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Catalyst of Ni and Co dependencies for carbon nanotube synthesis by CVD method

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ABSTRACT

In this research, the effect of catalyst type on the CNTs synthesis was investigated. The carbon nanotubes (CNTs) were produced on stainless steel substrates and two of catalyst with different characteristics by using Thermal chemical vapor deposition (TCVD) method. The catalysts have the important role for the growth carbon nanotubes (CNTs). Acetylene gas (C_2H_2) diluted by NH_3 was used as the reaction gas as a source of carbon. The formation of carbon nanotube structures were confirmed by Raman spectroscopy and scanning electron microscopy (SEM) methods. It was found that the type of catalyst play has an important role on the quality of the nanotubes.

Keywords: Carbonnanotube; Nickel; Cobalt; Atomic force microscopy (AFM); Raman spectroscopy; scanning electron microscopy (SEM)

INTRODUCTION

Carbon nanotubes (CNTs) that were discovered in 1991 by Ijima [1] are designated as one of the most attractive carbon nanostructures for reinforcing the material in compounds and unique physical, chemical and electronic properties as well as their wide potential applications [2-6]. Intensive research activities to improve the synthesis methods [7-8] and conditions and quality in other research experiments that chemical vapor deposition (CVD) techniques are the catalytic decomposition of hydrocarbon feed stock with aid of supported transition metal catalysts. The CVD methods [9-11] are the most suitable low-cost mass, purity and large-scale production technique of carbon nanotubes [12]. Thermal assisted CVD (TCVD) is one of the most commonly used catalytic CVD methods for synthesis of carbon nanotube structures. In this technique, a heat is utilized to decomposing the hydrocarbon-hydrogen gasses. The decomposition products usually consist mainly of active radicals and atomic hydrogen as well as unreacted hydrocarbons which they are crucial and important for carbon nanotubes formation [13]. Most of carbon nanotube synthesis techniques require introduction of catalyst in the form of gas particulates or as a solid support in different substrates surface. The selection of a metallic catalyst may affect the growth and morphology of carbon nanotubes that widely used catalyst material in carbon nanotubes synthesis are nickel, cobalt, titanium, iron and compounds of these metals [14]. Most

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widely used carbon precursors are acetylene, methane, ethanol, ethylene, toluene and 2-propanol.

The growth conditions such as reaction time, temperature, and flow rates of carbon source, inert gas and catalysts are important factors to produce high yield and high purity of carbon nanotubes [11]. Here we report that the present TCVD technique can synthesize high purity carbon nanotubes with different diameter and quality and quantity in this research work. Here, ammonia is used as a Carbon source and etching gasses. We observed the influence of type catalyst on structure formation of carbon nanotubes. By optimizing the catalyst, both carbon nanotubes could synthesized, depending on the reaction conditions. The obtained carbon nanotubes compounds are characterized by scanning electron microscopy (SEM), Raman spectroscopy.

EXPERIMENTAL

Stainless steel (type 304) plates cut into 10×10mm^2 rectangular pieces and were used as substrates for growing carbon nanotubes. Untreated steel substrates were cleaned in the ethanol, acetone and Di-ionized water solutions by an ultrasonic cleaning machine. Then the nanoparticles of Ni and Co were deposited on the plates using sputtering technique by PECVD system. The synthesis of carbon nanotube arrays was carried out in horizontal TCVD system. As-prepared steel substrates were placed in a quartz boat, and transferred into the reaction chamber. The reaction zone was heated up to the synthesis temperature of 910°C. Before deposition, the substrates were pretreated in Ar gas environment for a short time to activate and refine the catalyst nanoparticles. Mixtures of C_2H_2 and NH_3 gasses at ratios 1/2 were then introduced into the reaction chamber for 19 min. After completing experiments, the samples were then furnace cooled slowly in a H_2 gas environment. The molecules of the gas employed in the experiment are all higher than 99.6% in this paper. The morphology of Ni and Co catalyst nanoparticles were investigated using an atomic force microscopy (AFM) technique. The morphology and quality of the carbon nanotubes were analyzed using scanning electron microscopy (SEM), and Raman spectroscopy respectively.

RESULTS AND DISCUSSION

The process of synthesis of carbon nanotubes by TCVD method involves catalyst preparation and growth of carbon nanotube structures. It was possible to render the substrate surfaces covered with grains of Ni and Co catalyst of a certain size. Here, the nanoparticles were deposited using sputtering technique by PECVD system. Proper sputtering technique of the substrates is very important for the successful synthesis of carbon nanotubes. This section starts with growing separated nanotubes on a substrate and handling nanotubes by AFM (Atomic Force Microscope) techniques. The morphology of the catalysts of Ni and Co nanoparticles used in the synthesis of carbon nanotubes is studied using AFM technique. Figure 1 shows typical AFM images of the Ni and Co nanoparticles deposited on stainless steel substrates. The diameter size of Co catalyst around 70nm and the Ni catalyst with different of size diameters ~ 80nm to 170nm in this paper. We suggest that because of floating sputtering, etching of the Co layer on the steel substrates could be more effective and therefore the Co nanoparticles were more uniform. The morphology of surfaces of Ni catalyst layer seems to be inhomogeneous and it is attributed to the non-uniform surface of steel substrates before the sputtering process.

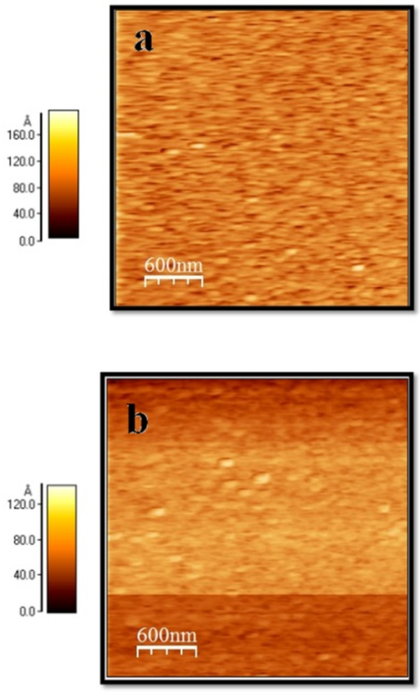

Fig.1. AFM images of the **(a)** Co and **(b)** Ni catalysts on stainless steel substrates by TCVD method.

This is a technique that uses a focused SEM Electron beam to dissociate organic species in a specific area and deposit the residual ionised organicgas molecules on the junction of the CNT with the measuring system.

Fig. 2a-2b shows the SEM images of the deposited structures on our desired samples. It can be seen in Fig 2a that the tubes are grown uniformly over the entire stainless steel substrate with a relatively high growth density. In both figure, carbonaceous particles (amorphous carbon) can be seen. These are seen to be having long noodle shape structure and appear like wounded nanotubes. Carbon nanotubes were densely grown all over the stainless steel substrates. They were not straight, but curly in shapes, tens of microns in length and 50 to 250 nm in diameter, roughly the same size of grains on substrate coated with Co catalyst in this paper. The diameter of carbon nanotubes, is correlated to the size of catalyst islands formed from the deposited nanoparticles. Transformation of catalyst layer to particles can be carried out before or during CVD method conditions. In the case of transforming of nanoparticles into islands on a substrate by the size of islands, and thus the diameter of carbon nanotubes, is depended on the size of the deposited nanoparticles or sputtering conditions for the nanoparticles coating in the case of DC-PECVD method. From SEM micrographs we can estimate a representative diameter of carbon nanotubes of Fig 2a, Fig 2b as around 100nm and 150nm to 1 micrometer respectively. The diameter of carbon nanotubes with Ni catalyst is different. Thus we can observe that there is correlation between the diameter of carbon nanotubes and size of the grains on substrate surface. The carbon nanotubes synthesized in this study were curly and not well aligned. One of the reasons for this is that the substrate surface became rough after etching and the growth direction was not uniform in this desired experiment. The way in which nanotubes are formed on substrates is not exactly known yet. There are several theories on the exact growth mechanism for nanotubes that basically, two main mechanisms, namely the tip growth mechanism and base (or root) growth mechanism and here, we explained by the decomposition of hydrocarbon (Acetylene) molecules at the Ni and Co surfaces, with the carbon dissolved and saturated in the Ni and Co nanoparticles. In both mechanism, the catalysts islands formed act as nucleation seeds for the carbon growth, that the carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below in different experiments.

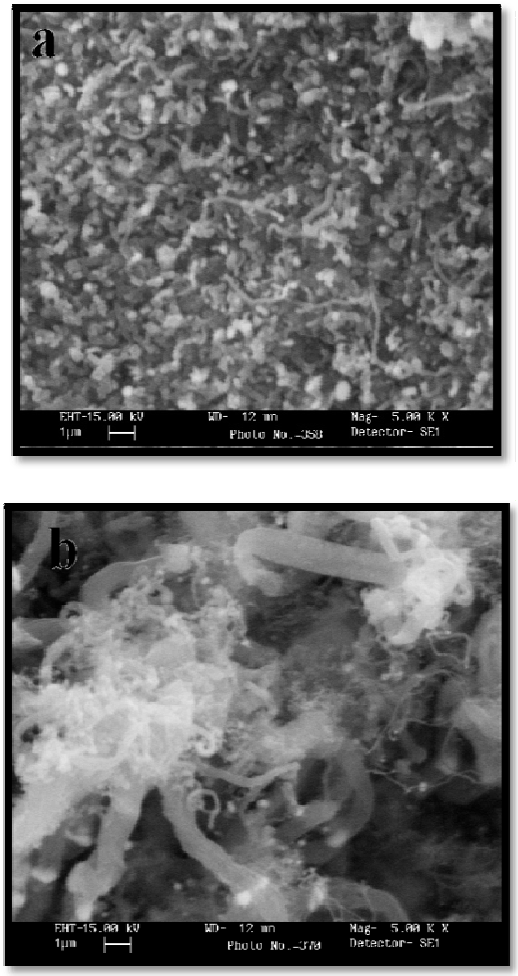

Fig. 2. SEM micrographs of carbon nanotubes deposited on stainless steel Substrates by (a) Co and (b) Ni catalysts.

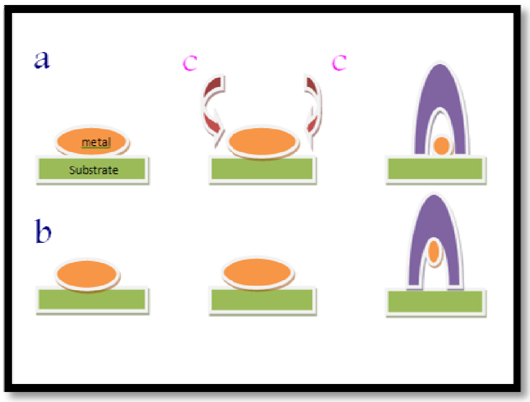

Fig. 3. Visualization of possible carbon nanotubes growth mechanisms of (a) root growth and (b) top growth.

The root growth mechanism, when the hydrocarbon passes over the catalyst nanoparticles, the carbon molecules diffuse into the particles through the edges and saturate it and then the catalyst remain at the bottom of the nanotube synthesized on the substrates, and in tip growth mechanism, carbon molecules decomposed and dissolved in the catalyst nanoparticles in the growth process. When saturation of the catalyst nanoparticles is reached, because of the further diffusion of carbon, the carbon molecules below the catalyst particles forms sheets of graphite and this pushes the catalyst particles upward where it stays at the tip of the nanotubes grown on substrates in desired of research studies [13-16]. In both fig 2a and 2b, the tip growth mechanism observed for synthesized carbon nanotubes by Ni and Co nanoparticles of catalyst.

Raman spectroscopy is most extensively and useful tool utilized to characterize CVD Carbon nanotubes of structures because to distinguish between different allotropes of carbon structures [10-11]. Fig 4a and 4b shows the Raman spectra of the carbon nanotubes grown on the stainless steel substrates. The Raman spectra of the carbon nanotubes are observed to have two peaks at ~1385 cm^{-1} (noted as D- band) and ~1535 cm^{-1} (noted as G- band) with Co catalyst and for Ni catalyst two peak at ~1335cm^{-1}(noted D-band) and ~1575 (noted G band) with intensity ratio I_D/I_G 0.8 and 0.9 respectively. The intensity ratio of D and G band can be utilized to indicate the purity samples and nanostructures crystallinity in desired studies. The D peak corresponds to the SP^3 hybrid and defects such as amorphous carbon whereas G peak correspond to SP^2hybrid in structures and graphite sheets [14].

These results show that better crystalline and quality of carbon nanotubes was produced by Co catalyst with lesser amount of diameter.

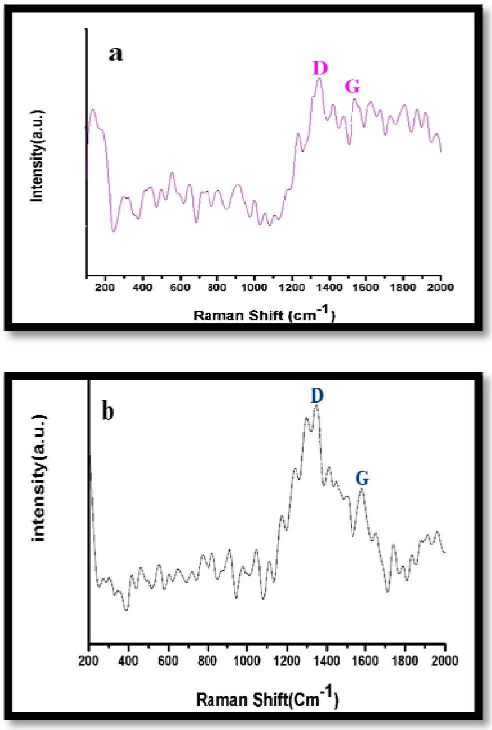

Fig. 4. Raman spectra of carbon nanotubes with (a) Co and (b) Ni catalysts by TCVD method.

CONCLUSIONS

We had successfully grown nanotubes from acetylene and ammonia directly on stainless steel coated with Co and Ni catalysts by TCVD method. Mechanism of synthesized carbon nanotubes with the both catalyst (Ni and Co) is of tip growth. The synthesized carbon nanotubes with Co and Ni catalysts have the diameter of about 100 nm and 150nm to 1micrometer, respectively and the length of different about 30nm to several micrometers, which were more uniform compared to those grown on stainless steel coated with Co catalyst. Mechanism of synthesized carbon nanotubes is tip growth for both of catalystIt was found that type of catalyst was very important for successful synthesis. In conclusion, the carbon nanotubes with the best crystalline structure and diameter obtained by Co catalyst and the most suitable catalyst for synthesis this carbon nanostructure on stainless steel substrates in this research work.

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