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The effects of Fe/Al_2O_3 preparation technique as a catalyst on synthesized CNTs in CVD method.

Ali.A.Hosseini*, F.Sh.Abhari, F.Taleshi

Department of Physics, University of Mazandran, Babolsar, 47416-95447, IRAN
*Correspondions autours e- mail; hos-a-p1@umz.ac.ir

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Abstract
In this research, the growth of CNTs is carried out on Fe/Al_2O_3 substrate by CVD method. Preparation of Fe catalyst nanoparticle supported on Al_2O_3 substrate as catalyst system for growth of CNTs, were carried out by two different methods, in order to, investigate its effects on the quality of synthesized CNTs. In the first method, Fe nanoparticles (with the size of less than 60nm) were mixed with alumina powder, and in the second one impregnation method were employed to synthesis catalyst particle on alumina substrate from $Fe(NO_3)_3.6H_2O$ salt. The qualities of CNTs growth on the substrates produced by above methods were compared using SEM images and XRD pattern of the produced samples.

Key words; catalyst, Fe/ Al_2O_3, CVD, CNT, impregnation, SEM, XRD

1-Introduction:

In recent years, carbon nanotubes (CNTs) were investigated extensively because of their unique properties and potential applications. So far, many efforts were performed toward control of the growth process of CNTs. [1-3]

Among the conventional methods in the synthesis of CNTs, chemical vapour deposition method (CVD) is known as more appropriate due to its high production yield, high possibility of growth as well as the desired economic justification. In the synthesis of carbon nanotubes using CVD, various parameters can be effective on the growth characteristics of the nanotube. These parameters include the type of hydrocarbon feed gas, type of metallic catalyst, catalyst particle size, substrate type and its surface geometry, flow rate of carrier gas and hydrocarbon gas, furnace temperature and growth time [1]. Studies indicate that, often for the nanotube growth using CVD, a variety of porous substrates such as MgO, Al_2O_3 and SiO_2 is used. Depending on the context, interaction between substrate and catalyst particles can affect parameters such as particle size and geometry, so that these parameters play important roles in the nanotube growth process [1, 5].

Interaction between catalytic nanoparticles and substrate can be a physical or chemical interaction. In physical interaction, catalyst particle size can be controlled by the presence of porosity on the substrate. But in the case of chemical, the interaction between catalyst particle and substrate occurs during the process of formation of catalyst. [4, 9]

One of the most important applications of CNTs is using them as a fabricating phase in the field of ceramics composite, in order to

improve the physical and mechanical properties of these highly industrial used materials. The quality of the fabricated ceramic Nano composite depends on the degree of the uniformly dispersion of nanotubes throughout the ceramic matrix as well as creation of suitable link between the substrate surface atoms and the nanotube surface. [6, 8].Thus to achieve a precise control over the nanotube growth process is very important. In this research, we consider the effect of iron catalyst preparation method, on the synthesis of CNTs. In this study first, synthesis of CNTs at different temperatures were assigned to obtain optimal temperature conditions on the growth of CNTs in the vicinity of iron/Alumina catalytic substrate. Therefore, to achieve optimal growth temperature, the effect of synthesizing temperature on the quality and quantity of nanotube, three temperatures 865° C, 925° C and 985 ° C were studied as the growth temperatures. It has been reported that the synthesizing temperature is an important factor affecting the size and structure of CNTs [4, 7] the knowledge of temperature effect could help us to investigate the effects of catalytic substrate preparation method on the quality of CNTs produced and the optimum conditions for synthesizing CNTs could be achieved. For preparation of catalytic two different methods were employed.

2-Experimental-section:

2-1 Materials and Devices:

In this project the following materials were used: Alumina powder (radioactive alpha alumina powder with average grain size of two micron Merck with purity 99%) as a substrate raw material, nanoparticles of iron with the dimensions of less than 60 nm and iron salts $Fe\ (No_3)_3.9H_20$ (Merck, purity >99%), CVD system equipped with Ethylene and Argon gasses as feed and carrier gas respectively for synthesis of CNTs, X-ray diffraction system (XRD, GBC,Cu(Kα), λ=1.54Å), at the Department of physics, Mazandaran University for catalyst and MWNT analysis and Scanning Electron Microscope from ETC department of Tarbiat Modarres University (SEM, Philips, 15KV, 30000X, SE), was used for analysis of the samples..

2-2 Catalytic substrate preparation:

2-2-1 First method, preparation of Catalytic Fe (nm) / Al_2O_3 substrate was carried out by direct combination of nanoparticles of commercial iron with alumina powder. Iron nanoparticles with dimension of less than 60 nm have been used as a catalyst. In the first method of preparing catalytic substrate, iron nanoparticle with 10 weight percent relative to alumina were mixed with ethanol under reflux processes for 10 minutes using Ultrasonic bath. Alumina powders were gradually added to the mix during 30 minutes while the mixture was under reflux. As the last processes the mixture were dried on a hot plate in order to remove ethanol from the sample.

2-2-2 In the second method of preparing the catalytic Fe_2O_3/Al_2O_3 substrate, powder of nano size particles of iron catalyst were synthesized using nitrate salts of iron employing impregnation processes on alumina substrate(3).

In this method desired weight percent of catalyst (Iron Oxide) and alumina powder were separately solved in 25 ml and 100 ml of ethanol respectively in an ultrasonic bath under reflux processes for 30 seconds The mixture were stirred with magnetic stirrer under a temperature of 80 C during which the iron nitrite salt was gradually added to the mixture in a period of 30 minutes. Finally the mixture was dried at 120º C on a hot plate followed by grinding of the product in to a fine powder by means of using a mortar until a uniform powder was achieved. For the last treatment the sample was calcinated in an oven under 450º C for 2 hours. Fe_2O_3/Al_2O_3 catalytic substrates were prepared for different concentration ratio of $Fe\ (No_3)_3.9H_20$ /alumina ratios (10 % wt,

20% wt, 30% wt and 40% wt of Fe $(No_3)_3$, $9H_20$

2-3 Synthesis of carbon nanotubes

Initially 500 mg of catalyst powder prepared by the above methods was placed directly at the appropriate place in the furnace, while argon carrier gas with flow of 100 sccm has been established in the quartz reaction tube. The synthesis of CNTs was carried out by pyrolyzing of the hydrocarbon feed gas (ethylene) with flow rate of 15 s After synthesis of CNTs, the reactor was turned off and cooled down to room temperature under Argon atmosphere to remove carbon contamination, thermal oxidation was carried out for one hour at 480 ^{0} **C**. followed by, refluxing in distilled water for 10 minutes using ultrasonic wave and finally dried at around 100°C.

3 - Results and discussion:

3-1 Analysis of XRD pattern:

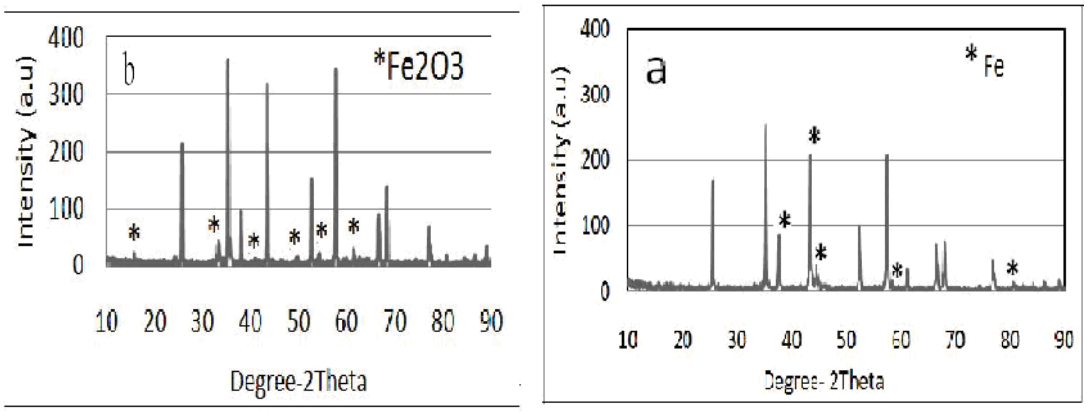

Fig1. XRD patterns of prepared catalyst a) Fe (nm)/Al_2O_3 and b) Fe_2O_3/Al_2O_3

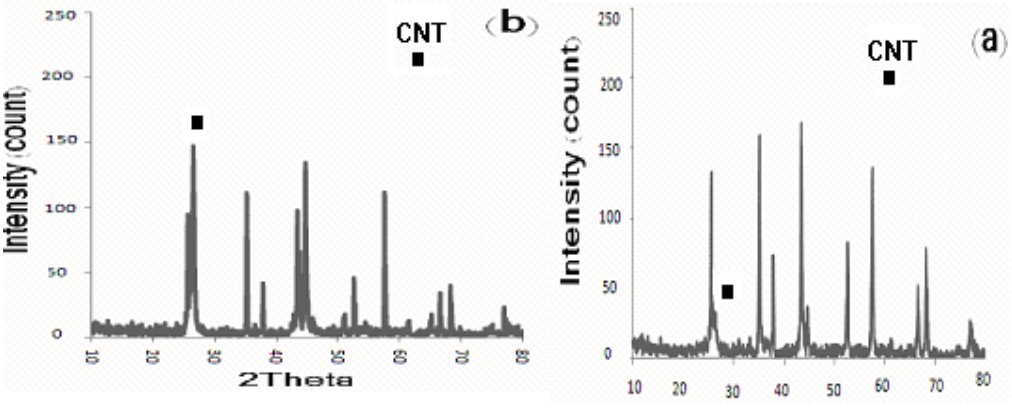

Fig2.XRD patterns of synthesised CNTs on prepared catalytic substrate, a) Fe (nm)/Al_2O_3, and b) Fe_2O_3/Al_2O_3 containing 40 % Salt).The peaks corresponding to CNTs are marked in the figure.

In order to investigate the effects of catalytic substrate preparation methods on produced CNTs the XRD patterns of the prepared substrates by two methods and the samples

were produced at room temperature by scanning the 2ɵ angle through 10 to 90^o, with the step value of 0.05 degrees The XRD patterns were produced by scanning 2ɵ angle through 10 to 90^o, with the step value of 0.05 degrees.

Fig (1) shows the XRD patterns of prepared catalytic substrates (a); Fe (nm)/Al_2O_3 and (b); Fe_2O_3/Al_2O_3 respectively.

The XRD patterns of synthesized CNTs on two substrates are shown in Fig (2).Peaks corresponding to Fe and **Fe_2O_3**, nanoparticles are marked by attics -a) and -b) respectively. Remaining peaks in the pattern corresponds other structures such as (002) plane of graphite, Alpha phase of alumina as indicated in the Figure

3-2 Nano structural analysis of samples using SEM images

3-2-1 Investigation of the CNTs growth on catalytic substrate Fe (nm)/Al_2O_3:

According to the images of SEM (Fig. 3), it was obvious the effect of substrate such as, when it was used no substrate in the synthesis process of CNTs, no growth observed, and all products are as black carbon (Fig. 3a). But using powder catalyst Fe (nm) / Al_2O_3 with the same growth conditions is caused high yield of CNTs. Therefore, employing Al2O3 substrate can affect catalytic activity of iron and affects the productivity increase of CNTs. (Picture 3b)For investigation of temperature effects on synthesis of CNTs three temperatures growth, was tested (875^0**C,** 925^0**C**, 975^0**C**) which according to these pictures, 925^0**C** has been recognized best conditions for growth of CNTs. As can be seen, the diameter and the yield of CNTs are optimized in this temperature**.** (Fig 3b, 3c and 3d)Outside diameter distribution of CNT growth on Fe (nm) /Alumina is evident that the highest percentage of the nanotubes have diameter about 45 nm which this amount is about average size of Fe nanoparticles. (Fig 4) method on the substrate on the growth of CNTs, preparing powder iron oxide catalyst on alumina substrate by second method, was performed.

We can control a catalyst nanoparticle size, by changing the salt concentration of Fe $(No_3)_3.9H_20$ to the alumina substrate.

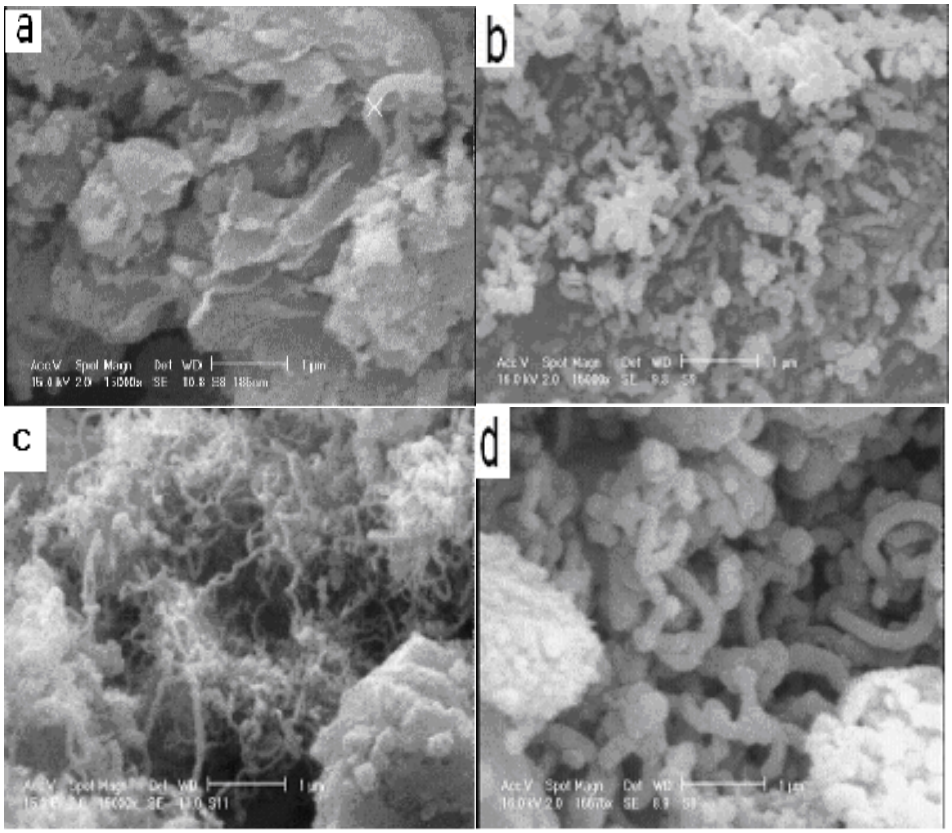

Fig3. SEM images of synthesized of CNTs on a) Fe nanoparticle without any substrate (compare a and c in which all of the synthesis conditions is same) and other images are related to Fe (nm)/Al_2O_3 under different growth temperatures b) 875°C c) 925°C and d) 985°C.As can be seen in 875°C CNTs are very short with low yield and in 985°C CNTs are very large diameters. (b and d)

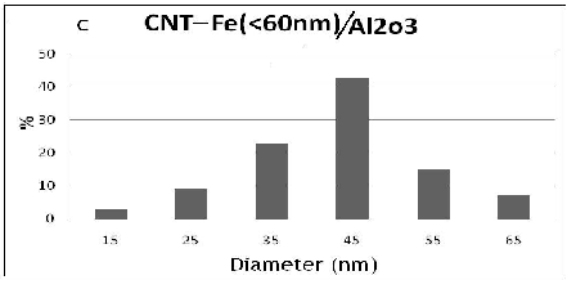

Fig4. Outside diameter distribution of CNT growth on Fe (nm) / Al_2O_3 which prepared by first method. (Only one weight percentage of Fe nanoparticles)

2-2-3 Investigation of the growth of CNTs in the vicinity of catalyst Fe_2O_3/Al_2O_3:

Considering the importance of using substrate to investigate the effect of catalyst preparation Comparing of SEM images (Fig.5), all that is changing the composition of different weight percentage of iron salt, the amount and range of diameter distribution also carbon pollution levels are

different. As can be seen the least carbon-related pollution mixed weight percentage of 30 percent iron oxide catalyst with a diameter less extensive distribution (range 55 to 105 nm) and the highest rate of pollution related to the mixed weight percentage is 40 percent (with a maximum range of diameter distribution , from 55 to 135 nm). In the mixed weight percentage of 40% CNT length is shorter than the other compounds weight. On the other hand comparing the SEM images of Figure 3 and 5, the synthesis of CNTs in the vicinity of Fe_2O_3/Al_2O_3 catalyst with respect to Fe (nm) / Al_2O_3 have been more appropriate conditions so that the lower amount of carbon pollution as well as better product we are witnessing.(fig 6)

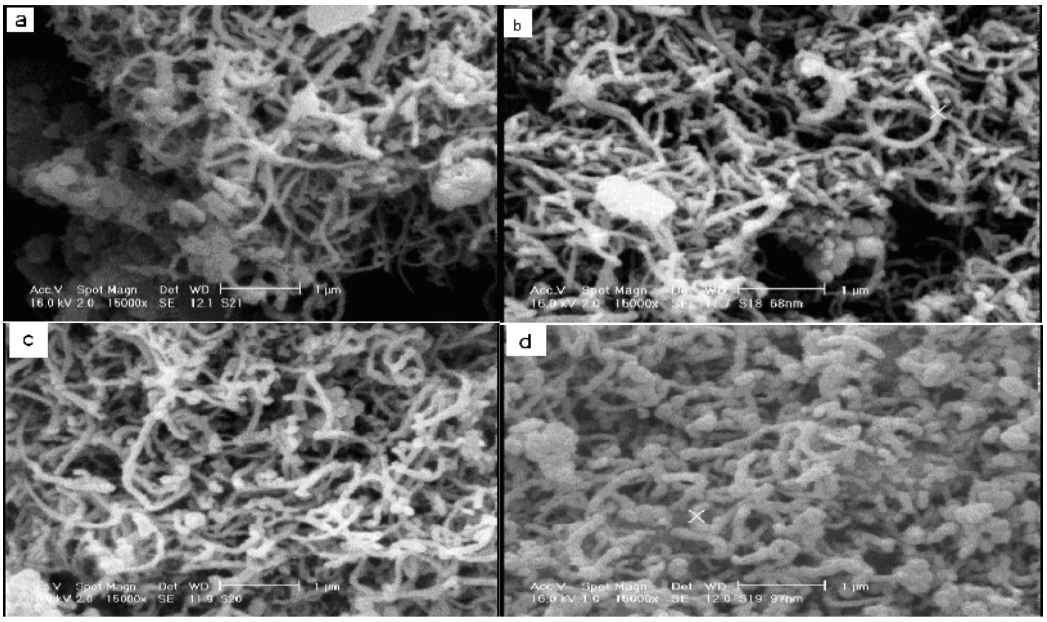

Fig5. SEM images of the growth of CNTs on Fe_2O_3/Al_2O_3 with different concentration of salt a) 10 wt%, b) 20 wt% , c)30 wt% and d)40 wt%

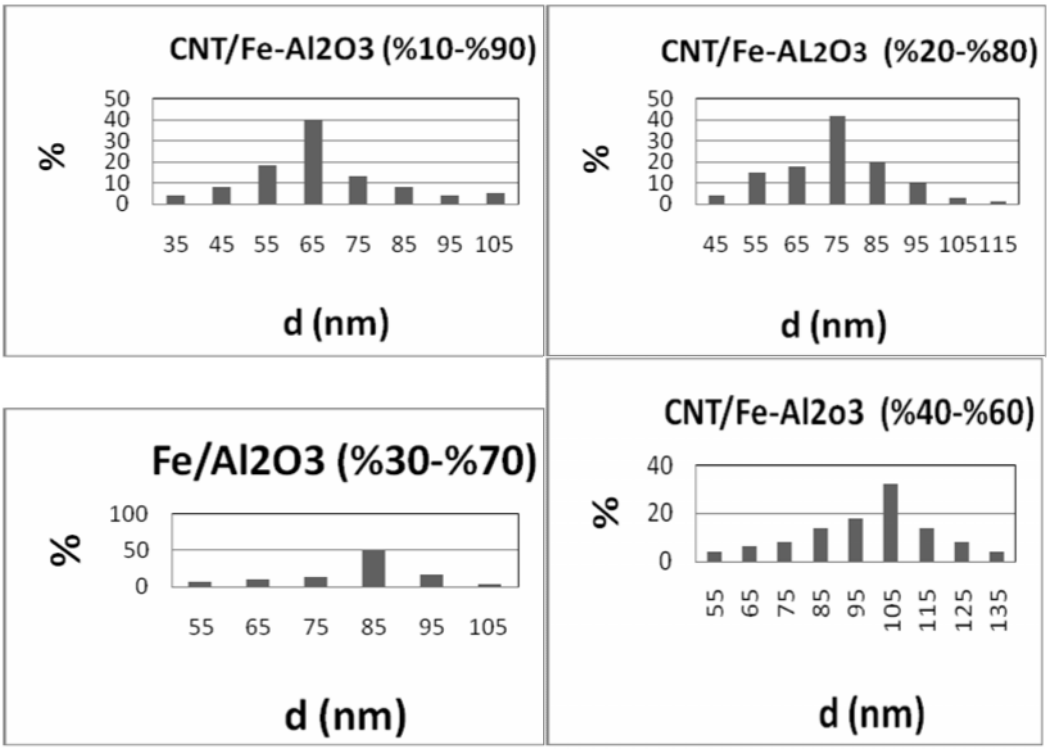

Fig6. Outside diameter distribution of CNT growth on Fe_2O_3/Al_2O_3 which prepared by second method with different concentration of catalyst. a)10 wt% , b)20 wt% , c)30 wt% and d)40 wt%

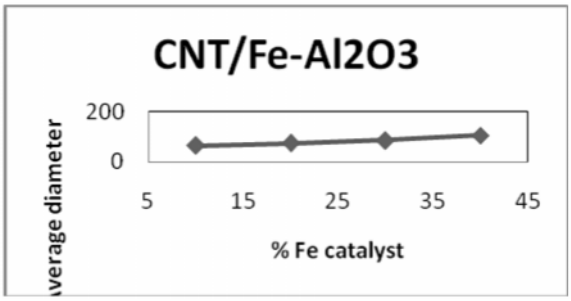

Fig7. Increasing of CNT 's outer diameter with incresing in concentration of Fe $(No_3)_3.9H_20$

Calculations found on outer diameter nanotubes synthesized by both methods indicate that, the most presence of the nanotubes, in terms of diameter value, are within the average size of catalyst particles used in the first method (40-30 nm) respectively (Fig.4) that is lower in respect to another one. In Column distribution, are shown outer diameter distribution of CNTs for the different percentages in which can be observed with increasing weight percentage of iron salt to the alumina substrate, the amount of 10% to 40%, the average diameter of the nanotubes are proportional to its 65 to 105 nm increases **.** Then can be said that in the same condition growth averge diameter of CNTs is more than synthesised CNTs in the frst method**.**

The effect of increasing of CNT 's outer diameter with incresing in concentration of Fe $(No_3)_3.9H_20$ in Figure 7 curve is drawn. Then we can easily control the diameter of CNTs with changes in concentration of salt.

5-Conclusion

Alumina substrate utilization can change temperature of catalyst activity and in addition to increasing of carbon yield, it will be caused to produce higher quality of nanotubes. The best temperature for growth of CNTs by using of ethylene gas is 925^0**C** in respect of quantity and quality. The SEM images obtained, a significant difference have been observed for the synthesis of nanotubes produced by two types of catalysts. Although preparation of the catalyst Fe(nm)/ Al_2O_3, the direct mixing of commercial iron nanoparticles with alumina substrate can be done easier and shorter time, but at a constant temperature of synthesis, the diameter of CNTs is near to catalyst particle therefore the control of CNT' s size is more easier because it' s enough to choose catalyst size, but using second method have some advantages such as in this way, by changing of concentration of salt the weight percentage of the catalyst and as a result the yield of the nanotube can be changed. In addition to in second method the nanotubes diameter also changes therefore can be obtain an optimum method for controlling the diameter of CNTs to achieve desired diameter of CNTs. While in preparing the catalyst by the first method, we only have a fixed measure range of nanoparticles.

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References:

[1] J. W. Ward and et al, Substrate effects on the growth of CNT by …, Chem. *Phys. Let*. **376**(2003) 717-725.

[2] Régis Philippe and et al, An original growth mode of MWCNTs on alumina supported iron catalysts, Journal of Catalysis

[3] William A. and et al, CNT reinforced ceramic and metals, materials today, ISSN: 1369 7021 ©Elsevier Ltd 2004

[4] Anne-Claire Dupuis, The catalyst in the CCVD of carbon nanotubes—a review**,** *Materials Science*, **Volume 50**, *Issue 8, November 2005, Pages 929-961*

[5] L. Kumari and et al, Synthesis, microstructure and electrical conductivity of carbon nanotube–alumina nanocomposites, *Ceramics International,* **Volume 35, Issue 5**, July 2009, Pages 1775-1781

[6] Jinwei Ning and et al, Fabrication and mechanical properties of SiO2 matrix composites
Reinforced by carbon nanotube, Materials Science and Engineering A357 (2003) 392_396

[7] E.Teredo, aligned carbon nanotube grown on alumina and quartz substrate by simple thermal CVD processe, *Diamond Related Materials* **15**(2006), July 2009, Pages 1775-1781

[8] K. Balani and et al, (2008) , In situ carbon nanotube reinforcements in a plasma-sprayed aluminium oxide nanocomposite coating aluminium oxide nanocomposite coating, Acta Material 56, 571–579

[9] Ali A Hosseini, F Taleshi, Large diameter MWNTs growth on iron-sprayed catalyst by CCVD method under atmospheric pressure, Indian Journal of Physics, Vol.84, No. 7, (2010) 789-794