The 2013 World Congress on
Advances in Nano, Biomechanics, Robotics, and Energy Research (ANBRE13)
Seoul, Korea, August 25-28, 2013

Electrical Properties of Iron Oxide Nanoparticles Coated Carbon Nanotubes

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ABSTRACT

Iron Oxide nanoparticles are prepared via simple cost effective sol-gel route using $FeCl_3.6H_2O$ as precursor. Ethanol and deionized water is used as a solvent and sodium hydroxide as a gelation agent. The gel synthesis is achieved by controlling the amount of sodium hydroxide. Oleic acid is used as a surfactant to control the shape and size of nanoparticles. The detailed synthesis of iron oxide sol is reported earlier (Riaz 2013). Carbon nanotubes prepared by plasma assisted CVD are coated by iron oxide NPs. Carbon nanotubes are also annealed in controlled atmosphere to study the effect of annealing temperature on the phase and morphology of CNTs. Electrical properties are measured using four probe methods. It is observed that iron oxide coating enhanced the electrical properties of CNTs. Moreover, shape, size and volume to surface ratio of iron oxide Nanoparticles that are incorporated in CNTs have also remarkable effect on the electrical properties of carbon nanotubes.

1. INTRODUCTION

Carbon nanostructures are widely studied and used for variety of applications (Bhushan 2006). Their electrical and mechanical properties particularly at nano-scale make them an attractive candidate for electronic & storage devices/purposes, field emission tips for displays ((Bhushan 2006), electron sources for X-rays, electron microscopy and lithography (Pierson 1992, Masarapu 2007), scanning probe tips for atomic scale imaging (Wang 2005), in nanoelectronics as transistors and diodes (Wal 2003), an array of vertically aligned multiwalled nantubes/nanofibres for electrodes and biosensors (Yun 2007, Park 2003). Substrate, which offers a support for nanostructures, plays important role in all these applications, and mostly a conducting substrate is required (Bhushan 2006).. Growth of carbon nanowires & nanotubes directly on a metal/conducting surface increases their adherence to the electrodes and

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favour a better electron/thermal transfer. Stainless steel (SS) is the best option for growth of carbon nanostructures as it is not only a conducting substrate but it also provides a support for carbon growth and gives catalytic sites for the growth and nucleation at nano-scale.

Variety of techniques has been used for the growth of carbon nanostructures. These include arc-discharge method, laser-ablation and chemical vapour deposition (CVD) (Wang 2001). CVD is a unique and superior to rest of the two techniques as uniformity and alignment of nanotubes & nanowires can be achieved during the growth process (Wang 2001). Drawback of arc-discharge and laser-ablatiion is that the nanostructures have to be produced separately, purified and then transferred to the required substrate (Wang 2001).

In a CVD system, the growth of carbon nanotubes occurs through catalytic decomposition (Wang 2001) of a carbon source gas over nanoparticles/islands of catalyst metal. The quality of the grown carbon nanotubes depends on the substrate, catalyst used and the growth parameters. Most commonly used are plasma-enhanced CVD (Sinnott 2000), metal-organic CVD, laser CVD, low pressure CVD and thermal CVD (Sinnott 2000, Park 2003, Yun 2007).

In this paper we report on the simple method for the uniform growth of carbon nanotubes. Iron oxide nanoparticles, prepared by sol gel method, are used to coat carbon nanotubes. Electrical properties are measured using four probe method. Shape, size and volume to surface ratio of iron oxide Nanoparticles that are incorporated in CNTs have also remarkable effect on the electrical properties of carbon nanotubes.

2. EXPERIMENTAL DETAILS

Stainless steel of commercial grade (i.e. SS201, SS303, SS304, SS316, SS420 and SS430) were cut into 5×5 mm square pieces to be used as substrates during this research work. As surface morphology plays a critical role during the growth of structures at nanoscale (Ren 1998), therefore, SS substrates were pretreated at different conditions prior to deposition. These conditions involved degreasing, cleaning, polishing, etching and baking of substrates. Polishing was done mechanically at the early stages by using sand paper of different grades and then by electrochemically by using electro-polisher in order to get a mirror like surface. Then the substrates were cleaned in an ultrasonic bath with acetone and then IPA for 15 minutes. Etching of the substrates was done by using 38% concentrated HCl solution for 10 minutes. HCl etching increases the growth rate of carbon nanostructures. It provides particle like active catalytic sites which are required for the growth of carbon nanostructures (Okai 2000).

The objective of the pretreatment of the substrates was to generate these favorable growth sites. After etching and then washing with distilled water SS substrates were prebaked at 850^{o}C in N_2 atmosphere for 30 min. Prebaking the substratre surface at 850^{o}C favourizes the recrystallization process and generates nanometer scale grain structures providing particle like active catalytic sites such as surface defects (Okai 2000).

Pretreated SS substrates were put into the home-made Plasma Enhanced CVD furnace/reactor. Methane (CH_4) gas was used with the pressure of 0.75torr which

decomposed to provide carbon in the presence of arc discharge produced between the carbon electrodes (shown in the Fig. 1) by applying the high voltage of 30KV between electrodes. Carbon was deposited at reaction temperature of 850 for 20 minutes.

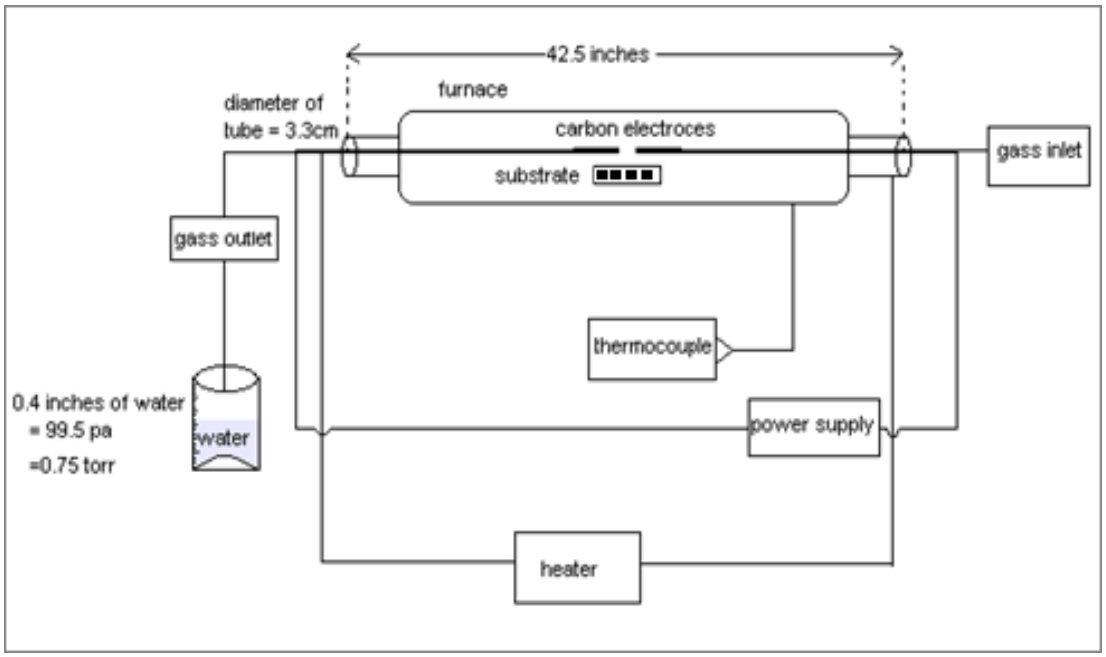

Fig. 1 Block diagram of home-made setup of Plasma Enhanced CVD

Leica DM-4000M Optical Microscope and Ambios-XP1 surface profilometer was used to examine the surface of substrates before polishing and then after every surface treatment. Hitachi S-3400 N scanning electron microscope was used to observe the growth and dimensions of carbon nanostructures deposited onto SS substrates. Structural Characterization was done by using Rigaku D-MAX-IIA X- Ray diffractometer. Metallic to semi-metallic nature with the change in resistance, after iron oxide NPs coating, was observed by using Everbeing microprober and Keithley 4200 semiconductor characterization system.

3. RESULTS AND DISCUSSION

Commercially available grades of SS steel substrates (i.e. SS420, SS304, SS201) were analysed for their surface properties and roughness values. Fig. 2(a-c) shows optical micrographs of SS substrates along with their surface profile.

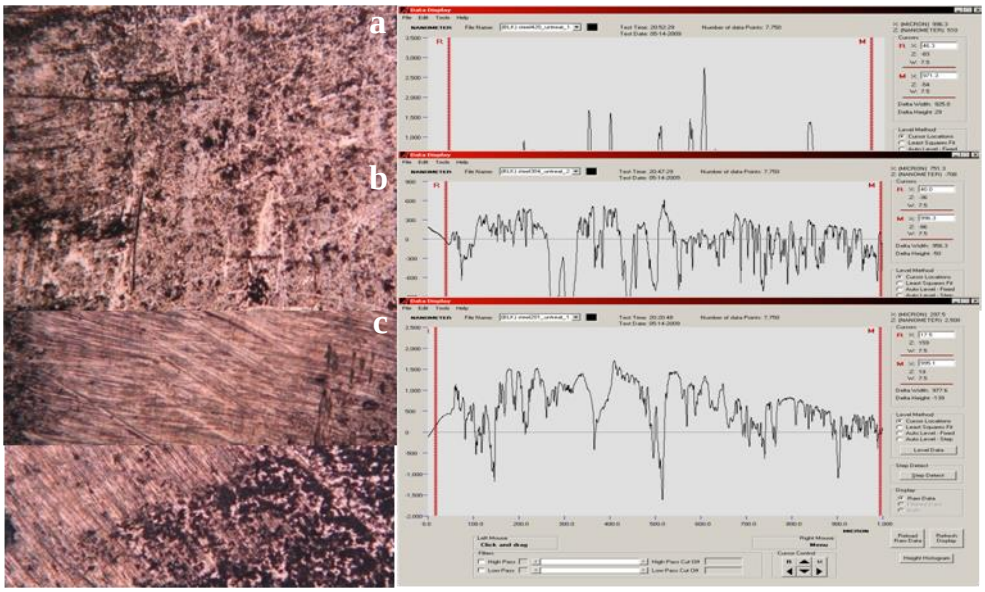

Fig. 2: Optical images (at 50x) and surface profile of (a) SS420 (b) SS 304, and (c) SS 201 showing surface roughness before polishing

Surface profilometery graphs are in close agreement with optical micrographs as both the results are showing an average roughness of less than 100 nm before any surface treatment. Surface treatment is essential for the growth of CNTs (Teo 2003, Merkulov 2001, Harris 2001). This treatment includes: Polishing, Etching and Baking.

Fig. 3 shows the smooth surfaces of SS420, SS304, SS201 at a magnification of 50X. Optical micrographs show that all the stains and contamination is removed from the substrates. Surface is now smooth with an average roughness value of15nm which is close/better than the value reported after polishing.

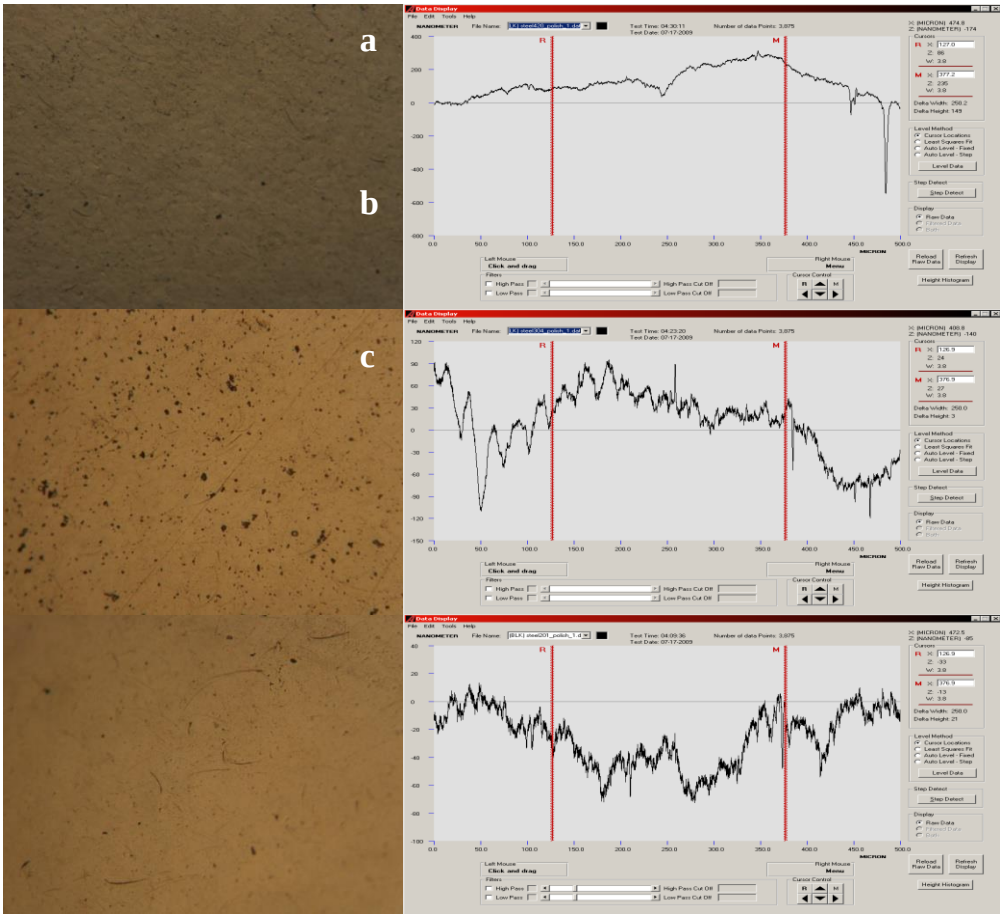

Fig. 3: Optical images (at 50x) and surface profile of (a) SS420 (b) SS 304, and (c) SS 201 showing smooth surface after polishing

Etching plays an important role for depositing carbon nanotubes (CNTs) without any additional catalytic coating on the substrate.

38% concentrated hydrochloric (HCl) acid was used to etch the surface of stainless steel substrates. Etching was done for 10 minutes. HCl preferentially etches chromium more than other metal compositions present in stainless steel (Hiramatsu 2010). This makes stainless steel substrates rich in iron. As a result of etching nucleation sites are formed on the surface of all SS substrates as observed from optical micrographs and confirmed from their surface profiles [Fig. 4]. These sites will favourize the growth process for CNTs (Hiramatsu 2010).

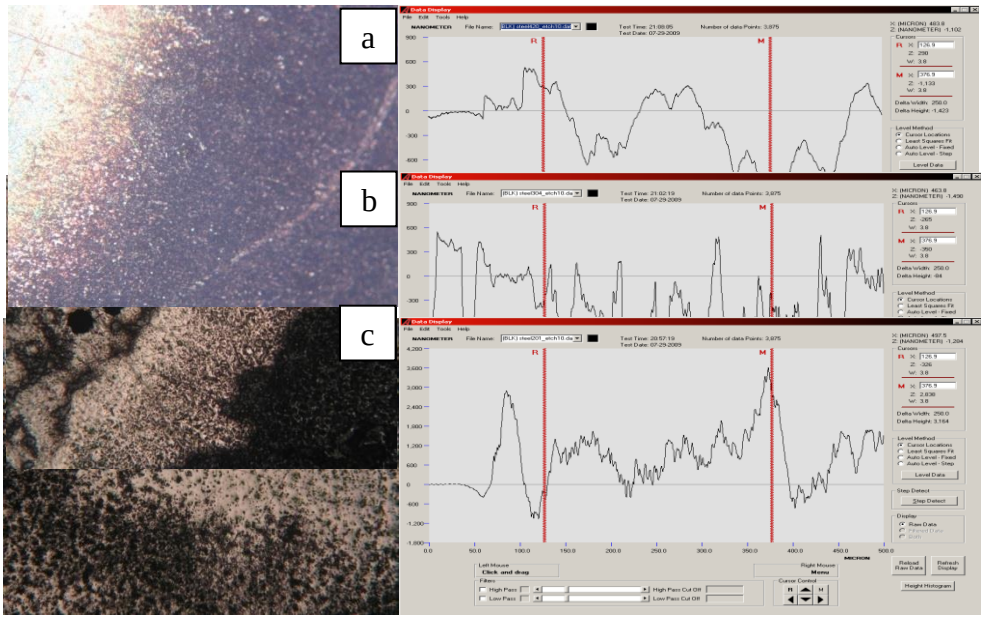

Fig. 4: Optical images (at 50x) and surface profile of (a) SS420 (b) SS 304, and (c) SS 201 showing surface roughness/nucleation sites after etching

Roughness of the substrate before and after polishing and then after etching is given in Table 1.

Table 1. Roughness in nanometer

Samples	Before Polishing	After Polishing	After etching
SS 420	1400-2800 nm	300-50 nm	300-600 nm
SS 304	400-600 nm	90-50 nm	200-600 nm
SS 420	1400-1700 nm	10-5 nm	1899-3600 nm

SS 420 substrate was placed at a distance of 12mm horizontally and 2.5cm vertically from the centre of electrodes. The distance between the electrodes is 3mm. Thermocouple is attached at the centre of the furnace. To carry out a comparative study carbon was deposited on etched as well as un-etched SS substrates.

After polishing and etching substrates were placed in CVD furnace for carbon deposition. Deposition conditions are given in experimental section. After deposition, carbon nanotubes were peeled off from the substrates and were purified chemically at 200^{o}C. After purification and filtration carbon nanotubes were functionalized before the coating of iron oxide nanoparticles. In-situ coatings of NPs were performed in this work.

Figure 5 show SEM image of iron oxide coated carbon nanotubes.

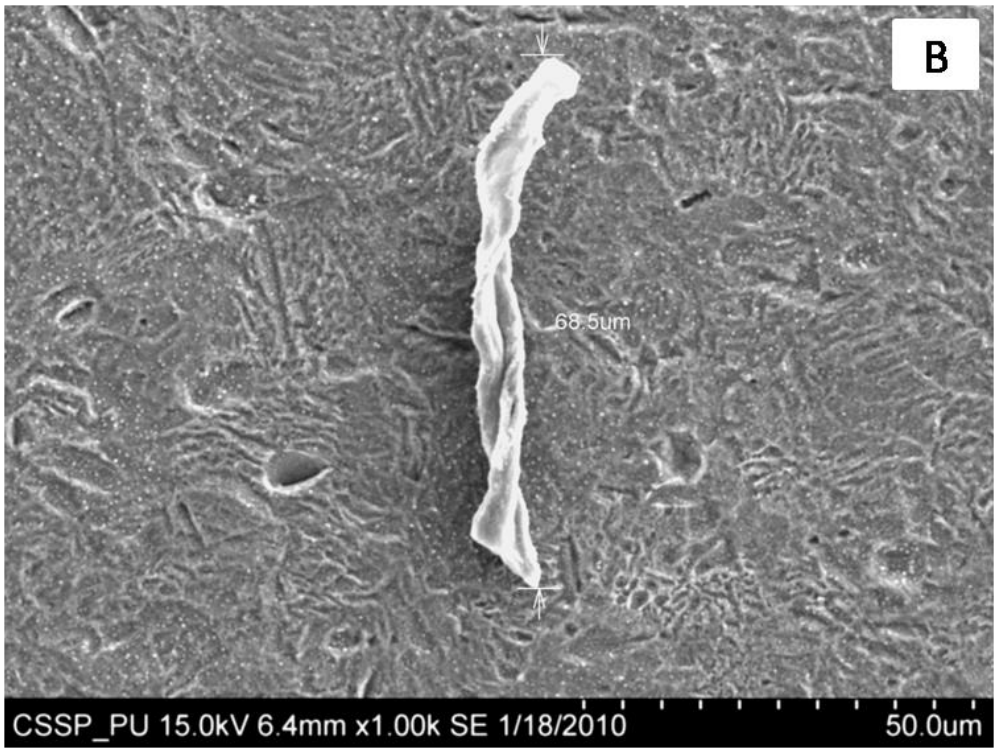

Fig. 5 SEM image iron oxide NPs coated bundles of Carbon nanotube

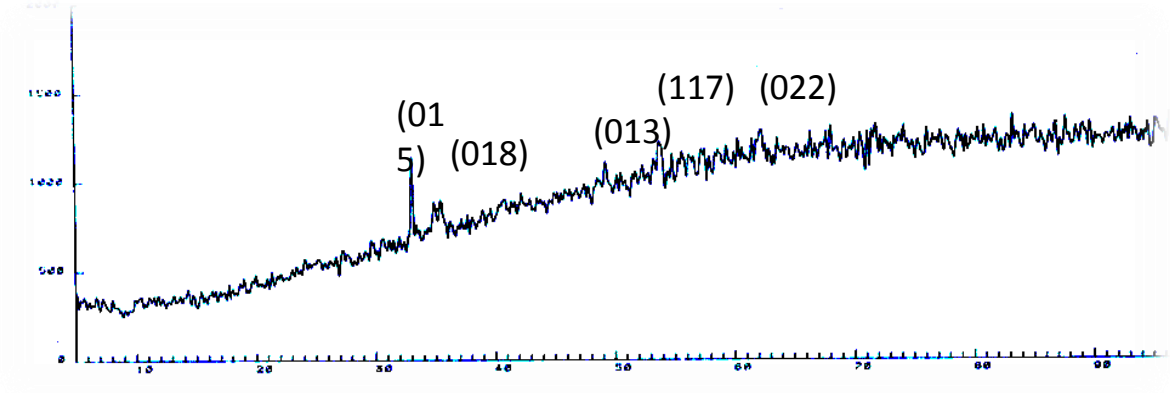

Fig. 6 XRD result of iron oxide coated carbon nanotube

I-V characteristics of coated carbon nanotubes is shown in Fig. 7. The resistance of the sample with iron oxide coating was 436 Ω which is smaller as compared to the uncoated sample

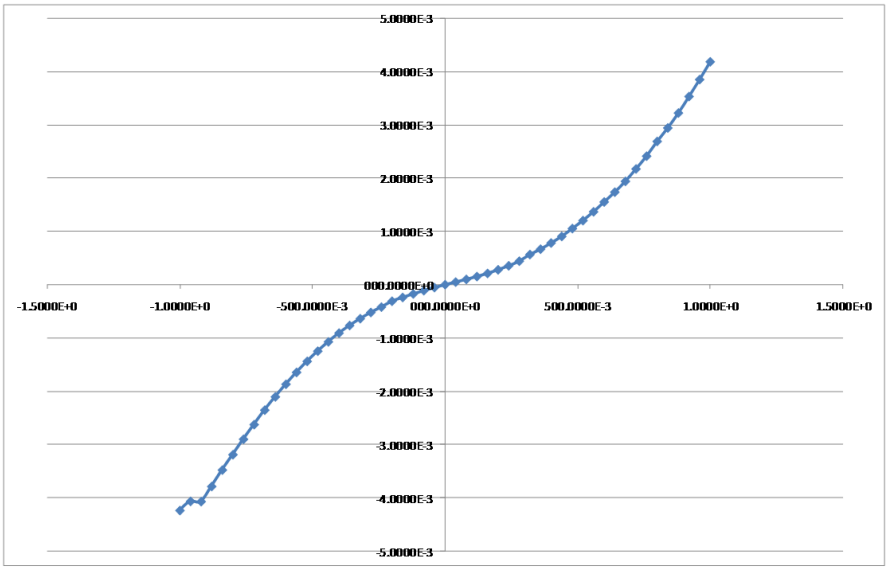

Fig. 7 I-V characteristics of iron oxide coated carbon nanotubes

4. CONCLUSIONS

Carbon nanotubes were prepared by plasma assisted CVD method. SS Substrates were polished and etched to create the nucleation sites. Deposition was carried out at 850^{o}C. Carbon nanotubes were also annealed in controlled atmosphere to study the effect of annealing temperature on the phase and morphology of CNTs. Iron Oxide nanoparticles are prepared via simple cost effective sol-gel route using $FeCl_3.6H_2O$ as precursor. Ethanol and deionized water was used as a solvent and sodium hydroxide as a gelation agent. In-situ NPs coating method was used to coat carbon nanotubes by iron oxide nanoparticles. Electrical properties are measured using four probe method. It is observed that iron oxide coating enhanced the electrical properties of CNTs. Moreover, shape, size and volume to surface ratio of iron oxide Nanoparticles that are incorporated in CNTs have also remarkable effect on the electrical properties of carbon nanotubes.

REFERENCES

Bhushan, B. (2006), *Springer Handbook of Nanotechnology,* Springer, Newyork.

Harris, P.J.F. (2001), *Carbon Nanotubes and Related Structure,* Cambridge University, UK.

Hiramatsu, M. and Hori, M. (2010), *Carbon Nanowalls Synthesis and emerging Applications*, Springer Wien, New York.

Masarapu, C. and Wei, B. (2007), “Direct Growth of Aligned Multiwalled Carbon Nanotubes on Treated Stainless Steel Substrates”, Langmuir, **23**, 9046–9049

Merkulov, V.I., Guillorn, M.A., Lowndes, D.H. and Simpson, M.L. (2001), “Shaping carbon nanostructures by controlling the synthesis process,” *Appl. Phys. Lett.*, **79**, 1178.

Okai, M., Muneyoshi, T., Yaaguchi, T. and Sasaki, S. (2000), “Structure of carbon nanotubes grown by microwave-plasma-enhanced chemical vapor deposition”, *Appl. Phys. Lett.*, **77**, 3468.

Park, D., Kim, Y.H. and Lee, J.K. (2003), “Pretreatment of stainless steel substrate surface for the growth of carbon nanotubes by PECVD”, *J. Mater. Sci.*, **78**, 4933-4939.

Pierson, H.O. (1992), *Hand book of Chemical Vapor Deposition,* Noyes Publications, Norwich, New York, U.S.A.

Ren, Z.F., Huang, Z.P., Xu, J.W., Wang, J.H., Bush, P., Siegal, M.P. and Provencio, P.N. (1998), “Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass”, *Science*, **282**, 1105-1107.

Sinnott, S.B., Andrew, R., Qian, D., Rao, A.M., Mao, Z., Dickey, E.C. and Derbyshire, F. (2000), “Model of carbon nanotube growth through chemical vapor deposition”, *Chem. Phys. Lett.*, **315**, 25-30.

Teo, B.K., Singh, C., Chhowalla, M. and Milne, W.I. (2003), *Encyclopedia of Nanosience and Nanotechnology*, Taylor and Francis, New York.

Wal, R.L.V. and Hall, L.J. (2003), “Carbon nanotube synthesis upon stainless steel meshes,” *Carbon*, **41**, 659-672.

Wang, N., and Yao, B.D. (2001), “Nucleation and growth of well-aligned, uniform-sized carbon nanotubes by microwave plasma chemical vapor depositon”, *Appl. Phys. Lett.*, **78**, 4028.

Wang, Z., Wu, Q., Zhang, F.Y. and Cui, Y.Y. (2005), “Synthesis of multi-walled carbon nanotube bundles with uniform diameter”, *Mater. Lett.*, **61**, 1955-1958.

Yun, Y., Gollapudi, R., Shanov, V., Schulz, M., Dong, Z. and Jazieh, A. (2007), “Carbon Nanotubes Grown on Stainless Steel to form Plate and Probe Electrodes for Chemical/Biological Sensing”, *J. Nanosci. Nanotechnol.*, **7**, 891-897.