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A one-step single source route to carbon nanotubes

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Abstract. Carbon nanotubes (CNTs) have been synthesized *via* directly pyrolyzing ferrocene in the autoclave. The nanotubes with several micrometers in length have outer and inner diameters in the range of 40–100 nm and 20–40 nm, respectively. An yield of ~70% of CNTs can be obtained without any accessorial solvents and catalysts. Experimental results showed that a temperature higher than 600°C in conjunction with proper pressure was favourable for achievement of the nanotubes. The growth mechanism of CNTs was also discussed.

Keywords. Carbon nanotubes; ferrocene; pyrolysis.

1. Introduction

Carbon nanotubes (CNTs) have been the focus of nanomaterials research for over a decade because of their wide range of applications (Baughman *et al* 1999; Fan *et al* 1999; Kim and Lieber 1999; Liu *et al* 1999; Luo *et al* 2005). Over the last few years, immense efforts have been made worldwide to optimize their synthesis and thus various synthesis methods have been developed such as chemical vapour deposition (Yokomichi *et al* 2001), electric arc discharge (Zeng *et al* 1998; Qiu *et al* 2003), pyrolysis (Jia *et al* 1999), laser ablation (Ma *et al* 2000), solvothermal (Jiang *et al* 2000) and hydrothermal processes (Libera and Gogotisi 2001; Kang *et al* 2003), etc.

Among these methods, the pyrolysis of organometallic compounds has emerged as a powerful approach to CNTs with large-scale production (Li *et al* 2000; Liu *et al* 2003). In particular, compounds containing transition metals such as ferrocene can not only act as a carbon source but also give rise to small catalytic metal particles as well; thus it was considered as a good alternative for the synthesis of CNTs (Rao *et al* 1997, 1998; Hou *et al* 2002; Wei *et al* 2002; Kumar and Ando 2003; Singh *et al* 2003; Zhang *et al* 2003). In most cases, chemical vapour deposition (CVD) process, needing multi-step and expensive carrier gas and substrate, was used to synthesize CNTs. On the other hand, in order to increase the yield of CNTs, some accessorial compounds (solvents) and catalysts were required with pyrolysis of ferrocene. However, it is necessary to prepare CNTs by a simple and cheap route.

Herein, we report the synthesis of CNTs with yield of ~70% by a one-step single source pyrolysis route. The synthesis process was simply achieved in an autoclave at 500–700°C by pyrolysis of ferrocene without any accessorial solvents and catalysts. In addition, the growth mechanism of CNTs is tentatively discussed based on the experimental results.

2. Experimental

1 mmol ferrocene powder was placed in a stainless steel autoclave with a capacity of 20 ml. The autoclave was kept at 700°C for 10 h, and then cooled to room temperature naturally. The resultant powder was collected from the autoclave. The obtained powder was added into diluted hydrochloric acid and maintained for sometime in order to remove the metal iron in it. Then the products were filtered off and washed with distilled water and absolute ethanol. Subsequently, the sample thus obtained was dried in a vacuum at 60°C for 4 h.

XRD patterns were recorded at a scanning rate of $0{\cdot}02°\ s^{-1}$ in the range, 2θ, from 10–70°, using Cu K_α radiation (λ = 0·154178 nm). SEM images were obtained on a JSM-6700F field emission scanning electron microscope. TEM images and SAED patterns were taken using a Hitachi Model H-800 transmission electron microscope. High-resolution electron microscopic images were taken on a JEOL-2010 transmission electron microscope. The Raman spectrum was investigated with a French Labram-HR confocal laser Raman microspectrometer with an argon-ion laser at an excitation wavelength of 514·5 nm.

3. Results and discussion

Figure 1 shows the XRD pattern of the product, which can be indexed to (002), (100) and (004) hexagonal graphite

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(JCPDS, 41-1487), respectively. The strong and sharp peaks suggest that the as-prepared products are well crystallized. There is no obvious impurity peak in the pattern.

Figure 2 shows the Raman spectrum of the product, which can allow us to draw further conclusion about the crystallography or morphology (Klinke *et al* 2002). The peak at 1580 cm^{-1} (G-band) corresponding to the Raman allowed optical mode, E_{2g}, of 2-dimensional graphite is closely related to the vibration in all sp^2 bonded carbon atoms in a 2-dimensional hexagonal lattice, such as in a graphite layer. The peak at 1350 cm^{-1} could be assigned to the vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite (Dresselhaus *et al* 1999).

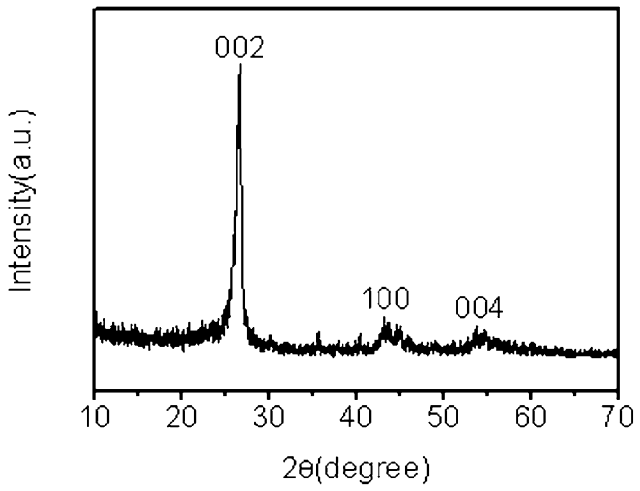

Figure 1. XRD pattern of the as-prepared product using Cu K_α X-ray as radiation.

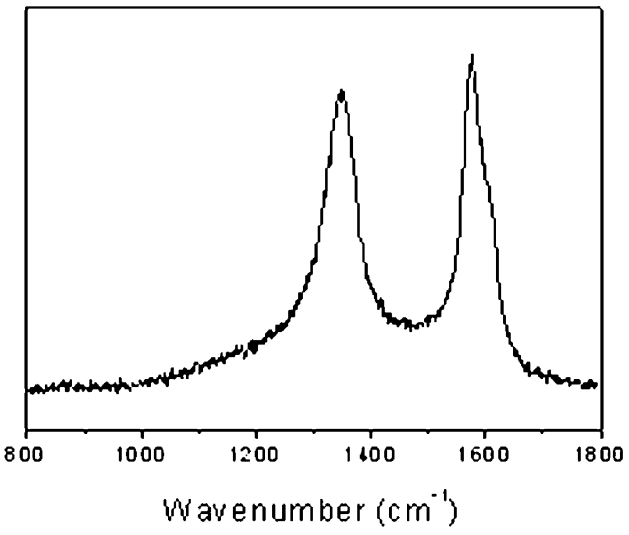

Figure 2. Raman spectrum of the as-prepared sample which shows two graphite peaks at 1350 and 1580 cm^{-1}.

Figures 3a and b show SEM and TEM images of carbon nanotubes, respectively. It can be seen that a large quantity of nanotubes can be achieved by this method. The yield of carbon nanotubes estimated through SEM and TEM observations of the as-prepared samples was 70%. Most of the carbon nanotubes with close ends and curly morphologies have outer diameters of 40–100 nm, inner diameters of 20–40 nm and length up to several micrometers, and no metal catalyst particles were detected from TEM image (figure 3b). The inset in figure 3b shows SAED pattern of the sample, and the three rings can be indexed to (002), (100) and (004) of graphite, which is in good agreement with XRD analysis. The diffuse ring patterns indicate that the nanotubes are well crystallized, and the appearance of a pair of strong spots (not arcs) for 002 diffraction indicates some orientation of the 002 planes and high graphatizability in the carbon tubes (Kyotani *et al* 1996). In addition, typical HRTEM image of a closed end of the carbon nanotube (inset in figure 4b) reveals that the interlayer spacing of the tip is about 0·34 nm, corresponding to the typical (002) lattice distance in hexagonal graphite.

In our synthesis process, temperature and pressure are found to be crucial for the formation of carbon nanotubes. Ferrocene is a highly volatile organometallic compound with excellent vapourizability. The decomposition of ferrocene can take place when temperature is higher than 400°C (Bernhauer *et al* 1994), while the obtained products were mainly amorphous carbons and a small quantity of the catalyst-coated carbon particles when the temperature was lower than 600°C. It was found that a temperature higher than 600°C, in particular, ~700°C, was favourable for the formation of carbon nanotubes under our experimental conditions. However, we cannot get nanotubes under the ambient pressure even if the temperature of the reaction reaches 700°C, and only a small quantity of nanotubes can be produced under ambient pressure even when the temperature of the reaction was heated to 900°C. So the pressure is also a very important factor for the formation of nanotubes.

In order to investigate the formation process of carbon nanotubes, some samples were obtained after a relatively short time of synthesis reaction and were not washed with diluted hydrochloric acid (figures 4a and b). It can be seen that the carbon nanotubes (figure 4a) have close ends and nearly straight morphologies, which are different from those as indicated in figure 3. The change in the shape of nanotubes with increasing reaction time probably resulted from changes in some conditions in the autoclave, such as the gradual decrease of carbon source and fluctuation of pressure with the consumption of starting materials. It is worth noting that there are obvious patches (marked by arrows) at the top of most of the carbon nanotubes (figure 4a), which were probably left behind by catalyst particles. At the same time, the catalyst particles at the top of some nanotubes (figure 4b) further indicates

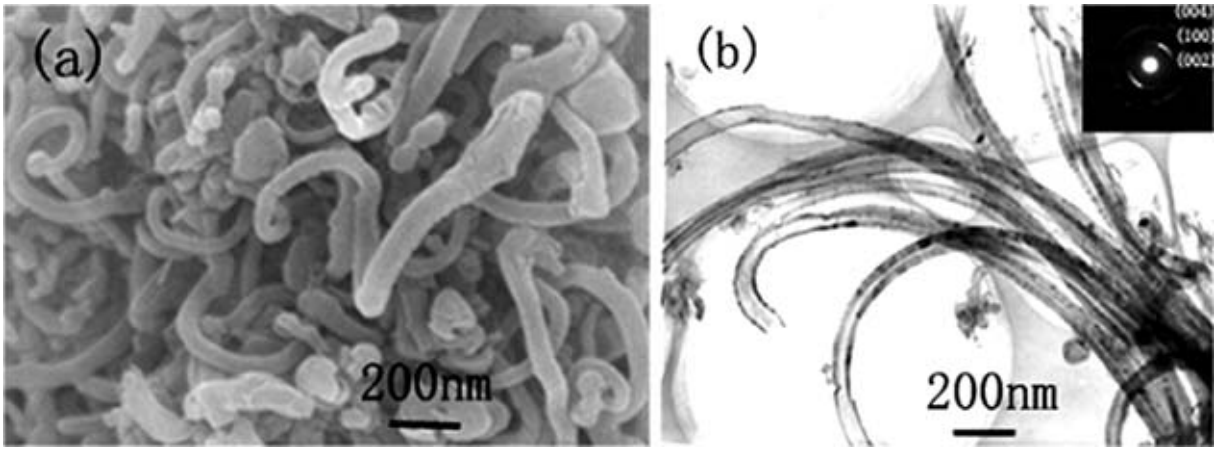

Figure 3. (**a**) SEM image and (**b**) TEM image of the carbon nanotubes; (inset **3b**) SAED pattern of individual carbon nanotube.

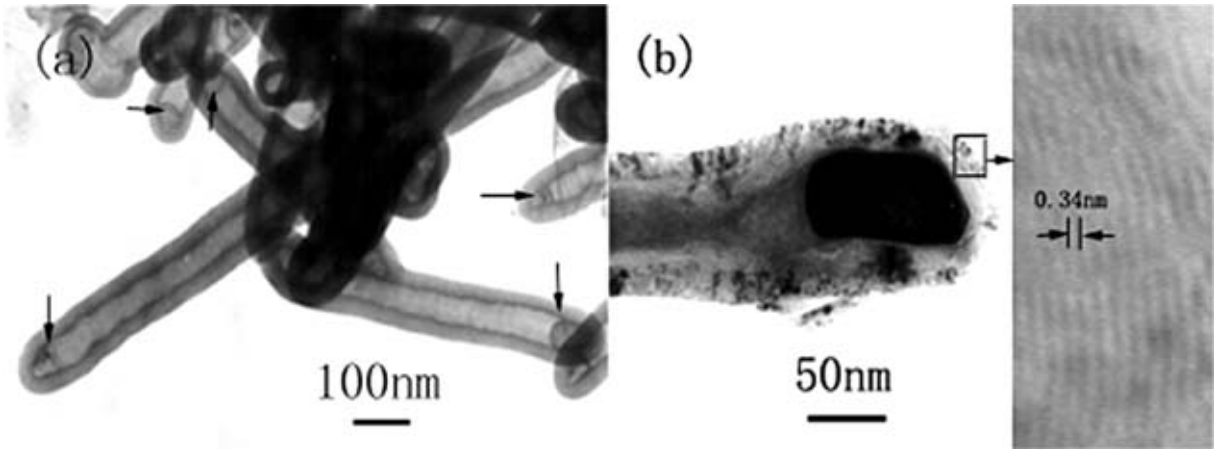

Figure 4. (**a**) **and** (**b**) TEM images of carbon nanotubes obtained after 5 h of reaction and washed without using the dilute HCl aqueous solution, respectively. Inset in figure **4b** is HRTEM image of the carbon nanotube.

that the catalyst particles existed at the top of the carbon nanotubes during their formation process. It is well known that ferrocene has been considered as a good catalyst precursor for the growth of nanotubes (Andrews *et al* 1999; Liu *et al* 2002). With the decomposition of ferrocene at high temperature, numerous micro-Fe and carbon particles were produced. Thereafter, the carbon clusters formed the graphitic sheets as caps on catalyst particles. As the cap lifted off the catalytic particles and carbon particles continued supply and the CNTs with hollow closed tip were produced. Of course, detailed formation mechanism of the CNTs needs further study.

4. Conclusions

The CNTs with yield, ~70%, have been obtained via a one-step pyrolysis of ferrocene in the autoclave at 700°C and the ferrocene acted both as catalyst and carbon source without adding any accessorial solvents and catalysts. In addition, the yield of CNTs is strongly affected by the temperature in conjunction with proper pressure in the autoclave. Here, the complex equipments and the separation of the raw material from the solvent are avoided, so it may be applied on the scale of industrial production.

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