The synthesis of single-walled carbon nanotubes over an \( \text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3 \) binary aerogel catalyst

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Abstract. An \( \text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3 \) binary aerogel was used as a catalyst for the synthesis of single-walled carbon nanotubes. The carbon products were synthesized by catalytic decomposition of methane or a \( \text{CH}_4/\text{H}_2 \) mixture at 820-960\(^\circ\)C for 30 min. The influence of preparation atmosphere on the growth of single-walled carbon nanotubes was investigated. The morphology and the structure of carbon products were investigated by TEM, HRTEM and Raman spectroscopy analyses. The carbon products prepared under a methane atmosphere are mainly amorphous. High-purity individual single walled carbon nanotubes (SWCNTs) and bundles were synthesized under the mixed atmosphere of \( \text{CH}_4/\text{H}_2 \). The results show that the atmospheres exhibit a close relationship to the yield and structure of carbon products formed.

1. Introduction

Various carbon nanotube synthesis technologies have been developed since their observation by Iijima in 1991 [1]. The potential application of carbon nanotubes has aroused interest worldwide. However, the high cost of the current production methods and the difficulty in manufacturing them on large-scale have slowed down commercial practice. For this reason, many research groups are working toward low cost, high purity and large-scale synthesis of single-walled carbon nanotubes (SWCNTs).

Currently, the major routes to SWCNTs production are based on electric arc growth [2], laser vaporization of a graphite electrode in the presence of a metal catalyst [3], and catalytic chemical vapour deposition (CCVD) processes [4]. Of these production methods only CCVD can provide large-scale yield of carbon nanotubes. The CCVD method involves the catalytic decomposition of hydrocarbons or CO over metal nanoparticles of either Fe, Co and Mo [5-6] supported on \( \text{SiO}_2, \text{MgO} \) or \( \text{Al}_2\text{O}_3 \) [7-8].

The influence of hydrogen when added to the carbon source gas on the growth of single-walled carbon nanotubes was investigated in this work. The aerogel catalysts were prepared by a sol-gel supercritical fluid drying (SCFD) process. The ratio between the catalyst and support can be controlled easily by this approach. This characterization study on the growth phenomenon of the SWCNTs was carried out by Raman spectroscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM).
2. Experimental

2.1 Preparation of binary aerogel catalysts

Al(NO₃)₃·9H₂O and Fe₂(SO₄)₃·xH₂O ethanol solutions at a mole ratio of 30:1 were mixed using magnetic stirring for 24 hours at room temperature to form an alcosol. The alcosol was then placed in an autoclave and dried under the supercritical conditions of 250°C temperature and 7.5MPa pressure for 0.5h after which the ethanol was slowly discharged at 250°C and the autoclave was cooled to room temperature with flowing nitrogen to obtain an Al₂O₃ / Fe₂O₃ binary aerogel.

2.2 The preparation of carbon nanotubes

The methane chemical vapor depositions over the Al₂O₃ / Fe₂O₃ binary aerogel were carried out in a quartz tube (28mm diameter) furnace equipped with temperature and gas-flow controls. 1g of binary aerogel catalyst in a quartz boat was first heated with a heating rate 5°C/min to 880-960°C under nitrogen which was then replaced by methane with a flow rate of 300sccm or a mixture of methane and hydrogen with flow rate ratio of 300sccm and 100sccm for 30 min at the required temperature. After reaction, the reaction gas was replaced by nitrogen and the furnace allowed to cool. The carbon products, dispersed in tetrahydrofuran, were purified in hydrofluoric acid (20wt%) under magnetic stirring for 24 hours in an attempt to remove the support and the catalyst. Finally they were thoroughly washed in water to neutralize the specimen for Raman spectroscopic analysis and TEM observation.

2.3 The characterization of carbon nanotubes

The Raman experiments were performed on a Renishaw inVia 2000 Raman microscope with the Ar⁺ 514.5 nm line as the excitation source at a power of 25 mW. Raman spectra were averaged from a number of sample regions.

The surface morphology and overall elemental composition analysis of the samples was studied with a Leo 1530 field emission scanning electron microscope (FEGSEM) and the more detailed morphology and structure of carbon nanotubes were evaluated in a FEI CM200 FEGTEM field emission gun transmission electron microscope equipped with an Oxford Instruments EDX detector and Gatan imaging filter.

3. Results and discussion

This work has investigated carbon nanotubes produced by catalytic decomposition of (i) pure methane and (ii) a mixture of methane and hydrogen. To clarify the role of temperature on nanotube growth, the reactions were conducted at a range of temperatures between 880–960°C.

Figure 1a shows the typical first-order Raman spectrum of carbon products grown under a methane atmosphere at 880°C for 0.5 hour. The D-line at about 1340cm⁻¹ and the G-line at around 1585cm⁻¹ are large with the former peak being dominant. The Raman spectra (not shown) of samples prepared at higher temperatures show a similar character. The high intensity of the D-line and the D/G intensity
ratio imply that the carbon products contain an abundance of disordered carbon. Figures 1(b-c) show typical SEM and TEM images of carbon products synthesized under a methane atmosphere at 880°C for 0.5 hour. It seems that the sample is mainly composed of sponge-like carbon plus a small number of spherical carbon nanoparticles. The TEM image shown in Figure 1c shows that the sponge-like carbon product is mainly composed of amorphous carbon sheets and nanoparticles with a diameter of 10-30nm; a few SWCNTs can be found by HRTEM observation. The formation of a large amount of amorphous or disordered carbon may be attributed to the extensive decomposition of methane leading to high concentrations of reactive carbon species. Figure 2A(a-e) shows the Raman spectra of carbon products prepared at 880–960°C under the atmosphere of mixed methane and hydrogen. In comparison to Fig.1a, the D/G intensity ratio is decreased, which indicates the decrease of defects or the disordered carbon product. It can be observed that the low frequency peaks (shown in Figure 2B), assigned to the radial $A_\text{r}$ “breathing” mode, and characteristic of SWCNTs, are very obvious. Based on the relationship between the tube diameter and band position: $v(\text{cm}^{-1}) = 6.5\text{cm}^{-1} + 232\text{nm/cm}/d(\text{nm})$ [9], the diameter of SWCNTs is mainly distributed between 0.90–1.55nm. The position of the peaks in Figure 2B shifts slightly to lower frequency with an increase in reaction temperature which implies that the diameter of the SWCNTs increases slightly with the synthesis temperature.

Figure 3a shows the SEM images of the sample synthesized under the mixed atmosphere of hydrogen and methane. Figure 3a illustrates some SWCNT ropes, with lengths of over 8mm. Inset in Figure 3a shows a higher magnification image of the long SWCNT rope in Figure 3a, which shows that this rope consists of SWCNTs bundles and a few carbon nanoparticles. Compared with Figure 1b, the yield of SWCNTs in the inset is obviously improved. Figure 3(b-c) and (d-e) show the TEM images of SWCNTs grown under mixed atmospheres at 880°C and 960°C respectively. The SWCNTs produced by this method are homogeneous and appear both isolated and in bundles with a small amount of amorphous carbon attached. The diameter of SWCNTs from HRTEM observation is mostly distributed around 1.5nm, in good agreement with Raman data. A few double walled carbon nanotubes can also be observed in Figures 3c and 3e. The morphology and microstructure of SWCNTs synthesized at 880°C and 960°C are similar. The results show that the introduction of hydrogen with methane has a remarkable influence on the structure and composition of carbon products. It is possible that hydrogen partially suppresses decomposition of methane, reducing the concentration of reactive carbon species. This may favour more gradual growth of SWCNTs rather than rapid formation of amorphous carbon.

4. Conclusion

Using an Al$_2$O$_3$/Fe$_2$O$_3$ aerogel as catalyst, carbon products were synthesized under atmospheres of both pure methane and mixed hydrogen and methane. The former product consists mainly of amorphous carbon while the latter is composed of high-purity individual SWCNTs (with a homogenous distribution of diameters) and bundles thereof. These results clearly demonstrate that admixture of hydrogen with
methane during CCVD assists the formation of clean SWCNTs in high yields.

Fig. 3 The (a) SEM of SWCNT ropes synthesized at 880°C and HRTEM images of SWCNTs synthesized at (b-c) 880°C and (d-e) 960°C for 0.5 hour under the mixed atmosphere of hydrogen and methane. The inset in Figure 3a is the magnified SEM image from the SWCNT rope in Figure 3a.

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