

ORIGINAL ARTICLE

## Role of growth temperature in CVD synthesis of Carbon nanotubes from Ni-Co bimetallic catalysts

Sepideh Sadat Madani<sup>1</sup>; Karim Zare<sup>1,\*</sup>; Mahmood Ghoranneviss<sup>2</sup>

<sup>1</sup>Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

<sup>2</sup>Department of Physics, Science and Research Branch, Islamic Azad University, Tehran, Iran

Received 29 November 2015; revised 26 February 2016; accepted 02 April 2016; available online 26 June 2016

### Abstract

The effect of temperature variation on the growth of Carbon Nanotubes (CNTs) using Thermal Chemical Vapor Deposition (TCVD) is presented. Nickel and Cobalt (Ni-Co) thin films on Silicon (Si) substrates were used as catalysts in TCVD technique. Acetylene gas was used in the CNTs growth process at the controlled temperature ranges from 850-1000 °C. Catalysts and CNTs characterization were carried out using Atomic Force Microscopy (AFM), Energy Dispersive X-ray (EDX), Field Emission Scanning Electron Microscopy (FESEM) and Raman spectroscopy. It was found that the CNTs diameters increased with the temperature. The CNTs diameters were continually increased from 70 nm to 180 nm in the temperature range. In addition, the degree of crystallinity of the grown CNTs decreased.

**Keywords:** Carbon nanotubes; DC-sputtering; Ni-Co catalyst; TCVD; Temperature.

### How to cite this article

Madani S S, Zare K, Ghoranneviss M. Role of growth temperature in CVD synthesis of Carbon nanotubes from Ni-Co bimetallic catalysts. *Int. J. Nano Dimens.*, 2016; 7(3): 240-246., DOI: [10.7508/ijnd.2016.03.007](https://doi.org/10.7508/ijnd.2016.03.007).

### INTRODUCTION

Carbon nanotubes (CNTs) are mono dimensional nanostructure material with properties such as high aspect ratio, high mechanical strength and modulus, high electrical conductivity and chemical stability has been attracting intensive theoretical and experimental interests in the past decades [1-4]. There are three main methods for growing of carbon nanotubes: Arc discharge, Laser ablation and Chemical Vapor Deposition (CVD) [5]. Among the different techniques of carbon nanotube growth, CVD is most popular and widely used due to its high production density, low set-up cost and ease of scale-up [6]. The CNTs growth by CVD technique consists of two steps: preparation of nanocatalyst substrates and growth of the CNTs on the substrates [2]. In this process, a hydrocarbon vapor in the presence of a metal nanocatalyst is decomposed [6]. The key parameters are chemical and physical characteristics of catalyst nanoparticles and their size, hydrocarbon source

\* Corresponding Author Email: [prof.zare@gmail.com](mailto:prof.zare@gmail.com)

and reacting environment during the CNTs growth [7].

A variety of nanoparticles such as Fe, Co, Mo, Ni, Cu, Au, etc. [8-13] have been used as catalyst either in pure metallic form or as alloys [14, 15]. These transition metal nanoparticles have popular advantages such as high melting temperatures, carbon solubility and carbon diffusion rates. A good catalyst should be monodisperse on the surface of a substrate. The catalyst should match with a suitable feeding rate of carbon and have appropriate interactions with substrates [16]. The size of nanocatalyst must be tuned to control the diameter or number of walls in the grown CNTs. Smaller sized particles results in less walled tubes. When the particle size is decreased, the amount of carbon that allows better nucleation of CNTs is reduced [17-20]. Recently, there has been great interest in the development of bimetallic catalysts for CNTs growth [18-23]. In this study, it is shown that the atomic-scale composition of bimetallic

catalyst influences CNTs density. The results are explained by considering the carbon solubilities as a function of metal composition. Although Co and Ni both have relatively high carbon solubilities compared to other metals and thus are favorable for carbon nanotube growth, the carbon solubility in Co is slightly higher than Ni. The implication of the current study is that the size of nanocatalyst alone does not determine CNTs densities, particularly in the case of bimetallic catalysts. The size of nanocatalyst and its composition must be carefully controlled to obtain a high density of CNTs for large-scale, cost effective and environment friendly production. Also, the effects of different reaction temperature on CNTs growth by Thermal CVD technique have been investigated.

## EXPERIMENTAL

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  $4 \times 10^{-1}\text{ Pa}$ . A nickel 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 nickel nanocatalysts were sputtered on Si substrates when the substrate temperature gradually increased up to  $100^\circ\text{C}$ . Deposition time for nickel sputtering was 20 minutes. In the next step, by the same method which mentioned above, the cobalt nanoparticles were deposited on the nickel thin layer film during 20 minutes and so the Ni-Co NPs were formed on Si substrates.

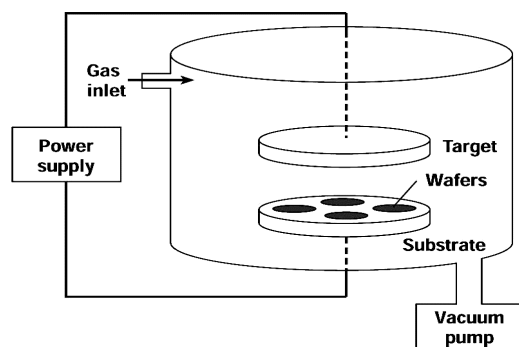


Fig. 1: Schematic diagram of DC-sputtering system.

The Thermal Chemical Vapor Deposition (TCVD) system in the experiment (Fig. 2) was an electric furnace composed of a horizontal quartz glass tube with an internal diameter of 7.5 cm 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  $750^\circ\text{C}$ . The samples were placed in the chamber and the temperature increased to  $850^\circ\text{C}$ . After that, Ar flow was switched off. For CNT growth, we used  $\text{C}_2\text{H}_2 / \text{NH}_3$  at 35 / 60 sccm for 15 minutes. The growth was terminated by turning off  $\text{C}_2\text{H}_2 / \text{NH}_3$  flow and the samples were allowed to cool down to room temperature under Ar gas flow. Same experiments were repeated with growth temperature as  $900^\circ\text{C}$ ,  $950^\circ\text{C}$  and  $1000^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The growth conditions except of the growth temperature were kept constant. Energy Dispersive X-ray (EDX) measurement was done to investigate the elemental composition of the Ni - Co (Fig. 3) catalysts deposited on Si substrates. Atomic percent of Co and Ni elements are 94.17 % and 5.83 %, respectively. Atomic Force Microscopy (AFM) in contact mode was used for analyzing the surface morphology of Ni-Co films deposited on Si substrates. 2D and 3D topography of the Ni-Co surface of the sample is shown in Fig. 4 (a, b). We used from WSxM 5.0 software for re-scaling AFM image. AFM images have been obtained in a scanning area of  $1\mu\text{m} \times 1\mu\text{m}$ .

For the analysis of the uniformity of catalyst distribution along the substrate surface, it is useful to calculate the roughness value. The average roughness is 4.97 nm and Root-Mean-Square (RMS) roughness was measured over the whole area and it was 6.29 nm.

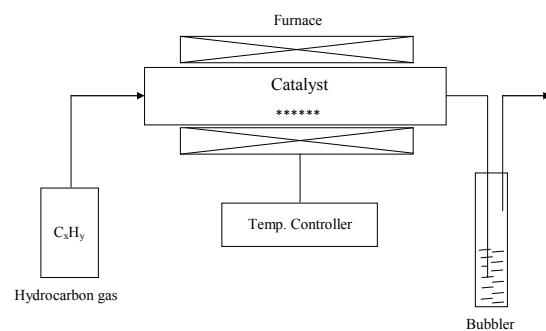


Fig. 2: Schematic diagram of TCVD system of nanotube synthesis

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. The surface morphology plays a significant effect on adherence. Adherence is a chemical-physical phenomenon responsible for the union of two surfaces when they come into contact with this union has force of high magnitude in conditions where there is a chemical bond with sharing of electrons or Coulomb attraction. The adhesion force reduces with increasing roughness [24]. Fig. 5 shows the histogram of the distribution of Ni-Co particle size on the surface of Si substrate. This histogram is fitted with a Gaussian curve and as can be seen from the histogram, this curve is asymmetric. The Gaussian diagram showed that the distribution of the Ni-Co nanoparticles on Si substrate is non-homogeneous. This may be due to agglomeration of the Ni-Co nanoparticles. The

histogram of this nanoparticles distribution can be used to interpret the distribution function of particle size [25]. From the Gaussian diagram, we can easily observe that the average particle size distribution is less than 35 nm. On the other words, on average, 1800 particles have a size distribution about 24 nm.

Fig. 6 (a-d) shows the FESEM images of CNTs grown on the Ni-Co bimetallic nanocatalyst at different growth temperatures 850 °C, 900 °C, 950 °C and 1000 °C. By increasing the temperature from 850 °C to 900 °C, growth density of CNTs on the surface is raised.

Moreover, the average diameters of grown carbon nanotubes for all samples were determined by Microstructure Measurement software. The average diameters of grown CNTs are 70, 80, 140 and 180 nm for growth temperatures of 850 °C, 900 °C, 950 °C and 1000 °C, respectively.

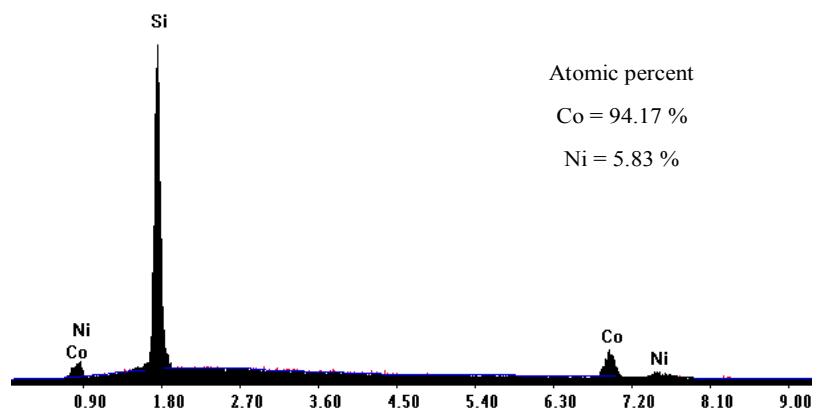


Fig. 3: Energy Dispersive X-ray (EDX) measurement shows the elemental composition of the Ni – Co nanoparticles deposited on Si substrate

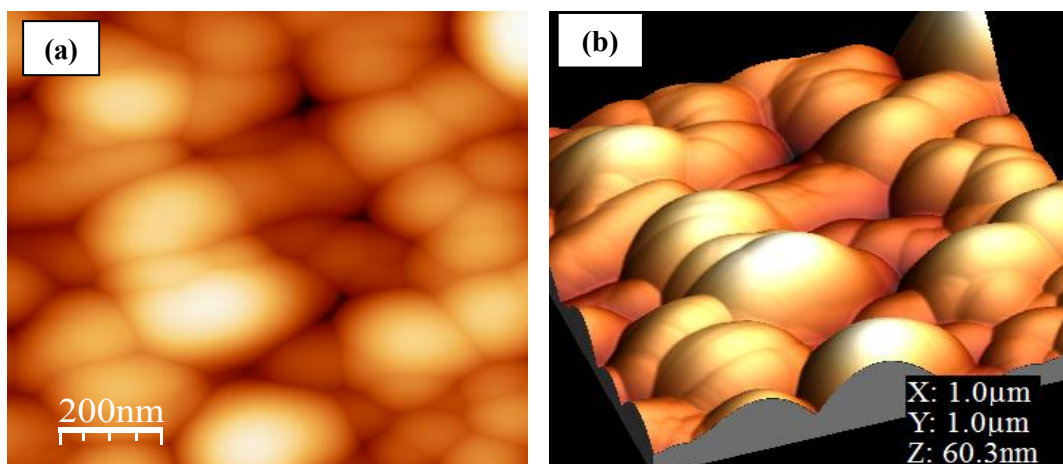


Fig. 4: (a) 2D and (b) 3D AFM Images of Ni-Co film deposited on Si substrates

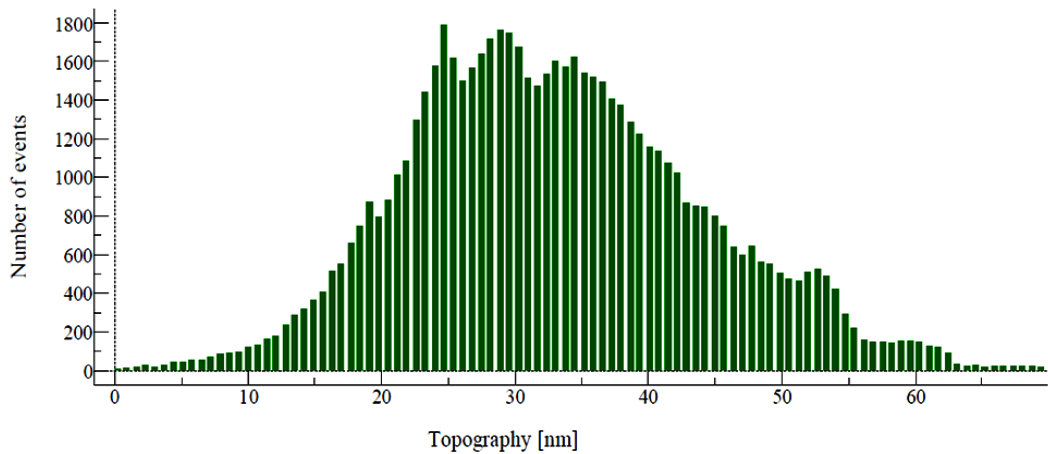


Fig. 5: Histogram of the size distribution of Ni-Co nanoparticles on the surface of Si substrate

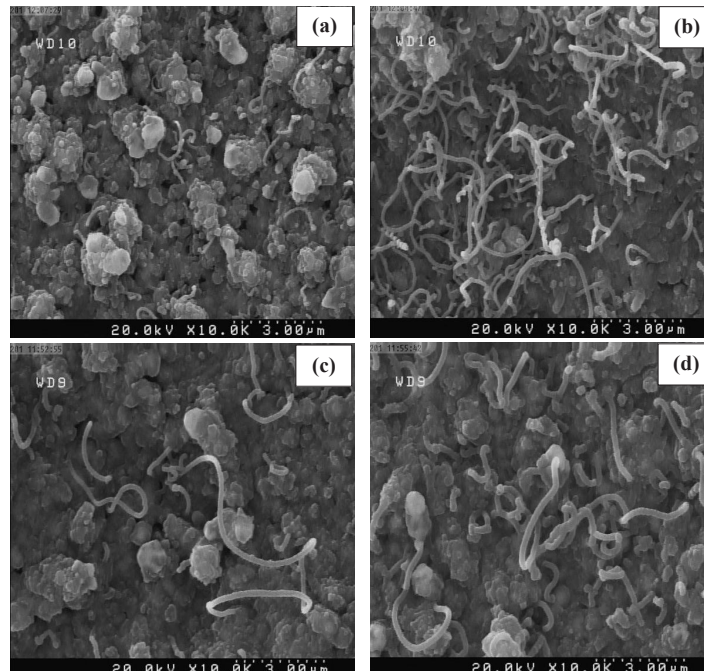


Fig. 6: The FESEM images of grown CNTs at different growth temperatures on the Ni-Co catalyst (a) 850°C, (b) 900°C, (c) 950°C and (d) 1000°C.

These results show that by increasing the growth temperature, average diameter of CNTs is increased. According to Charles law of kinetic theory of gases [26], when the growth temperature raises, then volume of gas, kinetic energy of gas molecules and diffusion rate of gas molecules in the growth chamber are increased. So, the decomposition rate of acetylene gas in CVD chamber increases and more carbon atoms are in contact with the Ni-Co catalyst. Therefore, the average diameter of grown carbon nanotubes

by raising the growth temperature increased. On the other hand, with increment in growth temperatures, the equilibrium between the decomposition of acetylene gas and diffusion rate of produced carbon atoms in Ni-Co catalyst nanoparticles is disturbed. Hence, some of these carbon atoms in the form of amorphous carbon are deposited on Ni-Co catalyst nanoparticles. These nanoparticles couldn't catalyze the CNTs growth and so, the density of CNTs decreased.

Structure and quality of CNTs highly depend on

properties and the type of catalyst composition. For this reason, it is essential to study the catalyst. Usually, with increasing the number of unfilled d-orbitals, the ability of transition metals to bond with carbon atoms increases and therefore the affinity for carbon raises from the right to the left of the periodic table [27]. The importance of carbon solubility is that when a carbon nanotube is nucleated, the diameter or number of walls in the tube can be determined by the amount of carbon atoms dissolved in the catalyst nanoparticle [28]. In multilayer metal films, a nanocatalyst metallic underlay can be used to control the surface characteristics of the catalyst or the deposition density.

Raman spectroscopy taken from all samples are shown in Fig. 7. It may be recalled here that first order Raman spectra of all graphitic materials, including CNTs, exhibit a G band at  $\sim 1580 \text{ cm}^{-1}$  (which is high-frequency  $E_{2g}$  first-order mode from graphitic-like  $sp^2$  type bonds), along with a D band at  $\sim 1300 \text{ cm}^{-1}$  (which is originated from diamond-like  $sp^3$  bonds). Since the origin of D band can be explained by the double resonance theory, it is also indicated as  $A_{1g}$  D mode – a band caused by

defects and disorder of the graphitic materials. In this study, relatively wider peaks of D and G bands show the presence of disorder induced features in the graphitic like ( $sp^2$ ) material and predominance of tubular structures in the CNTs, respectively. Moreover, a low ratio of  $I_G / I_D$  peaks ( $\leq 1.0$ ) shows that the multiwalled CNT structure has high defect density [29]. The  $I_G / I_D$  ratios were calculated to estimate the variation of CNT crystallinity at different growth temperatures using Ni-Co catalyst (Table 1). This reveals that the trend of CNT crystallinity varies with synthesis temperature. The results showed that with raising the growth temperature, The  $I_G / I_D$  ratio and therefore the CNT crystallinity is decreased.

It is believed that some defects could be observed at low growth temperatures due to nitrogen doping. However, it does not occur at higher temperatures because hydrogen and nitrogen species can react to form stable gaseous cyanide acid (HCN) which are expelled by the gases in the chamber [30]. 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.

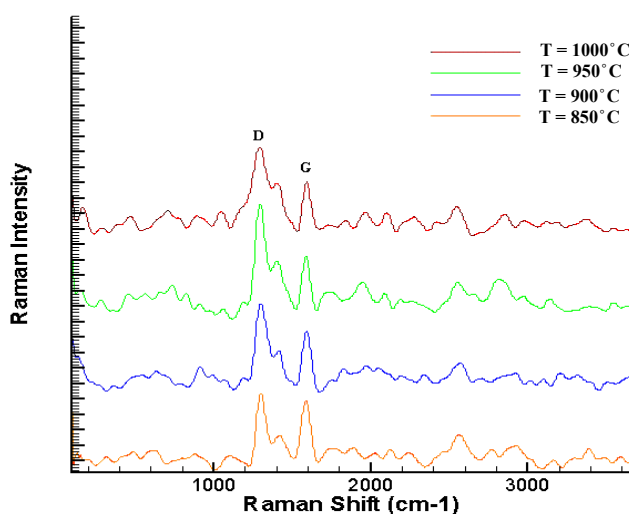


Fig. 7: The Raman spectrum of the grown CNTs on the Ni-Co catalyst at different growth temperatures

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

Catalyst	Growth Temperature	G band ( $\text{cm}^{-1}$ )	D band ( $\text{cm}^{-1}$ )	$I_G/I_D$
Ni-Co	850 °C	1586.26	1300.77	0.8806
Ni-Co	900 °C	1593.40	1293.64	0.6611
Ni-Co	950 °C	1586.26	1286.50	0.4907
Ni-Co	1000 °C	1593.40	1293.64	0.5708

## CONCLUSIONS

The effect of growth temperature using Ni-Co bimetallic catalyst composition on CNTs grown by TCVD technique was experimentally studied. The experimental findings suggest that CNTs yield is highly determined by the amount of carbon dissolved in these catalysts. The diameter of the CNTs was found to increase as the temperature increased. The increase in diameter was attributed to the higher activity of catalysts at a higher temperature. The formation of the graphitic layer on the catalyst surface seems to have been affected by the diffusion of carbon atoms in the catalyst metal. It was found that by raising the grown temperature, the degree of crystallinity of grown CNTs decreases.

## ACKNOWLEDGEMENT

The authors would like to express their thanks to Shahram Solaymani (PhD candidate, Young researchers and Elite club, Islamic Azad University, Kermanshah Branch, Iran) and Dr. Zahra Khalaj (Physics department, Shahre-Qods branch, Islamic Azad University, Tehran, Iran) for their help and cooperation.

## REFERENCES

- [1] Akbarzadeh Pasha M., Poursalehi R., Vesaghi M. A., Shafiekhani A., (2010), The effect of temperature on TCVD growth of CNTs from LPG over Pd nanoparticles prepared by laser ablation. *Physica B*. 405: 3468-3474.
- [2] Akbarzadeh Pasha M., Ranjbar M., Vesaghi M. A., Shafiekhani A., (2010), The evolution of catalyst layer morphology and sub-surface growth of CNTs over the hot filament grown Fe-Cr thin films. *Appl. Surf. Sci.* 257: 1511-1515.
- [3] Kuo D. H., Su M. Y., (2007), The effects of hydrogen and temperature on the growth and microstructure of carbon nanotubes obtained by the Fe(CO)<sub>5</sub> gas-phase-catalytic chemical vapor deposition. *Surf. Coat. Technol.* 201: 9172-9178.
- [4] Feng J. M., Li Y. L., Hou F., Zhong X. H., (2008), Controlled growth of high quality bamboo carbon nanotube arrays by the double injection chemical vapor deposition process. *Mater. Sci. Eng. A*. 473: 238-243.
- [5] Lee O., Jung J., Doo S., Kim S., Noh T., Kim K., Lim Y., (2010), Effects of temperature and catalysts on the synthesis of carbon nanotubes by chemical vapor deposition. *Met. Mater. Int.* 16: 663-667.
- [6] Kumar M., Ando Y., (2010), Chemical vapor deposition of carbon nanotubes: A review growth mechanism and mass production. *J. Nanosc. Nanotechnol.* 10: 3739-3758.
- [7] Gwan Hahm M., Kwon Y. K., Busnaina A., Jung Y. J., (2010), Structure Controlled Synthesis of Vertically Aligned Carbon Nanotubes Using Thermal Chemical Vapor Deposition Process. *J Heat Transfer*. 133: 031001-031004.
- [8] Moaisala A., Nasibulin A. G., Kauppinen E. I., (2003), The role of metal nano particles in the catalytic production of single-walled carbon nanotubes: A review. *J. Phys. Condens. Matter*. 15: S3011- S3035.
- [9] Zhou W., Han Z., Wang J., Zhang Y., Jin Z., Sun X., Zhang Y., Yan C., Li Y., (2006), Copper catalyzing growth of single-walled carbon nanotubes on substrates. *Nano Lett.* 6: 2987-2990.
- [10] Bhaviripudi S., Mile E., Steiner III S. A., Zare A. T., Dresselhaus M. S., Belcher A. M., Kong J., (2007), CVD synthesis of single-walled carbon nanotubes from gold nanoparticles catalysts. *J. Am. Chem. Soc.* 129: 1516-1517.
- [11] Takagi D., Homma Y., Hibino H., Suzuki S., Kobayashi Y., (2006), Single-walled carbon nanotube growth from highly activated metal catalysts. *Nano Lett.* 6: 2642-2645.
- [12] Yuan D., Ding L., Chu H., Feng Y., Mcnicholas T. P., Liu J., (2008), Horizontally aligned single-walled carbon nanotube on quartz from a large variety of metal catalysts. *Nano Lett.* 8: 2576-2579.
- [13] Liu B., Ren W., Gao L., Li S., Liu Q., Jiang C., Cheng H.-M., (2008), Manganese-catalyzed surface growth of single-walled carbon nanotubes with high efficiency. *J. Phys. Chem. C*. 112: 19231-19235.
- [14] Hofmann S., Blume R., Wirth C. T., Cantoro M., Sharma R., Ducati C., Hävecker M., Zafeirotos S., Schnoerch P., Oestereich A., Teschner D., Albrecht M., Knop-Gericke A., Schlögl R., Robertson J., (2009), State of transition metal catalysts during carbon nanotube growth. *J. Phys. Chem. C*. 113: 1648-1656.
- [15] Nunez J. D., Maser W. K., Mayoral M. C., Andrés J. M., Benito A. M., (2011), Platelet-like catalyst design for high yield production of multi-walled carbon nanotubes by catalytic chemical vapor deposition. *Carbon*. 49: 2483-2491.
- [16] Zhou W., Ding L., Liu J., (2009), Role of catalysts in the surface synthesis of single-walled carbon nanotubes. *Nano Res.* 2: 593-598.
- [17] Cheung C. L., Kurtz A., Park H., Lieber C. M., (2002), Diameter-controlled synthesis of carbon nanotubes. *J. Phys. Chem. B*. 106: 2429-2433.
- [18] Kondo D., Sato S., Awano Y., (2006), Low-temperature synthesis of single-walled carbon nanotubes with a narrow diameter distribution using size-classified catalyst nanoparticles. *Chem. Phys. Lett.* 422: 481-487.
- [19] Chiang W. H., Sankaran R. M., (2008), In flight dimensional tuning of metal nanoparticles by microplasma synthesis for selective production of diameter-controlled carbon nanotubes. *J. Phys. Chem. C*. 112: 17920-17925.
- [20] Rider A. E., Levchenko I., Chan K. K. F., Tam E., Ostrikov K., (2008), Size-selected Ni catalyst islands for single-walled carbon nanotube arrays. *J. Nanopart. Res.* 10: 249-254.
- [21] Bachilo S. M., Balzano L., Herrera J. E., Pompeo F., Resasco D. E., Weisman R. B., (2003), Narrow (n,m)-distribution of single-walled carbon nanotubes grown using a solid supported catalyst. *J. Am. Chem. Soc.* 125: 11186-11187.
- [22] Chiang W. H., Sankaran R. M., (2009), Linking catalyst composition to chirality distributions of as-grown single-walled carbon nanotubes by tuning Ni<sub>x</sub>Fe<sub>1-x</sub> nanoparticles. *Nat. Mater.* 8: 882-886.
- [23] He M., Chernov A. I., Fedotov P. V., Obratsova E. D., Sainio J., Rikkinen E., (2010), Predominant (6, 5) single-walled carbon nanotube growth on a copper-promoted iron catalyst. *J. Am. Chem. Soc.* 132: 13994-13996.
- [24] De Oliveira R. R. L., Albuquerque D. A. C., Cruz T. G. S., Yamaji F. M., Leite F. L., (2012), Atomic Force Microscopy-Imaging, Measuring and Manipulating surfaces at the atomic scale. In V. Bellitto (Ed.), *InTech*.
- [25] Ghodselahi T., Vesaghi M. A., Shafiekhani A., (2009), Study of surface plasmon resonance of Cu@Cu<sub>2</sub>O core-shell nanoparticles by Mie theory. *J. Phys. D: Appl. Phys.* 42: 1-6.

- [26] Tripathi N., Mishra P., Harsh, Islam S. S., (2014), Effect of growth temperature on the diameter distribution and yield of carbon nanotubes, *Physics of Semiconductor devices. Environmental Science and Engineering* (645-650). Springer.
- [27] Yazyev O. V., Pasquarello A., (2008), Effect of metal elements in catalytic growth of carbon nanotubes. *Phys. Rev. Lett.* 100: 156102-156106.
- [28] Deck C. P., Vecchio K., (2006), Prediction of carbon nanotube growth success by the analysis of carbon-catalyst binary phase diagrams. *Carbon.* 44: 267–275.
- [29] Lahiri I., Lahiri D., Jin S., Agarwal A., Choi w., (2011), Controlling the orientation of terraced nanoscale “Ribbons” of a poly (thiophene) semiconductor. *ACS Nano.* 3: 780-787.
- [30] Nitze F., Andersson B. M., Wagberg T., (2009), Ammonia assisted growth of multiwalled carbon nanotubes. *Phys. Status Solidi B.* 11- 12: 2440-2443.