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Preparation of $FeCl_3$ Catalytic Films Using Dip Dry Method for the Growth of Carbon Nanotubes

Mohan Lal [1,*], BharatBhushanSharma[2], PoornenduChaturvedi[1], PikaJha[1], Jaswant Singh Rawat[1], Partap Kumar Chaudhury[1]

[1]*Solid State Physics Laboratory, DRDO, New Delhi, India.*
[2]*D.A.V. Institute of Engineering and Technology, Jalandhar, Punjab, India.*

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Abstract

Catalytic films of $FeCl_3$ were coated on Si using simple and highly scalable technique of dip drying of silicon in aqueous $FeCl_3$ solution. The catalyst coated samples were pretreated at 850°C to reduce the deposited $FeCl_3$ into iron nanoparticles. The size distribution of nanoparticles was found to be strongly dependent on initial concentration of $FeCl_3$ in aqueous solution. The catalytic activity of nanoparticles was ascertained by growthof carbon nanotubes using Chemical Vapour Deposition. The $C_2H_2$was used as the carbon precursed along with the carrier gas of H_2 and NH_3.Characterization of the grown CNT revealed the direct relationship between the catalytic concentration and the diameter of carbon nanotubes.

Key words : *Carbon nanotubes; Catalytic films; Chemical vapour deposition; Dip dry method.*

1. INTRODUCTION

Catalyst plays an important role in controlling a wide variety of reactions. These range from biological reactions which are crucial for our existence to reactions used for extraction of elements and synthesis of compounds, polymers, etc. Transition metal compounds as catalysts have been used for various applications and are specifically used in the growth of carbon nanotubes.Carbon Nanotubes (CNT)which were discovered by (Iijima 1991) has got the attention of the research community because of its unique properties. The CNTwhich could be understood as a rolled upgraphenesheet, are mainly of two types single wall or multiwall.

Although because of their remarkable and extraordinary properties CNT have found applications invariety of fields like nanocomposites [Dalton et al., 2003; Yang et al.,), field emission displays (Saito et al., 2002; Choi et al., 1999) chemical sensors (Ting et al., 2008; Baughman et al., 2002) and physical sensors (Su et al.,) however difficulties related to synthesisof CNTfor specific type of applicationhas limited the commercial production of CNT based devices. The high quality CNT can be synthesized by different method like arc-discharge (Wang et al., 1995; Saito et al., 2003) laser ablation (Scott et al., 2001; Puretzky et al., 2002) and chemical vapor deposition (CVD) (Hart et al., 2006; Chakraborty et al., 2006). Among all of these techniques,CVD isused for the selective growth of CNT at particular location on the substrate and incorporatethem into the electronic devices.

The CVD technique require metal nanoparticle such as Fe, Co and Ni etc. which act as catalyst for the growth of CNT(Esconjauregui et al., 2009). A thin film of these metals is deposited over the substrate which is further treated to prepare metal nanoparticles. The catalyst film can be deposited on the substrate using different deposition technique like sputtering (Zheng et al.,), electron beam deposition (Hart et al., 2006), spin-

*Mohan Lal. Tel.:
E-mail : mohan.lal@sspl.drdo.in

coating (Kim et al., 2005)etc. Among the transition metal elements Fe is the most studied element for growth of carbon nanotubes. Researchers have used Fe is variety of forms which include elemental Fe (Chakraborty et al., 2006), iron oxides (Lee et al.,), iron salts (Hou et al., 2003) and even from biologically available Fe such as in ferritin (Durrer et al., 2007).

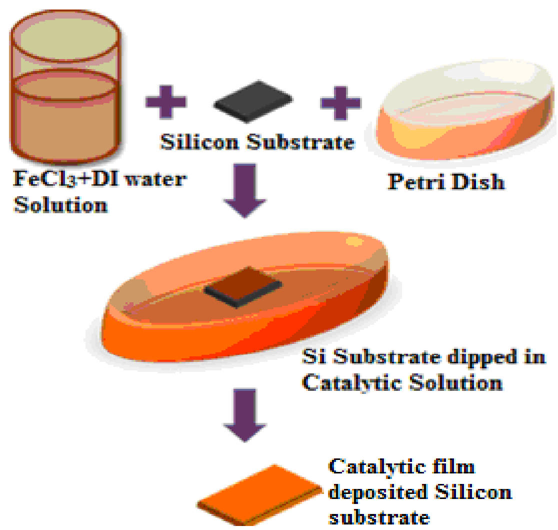

Fig. 1 : Sample Preparation by dip dry method

There are few reports about the growth of Carbon Nanotube using transition metal salts as the catalyst (Hou et al., 2003; Fu et al., 2004). In this paper, we have demonstrated thepreparation of catalytic films of Fe from aq. solutions of $FeCl_3$and used these films for the growth of CNT. Here the catalyst was deposited using a simple and highly scalable Dip Dry Method (DDM). Films with different concentration of $FeCl_3$ were prepared to explore the effect of initial concentration of $FeCl_3$ on the size distribution of nanoparticles. Further, the growth of nanotubes was carried out on the prepared films.

2. EXPERIMENTAL

2.1 Preparing catalytic film using Dip Dry Method

Dip Dry Method (DDM) was used to deposit the $FeCl_3$ salt as precursor for the formation of catalytic Fe nanoparticles. 2 mg, 4 mg, 8 mg of $FeCl_3$ salt was dissolved in 27 ml of DI water with different silicon wafers in the petri dish.The Si wafer was dipped in aqueous $FeCl_3$ solution and heated at 100°C temperature in the oven. After the sample is dried a film of $FeCl_3$ was formed over the substrate. These samples were used for further processing. The details of the process are depicted in Fig. 1. The optical microscope image of the sample B after $FeCl_3$ deposition is shown in Fig. 2

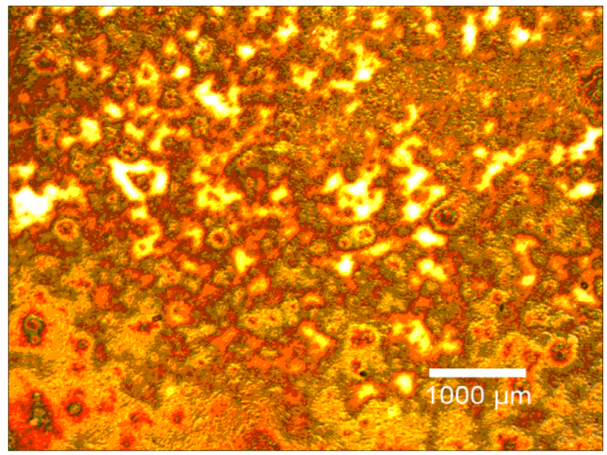

Fig. 2 : Optical image of catalytic film

Table 1. Indicating the three different samples with different weights of $FeCl_3$ salt

S. No.	Name of Samples	Quantity of $FeCl_3$ salt in 27 ml of water
1	Sample A	2 mg
2	Sample B	4 mg
3	Sample C	8 mg

2.2 Pretreatment and Nanoparticles formation

$FeCl_3$Each sample was broken into two pieces for studies after pretreatment and growth. One piece from each sample was loaded in the furnace for pretreatment. The samples were annealed at a temperature of 900°C in the environment of Hydrogen and Ammonia for 15 minutes. This step ensures the removal of Chlorine from the sample and aids in the formation of Iron Nanoparticles over the substrate.

2.3 Growth of CNT

The other half of the samples was loaded into the LPCVD 2Z75 system for the growth of CNT. This has a quartz furnace of 3" diameter and the gas flow is controlledby the MKS (1480 series) Mass Flow Controllers (MFC). These samples were also pretreated under same condition as in step 2 before carrying out the growth. The CNT growth was carried out at a temperature of 850 ^{o}C and by using Acetylene (C_2H_2) at flow of 0.1 SLM as the carbon source gas. The $H_2$and NH_3at a flow of 1 SLM and 0.5 SLM respectively were used as the carrier gas. The growth was done for the duration of 10 minutes. After the growth the samples were cooled till the 350 ^{o}C in hydrogen environment at 5 ^{o}C/min and then unloaded from the furnace

2.4. Result and discussion

The Fig.1shows the optical image of theas deposited catalytic film of $FeCl_3$ over the Si substrate. It can be observed that the ferric salt is continuously deposited over the substrate.These as deposited films were then characterized using EDAX.

Fig 3(a)shows the EDAX spectra of the as deposited $FeCl_3$ film for sample B. We can observe the peak of chlorine at 2.7 KeV along with the other peaks of iron and oxygen. The oxygen peak may be accounted for the oxidation of iron particles in the ambient enviroment. It is also observed that there is no peak of Silicon in the spectra and this happened because the film of as deposited $FeCl_3$ is thick enough and does not allow the penetration of electrons upto the Si wafer. To remove the Chlorine present in the samples and prepare the iron nanoparticles from the deposited films we carried out pretreatment of the samples. The removal of Chlorine is important for the formation of iron nanoparticles using the $FeCl_3$ salt. The pretreatment was carried out in the Hydrogen and Ammonia environment. The chlorine present on the substrate gets reduced in this environment. After the

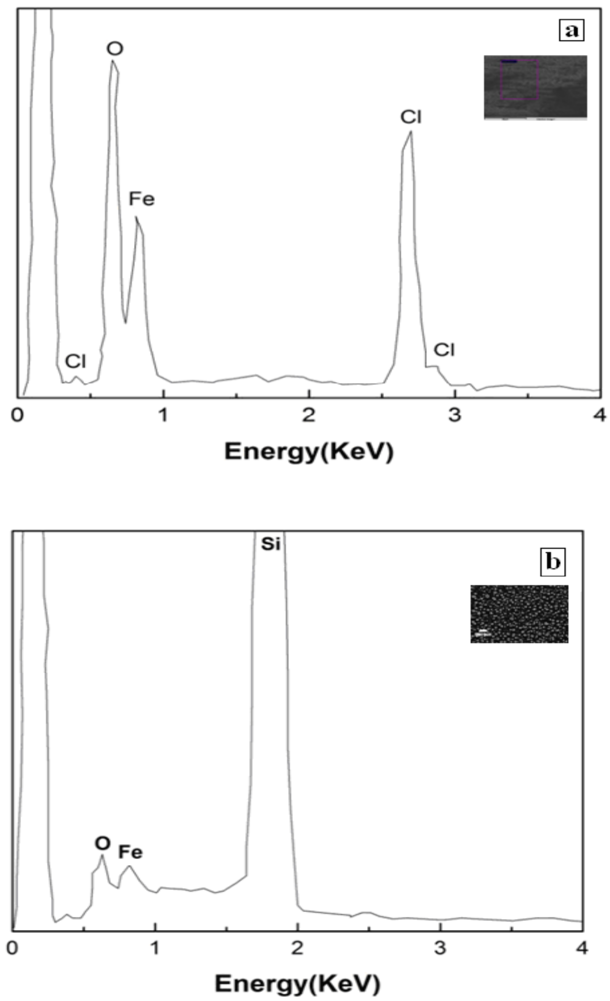

Fig. 3 : EDAX spectra of sample
(a) before pretreatment (b) after pretreatment

pretreatment the film of $FeCl_3$ gets reduced and only the particles of iron are left over the substrate. This canbe confirmed by studying the post annelead EDAX spectra. The Fig 3(b) shows the EDAX spectra after the pretreatment on the the sample B. In the spectra there is no peak for Chlorine at 2.7 KeV which was removed during the pretreatment. We can see in Fig 3that after the preteratment only iron nanopaticles are left over the Si substrate hence we observe a strong peak of the Si in the spectra. These particlesact as a grain for the growth of CNT. The density and size of these nanoparticles plays

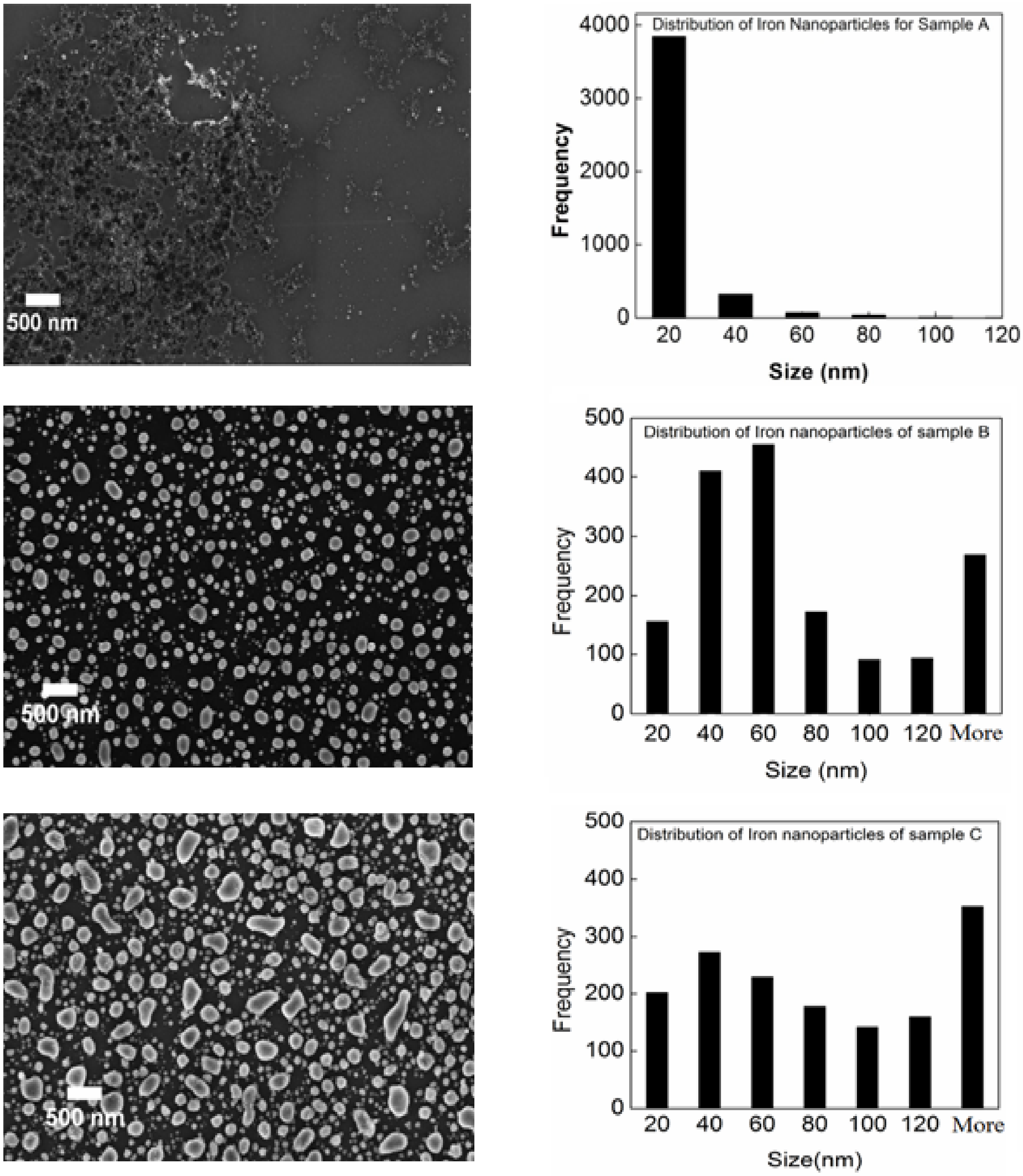

Fig. 4 : Iron Nanoparticles formed over Silicon after Pretreatment and respective particle size analysis

an important role in the growth of CNT[23].To further study the Nanoparticles formed after pretreatment FESEM ananlysis of all the three samples was done(Fig.4). It was observed that the particle distribution over the sample A was not uniform although it was observed that the diameter of Nanoparticle formed was having distribution in very narrow range aorund 20 nm. Nanoparticles in Sample B and C were uniformly distributed over the entire substrate but the diameter distribution in both of these sample was very high with nanopaticle diameter varying from 20nm to more than 120 nm. Fig 4 also shows the distribution of the iron naoparticles obtained on an area of 35 sq. micron. From the FESEM images and the obtained distribution we can see that the distribution shifts towards the larger particle size as we increase the amount of the salt used for the formation of the particles.

These samples were than put in reactor and growth ofmultiwall CNT was achieved over all the threesamples using acetylene as source gas. Fig. 5 showsthe FESEM micrographs of the three samples aftergrowth. The length of the grown CNT is in the rangeof 10-20 micron. While the CNT in sample A arelying on the substrate surface and not aligned in aparticular direction but the growth obtained in theother two samples is aligned in the verticle direction.

The inset in the Fig 5 shows the higher magnificationimages of the samples by which the diameter of thegrown CNT can be observed. From the SEM imagesone can easily observe that the density of gorwn CNT is very less in sample A while density is high in Sample B and C. This is very much expected from thedistribution of iron particle that we obtained. It was also observed that the average diameter increase from sample A to sample C ie. as we increase the salt concentration. This can be easily explained bystudying the size analysis of nanoparticle in Fig. 4. The diameter of grown CNT depend on the diameter of the Nanoparticle formed over the samples during the pretreatment now as the average diameter of the iron nanoparticle increases from sample A to C the average diameter of the CNT also increses in the same pattern. The approximate CNTdiamter observed was 25 nmsample A, 60 nm in sample B and 110 nm in sample C.

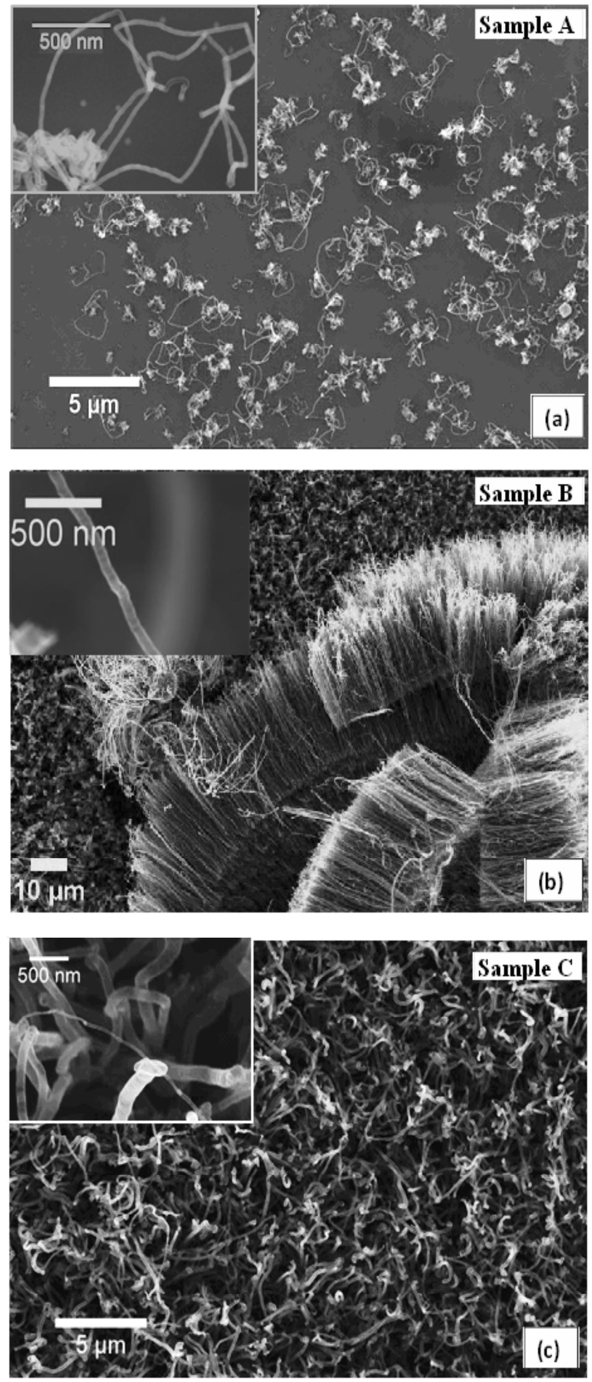

Fig 5: (a) (b) (c) FESEM images of the grown CNT. Inset shows the high magnification image of sample

3. CONCLUSION

Three samples with different concentrations of $FeCl_3$ were prepared using the Dip Dry Method. The samples were pretreated for the formation of iron nanoparticle and their distribution was seen to be dependent on the concentration of the salt used. Growth of CNT was done over these samples and the diameter of the grown CNT was also observed to increase with the increased concentration of the ferric salt.

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REFERENCES

Baughman, R.H., A.A. Zakhidov, and W.A. de Heer, Carbon nanotubes—the route toward applications. Science, 2002. 297(5582): p. 787-92.

Chakraborty, A.K., et al., *Chemical vapor deposition growth of carbon nanotubes on Si substrates using Fe catalyst: What happens at the nanotube/Fe/Si interface.* Journal of Applied Physics, 2006. **100**(8): p. 084321-6.

Choi, W.B., et al., Fully sealed, high-brightness carbon-nanotube field-emission display. Applied Physics Letters, 1999. 75(20): p. 3129-3131.

Dalton, A.B., et al., Super-tough carbon-nanotube fibres. Nature, 2003. 423(6941): p. 703-703.

Durrer, L., et al. *SWNT Growth by LPCVD on Ferritin-Based Iron Catalyst Nanoparticles Towards CNT Sensors*. in *Solid-State Sensors, Actuators and Microsystems Conference, 2007. TRANSDUCERS 2007. International*. 2007.

Esconjauregui, S., C.M. Whelan, and K. Maex, *The reasons why metals catalyze the nucleation and growth of carbon nanotubes and other carbon nanomorphologies.* Carbon, 2009. **47**(3): p. 659-669.

Fu, Q., S. Huang, and J. Liu, *Chemical Vapor Depositions of Single-Walled Carbon Nanotubes Catalyzed byUniform Fe2O3 Nanoclusters Synthesized Using Diblock Copolymer Micelles.* The Journal of Physical Chemistry B, 2004. **108**(20): p. 6124-6129.

Hart, A.J., A.H. Slocum, and L. Royer, *Growth of conformal single-walled carbon nanotube films from Mo/Fe/Al2O3 deposited by electron beam evaporation.* Carbon, 2006. **44**(2): p. 348-359.

Hart, A.J., et al., *Uniform and selective CVD growth of carbon nanotubes and nanofibres on arbitrarily microstructured silicon surfaces.* Nanotechnology, 2006. **17**(5): p. 1397.

Hou, H., et al., *Large-Scale Synthesis of Aligned Carbon Nanotubes Using FeCl3 as Floating Catalyst Precursor.* Chemistry of Materials, 2003. **15**(2): p. 580-585.

Iijima, S., Helical microtubules of graphitic carbon. Nature, 1991. 354(6348): p. 56-58.

Kim, D.Y., et al., *The density control of carbon nanotubes using spin-coated nanoparticle and its application to the electron emitter with triode structure.* Diamond and Related Materials, 2005. **14**(11â€"12): p. 2084-2088.

Lee, S.S., et al., *Control over the Diameter, Length, and Structure of Carbon Nanotube Carpets Using Aluminum Ferrite and Iron Oxide Nanocrystals as Catalyst Precursors.* The Journal of Physical Chemistry C. **116**(18): p. 10287-10295.

Mukul, K., *Carbon Nanotube Synthesis and Growth Mechanism*. 201

Puretzky, A.A., et al., *Investigations of single-wall carbon nanotube growth by time-restricted laser vaporization.* Physical Review B, 2002. **65**(24): p. 245425.

Saito, Y., et al., Field emission of carbon nanotubes and its application as electron sources of ultra-high luminance light-source devices. Physica B: Condensed Matter, 2002. 323(1–4): p. 30-37.

Saito, Y., T. Nakahira, and S. Uemura, Growth Conditions of Double-Walled Carbon Nanotubes in Arc Discharge. The Journal of Physical Chemistry B, 2003. 107(4): p. 931-934.

Scott, C.D., et al., *Growth mechanisms for single-wall carbon nanotubes in a laser-ablation process.* Applied Physics A: Materials Science & Processing, 2001. **72**(5): p. 573-580.

Su, C.C., et al., Two dimensional carbon nanotube based strain sensor. Sensors and Actuators A: Physical. 176(0): p. 124-129.

Ting, Z., et al., Recent progress in carbon nanotube-based gas sensors. Nanotechnology, 2008. 19(33): p. 332001.

Wang, X.K., et al., Carbon nanotubes synthesized in a hydrogen arc discharge. Applied Physics Letters, 1995. 66(18): p. 2430-2432.

Yang, K. and M. Gu, Enhanced thermal conductivity of epoxy nanocomposites filled with hybrid filler system of triethylenetetramine-functionalized multi-walled carbon nanotube/silane-modified nano-sized silicon carbide. Composites Part A: Applied Science and Manufacturing. 41(2): p. 215-221.

Zheng, R., et al., *The effect of ion sputtering of silicon substrates on the catalyst morphology and growth of carbon nanotube arrays.* Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. **268**(6): p. 568-572.