



Preparation of FeCl₃ Catalytic Films Using Dip Dry Method for the Growth of Carbon Nanotubes

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Abstract

Catalytic films of FeCl₃ were coated on Si using simple and highly scalable technique of dip drying of silicon in aqueous FeCl₃ solution. The catalyst coated samples were pretreated at 850°C to reduce the deposited FeCl₃ into iron nanoparticles. The size distribution of nanoparticles was found to be strongly dependent on initial concentration of FeCl₃ in aqueous solution. The catalytic activity of nanoparticles was ascertained by growth of carbon nanotubes using Chemical Vapour Deposition. The C₂H₂ was used as the carbon precursor along with the carrier gas of H₂ and NH₃. 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 CNT which could be understood as a rolled up graphene sheet, are mainly of two types single wall or multiwall.

Although because of their remarkable and extraordinary properties CNT have found applications in variety 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 synthesis of CNT for specific type of application has 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; Poretzky et al., 2002) and chemical vapor deposition (CVD) (Hart et al., 2006; Chakraborty et al., 2006). Among all of these techniques, CVD is used for the selective growth of CNT at particular location on the substrate and incorporate them 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-

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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 in a 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).

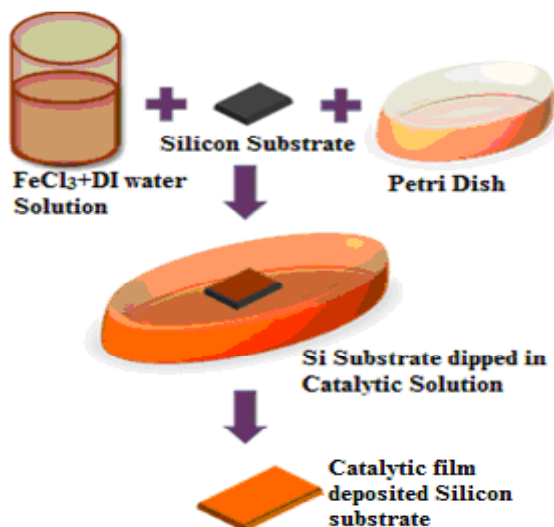


Fig. 1 : Sample Preparation by dip dry method

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 the preparation 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 concentrations 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

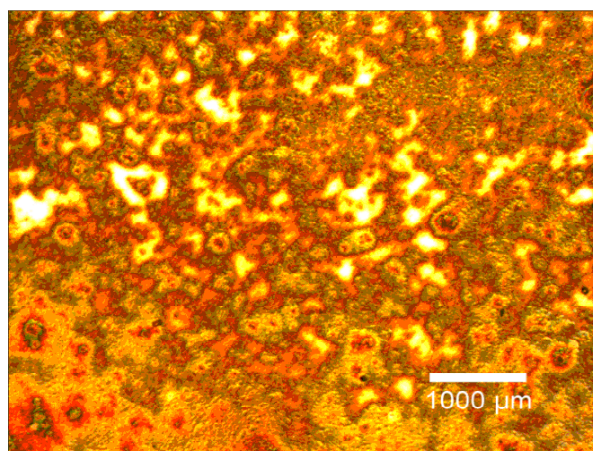


Fig. 2 : Optical image of catalytic film

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 controlled by 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 °C and by using Acetylene (C_2H_2) at flow of 0.1 SLM as the carbon source gas. The H_2 and NH_3 at 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 °C in hydrogen environment at 5 °C/min and then unloaded from the furnace

2.4. Result and discussion

The Fig.1 shows the optical image of the 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 environment. 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

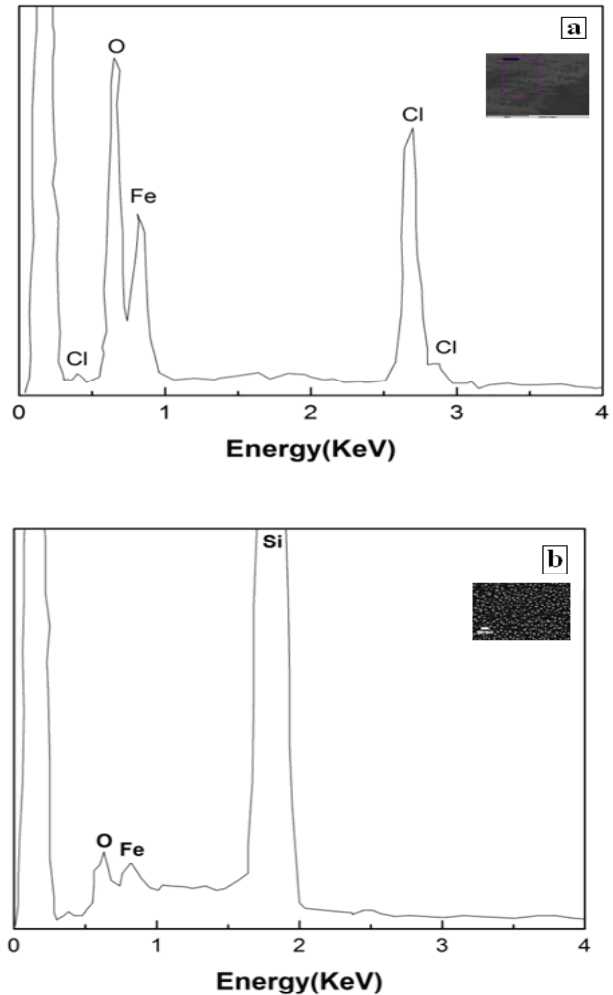


Fig. 3 : EDAX spectra of sample (a) before pretreatment (b) after pretreatment

pretreatment the film of $FeCl_3$ gets reduced and only the particles of iron are left over the substrate. This can be confirmed by studying the post annealed EDAX spectra. The Fig 3(b) shows the EDAX spectra after the pretreatment on 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 3 that after the pretreatment only iron nanoparticles are left over the Si substrate hence we observe a strong peak of the Si in the spectra. These particles act as a grain for the growth of CNT. The density and size of these nanoparticles plays

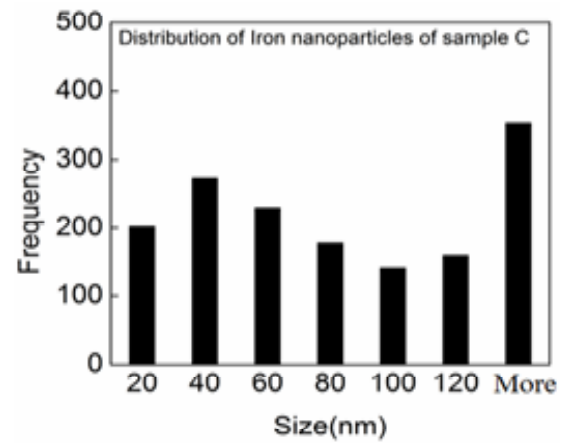
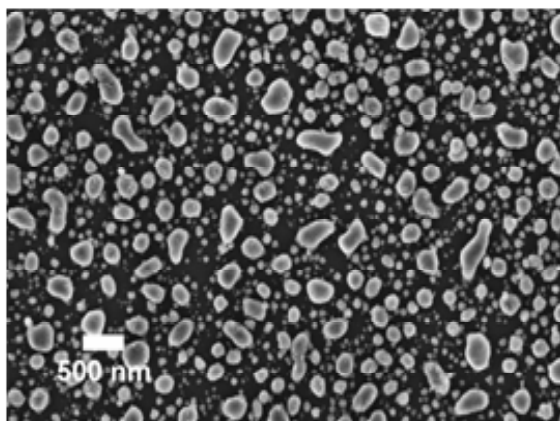
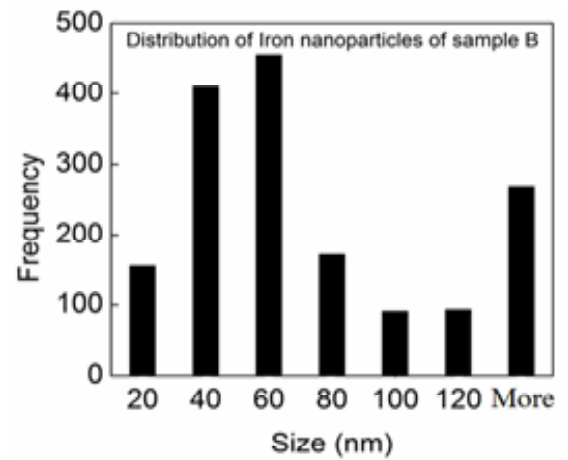
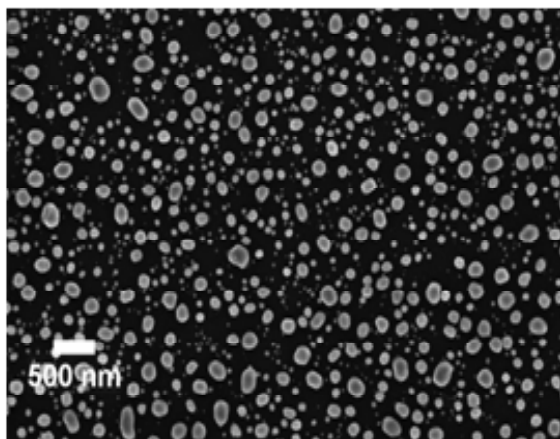
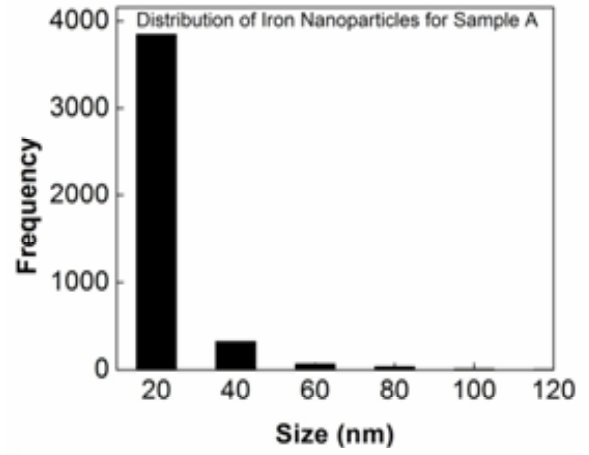
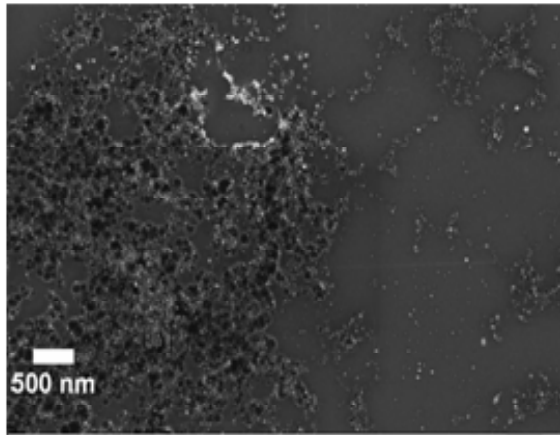


Fig. 4 : Iron Nanoparticles formed over Silicon after Pretreatment and respective particle size analysis

an important role in the growth of CNT[23]. To further study the Nanoparticles formed after pretreatment FESEM analysis 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 around 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 nanoparticle diameter varying from 20nm to more than 120 nm. Fig 4 also shows the distribution of the iron nanoparticles 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 then put in reactor and growth of multiwall CNT was achieved over all the three samples using acetylene as source gas. Fig. 5 shows the FESEM micrographs of the three samples after growth. The length of the grown CNT is in the range of 10-20 micron. While the CNT in sample A are lying on the substrate surface and not aligned in a particular direction but the growth obtained in the other two samples is aligned in the vertical direction.

The inset in the Fig 5 shows the higher magnification images of the samples by which the diameter of the grown CNT can be observed. From the SEM images one can easily observe that the density of grown CNT is very less in sample A while density is high in Sample B and C. This is very much expected from the distribution of iron particle that we obtained. It was also observed that the average diameter increase from sample A to sample C i.e. as we increase the salt concentration. This can be easily explained by studying the size analysis of nanoparticle in Fig. 4. The diameter of grown CNT depends 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 increases in the same pattern. The approximate CNT diameter observed was 25 nm in sample A, 60 nm in sample B and 110 nm in sample C.

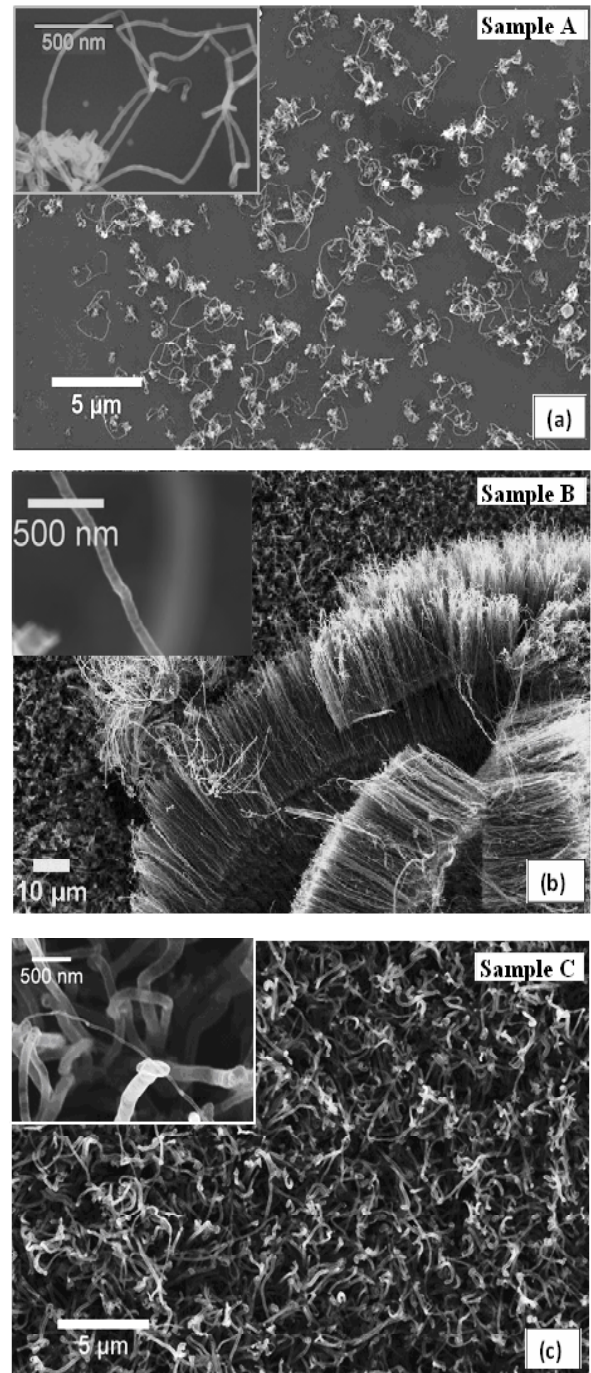


Fig 5: (a) (b) (c) FESEM images of the grown CNT. Inset shows the high magnification image of sample

3. CONCLUSION

Three samples with different concentrations of FeCl₃ 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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