

Synthesis and Characterization of Carbon Nanotubes Catalyzed by TiO₂ Supported Ni, Co and Ni-Co Nanoparticles via CCVD

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Abstract

Monometallic and bimetallic Ni and Co catalytic nanoparticles supported on Titanium dioxide (rutile phase) substrate were prepared by wet impregnation method. These nanoparticles were used as catalysts for synthesis of multiwalled carbon nanotubes (MWCNTs) from acetylene decomposition at 700°C by the catalytic chemical vapor deposition (CCVD) technique. The nanomaterials (catalyst and CNTs) were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Raman spectroscopy. In this paper, the usage of TiO₂ powder as catalyst support was examined and the effect of applied catalyst type on characteristics of grown CNTs was investigated. The results showed that the rutile phase of TiO₂ powder can be applied as a suitable catalyst support in CNT growth process. Furthermore, it was observed that the CNTs synthesized on Ni-Co bimetallic catalyst possess smaller average diameters, better quality and less amorphous carbon compared to Ni and Co monometallic catalyst types.

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1. Introduction

Carbon nanotube (CNT), as a fascinating one dimensional nanostructure material, has been attracting intensive theoretical and experimental interests in past two decades, due to its unique structural, mechanical, optical and electrical properties [1]. Since their first discovery in 1991 [2], research in the field of CNTs has grown exponentially. There are three principal methods in producing CNTs: Laser ablation, Arc discharge

and Catalytic chemical vapor deposition (CCVD) [3]. Among these, CCVD method has been more developed because of its advantages such as large-scale production of high quality CNTs, lower growth temperature, higher yield, lower cost and its benefits for semiconductor industries [4,5].

Usage of mesoporous substrates such as SiO₂ [6], Al₂O₃ [7], and zeolites [8] was widely reported and has revealed that these materials provide excellent substrates for the CCVD growth

of CNT. Currently, there are few reports which have utilized TiO_2 as substrate [9]. Here we examine the possibility of usage of this material as catalyst support in CNT growth process.

On the other hand, the most effective catalysts for chemical vapour deposition (CVD) growth of CNTs are transition metals from periodic table of elements, including Fe, Co, Ni and Mo [10]. The peculiar ability of these metals to promote the CNT growth is related to their catalytic activity for decomposition of the carbon feedstock (typically a hydrocarbon), the formation of metastable carbides, the carbon diffusion and the formation of graphitic sheets [11,12].

Previously, our group showed that using Ni-Co bimetallic catalyst supported over MgO substrate increases the CNTs growth yield and decreases the impurities of the end products compared to Ni and Co individual catalysts [13]. In this regard, Zare et al. investigated the effect of Ni and Co catalysts on growth of aligned CNTs by thermal chemical vapour deposition (TCVD). They found that compared to Ni catalyst, the CNTs originated from Co particles have lower densities and larger diameter, indicating that choose of catalyst element has an important role on the CNTs density, morphology and size of diameter [14]. In addition Chai et al. have studied the roles of metal oxides (CoO_x and NiO) and catalyst supports (alumina and silica) as well as the effect of synthesis temperature on the morphology and the yield of produced CNTs via CCVD of methane [15].

In this paper, we experimentally examine the effect of applying monometallic and bimetallic Ni and Co particles supported on rutile phase of TiO_2 for CNTs synthesis by thermal decomposition of acetylene via CCVD method.

2. Experimental procedure

The catalysts were prepared by wet impregnation method. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (supplied by Aldrich) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (supplied by Aldrich) salts were used as the source of Ni and Co particles to produce monometallic and bimetallic catalytic combinations. Metal nitrates were dissolved in distilled water separately and impregnated onto distilled water solution of rutile phase of TiO_2 powder (supplied by Merck) with concentration ratio of 20/80 wt% (monometallic type) and 10-10/80 wt% (bimetallic type) for catalyst/substrate, respectively. Then the mixture was executed under ultrasonic reflux, subsequently dried on a hot plate and calcinated in an oven at 500°C for 2 hours. At this stage, the nanostructure catalytic base was prepared.

The synthesis of carbon nanotubes was carried out by a TCVD system at atmospheric pressure in a horizontal tubular quartz reactor (length and diameter are 1200 mm and 50 mm, respectively) from thermal decomposition of acetylene. The precursor gas composed of acetylene and argon ($\text{C}_2\text{H}_2/\text{Ar} = 15/150$ Sccm) flows over the catalyst at 700°C for 15 minutes. For each run, 50 mg of the catalytic powder (uniformly distributed on a quartz boat) was loaded into the reactor. After CNTs synthesis, the reactor was cooled down to room temperature under argon atmosphere. Then the boat was removed from the reactor and the product (carbon deposit) formed along with the catalyst, was weighed and characterized.

The obtained carbon deposit and the catalytic powder were characterized by Scanning electron microscopy (SEM, Hitachi S4160), X-ray diffraction analysis (XRD, Bruker AXS, D8-Advance, $\text{Cu-K}\alpha$, $\lambda = 1.54 \text{ \AA}$) and Raman spectroscopy (Thermo Nicolet Almega Dispersive Micro-Raman Spectrometer, $\lambda = 532\text{nm}$).

3. Results and discussion

In order to determine the crystal structure of monometallic and bimetallic Ni and Co combination supported on rutile phase of TiO₂ substrate and estimation of catalytic nanoparticle sizes, the catalysts were characterized by XRD technique.

Fig. 1 shows the XRD patterns of the three catalyst samples. It shows the representative peaks of NiO, Co₃O₄ and rutile phase of TiO₂ substrate with different signs. As we expected, in each catalyst sample, the most intensive peaks correspond to TiO₂ crystal plates. The presence of Nickel oxide and Cobalt oxide representative peaks in the XRD diagram of catalyst samples indicates that the chemical reactions in wet impregnation process have proceeded successfully to synthesize metal oxide catalyst particles from initial metal salt materials.

Regarding to Fig. 1, diffraction peaks of each XRD pattern correspond to diffraction from different crystal plates, for example the peaks seen at $2\theta = 43.3$ in Fig. 1(b) and $2\theta = 36.9$ in Fig. 1(c) correspond to diffraction from [200] and [311] crystal plates, respectively. Also, diffraction peaks seen at $2\theta = 62.9$ and 36.9 in Fig. 1(a), can be assigned to diffraction from [220] and [311] crystal plates, respectively for Nickel oxide and Cobalt oxide nanoparticles formed on bimetallic Ni-Co/TiO₂ catalyst [16, 17]. The XRD analysis revealed that the resultant nanoparticles were Ni and Co nanoparticles with a cubic structure. The approximate sizes of crystallites were calculated using Debye-Scherrer equation, which is given by:

$$D = k \lambda / \beta \cos\theta \quad (1)$$

Where D is the crystallite size, k is the shape factor (0.89), λ is the X-ray wavelength (1.54 Å), β is the

peak broadening at half maximum and θ is the diffraction angle.

The approximate sizes of Ni and Co nanoparticles formed on bimetallic Ni-Co/TiO₂ catalyst are 20.1 nm and 15.9 nm, respectively. Also, the approximate sizes of Ni nanoparticles formed on monometallic Ni/TiO₂ catalyst sample and Co nanoparticles formed on Co/TiO₂ catalyst type are 29.6 nm and 29.5 nm, respectively.

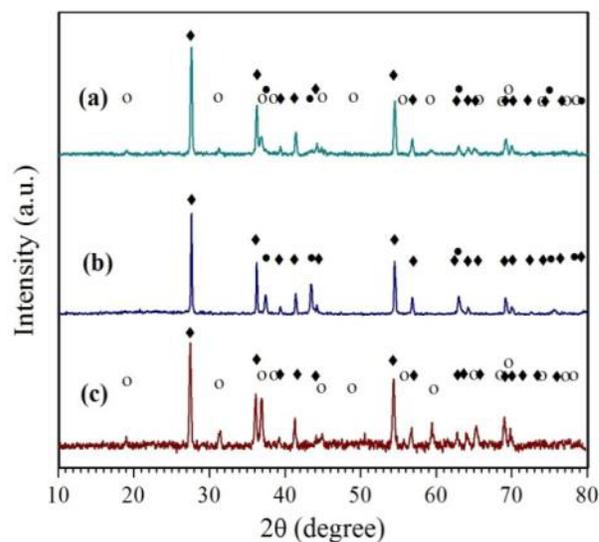


Fig. 1. XRD patterns of (a) Ni-Co/TiO₂; (b) Ni/TiO₂; and (c) Co/ TiO₂ catalyst samples. (●) NiO; (○) Co₃O₄; and (◆) TiO₂-rutile.

It means that at the same laboratory conditions smaller Ni and Co nanoparticles on bimetallic catalyst sample were produced compared to monometallic ones, which can be due to better dispersion of the Ni and Co particles over titanium dioxide matrix in bimetallic catalyst type.

The percentage of carbon yield and average growth rate of the carbon deposit were calculated according to the following equations [15, 18] and shown in Table 1:

$$\text{Carbon yield (\%)} = \frac{M_{\text{Total}} - M_{\text{Ca}}}{M_{\text{Ca}}} \times 100 \quad (2)$$

$$\text{Average growth rate} = \frac{M_{\text{Total}} - M_{\text{Cat}}}{\text{growth time}} \quad (3)$$

Where M_{Total} is the total mass of final product catalyst + carbon deposit and M_{Cat} is the initial mass of catalyst.

As shown in Table 1, Co/TiO₂ monometallic catalyst has the maximum carbon yield and maximum average growth rate of the carbon product among these three catalyst samples, thus Co/TiO₂ show better catalytic activity compared to the two other catalyst types.

Table 1. The carbon yield percentage and average growth rate of carbon deposit over the three types of catalysts.

Catalyst type	Carbon yield	Average Growth rate(mg/min)
Ni-Co/TiO ₂	120%	4
Ni/TiO ₂	40%	1.33
Co/TiO ₂	220%	7.33

Fig. 2 and 3 show the SEM images and diameter distribution diagrams of synthesized CNTs. It is clear that successful growth of CNTs on all three types of catalysts were obtained. It confirms that the transition metals Ni and Co have suitable catalytic activity over TiO₂ substrate indicating that the rutile phase of TiO₂ powder can be applied as an appropriate catalyst support in the CVD process of CNT production.

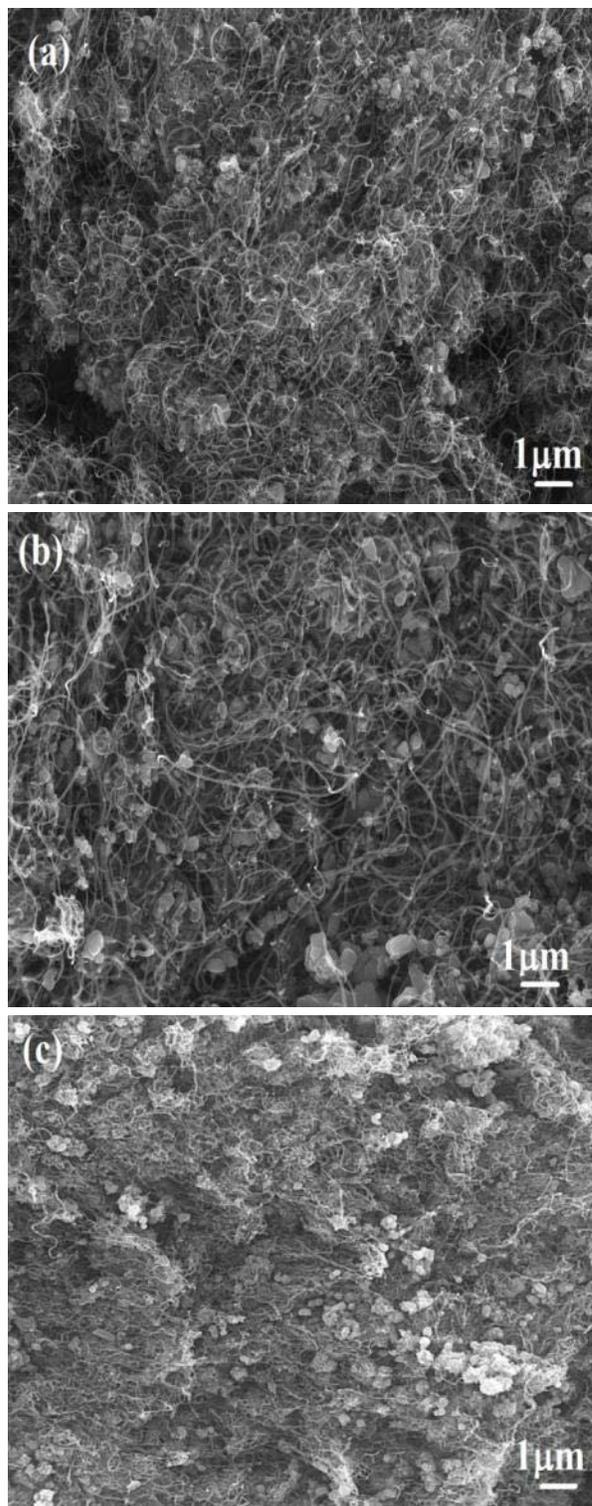


Fig. 2. SEM images of CNTs produced on (a) Ni-Co/TiO₂; (b) Ni/TiO₂; and (c) Co/TiO₂ catalysts.

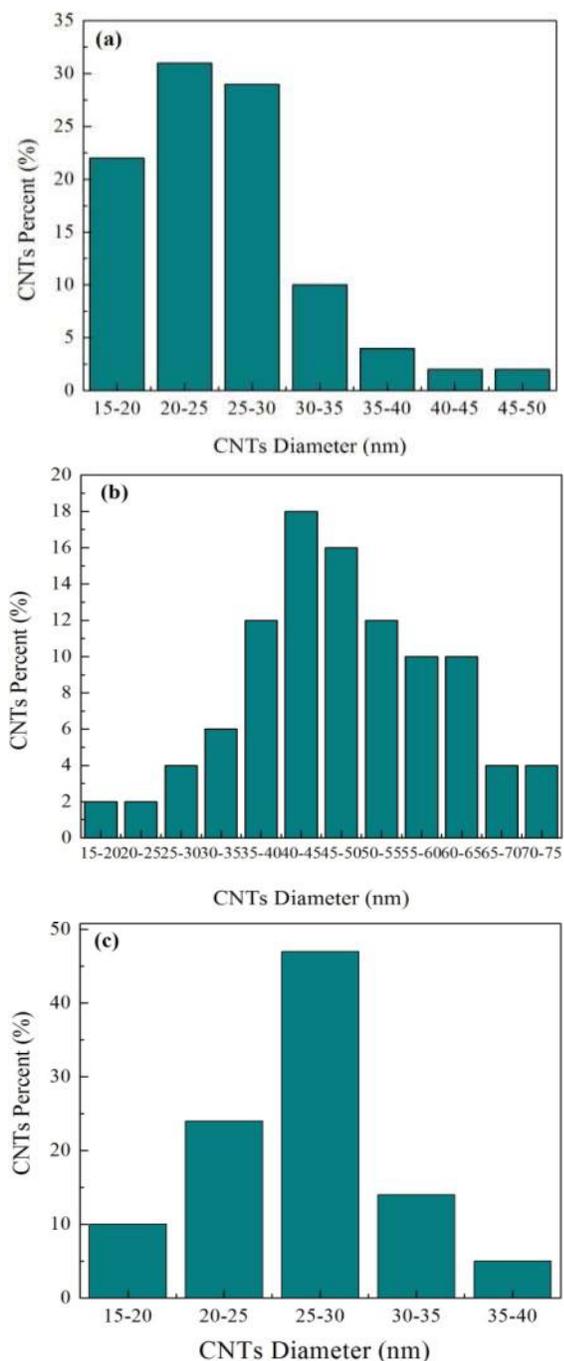


Fig. 3. Diameter distribution diagrams corresponding to SEM images of CNTs produced on (a) Ni-Co/TiO₂; (b) Ni/TiO₂; and (c) Co/TiO₂ catalysts.

According to distribution diagrams the average diameters of grown CNTs on monometallic Ni/TiO₂ and Co/TiO₂ and bimetallic Ni-Co/TiO₂ catalyst samples are 48, 27 and 25 nm,

respectively. Thus, the CNTs originated from the bimetallic Ni-Co/TiO₂ catalyst possess smaller average diameters, more homogeneous distribution and less amorphous carbon compared to Ni and Co monometallic catalyst types.

It is reported that Ni nanoparticles can easily congregate to form larger particles, thus formation of CNTs with maximum average diameter over Ni/TiO₂ catalyst sample is expected [19]. On the other hand, the grown CNTs over Co/TiO₂ catalyst sample have denser structure and higher carbon yield.

It can be concluded that in comparison with using Ni nanoparticles lonely (Ni/TiO₂ sample), adding Co nanoparticles to the catalyst composition (Ni-Co/TiO₂ sample) caused to increasing carbon yield and decreasing average diameter of synthesized CNTs. Moreover, these observations are in agreement with our previous results of XRD analysis that indicates the sizes of Ni and Co nanoparticles formed on bimetallic Ni-Co/TiO₂ catalyst is smaller than of the nanoparticles obtained on monometallic catalyst samples.

There are two general growth modes of nanotubes in CVD: “base-growth” and “tip-growth” modes. The interaction between metal catalyst particle and substrate is an important factor that influences the nanotube growth mode. The strong interaction between the catalyst particle and the substrate material results in the failure of catalyst particle separation from the substrate, caused to the formation of nanotubes by “base-growth” mode. In contrast, when the metal-substrate interaction is weak, the nanotube grows while carrying away a catalyst particle at the top by “tip-growth” mode [1, 2].

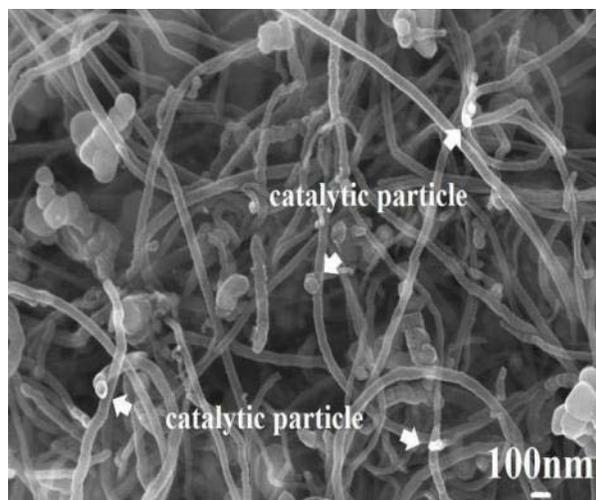


Fig. 4. High magnification SEM image of the CNTs produced on Ni/TiO₂ catalyst sample. White arrows represent catalytic particles stuck to the ends of CNTs.

Fig. 4. shows a high magnification SEM image of multiwalled CNTs (MWCNTs) originated from the Ni/TiO₂ catalyst sample. The white arrows in this figure represent the presence of some catalytic particles at the tips of the CNTs, which propose that the growth mode of the grown CNTs is “tip-growth” [15, 20].

In order to understand the structure and crystallinity of the grown CNTs, Raman spectroscopy was executed. Fig.5 represents the Raman spectra of the grown CNTs over the three catalyst samples. The Raman band appearing in 1500-1605 cm⁻¹ region of the wave number is attributed to G band (graphite band) and the one appearing in 1250-1450 cm⁻¹ spectral region is known as D band (disorder-induced band). The G band is assigned to C-C vibration frequency of the carbon material with a sp² orbital structure and the D band contributed to disorder-induced vibration of C-C band [21].

According to Fig. 5, two peaks corresponding to the D and G bands of MWCNTs were appeared in each spectrum. The intensity ratio of G band to D one, I_G/I_D is known as a rough measure for the

quality of produced CNTs [22]. This ratio for the carbon deposit obtained from the three catalyst samples are calculated and shown in Table 2.

Table 2. Intensity ratio of G band to D band of the carbon deposits over the three types of catalysts.

Catalyst types	I _G /I _D
Ni-Co/TiO ₂	0.826
Ni/TiO ₂	0.816
Co/TiO ₂	0.801

According to this table the CNTs produced on bimetallic Ni-Co/TiO₂ catalyst have better quality compared to Ni and Co monometallic catalyst samples that may be due to smaller sizes of catalytic particles over Ni-Co/TiO₂. It should be noted that increasing catalytic particle sizes can increase the possibility of creating carbon structures with defective crystalline discipline or amorphous carbon.

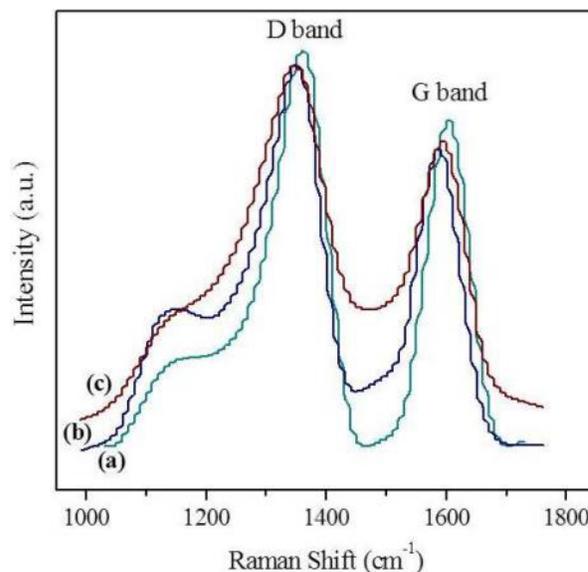


Fig. 5. Raman spectra of CNTs produced on (a) Ni-Co/TiO₂; (b) Ni/TiO₂; and (c) Co/TiO₂ catalyst samples.

4. Conclusion

MWCNTs were synthesized from acetylene decomposition at 700°C and atmospheric pressure

by CCVD over TiO₂ supported monometallic and bimetallic Ni and Co catalytic particles, prepared by wet impregnation method. The successful growth of nanotubes showed that TiO₂ powder can be applied as a suitable substrate for catalytic particles in CVD growth of CNTs.

It was observed that the produced CNTs over bimetallic Ni-Co/TiO₂ catalyst possess smaller average diameters, better quality, less amorphous carbon and denser morphology compared to monometallic Ni/TiO₂ and Co/TiO₂ catalyst samples. This may be due to better distribution and smaller sizes of catalytic particles over Ni-Co/TiO₂ catalyst type. On the other hand, the monometallic Co/TiO₂ catalyst has the most catalytic activity among these three catalyst samples.

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