

Growth Phenomena of Carbon Nanotubes Over Co-Mo/MgO Catalyst from the Decomposition of Acetylene

Md. Shajahan^a and A. K. M. Fazle Kibria^b

^aSchool of Chemical Engineering and Technology, Chonbuk National University, Chonju 561-756, Republic of Korea and ^bChemistry Division, Atomic Energy Centre, P. O. Box 164, Ramna, Dhaka-1000, Bangladesh

Abstract

Carbon nanotubes (CNTs) were grown over 12Mo:18Co:70MgO catalyst at 500, 700 and 900^o C from C₂H₂ decomposition for 30 minutes using chemical vapor deposition (CVD) method. The highest yield of CNTs was observed at 700^o C. The lowest diameter of CNTs appeared at 900^o C. Quadruple mass spectroscopy (QMS) study on the species generated from the catalytic decomposition of C₂H₂ identified that the catalyst consumed C species during the growth stage of CNTs. The consumption period of C varied with temperature and showed a close relationship with the carbon yield. At 500, 700 and 900^o C, the consumption periods were 12, 35 and 20 min, respectively, and the corresponding carbon yields were 7, 385 and 89 %. From the XRD analysis of catalyst surface, and XRD and Raman analysis of the CNTs, it was realized that Co particles released from Co₃O₄, CoMoO₄ and CoO-MgO were participated in CNTs growth at 500, 700 and 900^o C, respectively. The Co particles acted as the transporting medium of carbon to grow CNTs. The tubes are MWNTs and grown by tip growth mode.

Introduction

The demand of carbon nanotubes (CNTs) is going high because of their application possibilities as field emission displays (Saito *et al.* 2002, Yu *et al.* 2003), battery electrode (Frackowiak *et al.* 1999), capacitors (Chatterjee *et al.* 2003), hydrogen storage material (Ci *et al.* 2003), hydrogen evolution material (Prosini *et al.* 2003), etc. To fulfill this demand, it requires large-scale produc-

tion of CNTs. For large-scale production of CNTs, it is necessary to improve catalysts further with a better understanding of the role of catalysts and reactants during CNTs growth. In general, the species generated during the catalytic decomposition of hydrocarbon play an important role during the growth of CNTs (Otsuka *et al.* 2001, Lee *et al.* 2003).

Recently, Mo containing bimetallic supported catalysts such as Mo-Fe:Al₂O₃ and Co-Mo:SiO₂ are found effective in producing good amount of CNTs from CH₄, C₂H₄ and CO decomposition (Hafner *et al.* 1998, Herrera *et al.* 2001). However, reports on the reactive species generated during their decomposition and proof of their consumption during CNTs growth are rarely available. Support such as MgO can form solid solution with transition metals like Ni, Co and Fe whereas SiO₂ has no such a capability. So, it can be expected that the amount of exposed active metal on the catalyst surface and the size of metal particle should vary with changing the support. It seems essential to clear the role of MgO in exposing the metals on the catalyst in favor of CNTs growth and concurrently the roles of Mo and Co in producing CNTs.

Considering above importance, the present program has been taken to prepare a Co-Mo/MgO catalyst, and to investigate the capability of the catalyst in growing CNTs from decomposition of C₂H₂ at different temperatures. Attempt was taken to identify and measure the species produced during catalytic decomposition of acetylene to explore the species responsible for the growth of CNTs. The study also attempted to explore fundamentally the potential roles of Mo and Co in the catalyst for large-scale growth of CNTs.

Materials and Methods

A bimetallic supported catalyst of weight compositions 12Mo:18Co:70MgO was pre-

pared by impregnation method. To prepare the catalyst, alcoholic solutions of (NH₄)₆Mo₇O₂₄·4H₂O and Co(NO₃)₂·6H₂O salts were slowly mixed with support MgO powder and stirred at 70^o C to achieve a homogeneous mixture of metals and the support. The mixture was then dried at 100^o C for 12 h. The dry product was then calcined at 400^o C for 6 h in a box furnace and reduced in 100 sccm H₂ flow at 450^o C for 4 h under vacuum. To understand the surface condition of the catalyst, XRD study was carried out. Then the catalyst was subjected to synthesize CNTs.

Approximately 0.2 g of the catalyst was uniformly dispersed in an alumina boat and placed in the central region of a horizontal quartz tube reactor of diameter 6.5 cm and length 18 cm. There, the catalyst was activated at 500^o C for 1 h under 100 sccm H₂ flow and then the growth of CNTs was carried out. CNTs were grown at 500, 700 and 900^o C by flowing C₂H₂:H₂ mixture of 10:100 sccm for 30 min. Carbon yields were calculated using the procedure described earlier (Kibria *et al.* 2001).

The decomposition of C₂H₂ over the catalyst was investigated at 500, 700 and 900^o C using a quadruple mass spectrometer (QMS) directly connecting to the reactor. The species produced from C₂H₂ in the range of m/e value of 1 to 48 was scanned at 1s interval. Variation of partial pressure of C₂H₂ species and C species as a function of time was determined. The structure and morphol-

ogy of the grown CNTs were studied by scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD).

Results and Discussion

Figures 1(a)-(c) show the scanning electron microscopy (SEM) images of the CNTs grown over 12Mo:18Co:70MgO catalyst for 30 min at 500, 700 and 900°C, respectively. It can be seen that the highest density of tubes of average diameter 40 nm were grown at 700°C whereas the lowest density of tubes of average diameter 60 nm were grown at 500°C. The tubes grown at 900°C have diameter of about 20 nm. This finding informs that the diameter of tubes gradually decreased with increasing the growth temperature. Such a growth behavior of CNTs may appear due to the decrease in active metal crystallites size with increasing temperature. The size of metal crystallites is a crucial factor for the growth of CNTs (Kibria *et al.* 2001, Yudasaka *et al.* 1997).

At 500, 700 and 900°C, the observed carbon yields are 7, 385 and 89 %, respectively. It is notable that carbon yield was calculated using the formula: $[\text{Carbon yield (\%)} = \{(m_{\text{tot}} - m_{\text{cat}})/m_{\text{cat}}\} \times 100]$, where m_{cat} is the weight of the catalyst before CNTs growth and m_{tot} is the total weight of the catalyst and CNTs after the growth of CNTs (Kibria *et al.* 2001). It indicates that carbon yield (%) increased 55 folds with increasing temperature from 500 to 700°C and then decreased 4.3 folds with further increase in temperature 200°C.

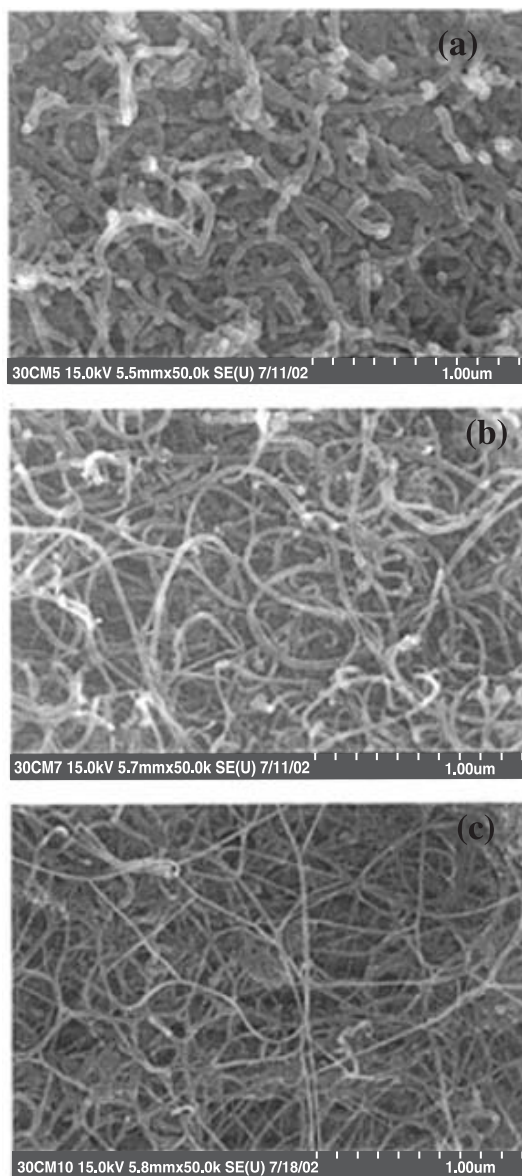


Fig. 1. SEM images of CNTs grown over 12Mo:18Co:70MgO catalyst for 30 minutes under 10/100 sccm $\text{C}_2\text{H}_2/\text{H}_2$ flow at (a) 500, (b) 700 and (c) 900°C

Figures 2(a)-(c) show the Raman spectra of the grown CNTs measured at the Ar^+ -laser excitation wavelength of 514.5 nm. It can be seen that three common peaks are appeared in the spectra at around 1345, 1572 and 2690 cm^{-1} , respectively. The first two peaks are associated with disordered carbonaceous products (Id) and tangential graphitized products (Ig), characteristic peaks for MWNTs (Kibria *et al.* 2001, Yudasaka *et al.* 1997). It can be seen that the Raman spectrum appeared for the CNTs grown at 500 $^{\circ}$ C shows two distinct peaks at around 330 and 942 cm^{-1} , respectively. The identification of these peaks and the reason of their appearance will be described later.

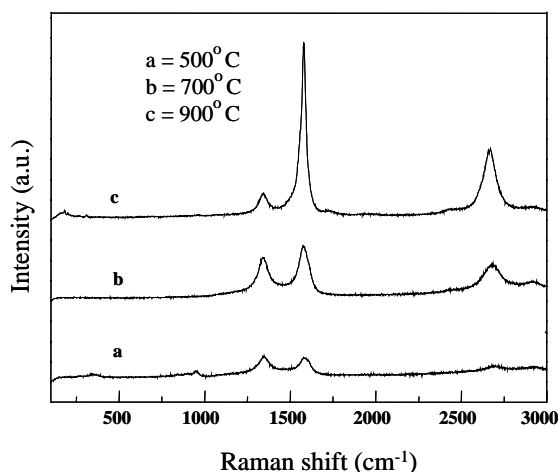


Fig. 2. Raman spectra for the CNTs grown over 12Mo:18Co:70MgO catalyst at (a) 500, (b) 700 and (c) 900 $^{\circ}$ C

Figures 3(a)-(c) show the QMS spectra for the species generated from C_2H_2 decomposition in H_2 atmosphere over the catalyst at

500, 700 and 900 $^{\circ}$ C. The normalized peak intensity is expressed in mole fraction. Mole fraction is calculated by dividing the partial pressure of each species by operating pressure of QMS. The operating pressure of QMS was 5×10^{-6} Torr. It can be seen that peaks related to the species C, CH, CH_4 , C_2 , C_2H , C_2H_2 , C_2H_3 , C_2H_4 and C_2H_5 are appeared at m/e values of 12, 13, 16, 24, 25, 26, 27, 28 and 29, respectively. It indicates that the used catalyst is capable to generate the required species C from C_2H_2 decomposition for the growth of CNTs at the experimental temperatures.

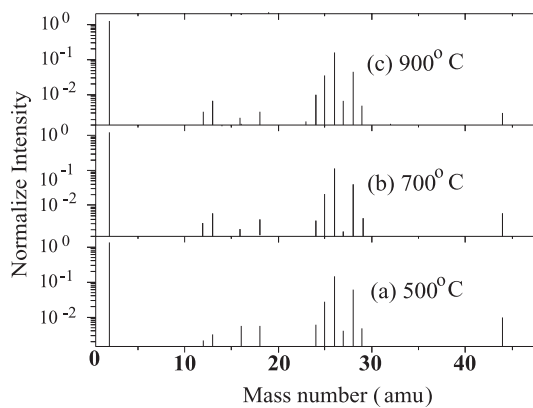


Fig. 3. Mass spectrum of the species formed during the decomposition of C_2H_2 over 12Mo:18Co:70MgO catalyst at (a) 500, (b) 700 and (c) 900 $^{\circ}$ C.

Figure 4 shows the variation of the partial pressure of C_2H_2 species as a function of time, with and without catalyst at 500, 700 and 900 $^{\circ}$ C, respectively. It can be seen that for the non-catalytic system, at a given

temperature, the equilibrium of partial pressure attains quickly and it is higher compared to that of catalytic system. For the catalytic system, the slow attainment of partial pressure equilibrium of C_2H_2 species and lower partial pressure compared to those of non-catalytic system are the consequence of the activity of catalyst in C_2H_2 decomposition, i.e., the decomposition of C_2H_2 occurred via the 12Mo:18Co:70MgO catalyst.

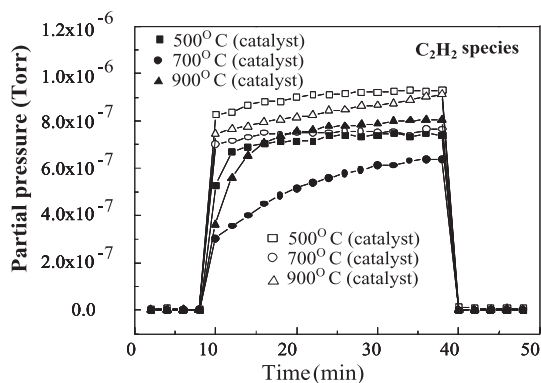


Fig. 4. Partial pressure vs. time plots for the C_2H_2 species with and without catalyst at (a) 500, (b) 700 and (c) 900 $^{\circ}$ C

Figure 5 shows the partial pressure vs. time trend for the C species in catalytic and non-catalytic conditions at different temperatures. It can be seen that the non-catalytic system attains quick equilibrium of partial pressure but for the catalytic system equilibriums seemed attain after 12, 35 and 20 min at 500, 700 and 900 $^{\circ}$ C, respectively. The consumption of C species up to the time of equilibrium attainment may be considered as the con-

sequence of carbon yield, i.e., the production of CNTs. It is notable that carbon yield 7, 385 and 89 % are observed at 500, 700 and 900 $^{\circ}$ C, respectively. On the other hand, longest equilibrium achieving time and the highest yield of CNTs at 700 $^{\circ}$ C may have a correlation with the abundance of the highest number of active particles to receive carbon fruitfully to grow CNTs.

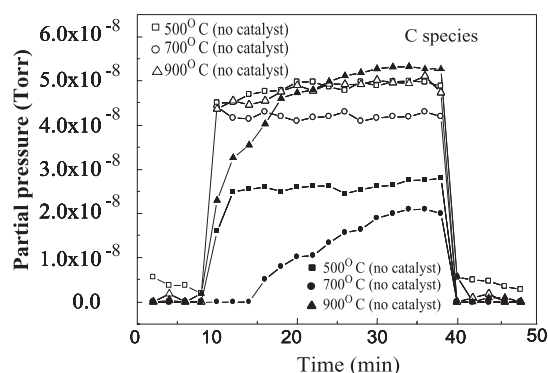


Fig. 5. Partial pressure vs. time plots for C species with and without catalyst at (a) 500, (b) 700 and (c) 900 $^{\circ}$ C

It has been reported that no tubes were grown over the 30Mo:70MgO catalyst. The catalyst 30Co:70MgO grown CNTs of 39% carbon yield (Kibria *et al.* 2004). This report indicates that on addition of Mo with Co, favorable sized active metal particles to grow CNTs were enormously exposed to the catalyst surface by a phenomenon at 700 $^{\circ}$ C during the growth stage. XRD analysis of the catalyst in different state and that of CNTs sample can be an informative of this phe-

nomenon. Considering it, XRD analyses of the catalyst and CNT samples were carried out.

Figure 6(a)-(d) shows the X-ray diffraction (XRD) patterns of the support MgO, raw, calcined and reduced catalysts. It can be seen that XRD patterns of the calcined and reduced catalysts are different from that of raw catalyst but analogous to that of MgO. It represents the appearance of CoO-MgO solid solution (Radwan *et al.* 2003, Ullah *et al.* 2001, Wang and Ruckenstein 2002). The decomposition temperature of this phase is above 800^o C. For the raw catalyst, various sharp peaks are appeared at 2 θ value of 18.6, 38, 51 and 58.8^o, respectively. Up to 2 θ value 40^o, four weak peaks are observed at 12.5, 28.8, 33.3 and 35.4^o, respectively. The peaks indicate the appearance of Co₃O₄, CoMoO₄, MoO₃ and Mg₂Mo₂O₇ (Radwan *et al.* 2003, Ullah *et al.* 2001, Wang and Ruckenstein 2002, Ning *et al.* 2002, Xiao *et al.* 2002). CoMoO₄ species decomposes at around 550^o C (Herrera *et al.* 2001). MoO₃ reduces at around 1000^o C (Radwan *et al.* 2003). So, no peak for Mo appeared at the XRD spectrum of the reduced catalyst. Although cobalt oxide reduces at 400^o C, it can partially consume by reacting with MoO₃ and resulting CoMoO₄ species ((Radwan *et al.* 2003). Moreover, very small amount of reducible Co₃O₄ species be appeared in Co/MgO catalyst up to 600^o C compared to unsupported Co₃O₄ (Ullah *et al.* 2001). It indicates that in the catalyst, the amount of reducible Co₃O₄ species was low.

The Co particles produced on reduction was small in size or in the form of cluster and highly dispersed over the catalyst surface. So, no diffraction peak for Co appeared in the spectrum of the reduced catalyst.

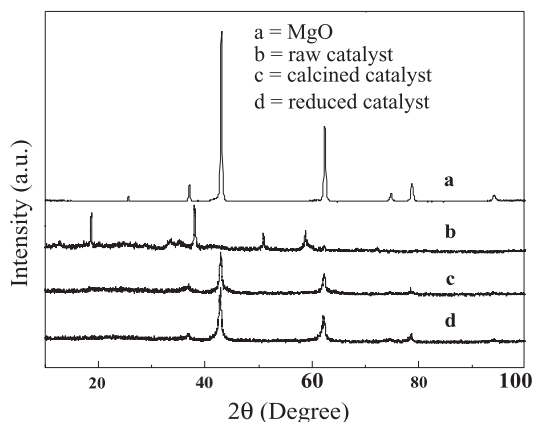


Fig. 6. XRD spectra of (a) support MgO, (b) raw catalyst, (c) oxide catalyst and (d) reduced 12Mo:18Co:70MgO catalyst.

Figure 7(a)-(d) shows the XRD spectra of the as-grown CNTs at 500, 700, 900^o C and the reduced catalyst, respectively. It can be seen that except for the CNTs grown at 500^o C, a peak appeared at 2 θ value of 26^o for the 002 graphite face of CNTs (Kibria *et al.* 2001). At 500^o C, the appearance of a hump peak at around 26^o informs the growth of poorly graphitized tubes at this temperature. The value ~ 1 of the ratio of the intensities, (I_d/I_g), of disordered carbonaceous product peak and tangential graphitized product peak obtained from Raman spectrum (Fig. 2) also informed the growth of poorly graphitized tubes at 500^o C. At 900^o C, the appearance of Mo₂C

peak at 39° and Co peak at 44.5° is suggesting the phase change of catalyst during the CNTs growth stage (Xiao *et al.* 2001).

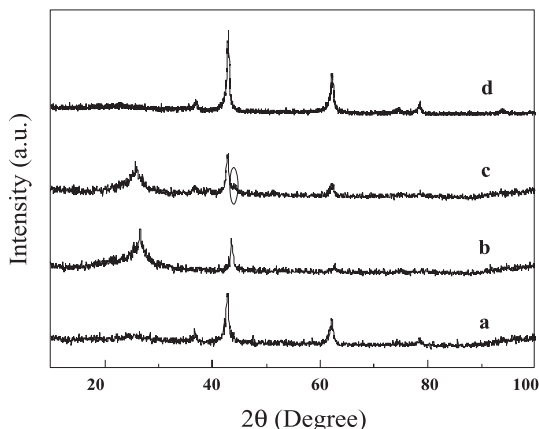


Fig. 7. XRD spectra of CNTs grown over 12Mo:18Co:70MgO catalyst at (a) 500, (b) 700 and (c) 900 $^\circ$ C and (d) reduced 12Mo:18Co:70MgO catalyst.

In the Raman spectrum for the CNTs grown at 500 $^\circ$ C, the peak appeared at 942 cm^{-1} (Fig. 2) represents the appearance of undecomposed CoMoO_4 species (Xiao *et al.* 2001). The absence of such a peak at higher than 500 $^\circ$ C, indicates that this phase was decomposed during the growth stage of CNTs. The cobalt oxide precursor released from the decomposition of this phase can easily be reduced to Co at 700 and 900 $^\circ$ C. In the Raman spectrum for the as-grown CNTs at 500 $^\circ$ C, the peak appeared at 330 cm^{-1} (Fig. 2) represents the appearance of MoO_3 . The disappearance of MoO_3 peak at other temperatures indicates that MoO_3 is rarely transforms to its carbide at 500 $^\circ$ C. This observation coincides with the findings of

others (Xiao *et al.* 2002).

In the present case, the highest carbon yield achieved at 700 $^\circ$ C which then decreased at 900 $^\circ$ C. The XRD spectrum of the as-grown CNTs samples showed a clear peak at 44.5 $^\circ$ for metallic Co at 900 $^\circ$ C, whereas such a peak was not appeared for the samples grown at the lower temperatures. It indicates that the size of Co particles increased after 700 $^\circ$ C. Particle size of Co increased by coalescence with the neighboring particles i.e., formation of agglomeration with increasing temperature. Authors (Wang and Ruckenstein, 2002) have reported a decrease in surface area of Co:MgO catalyst about 13 folds owing to coalescence of Co particles when the reduction temperature increased from 800 to 900 $^\circ$ C. In case of Co-Mo catalyst, the authors (Hada *et al.* 2002) observed more than 2.5 folds higher surface area while increasing temperature from 500 to 650 $^\circ$ C, but it then decreased about 4 folds owing to agglomeration of active metals on further increasing temperature to 800 $^\circ$ C. It can be speculated that the surface area of the catalyst increased at 700 $^\circ$ C and then decreased with increasing temperature. The decrease in surface area corresponds to the appearance of larger particles and decrease in CNTs growth because the active metal particle size is a decisive factor to grow CNTs (Yudasaka *et al.* 1997).

It is not clear at this moment how the narrowest diameter CNTs grown at 900 $^\circ$ C. It seems that these tubes were originated from

the active particles generated further in the catalyst at this temperature. It has been reported that the decomposition of CoO-MgO solid solution begins at above 800°C. The released cobalt oxide can easily be reduced to metallic Co at this temperature. With increasing temperature, the decomposition of solid-solution phase highly increases and complete decomposition of it occurs at above 1000°C (Wang and Ruckenstein, 2002). So, it can be speculated that in the present case, the CoO-MgO solid solution phase decomposed at 900°C. The appearance of higher peak intensities at 900°C compared to those of reduced catalyst (Fig. 7) can be taken as an informative of it. Authors (Wang and Ruckenstein, 2002) have reported that the decomposition of CoO-MgO solid solution and simultaneous reduction generates fine Co particles and Co clusters. These metallic Co and Co clusters seem responsible in growing narrowest diameter CNTs at 900°C.

On compiling the XRD, Raman and SEM information, it can be said that the Co particles contributing in CNTs growth were generated from Co_3O_4 , CoMoO_4 and CoO-MgO solid solution. The appearance of CNTs at 500°C indicates that the catalyst surface contained metallic cobalt in the form of cluster those were originated from Co_3O_4 . At this temperature, very low carbon yield, i.e., about 7 % indicates that the amount of Co cluster in the catalyst surface was very small (Ullah *et al.* 2001). It seems that at 700°C,

Co cluster, and Co crystallites originated from CoMoO_4 phase were participated in CNTs growth. At 900°C, mostly the Co crystallites and clusters originated from CoO-MgO solid solution grown CNTs.

In the present case, the grown tubes are MWNTs. In a close look on the SEM images (Fig. 1), it can be seen that each tube ended by showing a white spot. These white spots originated from metal (Kibria *et al.* 2001). It indicates that CNTs were grown by tip growth mode. It means that the necessary carbon feed stock supplied from the catalytic decomposition of acetylene dissolved in metallic Co to form cobalt carbide eutectic, i.e., metastable cobalt carbide. This cobalt carbide eutectic on dissolving more carbon became oversaturated which then precipitated graphitic carbon in forms of tubes by keeping metallic cobalt cluster at the top end of the CNTs.

Conclusions

MWNTs were grown over 12Mo:18Co:70MgO catalyst from the decomposition of C_2H_2 . It was observed that growth density and diameter of CNTs are highly dependent on the growth temperature. Catalyst particle size controlled the CNTs growth. Quadruple mass spectroscopy (QMS) study identified that carbon species consumed during CNTs growth, and the consumption period of carbon varied with temperature. Carbon yield increased with increasing carbon consumption period. The Co particles participating in

CNTs growth seemed originated from three precursors as Co_3O_4 , CoMoO_4 species and CoO-MgO solid solution. The Co particles worked as the transporting medium of carbon to grow CNTs.

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