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Studying the Bimetallic Catalyst Effects on the Synthesis of Multi-Walled Carbon Nanotubes via CVD Method.

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were synthesized using assembled chemical vapor deposition (CVD) setup reactor at temperature of 850 °C, over different types of bimetallic Mo-based catalyst as Fe-Mo and Ni-Mo using MgO as supporting material. The high resolution transmission electron microscope investigation is used to prove the mass production of MWCNT. For Ni-Mo as a catalyst; the only formed were spheres of carbon and low amount of MWNTs, while for Fe-Mo; elongated MWCNTs were produced with an average diameter 25 nm. The formation of MWNTs was further proved with the data obtained from X-ray diffraction, Raman spectroscopy, Field Emission Scanning electron microscope and EDX spectroscopy analysis.
Keywords: Multi-walled Carbon nanotubes, bi-metallic catalyst, CVD method.

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INTRODUCTION

Among nanomaterials, Carbon nanostructures have attracted scientific interest because of their extensive prospective applications. All of these nanostructures are made up of carbon element to form graphene, fullerene, diamond or more complicated structure such as Carbon nanotubes (CNTs) [1].

CNTs could be represented as one of the most interested materials in the last years in the field of nanotechnology since there was first discovered by Iijima in 1991 [2]. That is because of their unusual properties as mechanical, electronic, thermal, optical and chemical properties [3-5]. From that time, a lot of researchers focused their attention and activity on the ways of preparation, characterization, and potential applications of CNTs in several fields.

CNTs could be prepared by three methods: electrical arc discharge [6-10], Laser ablation enhancement [11-12], and chemical vapor deposition (CVD) [13-21]. CVD method could be represent the most popular and suitable method compared to others because their high mass production property and low cost. Moreover, the ability to control the resulted CNTs characteristics as diameter, length and number of walls [22]. It also utilizes plenty of hydrocarbons in all forms as solid, liquid or gas and different substrates. Also CVD could be used to grow CNTs in different forms like aligned or entangled, straight or coiled nanotubes on pre-defined cites of a patterned substrate.

In CVD technique, there are number of factors affected on the quality and the amount of the resulted CNTs like carbon source, metal catalyst, supporting material, and temperature of tube furnace [23]. Supporting materials help to form metal catalyst in the nanoscale that will hold CNTs on its island structure such as Al, Mg, Cu, and Ag, while the metal catalyst could be single metal (e.g. Ni, Fe, and Co) or bimetallic (e.g. Co-Ni, Fe-Co, and Co-Mo) [24-29] and is considered as the nuclei for growing CNTs .

In this work, we report the synthesis of CNTs with two types of bi-metallic catalyst Fe-Mo/MgO and Ni-Mo/MgO using CVD techniques; and high resolution transmission electron microscope (HRTEM) and FESEM were used to make a comparative study between the output product of MWCNTs and to propose the possible mechanism of growing CNTs on the supporting materials.

MATERIALS AND METHOD

Material

The materials used are Ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), Nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), ammonium oxide and magnesium oxide (MgO). All chemicals used in this research were purchased from sigma-Aldrich and used without further purification.

Preparation of catalyst

The used catalysts Fe-Mo/MgO and Ni-Mo/MgO were prepared by wet impregnation method with molar ratio 1:6:30 as follow: 2 g of MgO powder was steeped in a 50 ml NH_4OH (0.3 wt.%), and the suspension was subsequently stirred at 70°C for 30 min. Then ammonium heptamolybdate was added to the suspension, and it was stirred for 10 min. Lastly, 10 ml of a water-based solution of ferric nitrate $Fe(NO_3)_3{\cdot}9H_2O$ or $Ni(NO_3)_2{\cdot}6H_2O$ was infused, and the suspension was stirred additionally for another 10 min and as a consequence, the color of the suspension turns into orange in case of Fe and to pale green in case of Ni. The powder mixture of both was dried at 90°C over night. After drying, the catalyst powder was ground in an agate mortar and no further calcination was applied.

Synthesis of CNTs

MWCNTs were grown via CVD process in a tubular furnace reactor with a quartz tube around 120 cm long and 40 mm diameter, and temperature controller. The prepared two catalysts were placed separately on two ceramic boats. Then each boat was exposed to be placed in the middle of the tube and the two catalysts were inserted in the furnace separately with the same condition. The furnace was heated with rate of 10

°C/min and at temperature of 850°C while the furnace was purged with 150 cm3/min of Argon. Once the target temperature was kept constant at 850 °C, the methane (CH4) with a flow rate of 50 cm^3/min was introduced into the quartz tube for 20 min for the fabrication of carbon nanotubes. After 20 min, the CH_4 flow was set to zero. The CNT growth process was stopped by switching off the CH_4 flow, and the product was immediately cooled down to the room temperature under Argon flow.

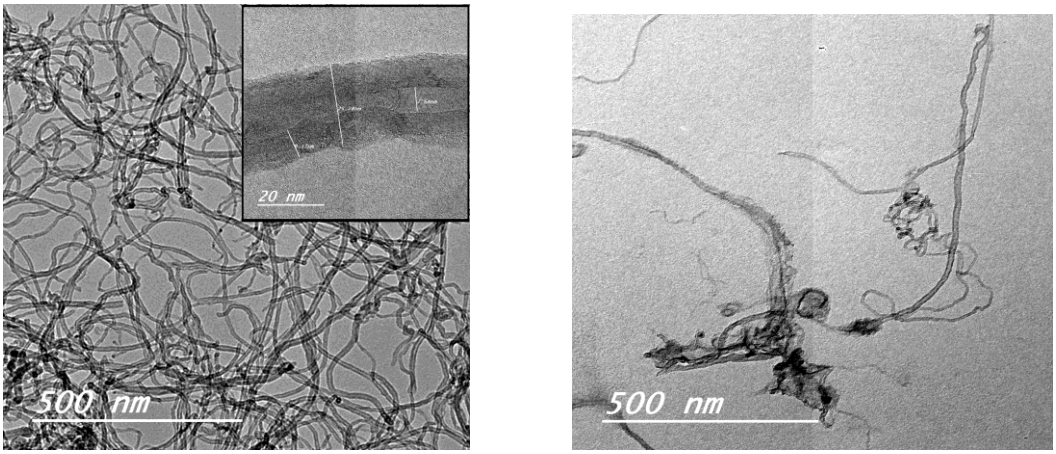
Characterization techniques

The size and shape of the nantubes were observed on a high resolution transmission electron microscope (HRTEM) JEOL–JEM-1011, Japan. Images were recorded at a rate of 200 kV. For each sample, low concentration of suspension dispersion was deposited on a carbon copper grid and left to dry at room temperature. Field emission scanning electron microscope (FE-SEM) on a Quanta FEG 250 (Czech Republic) electron microscope was used to investigate the morphology analysis cooped with Energy Dispersive X-ray spectroscopy analysis (TEAM –EDX Model).

The crystalline structure of samples was characterized using X-ray (XRD) diffractometer (Schimadzu 7000, Japan) operating with Cu Kα radiation (λ=0.154060 nm) generated at 30 kV and 30 mA with scanning rate of 4ºmin-1 for 2θ values between 10 and 80 degrees. Raman measurement was carried out with BRUKER SENNTRRY, Micro Raman spectroscopy operating at 532 nm laser, and embedded wavelength 88 to 4000 cm^{-1} spectral range and up to 3 cm^{-1} resolution.

RESULTS AND DISCUSSION

The HRTEM images of the prepared MWCNTs using MgO as supporting materials with different bimetallic Mo-based catalyst showed that in the case of Ni-Mo as a catalyst, the only formed was circular shaped carbon nanospheres and very low amount of MWCNTs as in figure 1(a). However, in the case of Fe-Mo as a catalyst, it was cleared that high yield of thin and highly uniformed elongated MWCNTs with an average diameter 25 nm were formed over the catalyst as in figure 1(b). This could be explained as follow: in case of Fe-Mo/MgO, the interaction between bimetallic catalyst Fe-Mo and the supporting MgO were not very strong forming an acute contact angle So the hydrocarbon decomposes on the top surface of the metal then carbon diffuses down through the metal, and CNT get out across the metal bottom, pushing the whole metal particle off the substrate as in figure (2a) and the metal's top is open for fresh hydrocarbon decomposition more allowing more carbon diffusion, and CNT continues to grow longer and longer "tip-growth model" helping the yield to increase while in the case of Ni-Mo/MgO the catalyst-substrate interaction is strong forming an obtuse contact angle and what happened is similar to that in the tip-growth case, but the CNTs precipitation fails to push the metal particle up as in figure(2b) stopping more carbon diffusion so the carbon crystallizes out as a hemispherical dome forming closed-carbon network on a spherical nanoparticle and the growth is stopped "base-growth model" leading to low yield of CNTs[30].



1(a) **1(b)**

Figure 1: TEM images of the prepared MWCNTs over (a) Fe-Mo catalyst, and (b) Ni-Mo catalyst.

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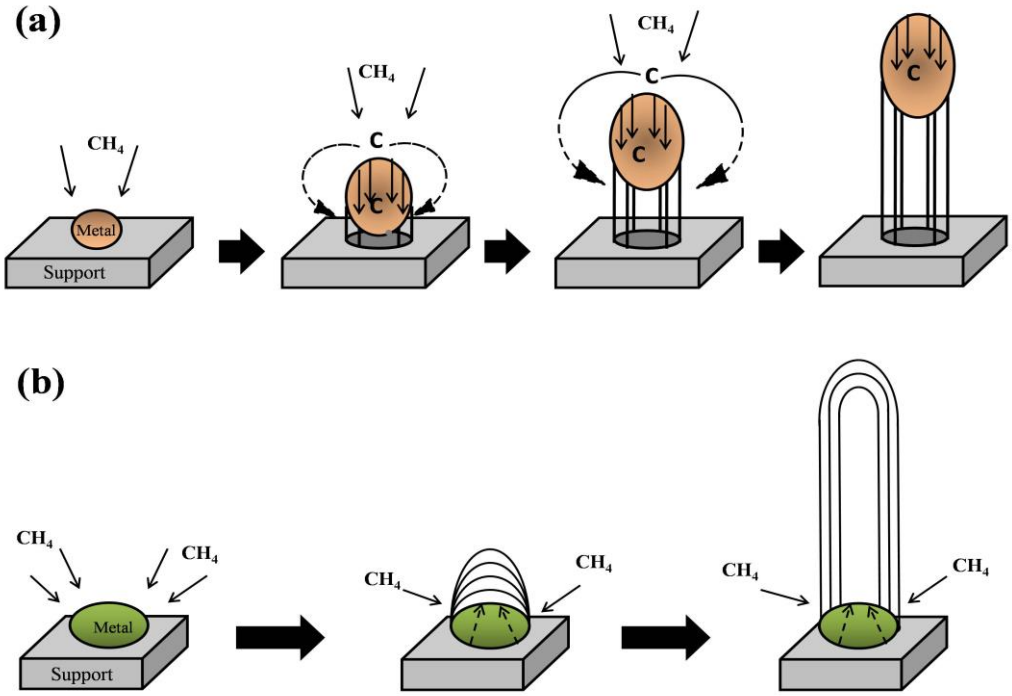

Figure 2: Growth mechanism of MWCNTs

The carbonized structure was obtained using Raman micro-spectroscopy for Fe-Mo catalyst as shown in figure (3). The peak at 1345 cm^{-1} is corresponding to the non-crystalline carbon which so-called disordered band (D-band) at the range of 1350-1380 cm^{-1}, while the peak at 1591 cm-1 is corresponding to the carbon atoms with graphite-like symmetry which so-called graphite band (G-band) at the range of 1580-1600 cm^{-1} [31-32]. The G and D bands represent the most intense peak in the spectra for CNTs which are features of all sp^2 bonded carbon materials and sp^3 bonding defects in the nanotubes, respectively. From the values of intensities of D and G bands, the quality of CNTs can be obtained from the intensity ratio I_D/I_G of D band to G-band [33-34].

$$I_D/I_G = 1.02$$

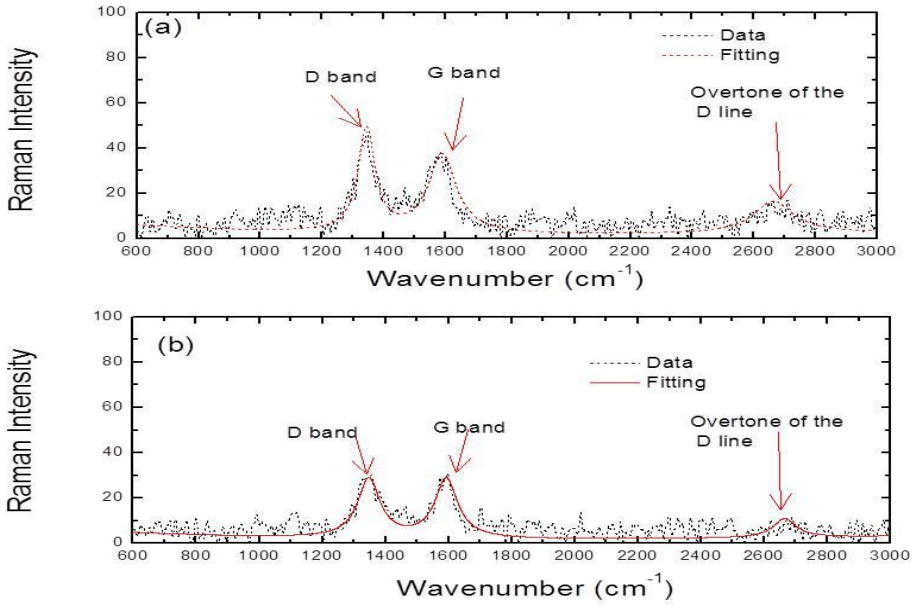

figure 3: Raman spectra of the prepared MWCNTs over (a) Fe-Mo catalyst, and (b) Ni-Mo catalyst.

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According to experimental and theoretical results [35-39], the D mode is very weak in well-ordered graphene structure. The intensity of the D band is increased for the disordered carbonaceous materials. Obviously, the Raman spectra are strongly affected by the disordered of the hexagonal structure in MWCNTs. The significant increase of D/G intensity ratio can be attributed to the partial decrease of the size of the in-plane sp^2 hybridization due to the randomly distribution of the most outer wall of the MWCNTs and partially ordered graphene crystal structure. Accordingly, the first raman spectrum (Figure a) for sample which shows less amount of MWCNTs (with highly disordered graphene structure in the most outer wall of the MWCNTs), while (Figure b) for the sample with high amount of MWCNTs (less disordered of the graphene structure in the most outer wall of the MWCNTs) .These results prove the presence of CNTs and are in good agreement with the Images of MWCNTs obtained from HRTEM.

Figure 4 shows XRD pattern of the prepared MWCNT by using catalyst of Fe-Mo. In this pattern, the distributions of prominent diffraction peaks match well with rombohedral structure of graphite structure derived from (JCPDS card No. 75-2078). The diffraction peaks were shown at (2Θ) of 25.9°, 43.03°, 52.11°, 53.7°, and 78.7° which are assigned to the (111), (010), (222), (112), and (110) crystal plane [33].

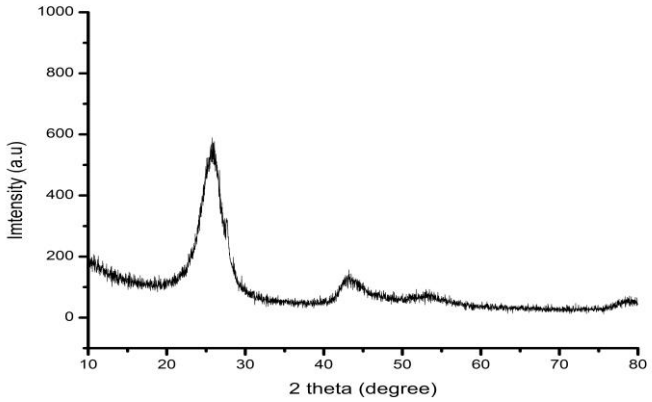
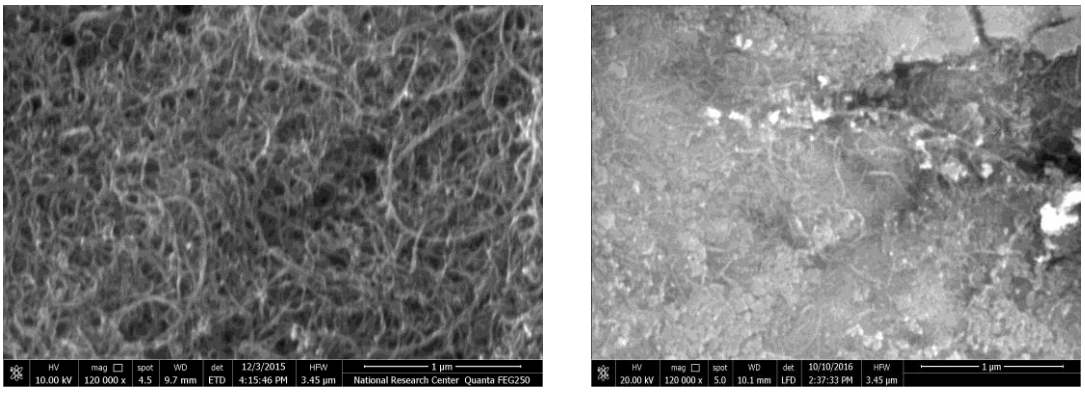


Figure 4: XRD pattern of the prepared MWCNTs over Fe-Mo catalyst

FESEM images of the prepared MWCNTs when Fe-Mo and Ni-Mo were used as a catalyst are presented in figures (5a) and (5b) respectively to display the morphology and topography of the two prepared MWCNTs samples. It is clearly observed that the MWCNTs are elongated and are present in a large quantity in case of Fe-Mo catalyst while in case of Ni-Mo as acatalyst only very low tubes are appeared but the majority are carbon spheres and unreacted metal catalyst nanoparticles and EDX measurements could be support these results as in figure 6(a) in case of Fe-Mo that the elemental analysis showed that the sample is only contain carbon atoms of the formed MWCNTs while in case of Ni-Mo as a catalyst as in figure 6(b) there are traces of Ni, Mo and Mg of un reacted catalyst.



5(a) **5(b)**

Figure 5: SEM of the prepared MWCNTs over (a) Fe-Mo catalyst, and (b) Ni-Mo catalyst.

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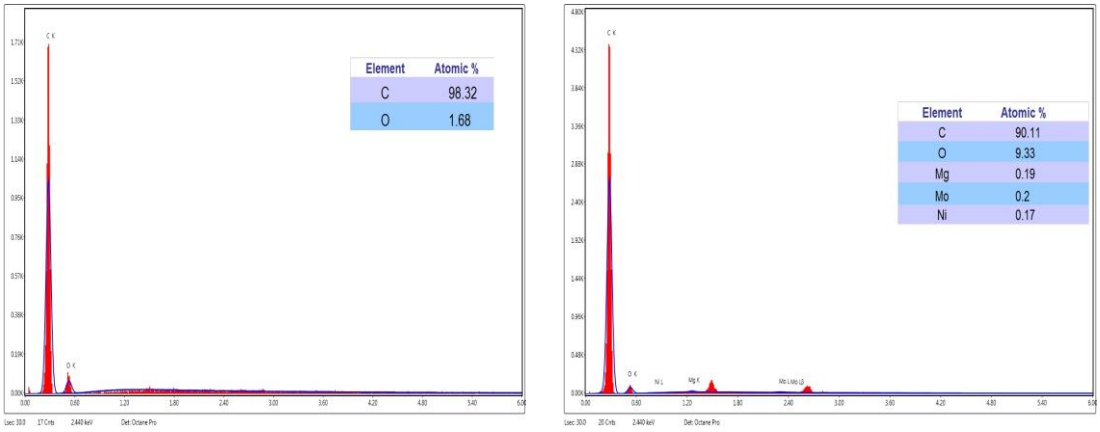

6(a) 6(b)

figure 6: EDX of the prepared MWCNTs over (a) Fe-Mo catalyst, and (b) Ni-Mo catalyst.

CONCLUSION

The synthesized MWCNTs were tested over different types of bimetallic of Mo catalyst, Fe-Mo and Ni-Mo, using supporting material of MgO via methane CVD method at the temperature of 850°C using Ar/CH4 with gas ratio of 3:1. The high resolution transmission electron microscope confirms that high yield and more uniformed and elongated MWCNTs were formed using Fe-Mo rather than in case of Ni-Mo as a catalyst. Also the images obtained from FESEM and the spectrum obtained from XRD and Raman spectroscopy confirmed the formation of MWCNTs.

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