



Evaluation of the Effect of Ni-Co NPs for the Effective Growth of Carbon Nanotubes by TCVD System

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Abstract

A systematic study was conducted to understand the influences of catalyst combination as Ni-Co NPs on carbon nanotubes (CNTs) grown by Chemical Vapor Deposition (TCVD). The DC-sputtering system was used to prepare Co and Ni-Co thin films on silicon substrate. Ni-Co nanoparticles were used as metal catalyst for growing carbon nanotubes from acetylene (C₂H₂) gas in 850° C during 15 min. Carbon nanotubes grown on Co and Ni-Co deposited on Si substrates was characterized by Field Emission Scanning Electron Microscopy (FESEM) and Raman spectroscopy. Energy Dispersive X-ray (EDX) measurements were used to investigate the elemental composition of the nickel and cobalt nanocatalysts deposited on Si substrates. Atomic Force Microscopy (AFM) was used to characterize the surface morphology of the nanocatalysts. It was found that by the addition of Ni NPs thin layer on Si substrate for Co NPs catalyst, density of the grown CNTs is much decreased in comparison to Co NPs on Si substrate.

Keywords: Carbon nanotubes, Ni-Co NPs, Nanocatalyst, Thermal Chemical Vapor Deposition (TCVD).

Introduction

For approximately twenty years, since the discovery of carbon nanotubes (CNTs), they have been investigated for their potential nanotechnology applications. These hollow

structures are lightweight, have varying electrical and optical properties and great applications in the fields of medicine and biology which are notably powerful than all structural material used today. However, the

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progress of CNTs is a great disadvantage in the application of carbon nanotubes in current technologies. Systematic and cost effective growth techniques are the key to mass production of carbon nanotubes [1-5]. On the prospects of achieving this purpose, researchers across the world are working to realize and control the methods of CNT growth.

Four fundamental parameters affect CNT growth in a chemical vapor deposition (CVD) technique: temperature, pressure, gases and the interaction between metal and support [6]. The catalyst particles necessarily act as an origin for the growth of the CNT. The key challenge in CNT growth is mass production with low cost [7]. The capability of those catalysts was related to its catalytic activity for the decomposition and diffusion of hydrocarbon precursor on the active site, the shaping of C-hexagon as well as the catalyst deactivation and the formation of meta-stable carbides [8, 9]. The catalyst itself can be used either separately or combined together to form bi or tri-catalyst combination [10]. Each single catalyst has its own character, a cooperative effect was expected when the catalyst were combined. The metal particle catalyzes the dissociation of the gas, allows carbon parts to diffuse on the surface and/or in the bulk of the particle, and supports the nucleation and growth of the nanotube.

Transition metals, such as Fe, Ni, and Co, due

to their high carbon solubilities are common catalysts for carbon nanotube growth [11, 12]. Previous experimental [13–15] and theoretical [16] studies have shown that the diameter or number of walls in the as-grown carbon nanotubes can be controlled by the catalyst size. By decreasing the particle size, fewer walled tubes produce. Also, smaller particle size causes the amount of carbon reduces that precipitates and allows preferential nucleation of SWCNTs [17]. Bimetallic catalysts have been shown to grow chirally-enriched SWCNTs which is important to their application in nanoelectronics [18–21], as well as other technological fields [20].

The chemical vapor deposition (CVD) provides a dependable process to grow carbon nanotubes on different substrates and is acceptable for scaled growth of high purity multi-walled and single-walled CNTs. Moreover, CVD works at essentially lower temperatures than that in laser ablation and arc discharge methods [22].

There are two usual growth modes of nanotubes in CVD: “base-growth” and “tip growth” modes. The interaction between metal catalyst NPs and substrate is an important factor that influences the nanotube growth mode. The strong interaction between the catalyst NPs and the substrate material results in the failure of catalyst NPs separation from the substrate, lead to the formation of nanotubes by “base growth” mode. In opposition, when the metal

substrate interaction is weak, the nanotube grows while carrying away a catalyst NPs at the top by “tip-growth” mode [23].

Here, we indicate that the mixture of bimetallic catalysts influences CNTs density. After collecting the as-grown carbonaceous product and characterizing of CNTs, we find that the density of CNTs is highest for pure Co catalyst.

Experimental

In the present investigation, p-type Si (400) wafers with the size of $1\text{cm} \times 1\text{cm}$ were used as substrates. The wafers were cleaned by ultrasonic method in acetone and ethanol solutions to remove potential residual contaminants prior to deposition. The samples were introduced into the planar DC-sputtering system and then pumped down to a base

pressure of 4×10^{-1} Pa. A cobalt plate was used as a cathode and was placed in parallel with the oven which was grounded. The distance between the cathode and anode was about 1 cm (Fig. 1). Argon was introduced into the chamber with a flow of 200 Standard Centimeter Cubic per Minutes (sccm). The cobalt nanocatalysts were sputtered on Si substrates when the substrate temperature gradually increased up to 100°C . Deposition time for cobalt sputtering was 20 minutes. In the next step, by the same method which mentioned above, the nickel nanocatalysts were sputtered on Si substrates in 20 minutes and again, cobalt nanoparticles were deposited on the nickel thin layer film during 20 minutes and so the Ni-Co NPs were formed on Si substrates.

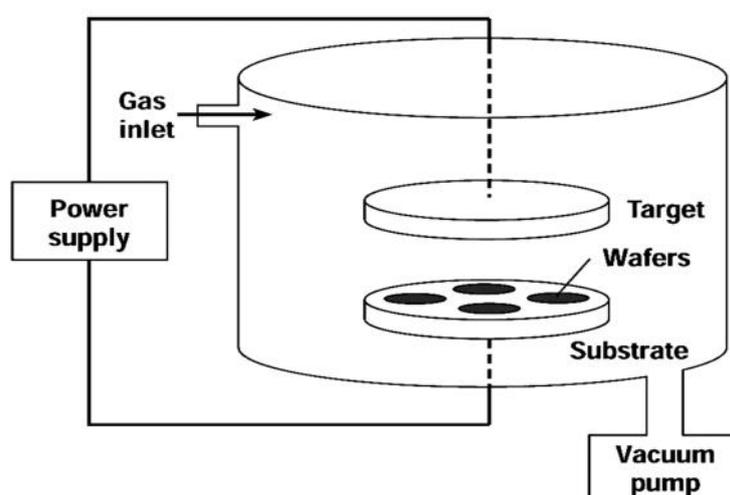


Figure 1. Schematic diagram of DC-sputtering system.

The Thermal Chemical Vapor Deposition (TCVD) system in the experiment (Figure 2) was an electric furnace composed of a horizontal quartz glass tube with an internal diameter of 7.5cm and a length of 80cm which was operated at atmospheric pressure.

Argon gas with a flow rate of 200 sccm was supplied into the CVD reactor to prevent the oxidation of catalytic metal while raising

the temperature to 750°C. The samples were placed in the chamber and the temperature increased to 850°C. After that, Ar flow was switched off. For CNT growth, we used C_2H_2 / NH_3 at 35 / 60 sccm for 15 minutes. The growth was terminated by turning off C_2H_2 / NH_3 flow and the samples were allowed to cool down to room temperature under Ar gas flow.

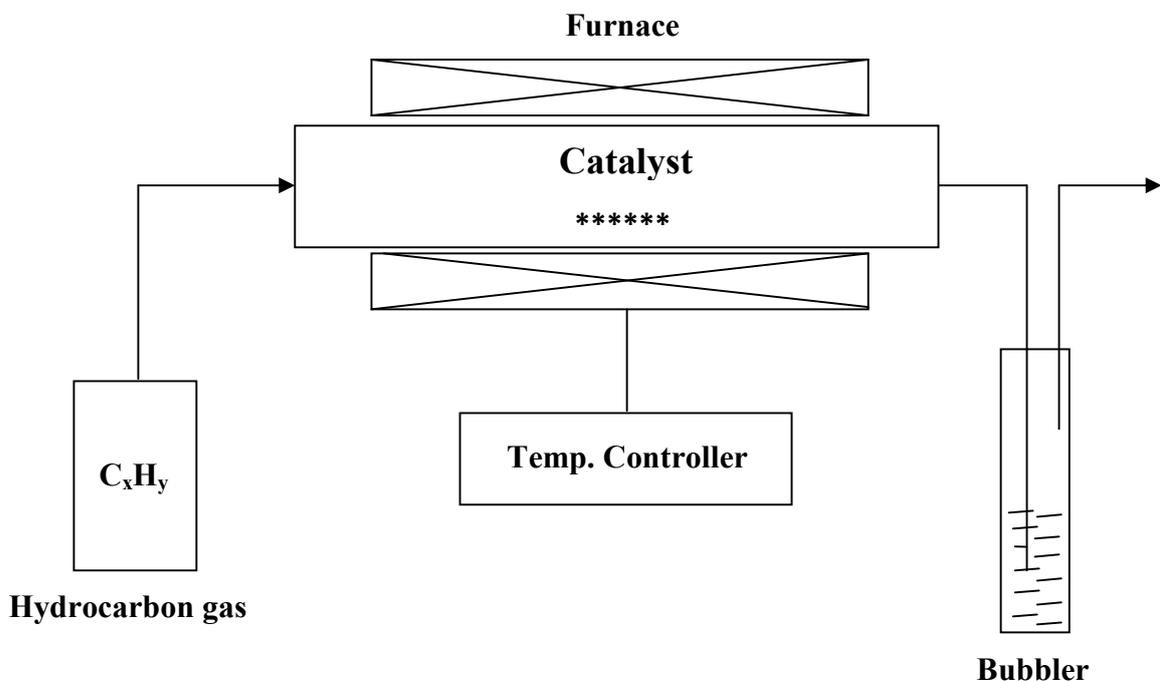


Figure 2. Schematic diagram of TCVD system of nanotube synthesis.

Results and discussion

In this work, all the growth conditions except of the catalyst type were kept constant. Energy Dispersive X-ray (EDX) measurements were

done to investigate the elemental composition of the Co (Figure 3a) and Ni - Co (Figure 3b) catalysts deposited on Si substrates.

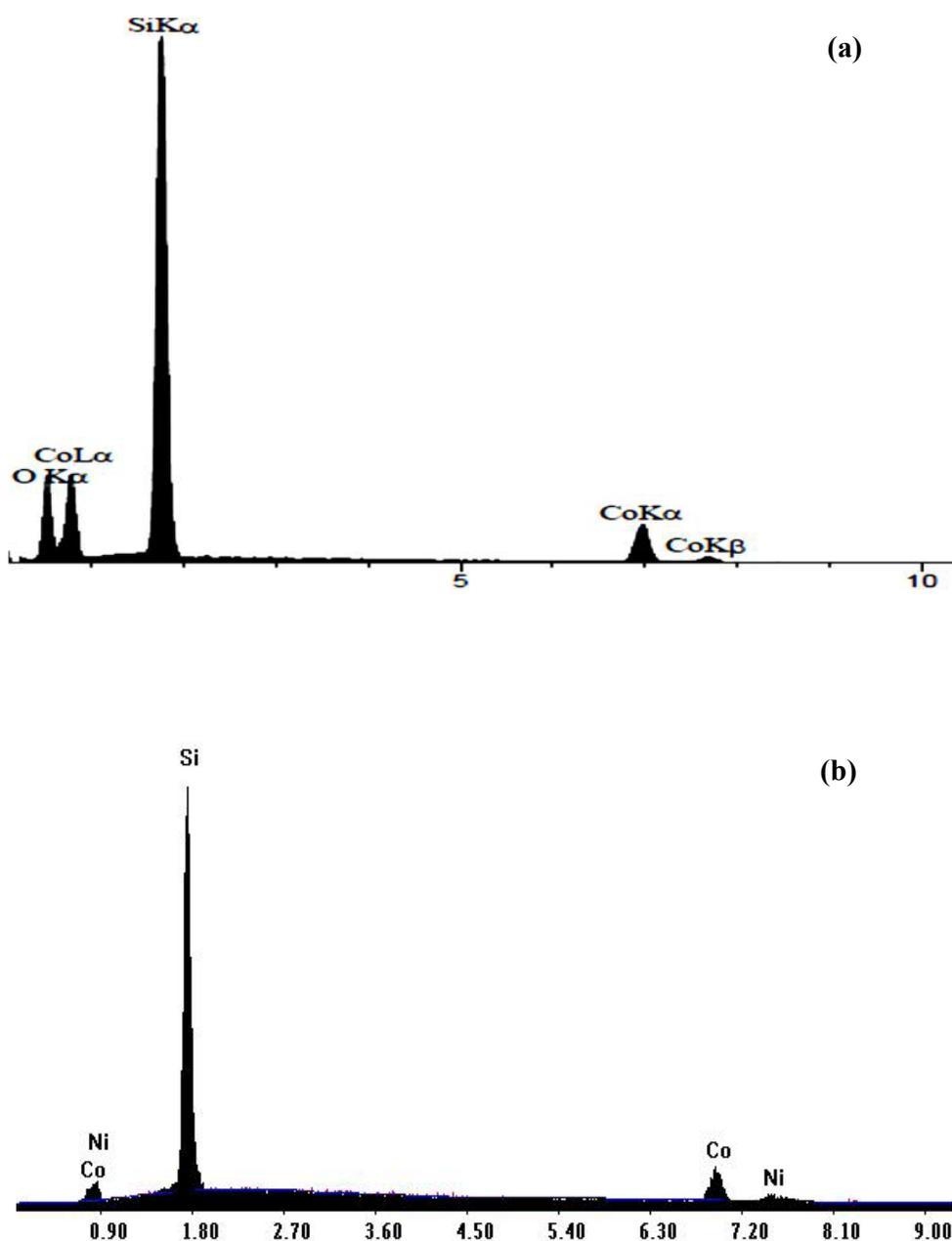


Figure 3. Energy Dispersive X-ray (EDX) measurements show the elemental composition of the (a) Co and (b) Ni – Co NPs deposited on Si substrates.

Atomic Force Microscopy (AFM) in contact mode was used for analyzing the surface morphology of Co and Ni-Co films deposited on Si substrates (Figure 4 (a-d)). AFM images have been obtained in a scanning area of $3\mu\text{m}$

$\times 3\mu\text{m}$. As it is clear, the generation of catalyst NPs with a comparatively smooth surface can be observed. For the analysis of the uniformity of catalyst distribution along the substrate surface, it is useful to calculate the roughness

value. The average roughnesses are 1.91 nm and 4.97 nm for Co and Ni-CoNPs, respectively. Root-Mean-Square (RMS) roughnesses of both samples were measured over the whole area and it was 2.44 nm and 6.29 nm for Co and

Ni-Co, respectively. The RMS roughness of a surface is like to the roughness average, with the just difference being the mean squared absolute values of surface roughness profile.

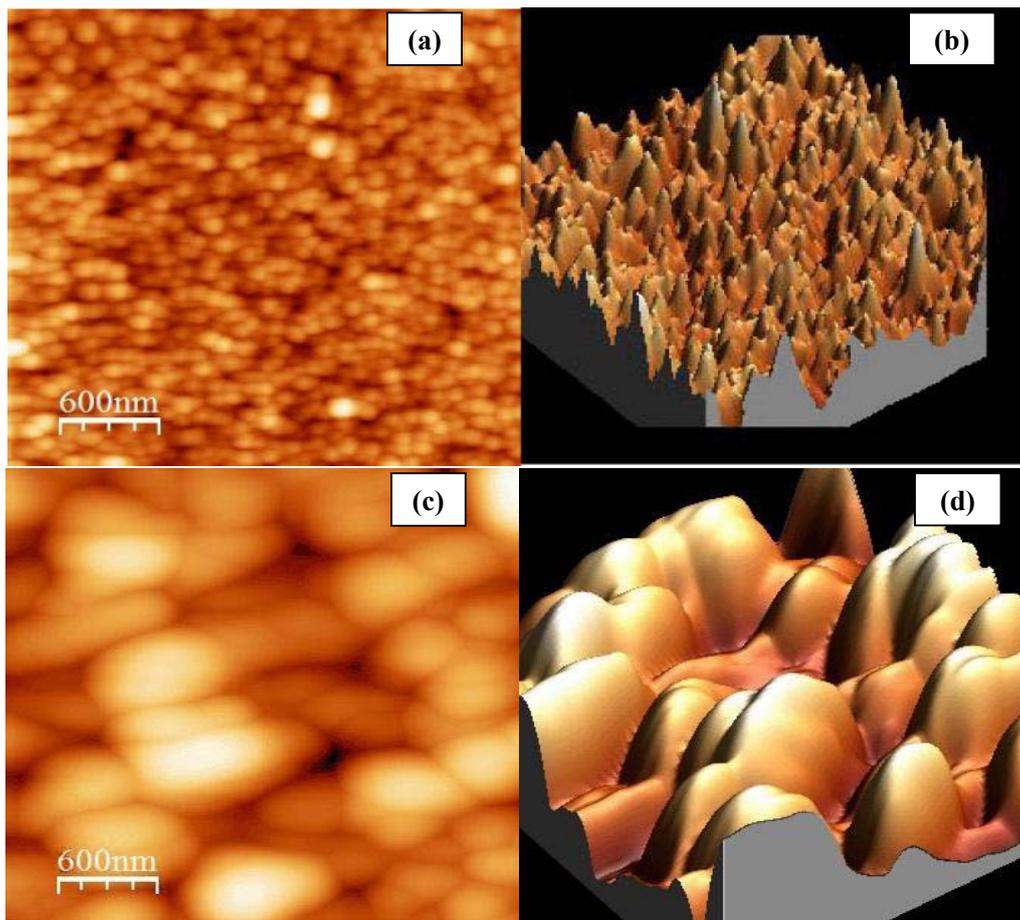


Figure 4. (a) 2D and (b) 3D AFM Images of Co film, (c) 2D and (d) 3D AFM Images of Ni-Co film deposited on Si substrates.

Figure 5 shows the histogram of distribution of Co and Ni-Co particle size on the surface of Si substrates. For Ni-Co sample, The Gaussian diagram showed a non-homogeneous distribution of the Ni-Co nanoparticles on a substrate. The histogram of the nanoparticles

distribution can be used to interpret the distribution function of particle size [24]. By the Gaussian diagram, we can easily observe that the average particle size distribution of Co and Ni-Co samples are less than 15 and 50 nm, respectively.

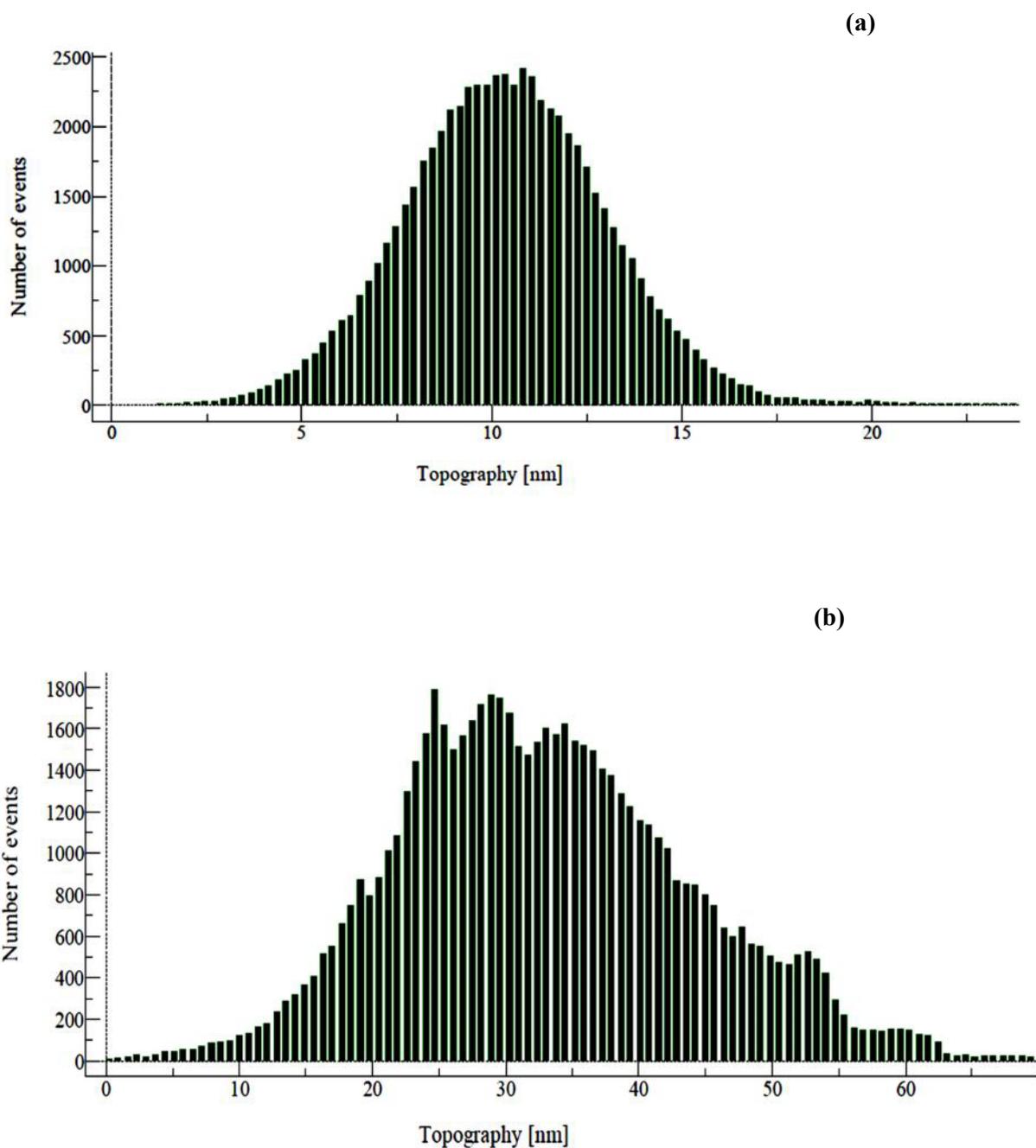


Figure 5. Histograms of the size distribution of (a) Co and (b) Ni-Co nanoparticles on Si substrates.

The FESEM images of CNTs grown on Co NPs without Ni NPs thin layer and Ni-Co NPs on Si substrates are shown in Figures 6a and 6b, respectively. By addition of Ni NPs thin layer on Si substrate for Co NPs catalyst, the density of the grown CNTs is much decreased in comparison to Co NPs on Si substrate.

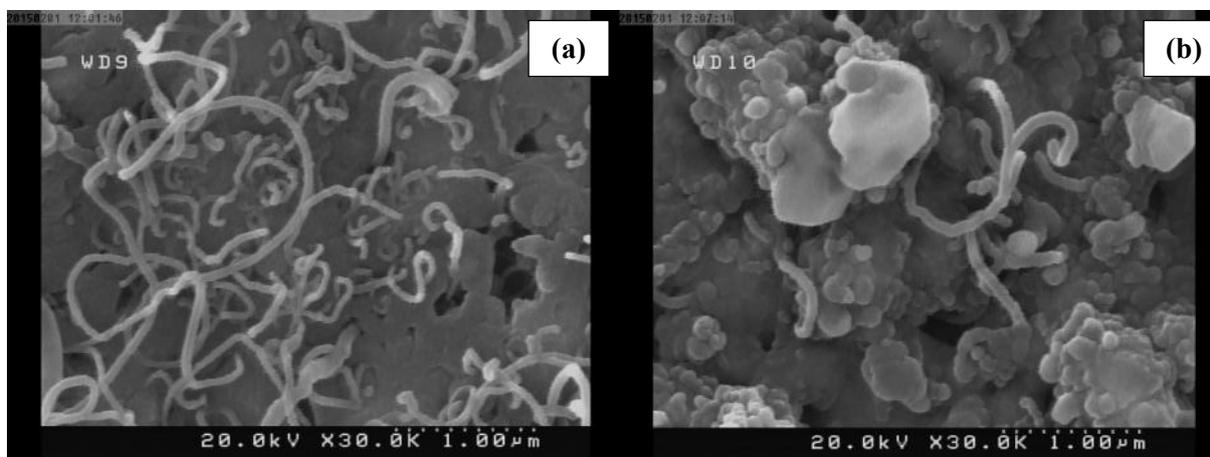


Figure 6. The FESEM images of CNTs grown on (a) Co NPs without Ni NPs thin layer and (b) Ni-Co NPs on Si substrates.

The carbon solubility in catalyst nanoparticles and the precipitation rates of carbon from catalyst nanoparticles indicate strong dependence on the size of catalyst nanoparticles, because quantum size effects significantly influence the characteristics of the catalyst nanoparticles when the size of particles is below ten nanometers [25]. Under a given CVD parameters, there is an optimal particle diameter to nucleate CNTs with a stable feeding rate of carbon. Smaller nanoparticles are simply poisoned because of “overfeeding” and larger nanoparticles are inactive because of “underfeeding” [26]. In order to get greatly efficient growth of CNTs with equal diameters on surfaces, both exact control of the size of catalyst nanoparticles and choice of a relevant feeding rate of carbon necessary.

When the metal thin film is heated up to a high temperature (like the growth temperature), the thin film disintegrates and merges to produce nanoclusters owing to increased surface mobility and strong cohesive forces of the metal atoms. Then, the growth of the carbon nanotubes catalyzed by these nanoclusters. In general, the size of the nanoclusters formed can be controlled by the temperature, by the thickness of the catalyst film or by the annealing time. Films with higher temperatures, thick and lengthy annealing times lead to the production of bigger metal clusters because of increased surface migration of the metal atoms [27]. Even though, these parameters may be used to control the average size of the nanoclusters (such as diameter of grown carbon nanotubes), one should note that the

production of nanoclusters from the metal film is a random process and so there will still be a distribution in the diameters of the structures.

The interactions between catalysts and substrates can be universally described as van der Waals forces and chemical reactions.

In the nucleation step of CVD growth, the interactions between nanocatalysts and substrates play a commanding role. Co and Ni are known to diffuse into silicon at temperatures close to those used for nanotube growth. Poor growth density or no growth happens when Ni nanocatalyst diffuses into the Si substrate to produce NiSi_x at temperatures above 450 °C [28]. A same problem may appear when Ni-Co is used directly on metal substrates, since the metals may generate an alloy at high temperatures.

Generally, the capability of transition metals to bond with carbon atoms enhances with the number of unfilled d-orbitals. Metals with few d-vacancies such as Ni and Co show limited carbon solubility. For transition metals, the affinity for carbon consequently enhances from the right to the left of the periodic table

[29-31]. Graphitic carbon will be allowed to form if the carbon concentration overcomes the solubility of carbon in the catalyst nanoparticle.

Raman spectroscopy was used to study general details of the structure and crystallinity of the grown MWCNTs. The Raman spectrum of the prepared CNTs using Co and Ni-Co NPs on Si substrates is shown in Figure 7. There are two main peaks in these spectra. G-band at 1590 cm⁻¹ shows the formation of graphitized MWCNTs and the D-band at 1300.77 cm⁻¹ which shows the existence of the disorder carbon such as amorphous carbon particles or defective graphite structure. The peak intensity ratio IG /ID is used as a rough measure of sample quality because it shows the relative feature of graphite carbon to imperfect carbon. The IG /ID ratios were calculated and are presented in Table 1. These results showed that the grown MWCNTs using Ni-Co NPs on Si substrate have greater IG /ID ratio and this means that they have better crystallinity of graphite sheets.

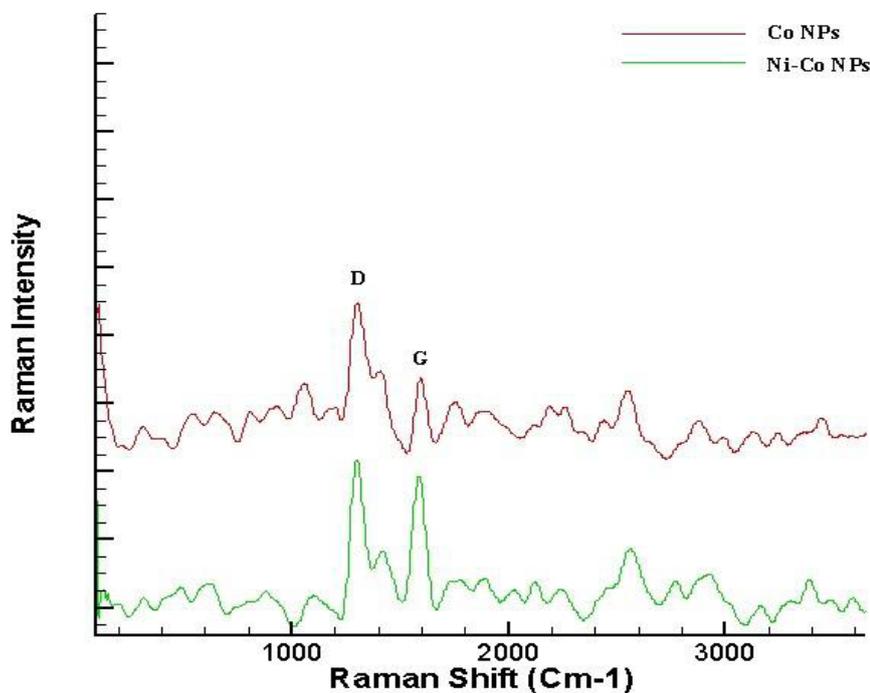


Figure 7. Raman spectrum of the prepared CNTs using Co and Ni-Co NPs on Si substrates.

Table 1. The ratios of the intensities of G and D peaks, I_G/I_D for produced CNTs by Co and Ni-Co catalysts.

Catalyst	G band (cm^{-1})	D band (cm^{-1})	I_G/I_D
Co	1593.40	1300.77	0.44
Ni-Co	1586.26	1300.77	0.89

It is believed that some defects could be observed at low growth temperatures due to nitrogen doping, while this is not the case at higher temperatures because hydrogen and nitrogen species can react to form stable gaseous cyanide acid (HCN) which are transported away by the gases in the chamber [32]. This will lead to a lower amount of nitrogen which it's available for doping and it causes the temperature defects replaces the nitrogen induced.

Conclusion

In this study, MWCNTs were grown by TCVD from the acetylene gas as carbon source in 850 °C during 15 min using the Co and Ni-Co NPs deposited on Si substrates. The results showed that the CNTs grown using Co NPs were denser in morphology compared to the CNTs grown using Ni-Co NPs. Furthermore, Raman spectra results indicated that the grown MWCNTs using Ni-Co nanoparticles due to greater ratio of I_G/I_D , have better crystallinity of graphite

sheets. For transition metals, the affinity for carbon increases from the right to the left of the periodic table. So, the affinity of cobalt for carbon is greater than the affinity of nickel. It's clear that when the bimetallic catalyst thin films used, the underlay nanocatalyst can be used to control the catalyst surface properties or CNTs deposition yield.

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