SYNTHESIS OF CARBON NANOTUBES BY CATALYTIC CVD USING Fe-Mo/MgO AND Fe-Mo/Al$_2$O$_3$ CATALYSTS

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Abstract

Carbon nanotubes (CNTs) were synthesized by catalytic chemical vapor deposition using Fe-Mo/MgO and Fe-Mo/Al$_2$O$_3$ catalysts. Methane was used as the carbon source. The catalysts were prepared by impregnating MgO or Al$_2$O$_3$ catalyst support with a Fe-Mo solution. Two different iron sources, Fe(NO$_3$)$_3$ and Fe$_2$(SO$_4$)$_3$, were used to prepare the catalyst. Experimental results indicate that addition of molybdenum favors the formation of CNTs and that the growth temperature is lower when Fe$_2$(SO$_4$)$_3$ is used as the iron source. SEM observations show that large quantities of entangled CNT bundles with a layer network morphology can be synthesized and that very small amount of amorphous carbon is observable. Under optimum growth condition, compacted CNT bundles of several micrometers in length, protruded out of the catalyst surface, can be grown and the yield can be increased significantly. Most of the CNT products are double-walled CNTs by TEM observations.

Introduction

Carbon nanotubes (CNTs) have attracted a lot of attention in the last decade due to their fascinating properties. Many potential applications are wide open, which extend from composite reinforcement to nanoelectronics [Popov 2004]. For the commercial applications, a process method to grow high quality CNTs with a large quantity and controlled morphology and structure is desired. Among the three main techniques used to synthesize CNTs, arc discharge, laser ablation and catalytic chemical vapor deposition (CVD), large scale syntheses of CNTs are mainly carried out by the catalytic CVD technique due to the high yield, high selectivity and low cost [Gulino et al. 2005].

Using catalytic CVD, Fe and Fe-Mo catalysts have shown potential to grow single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs) and multi-walled CNTs (MWCNTs) in a large scale [Lyu et al. 2004a,b; Gulino et al. 2005; Cassell et al. 1999]. In this study, two different iron sources and two different catalyst supports were used to prepare the Fe and Fe-Mo catalysts and their influences on the growth of CNTs were investigated.

Experimental

Growth of CNTs

Two different iron sources, Fe(NO$_3$)$_3$•9H$_2$O and Fe$_2$(SO$_4$)$_3$•5H$_2$O, were used in the catalyst preparation. Iron catalysts were made by impregnating support materials in the Fe(NO$_3$)$_3$•9H$_2$O or Fe$_2$(SO$_4$)$_3$•5H$_2$O aqueous solution. For the Fe-Mo catalysts, suitable amount of (NH$_4$)$_6$Mo$_7$O$_{24}$•4H$_2$O was added in the solution. Two kinds of catalyst supports, MgO and Al$_2$O$_3$, were adopted. CNTs were synthesized by CVD in a horizontal tube furnace. The catalysts were positioned in the center of the furnace and then heated up to the reaction temperature under a argon flow. The reaction gas mixture was CH$_4$ and Ar with a flow ratio of CH$_4$/Ar = 4.

Characterization

The morphology of as-grown CNTs was observed by field-emission scanning electron microscopy (FE-SEM, LEO 1530). The oxidation behavior of as-grown CNTs was explored using a thermogravimetry analyzer (TGA, TA Instrument 5100). Data were obtained in flowing air using a heating rate of 5℃/min up to 900℃. The arrangement of graphene layers in the CNTs was characterized by the high resolution transmission electron microscopy (HRTEM, JEOL, JEM 2010).

Results and Discussion

Growth of CNTs using different catalyst supports and iron sources

Figure 1 shows the FE-SEM images of CNTs synthesized using different catalyst supports and iron sources. Figure 1(a) and (b) present the CNTs grown using MgO as the catalyst support and Figure 1(c) and (d) present the CNTs grown using Al$_2$O$_3$ as the catalyst support. As shown in Figure 1(a) and (b), the Fe/MgO catalysts were almost fully covered with entangled CNT bundles, forming a network-like layer. very small amount of amorphous carbon is observable. On the contrary, only small amount of CNTs were obtained when the Al$_2$O$_3$ support was used. For the Fe$_2$(SO$_4$)$_3$/MgO catalyst, the

yield of CNTs could be increased significantly by growing the compacted CNT bundles at a lower temperature of 800℃ (Figure 1(e)). As indicated in Figure 1(e), compacted CNT bundles of several micrometers in length, protruded out of the catalyst surface, could be observed.
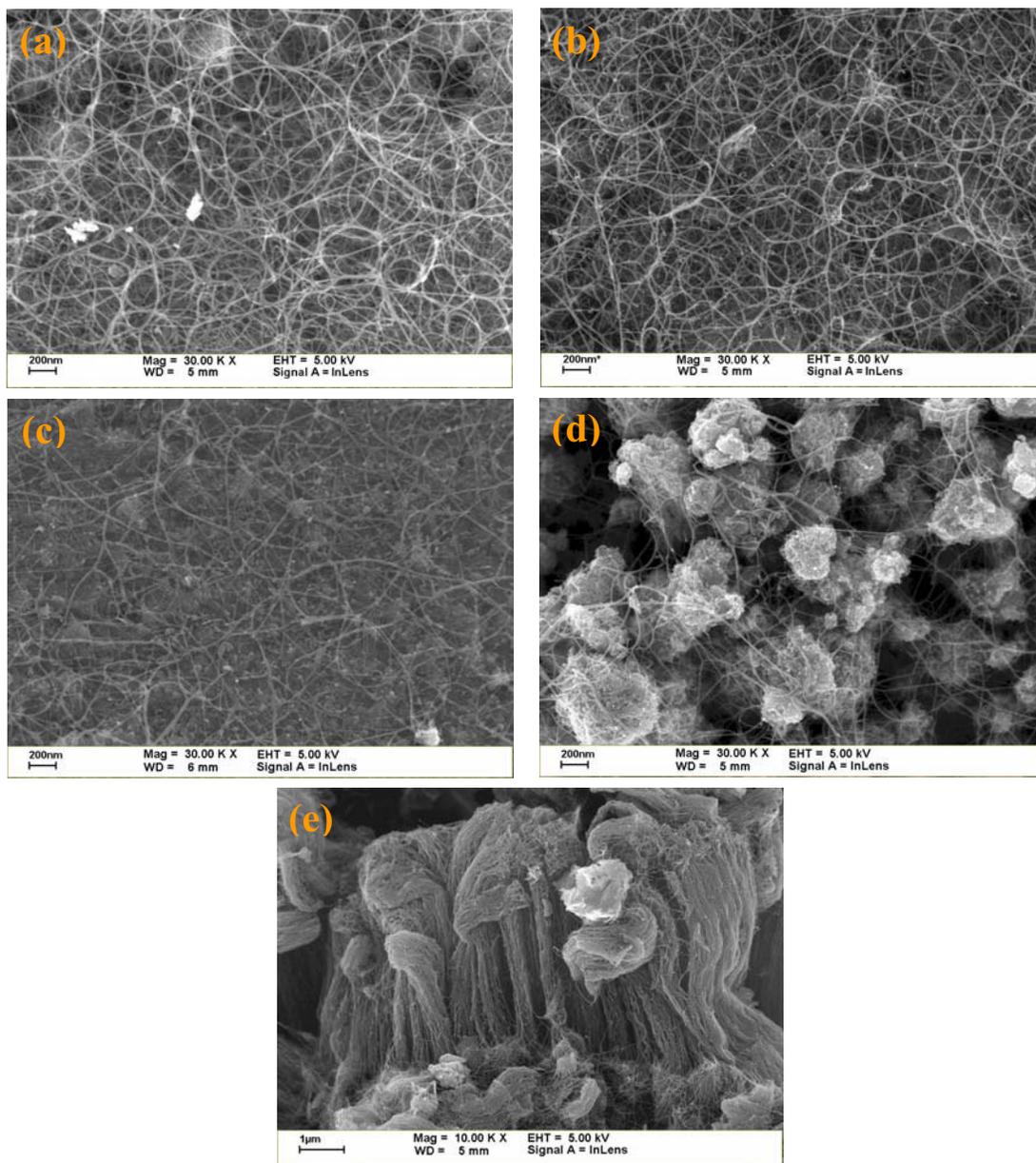

Figure 1. FE-SEM images of CNTs synthesized using different catalyst supports and iron sources: (a) $Fe(NO_3)_3$/MgO, 5wt%, 900℃, (b) $Fe_2(SO_4)_3$/MgO, 5wt%, 900℃, (c) $Fe(NO_3)_3$/Al_2O_3, 10 wt%, 950℃, (d) $Fe_2(SO_4)_3$/ Al_2O_3, 10wt%, 850℃ and (e) $Fe_2(SO_4)_3$/MgO, 5wt%, 800℃.

Comparison between the CNT growth using $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$ as the carbon sources showed that the growth temperature is lower when $Fe_2(SO_4)_3$ is used as the iron source. Addition of sulfur had been shown to increase significantly the yield of vapor-grown carbon fibers [Katsuki et al. 1981;Tibbetts et al. 1994] and also the CNTs recently [Cheng et al. 1998; Ci et al. 2002; Wei et al. 2004]. Tibbetts et al. [1994] pointed out that small amounts of sulfur in iron cause some liquefaction of the particle which increases the rate of filament nucleation. Due to the decrease of the melting point of iron particle when using $Fe_2(SO_4)_3$ as the carbon source, lower growth temperatures were observed for both $Fe_2(SO_4)_3$/MgO and $Fe_2(SO_4)_3$/Al_2O_3 catalysts.

Effect of Mo Addition

Figure 2 shows the FE-SEM images of CNTs synthesized using different catalyst supports and iron sources with the addition of Mo. As shown in Figure 2(a) and (b) for the MgO surpport, entangled network-like CNT bundles were also observed to cover the entire catalyst surface. Higher yield was measured according to the TGA results (Figure 3) when the Mo was added. For the Al_2O_3 support (Figure 2(c) and (d)), significant increase of growth yield was found for both the $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$ carbon sources. Above results indicate that the increase of CNT yield by the addition of Mo seems to be independent of the support materials. It is also noted that for the Al_2O_3 support the optimized growth temperatures were ~50℃ lower for both the $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$ carbon sources than those without Mo addition.
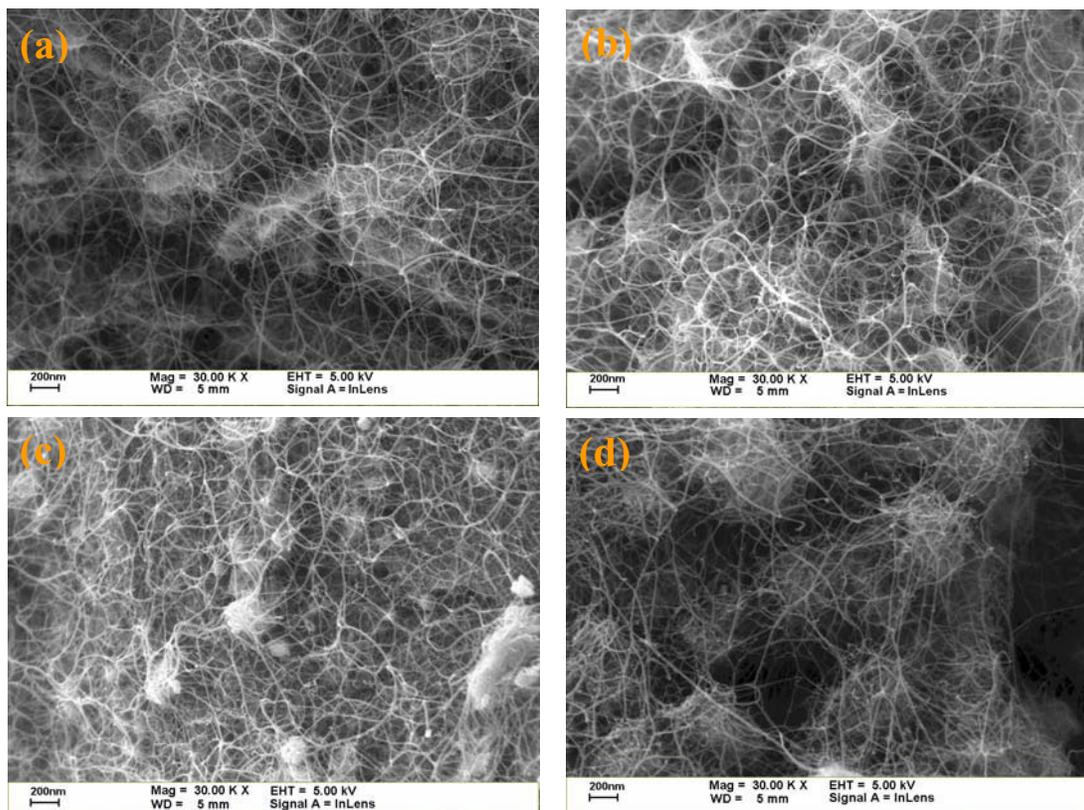

Figure 2. FE-SEM images of CNTs synthesized using different catalyst supports and iron sources with the addition of Mo: (a) $Fe(NO_3)_3$-Mo/MgO, 5wt%, Mo/Fe= 0.1, 900℃, (b) $Fe_2(SO_4)_3$-Mo/MgO, 5wt%, Mo/Fe= 0.1, 900℃, (c) $Fe(NO_3)_3$-Mo/Al_2O_3, 10 wt%, Mo/Fe= 0.5, 900℃ and (d) $Fe_2(SO_4)_3$-Mo/Al_2O_3, 10wt%, Mo/Fe= 0.1, 800℃.

Figure 3 shows the TGA-DTG results of as-grown CNTs synthesized using different Mo/Fe ratio in the $Fe(NO_3)_3$-Mo/MgO catalysts. In addition to the increase of carbon yield, the oxidation temperature was found to shift to the higher temperature as the Mo/Fe ratio was raised. It has been reported [Herrera and Resasco 2003; Li et al. 2004] that the oxidation sequence of the carbon phases is amorphous carbon, SWCNTs and MWCNTs in order of increasing temperature. Li et al. [2004] showed that amorphous carbon is oxidized below 450℃, SWCNTs are oxidized between 450 and 600℃ and MWCNTs between 600 and 700℃. As indicated by the TEM images (Figure 4(a)), most of the products are DWCNTs and the oxidation temperatures measured are in the range of 455~601℃, which are close to the reported values of SWCNTs. Although most of the products were DWCNTs, the probability of finding CNTs with the number of graphene sheet greater than two is higher when the Mo/Fe ratio was increased. This might contribute a little to the increase of the oxidation temperature. Further investigation is needed to elucidate the problem.

TEM Study

Figure 4 shows the TEM images CNTs synthesized using two catalysts, $Fe(NO_3)_3$-Mo/MgO and $Fe_2(SO_4)_3$-Mo/MgO, with different iron sources. As presented in Figure 4(a) and (b), most of the products were DWCNTs. Some CNTs with the number of graphene sheet greater than two, as indicated by the arrow sign in Figure 4(b), were also observed.
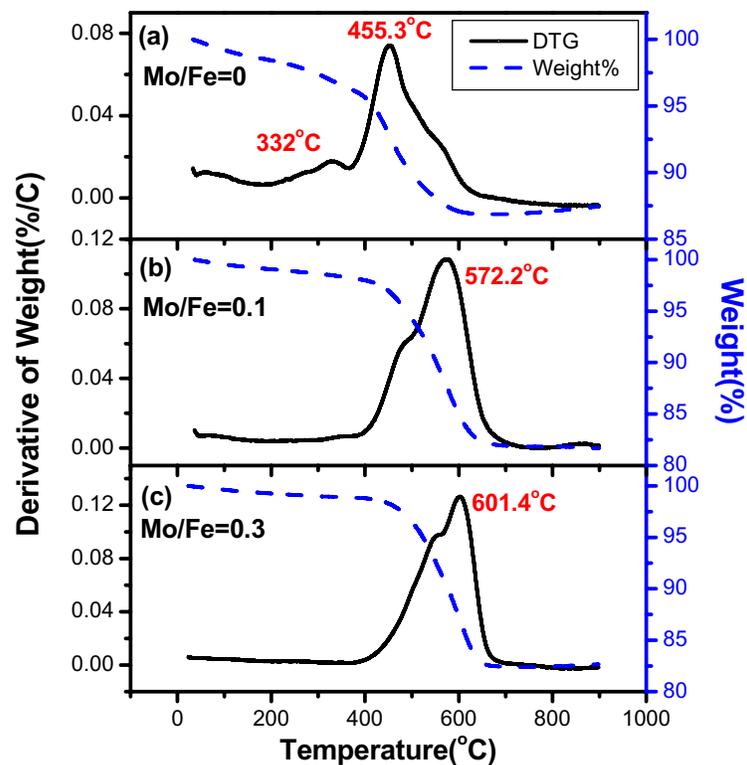
Figure 3. TGA-DTG analyses of as-grown CNTs synthesized using different Mo/Fe ratio in the Fe(NO$_3$)$_3$-Mo/MgO catalysts: (a) Mo/Fe= 0, (b) Mo/Fe= 0.1 and (c) Mo/Fe= 0.3.
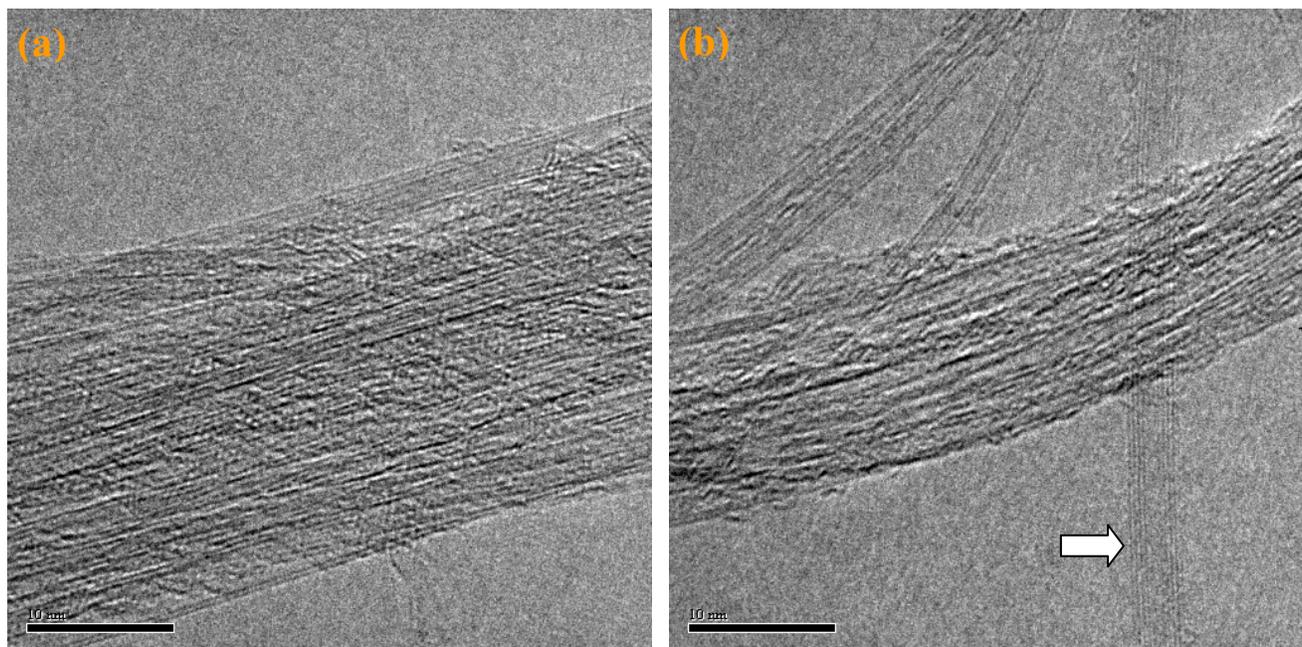

Figure 4. TEM images of CNTs synthesized using different catalysts: (a) Fe(NO$_3$)$_3$-Mo/MgO, 5wt%, Mo/Fe= 0.1, 900 ℃ and (b) Fe$_2$(SO$_4$)$_3$-Mo/MgO, 5wt%, Mo/Fe= 0.1, 900℃. Scale bar = 10 nm.

Conclusions

Two different iron sources, $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$, and two different catalyst supports, MgO and Al_2O_3, were used to prepare the Fe and Fe-Mo catalysts and their influences on the growth of CNTs by catalytic CVD were investigated. Experimental results indicate that addition of molybdenum favors the high yield of CNTs and that the growth temperature is lower when $Fe_2(SO_4)_3$ is used as the iron source. SEM observations show that large quantities of entangled CNT bundles with a layer network morphology can be synthesized and that very small amount of amorphous carbon is observable. Under optimum growth condition, compacted CNT bundles of several micrometers in length, protruded out of the catalyst surface, can be grown and the yield can be increased significantly. Most of the CNT products are double-walled CNTs by TEM observations.

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