Synthesis of Fe catalyst nanoparticles by solution process towards carbon nanotube growth

M. A. Azam*, Z. M. Nawi, N. M. Azren and N. N. Zulkapli

The iron catalyst nanoparticles were prepared on silicon wafers by solution process, which first spins coat the solution of iron (III) nitrate nonahydrate and colloidal solution, and then are heated to obtain the formation of iron nanoparticles. The effects of different spin speed and heat treatment parameters during the solution process were investigated. As a result, the smallest thickness of the Fe catalyst thin films is 78 nm, and the smallest Fe catalyst nanoparticles, i.e. 9·67 nm, were obtained at the highest spin speed of 8000 rev min^{-1} and 500°C. The uniformity of the thin films was also found to increase with increasing spin speed. The particle and thickness analysis was performed by means of field emission scanning electron microscopy.

Keywords: Spin coating, Fe catalyst, Fe nanoparticles, Catalyst thin films, Field emission scanning electron microscopy

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Introduction

The synthesis of carbon nanotubes (CNTs) especially single walled (SWCNTs) by catalytic chemical vapour deposition method has been widely studied due to their extraordinary electrical, mechanical and thermal properties, accompanied with cost effective and good quality CNTs produced.[1] The transition metals such as Fe, Ni and Co have been widely used as the metal catalyst in the synthesis of multiwalled CNTs and SWCNTs by this method.[2–4] These metals have high solubility of carbon at high temperature and high diffusion rate, which is very helpful during the CNT growth process. The catalyst particles formed on the substrates provide active sites for the nucleation of CNTs, and the size of catalyst particles vigorously corresponds to the diameter of CNTs produced.[5]

Various methods of synthesis can be applied in order to grow the CNTs,[6] such as arc discharged and laser ablation. Physical vapour deposition is the common method to deposit catalyst thin films onto selected substrates due to the process able to deposit more uniform thickness of catalyst thin films, which will affect the size of the nanoparticle formation.[7] Several studies have been reported regarding the formation of catalyst thin films thickness $<1{\cdot}0$ nm.[8,9] However, the employment of physical vapour deposition leads to the cost ineffectiveness in the electronic devices manufacturing due to the need of high power of electrical supply in order to provide a vacuum condition in the system. Thus, other deposition techniques, spin coating,[10–12] dip coating,[6,13] spray coating[14] and patterning,[15] which are based on the solution based catalytic precursors, have been progressively prominent to gain uniform thin films. Out of these techniques, spin coating is favourable due to the easiness in preparing uniform catalyst thin films to directly grow CNTs onto the substrates. In addition, it has the ability to achieve smaller thickness of thin films.

In this paper, the effect of spin speed on thickness of Fe catalyst thin films produced by spin coating technique was investigated. The main aim for this research is to achieve smaller thickness of thin film, which will be used to grow CNTs on the Si substrates. The thickness of Fe catalyst thin films over various spin speed of spin coating was studied.

Experimental

Fe catalyst nanoparticles were prepared by diluting iron (III) nitrate nonahydrate, $FeN_3O_9.9H_2O$, in colloidal solution, which is a combination of absolute ethanol–polyethelyne glycol 400 (PEG-400) to produce a solution with a concent ration of 40 mmol L^{-1}.[16] The solution was stirred for 30 min and then sonicated for another 30 min to ensure the homoginity of the solution. Materials for catalyst film preparation are shown in Table 1. Silicon (Si) wafer 4 inches in diameter with one sided polished and 1000 Å thermal oxide layer was used as substrate. The substrate was cut into squares of 15×15 mm^2. Next, the wafers were cleaned using piranha solution by immersing the Si wafer into the solution of hydrogen peroxide 30% and sulphuric acid for 15 min, and then rinsed in deionised water. The Si wafers were dried using a spin coater with spin speed of 8000 rev min^{-1} for 30 s to clean the substrate surface from organic and inorganic conteminent.[11]

Iron nitrate nonahydrate/colloidal solution was spin coated on the cleaned Si wafer at spin speed of 7500,

Carbon Research Technology Research Group, Faculty of Manufacturing Engineering, UniversitiTeknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

*Corresponding author, email asyadi@utem.edu.my

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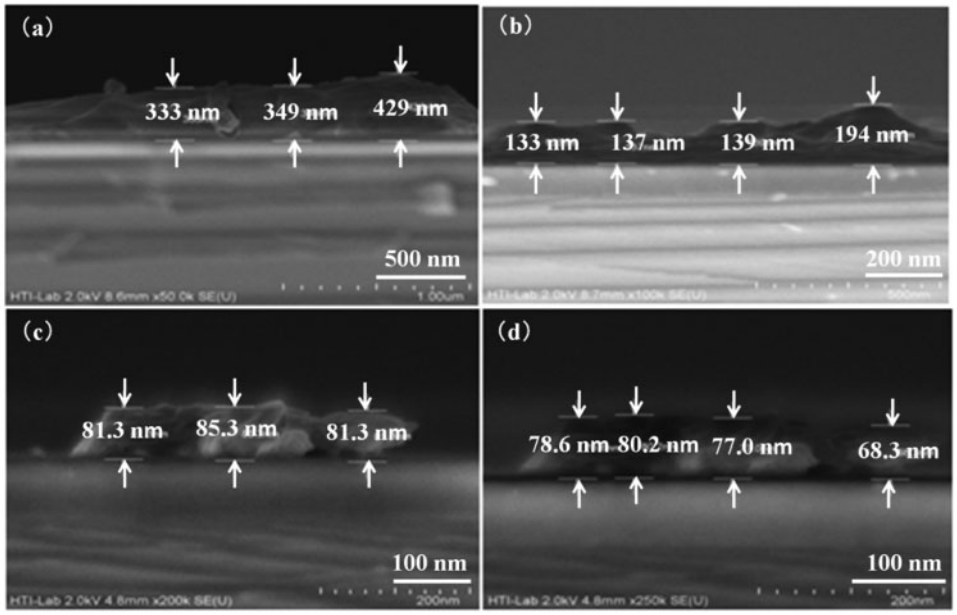


1 Field emission SEM images of Fe catalyst thin films at spin speed of *a* 6500, *b* 7000, *c* 7500 and *d* 8000 rev min^{-1} and preheated at 250°C; note that different scales were used in order to get clearer images

8000, 8500 and 9000 rev min^{-1} for 30 s. The coated wafers were quickly preheated at 100°C for 1 min to vapourise the solvent, leaving Fe catalyst thin films on the wafers. Then, the preheated wafers were placed in a vacuum furnace for heat treatment process of 450, 500, 550 and 600°C for 10 min to obtain Fe catalyst nanoparticles. A field emission scanning electron microscope (Hitachi SU8100) was used to analyse the morphology of the samples in the range of 2·0–5·0 KV depending on the suitable magnification.

In addition, the work has been elucidated following the parameter and samples tabulated in Table 2. Similar experiment was performed several times to confirm the work's reproducibility and consistency of results.

Results and discussion

Influence of spin speed to catalyst thin film thickness

The formation of catalyst thin film on the Si wafer before the heat treatment process with four different spin speeds is shown in Fig. 1*a–d*. A variation in the thin film thickness obtained showed that the deposited thin films were developed in continuous pattern. A dramatic decrease in thickness at 6500 and 7000 rev min^{-1}, the thickness reduced from 343 to 137 nm, which is mainly due to the increasing speed (Fig. 2). When the spin speed reached a stable thickness, the thickness did not dramatically decrease as shown in spin speed of 6500 to 7000 rev min^{-1}. The decreasing of thickness reduced ~20 to 30 nm when the spin speed is increased to 7500 and 8000 rev min^{-1}. The pattern of the result showed that, by increasing the spin speed, the thickness of the catalyst thin film becomes thinner.

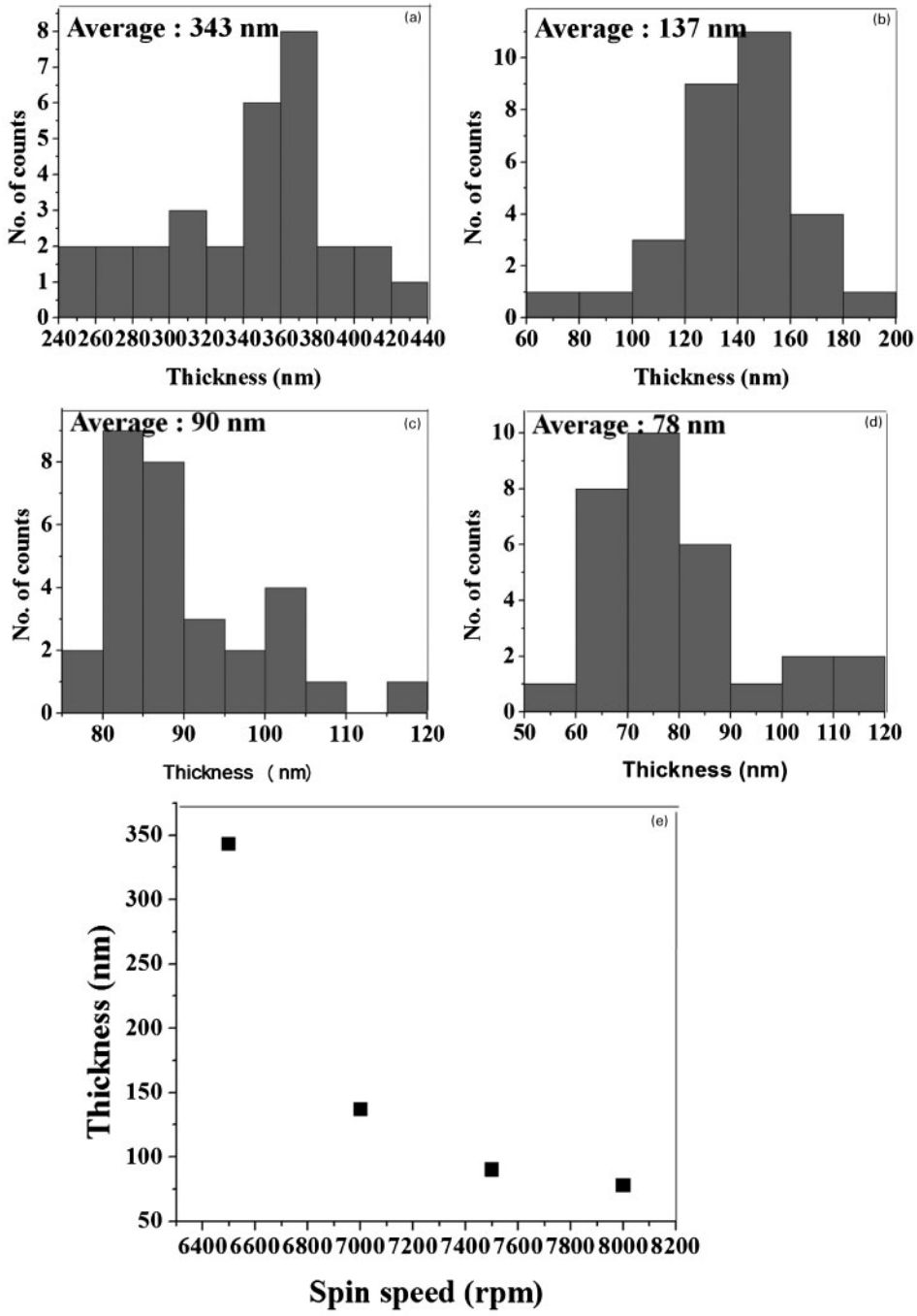
The decreasing thickness of thin film by increasing the spin speed of spin coating was due to the thinning process. It is suggested due to the centrifugal force, which developed to reduce thickness of the thin film. By increasing the spin speed, more centrifugal force was created, causing the centrifugal force to create a force that acts downward to push the thin film and make it thinner as shown in Fig. 3. It is also supported by a simple mathematical model of spin coating process

Table 2 Design of experiment for spin coating and heat treatment parameter (spin duration and volume of solution fixed to 30 s and 50 μm respectively)

Spin speed/rev min^{-1}	Heat treatment temperatures/°C	Level of sample
7500	450	L1-1
	500	L1-2
	550	L1-3
	600	L1-4
8000	450	L2-1
	500	L2-2
	550	L2-3
	600	L2-4
8500	450	L3-1
	500	L3-2
	550	L3-3
	600	L3-4
9000	450	L4-1
	500	L4-2
	550	L4-3
	600	L4-4

Table 1 Materials for Fe catalyst thin film preparation

	Materials (and its ratio)
Precursor	Iron nitrate nonahydrate ($FeN_3O_9.9H_2O$)
Colloidal solution	Ethanol/PEG-400 (1/1) (v/v)
Substrate cleaning solution (piranha solution)	H_2SO_4/H_2O_2 (1/1) (v/v)



2 Histograms of Fe catalyst thin films thickness of *n*=30 with spin speed of *a* 6500, *b* 7000, *c* 7500 and *d* 8000 rev min^{-1} and *e* graph of average thickness of Fe catalyst thin films at four different spin speeds

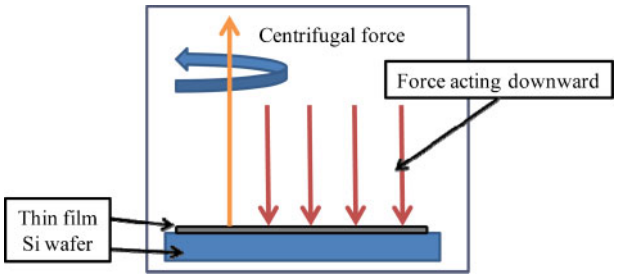
proposed by Emslie's group to predict the film thickness as a function of a number of physical parameters as follows, where h_o is the initial film thickness, ω the spin speed and η the viscosity[16]

$$h = \frac{h_o}{\left(1 + \frac{4\omega^2 h_o^2 t}{3\eta}\right)^{1/2}} \quad (1)$$

Controlling the thickness of the catalyst thin film is very important because it will affect the diameter of the catalyst nanoparticle. Thus, if the thickness of the thin film is thick, the diameter of the catalyst nanoparticles will be larger. However, if one can control the thin film thickness, smaller nanoparticle formation is possible, which will lead to the efficient growth of SWCNT rather than multiwalled CNT.[17]

Influence of heat treatment to particle formation

Figure 4 depicts the formation of Fe nanoparticle on the Si wafer after the post-heat treatment process with four different temperatures. In the case of 350 and 400°C heat treatment temperatures, the particle agglomerates and becomes one large cluster (Fig. 4*a* and *b*). As the temperature increased to 450 and 500°C, Fe particles start to form without agglomerate and are well dispersed on the substrate. In addition, from the average diameter analysis using histogram in Fig. 5, it was found that with the increasing heat treatment temperature, the diameter of Fe catalyst particles gradually decreased. The



3 Schematic mechanism of thinning process

formation of Fe catalyst nanoparticles is strongly influenced by post-heat treatment temperature.

Schematic illustration of particle formation at different temperatures is shown in Fig. 6. It is conceivable that at lower temperatures, the particles tend to agglomerate and become large cluster. When the temperature is equal or >450°C, the particles bonding started to break and cause the particles to fall apart, and this is known as bond breaking. The chemical bond breaking was due to the absorbed energy by the cluster. When the supplied energy was increased, the atoms inside the particles started to repel from each other. Once the iron particles have enough energy to be independent, then the chemical bonding between each particle started to break.

As evidenced in SEM image in Fig. 5, when the temperature increased to 450°C, the particles are no longer combining as a cluster, but the particles are still in irregular (not spherical) shape. When the temperature increased to 500°C, the particles have gained enough energy to form round shape of particles. The round shape of particles indicated that the particles were in a stable state condition. This condition was also related to the good interaction between the catalyst particles and silicon substrate. Thus, this phenomenon caused well distribution of particles on the substrate. The formation of Fe catalyst nanoparticles is very vital for the CNT growth because it will act as the cap for the CNT to growth.[7]

Suggested mechanism of thin film and particle formation

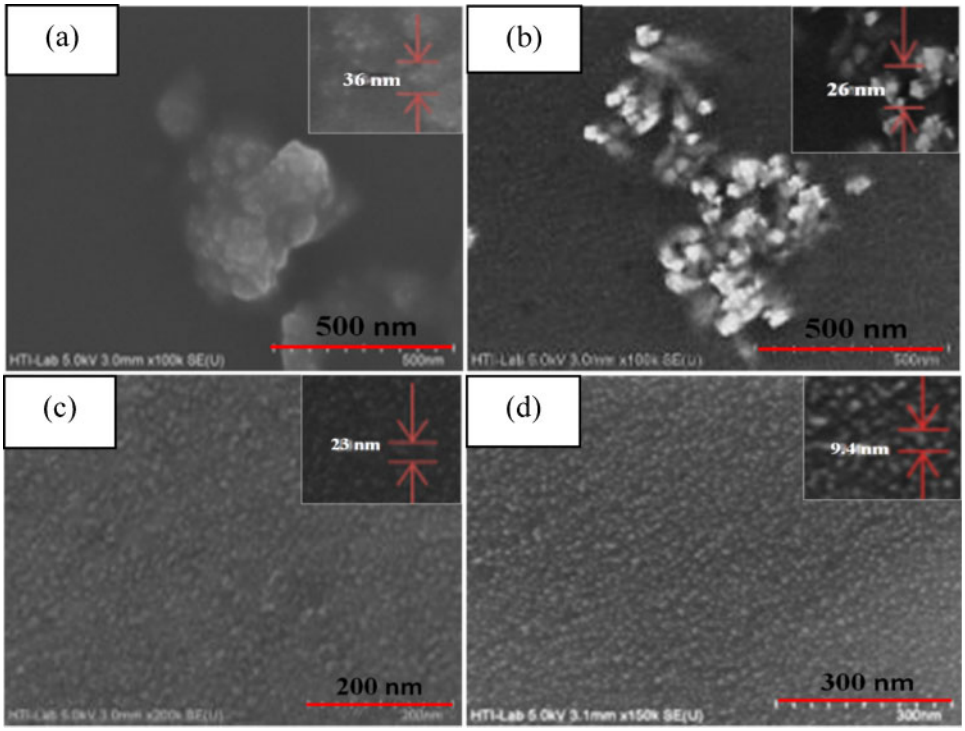
Catalyst thin film and particle formation is correlated to each other. The thickness of the deposited thin film will influence the size of catalyst particles formation. Larger size of catalyst particles will be formed from the thick thin film. In order to produce good thin film and catalyst particles, the spin speed of spin coater and the heat treatment temperature of heat treatment needs to be controlled. The size of particles is very important for the CNT growth.[5] By controlling spin speed of spin coating and post-heat treatment temperature, a production of uniform thin film, consequently fine size of catalyst nanoparticles, is possible.

The suggested mechanism of thin film and particle formation in Fig. 7 shows that the relationship of spin coating and heat treatment process is very important in producing thin film, as well as to promote the formation of particles. As the process is moving from spin coating to heat treatment, parameter-like spin speed and heat treatment temperatures are very crucial in achieving good particle formation to grow CNTs.

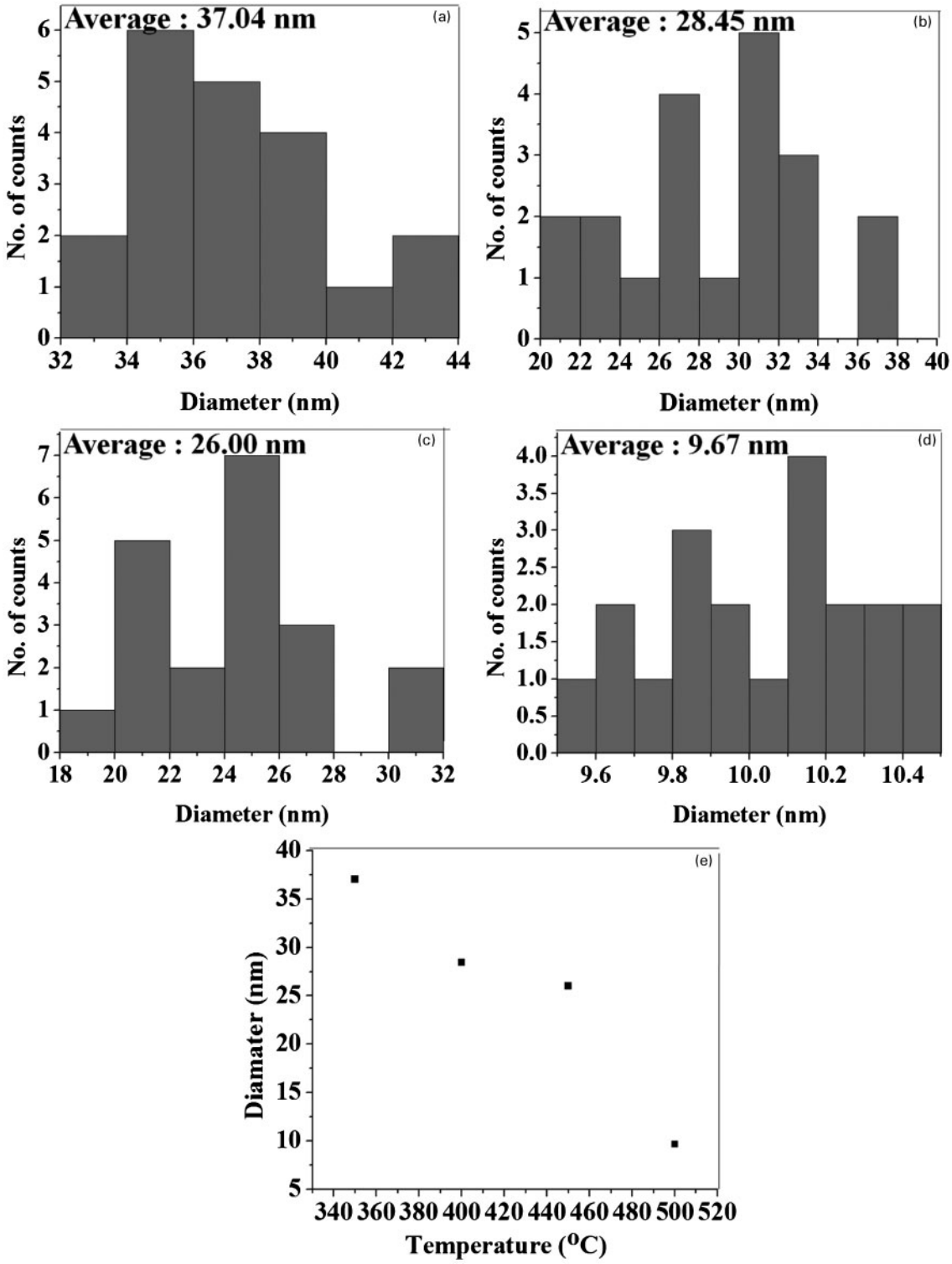
Conclusions

From the work, it was found that.

1. Formation of Fe thin films is possible by spin coated Fe based solution with a concentration of 40 mmol L^{-1}. By controlling the spin speed of spin coating, the optimum thickness of Fe thin films can be achieved. Fe thin film with an average thickness of 78 nm was achieved at spin speed of 8000 rev min^{-1}.



4 Field emission SEM images of Fe catalyst nanoparticles at temperatures of *a* 350, *b* 400, *c* 450 and *d* 500°C spin coated at 8000 rev min^{-1}; samples are in different scales



5 Histograms of Fe catalyst thin films diameter with temperature of *a* 350, *b* 400, *c* 450 and *d* 500°C and *e* plot of average diameter of Fe catalyst nanoparticles at four different temperatures (n=20)

2. By increasing the post-heat treatment temperature from 350 to 500°C, the cluster formed at lowest temperature started to break down into small particles at the highest temperature. Fe nanoparticles were formed at post-heat treatment temperature of 500°C. Average particle size at 500°C was 9·67 nm.

3. It is suggested that, by controlling spin speed of spin coating and the post-heat treatment temperature, a thin film with a fine size of particles can be achieved. In addition, the size of catalyst nanoparticles is very critical because it may influence the formation and growth of CNT.

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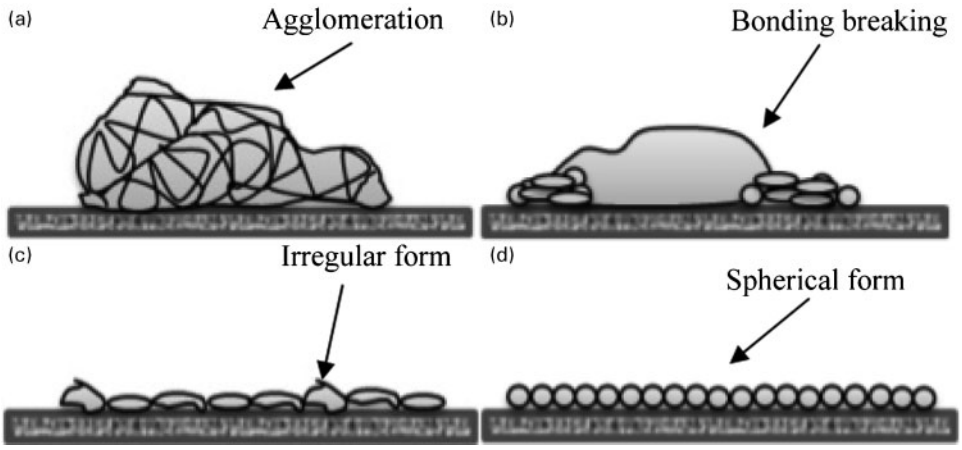
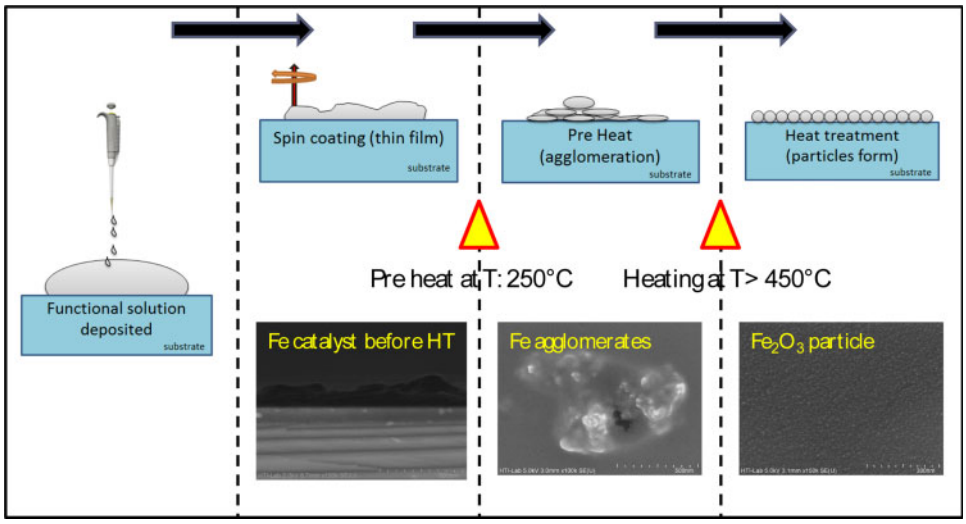


6 Schematic illustration of particles formation at various temperatures



7 Suggested mechanism of thin film and particles formation

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