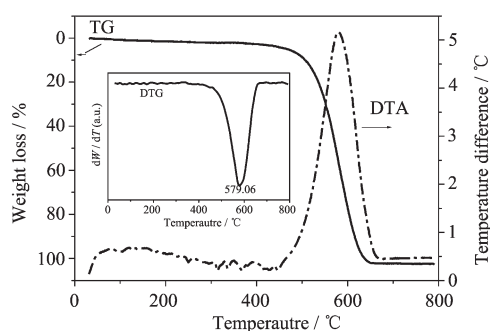
The full and dotted curves are the TG and DTA curves, respecti
vely. The inset is the DTG curve

Fig.3　TG (DTG)-DTA curves of the CNTs grown over
1.51 mmol·g^{-1} Fe-1.51 mmol·g^{-1} Co/γ-Al$_2$O$_3$
catalyst. The catalysts were removed by
condensed hydrochloride before the experiments

DTG) and the single exothermic peak in DTA also reflects the high homogeneity of the CNTs synthesized by this route. This may relate with the h-C$_6$ growth mechanism.

　　According to the above results, well-graphitized quasi-aligned CNTs of high purity could be synthesized in high yield by thermal CVD method with benzene precursor. Subsequently, the typical influence factors, i.e., chemical component of catalysts, catalyst dosage, flux of benzene vapor, and growth temperature were investigated to obtain high productivity of CNTs. Fig.4a shows the typical relationship between carbon deposit and the decomposition temperature for two high-productive catalysts, i.e., 1.00 mmol·g^{-1} Fe-2.00 mmol·g^{-1} Co/γ-Al$_2$O$_3$(i) and 0.60 mmol·g^{-1} Fe-2.40 mmol·g^{-1} Co/γ-Al$_2$O$_3$(ii). With the deposition temperature lifting, the yield of carbon deposit reaches the maximum around 660 ℃ and then decreases. The maximum of 609 wt%

can be reached at 660 ℃ on 0.60 mmol·g^{-1} Fe-2.40 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst while the maximum of 743wt% occurs at 670 ℃ on 1.00 mmol·g^{-1} Fe-2.00 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst. Therefore, about 660 ℃ can be taken as the optimal synthesis temperature range for growing CNTs through the catalytic decomposition of benzene vapor. Fig.4b displays the relationship between carbon deposit and the temperature of benzene saturator. Four temperatures of benzene saturator are investigated, namely, 25, 40, 60, and 70 ℃. The higher the temperature of benzene saturator, the higher carbon deposit. Up to 857wt% of carbon deposit can be reached on 1.00 mmol·g^{-1} Fe-2.00 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst at 70 ℃ of benzene saturator. For 0.60 mmol·g^{-1} Fe-2.40 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst, after the temperature of benzene saturator exceeds 60 ℃, the changes of carbon deposit become slow. Thus, 60~70 ℃ can be selected as the optimal temperature of benzene saturator. Furthermore, influence of catalyst dosages on carbon deposit is indicated in Fig.4c. Under 60 ℃ benzene saturator, with the catalyst dosages increasing, carbon deposits firstly decrease, then increase and reach the maximum at 300 mg catalyst dosage, and then decrease again. For 0.60 mmol·g^{-1} Fe-2.40 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst, carbon deposit can reach up to 859wt% as shown in Fig.4c(ii). It implies that the flux of benzene vapor is too high to the deposition rate of CNTs in lower catalyst dosages and is not sufficient to higher catalyst dosages. Based on the results, 300 mg is considered as the appropriate catalyst dosage by using 75 sccm nitrogen as carrier gas passing through 60 ℃ of benzene saturator.
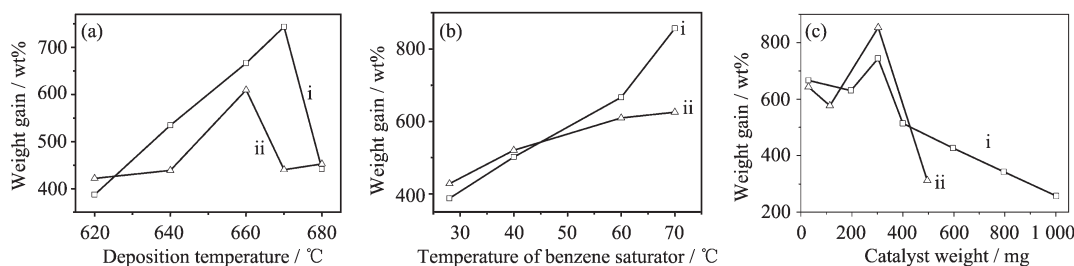
The ratios of iron and cobalt correspond to 1:2(i) and 1:4(ii)

Fig.4　Relationship between weight gain and synthesis conditions, namely, deposition temperature (a), temperature
of benzene saturator (b), and catalyst dosages (c)

3　Conclusions

In summary, high-yield and high-quality quasi-aligned CNTs were prepared by catalytic decomposition of benzene over γ-Al$_2$O$_3$-supported iron-cobalt binary component catalysts under the appropriate growth conditions. The as-prepared MWCNTs possess very well-graphitized degree and high purity with a diameter of ca. 20 nm. Several key factors for growing CNTs have also been optimized, *e.g.*, chemical component of catalysts, catalyst dosage, flux of benzene vapor, and growth temperature. The carbon deposits can very easily exceed 600wt% and even the maximum yield of CNTs is even as high as 859wt% on 300 mg 0.60 mmol·g^{-1} Fe-2.40 mmol·g^{-1} Co/γ-Al$_2$O$_3$ catalyst.

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