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DEPOSITION OF IRON CATALYST ON CARBON FIBRE

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ABSTRACT

Catalyst deposition is a key step in synthesis of carbon nanotubes. In this work, iron catalyst has been deposited on to carbon fibre surface by impregnation method. The carbon fibre was impregnated in difference concentration of iron nitrate solution (5wt%, 1wt%, 0.5%, 0.1wt% and 0.01wt%). In order to get a good dispersion of iron catalyst, the fibre was treated by oxidation in reflux of 12 M hydrogen peroxide (H_2O_2). The treatment has improved the bond between fibre and iron catalyst. XRD results proved the existence of iron oxide as iron precursor on the fibre surface but for the fibre impregnated at very low concentration (0.01wt%), the peaks of iron oxide were not exist. However EDX and TGA analysis revealed that iron oxide has been deposited on the fibre even impregnated at very low concentration of iron nitrate but at little amount. More, SEM micrographs showed that when impregnated at very high concentration of iron nitrate solution (more than 1wt%), the catalyst precursor tended to coat the fibre surface with a thick layer, while a thin layer will be formed when impregnated in low concentration (less than 1wt%).

Keywords: iron catalyst deposition, fibre treatment.

INTRODUCTION

Carbon nanotubes (CNTs) are considered as a fascinating material. With their unique and tremendous mechanical, electrical and thermal properties make them potential in wide range applications. For instance, CNTs have been combined with polymers or alumina ceramic to construct materials with good electrical conductivity and high mechanical strength [1].

In composite field, CNTs are been used to increase the mechanical properties of composite. It has been reported that CNTs can improve the delamination problem which one of the major fail in composite application. For this purpose, CNTs were directly growth on carbon fibre. This idea is to create more interlocking between carbon fiber surface and matrix. Therefore it will increase the surface adhesion between them [2].

Growth mechanism of CNTs is based on "adsorption-diffusion-deposition" model. In this theory, the adsorption and decomposition of hydrocarbon compounds on the active surface of catalyst metal nanoparticles is the important step to the production of CNTs. The hydrocarbon is decomposed to carbon atoms and these atoms are diffusing through metal particles to the other side of the face and will deposit on the substrate to form CNTs. Therefore, the diameters of the catalyst determine the CNTs. The smaller catalyst particles are tended to form finer CNTs. In contrast, when the concentration of the metal catalyst particles is higher, the particles are more likely to agglomerate and grow up to form CNTs with larger tube diameters [3, 4]. In has been reported that the size of catalyst particle need to be controlled under 100nm in order to produce carbon nanotubes [5].

It is well understood that metal catalyst has affected to the growth and structure of carbon nanotube. Therefore, preparation of catalyst nanoparticle plays a very important role in the synthesis of CNTs. In this study, iron precursor was deposited on carbon fibre by impregnation in different concentration of iron nitrate solution. Prior to the catalyst deposition, a treatment was introduced to the carbon fiber. The effects of various concentrations of iron nitrate solution and fibre treatment on the catalyst loading and fibre morphology were examined. These parameters were optimized in order to form good catalyst for carbon nanotubes production.

EXPERIMENTAL

The carbon fibre bundle used is a sized fibre and contains of 3K filament. Sized fibres are typically produced via a proprietary process and involve coating the fibre with thin polymer-based materials that specifically formulated to enhance tensile and interfacial properties during handling and final use. To remove the fibre sizing, which may otherwise adversely affect CNT growth, the fibre bundle was immersed into acetone at room temperature for 2 hours under continuous mixing. The fibre bundle was then washed by pure water and dried in an oven at 120 °C for 12 hours. The dried fibre bundle was chemically treated with a refluxed of 12 M hydrogen peroxide (H_2O_2) for 3 hours under a continuous mixing. This treatment caused the attachment of oxygen species to the fibre surface.

Iron (Fe) precursor was deposited on to fibre surface by impregnation method. For initial, the carbon fibre bundle was dipped into iron nitrate solution with different concentration (5, 1, 0.1 and 0.01 wt%). In this preparation, the iron nitrate solution was prepared by dissolved in acetone. This solution was mixed for 30 minutes at room temperature and then was heated to 70 °C to evaporate the solution. The fibre deposited with iron precursor was dried at 120 ˚C for 2 hours, calcined at 400 ˚C for 4 hours before reduced with 80% H_2 at 700 ˚C for 2 hours.

XRD analysis was carried out using CuKα radiation to confirm the existence of iron precursor on the fiber surface. The morphology of carbon fiber after

oxidation treatment and catalyst deposition were characterized by scanning electron microscopy (SEM) and the specific amount of catalyst loading were calculated from Thermogravimetric (TGA) analysis. For TGA, the sample was heated up to 1000 ºC with heating rate of 10 ºC/min in air atmosphere.

RESULTS AND DISCUSSIONS

In order to improve the dispersion of catalyst on the fibre surface, a treatment was introduced to the fibre. Surface morphology of treated fibres and untreated fibre are shown in Figures 1 (a) and (b). From these figures, there was no significant difference observed between treated and untreated fibre surface. However when compare to the previous research, the morphology surface of treated fibre was not similar with the observation in other works. They claimed that the oxidation process basically will etch the fiber surface. The surface became rougher and the grooves became deeper [4, 6].
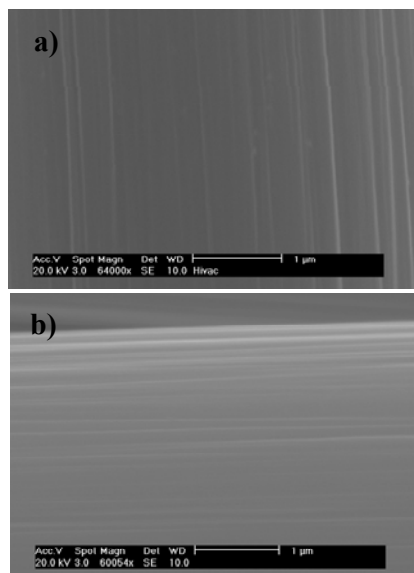

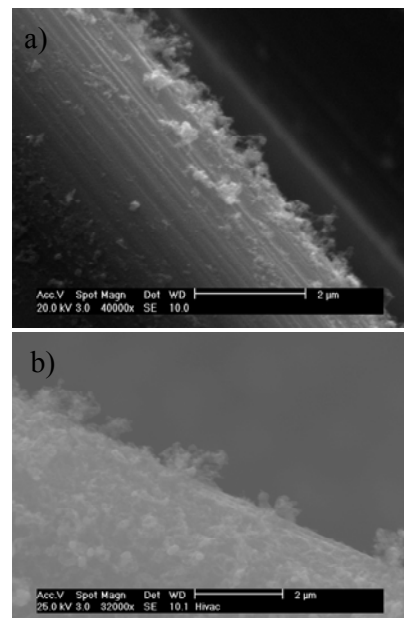**Figure-1.** SEM images of a) untreated fibres, b) treated fibre.

Figure-2. SEM images of deposited carbon nanostructure on carbon fibre a) untreated fibre, b) treated fibre.

However the fibre treatment is still believed has increased the catalyst loading. Based on the SEM micrographs of surface morphology of treated fibres and untreated fibre after carbon nanostructure deposition are shown in figure. 2 (a) and (b), it is observed that a large amount of carbon nanostructure was deposited on the treated fibre surface. Comparing to the surface of untreated fibre, the carbon nanostructure were deposited sparsely. This is indicates that the treatment has improved the compatibility between fibre and iron precursor. It was hypothesized that when the fibre were oxidized in hydrogen peroxide, oxygen species were introduced on to the fibre surface and created functional group [6]. This function reacts to form good bonds between fibre and catalyst.

XRD analysis was carried out on the carbon fibre and carbon fibre deposited with different weight percentage of iron nitrate solution. The results from the XRD analysis are shown in figure-3 and 4. As can be seen in figure-3, broad diffraction peak are showed at 26°of 2θ and 43°of 2θ. These two diffractions are corresponding to the carbon. While figure-4 shows representative X-ray diffraction of carbon fibre deposited with iron nitrate in difference concentration. The diffraction peaks are observed at 33°, 35°, 49°, 54° and 62°, corresponding to iron oxide (Fe_2O_3) reflected to calcinations of iron nitrate. When the concentration of iron nitrate is decreased, it is observed that the diffraction peak of iron oxide decreased. The XRD pattern of fibre deposited with 0.1wt% of iron nitrate showed only one iron oxide diffraction peak at 35° and no iron oxide peaks are clearly seen in XRD pattern of fibre deposited with 0.01wt% of iron nitrate solution.
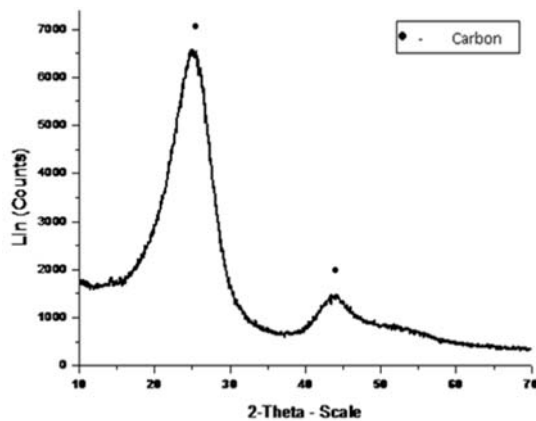
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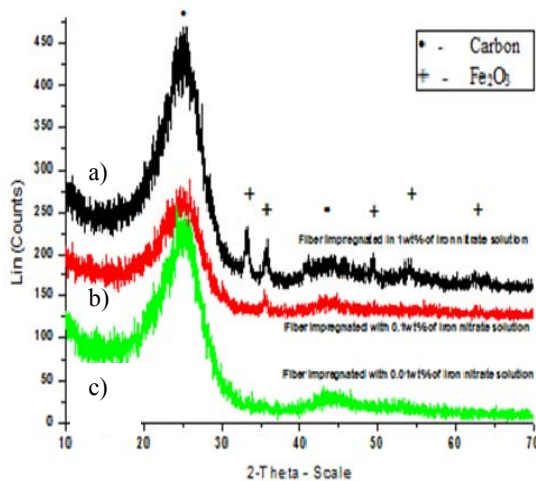

Figure-3. XRD patterns of carbon fibre.

Figure-4. XRD patterns of fibre deposited with different concentration of iron nitrate solution; a) 1wt%, b) 0.1wt% and c) 0.01wt% of iron nitrate solution.

Based on Scherrer formula, the broad and sharp peak was principally due to the formation of small crystallite size and bigger crystallite size. From the figure 4, the Fe_2O_3 diffraction peak for higher concentration samples is observed are much sharper than lower concentration. It is assumed that this reflected to the bigger crystallite size of catalyst [3]. Then it is suspected when heating at high temperature, the catalyst layer will be formed bigger catalyst particle [3, 7].

SEM images for carbon fibre deposited with different concentration of iron nitrate solution shown in figure-5. Figure-5a shows a micrograph of fibre impregnated in 5%wt of iron nitrate solution. It is clearly seen that the iron precursor were fully coated on the fibre surface with very thick layer. Due to high concentration, at certain area, the iron precursor also seen like to formed a flake. In contrast, when reduced the concentration of iron nitrate solution to the 1wt% and 0.1wt%, the iron precursor were deposited on the fibre surface as thin film.

However when the concentration is decreased 0.01wt%, seem like no iron precursor layer was deposited on fibre surface.
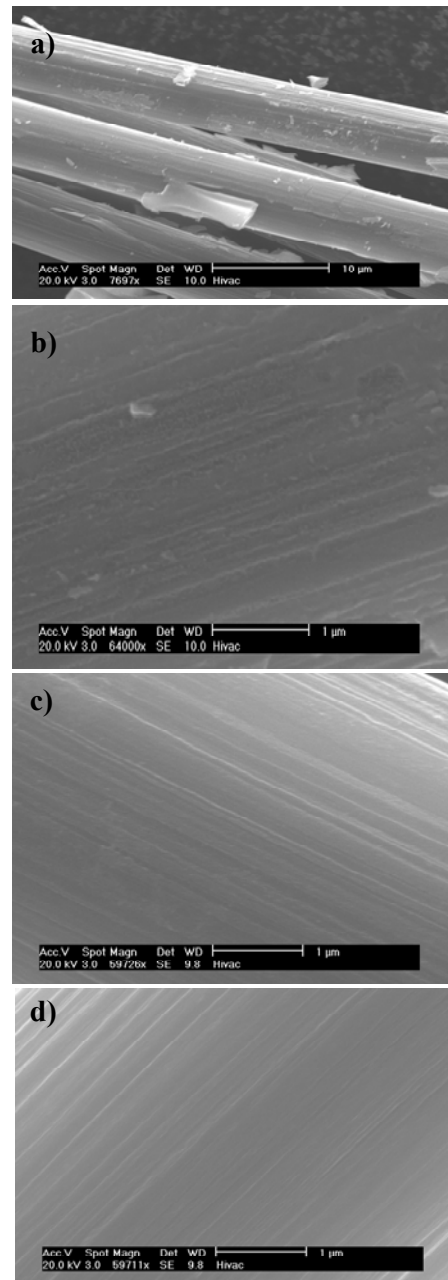

Figure-5. SEM images of fibre deposited with a) 5wt% of iron nitrate solution, b) 1wt% of iron nitrate solution, c) 0.1wt% of iron nitrate solution, d) 0.01wt% of iron nitrate solution.

Further, EDX analysis has been carried out on the fibre deposited with 0.01wt% of iron nitrate solution. The purpose was to identify the existence of iron on the fibre surface. Based on the analysis shown in figure-6, it is confirmed that iron precursor was deposited on the fibre even from the SEM images was not clear. However the

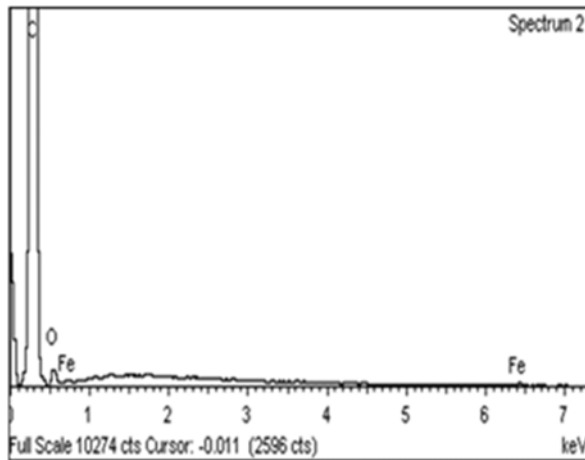amount percentage of the deposition was very low about 0.22%.

Figure-6. EDX analysis of fibre deposited with 0.01wt% of iron nitrate solution.

The loading of iron catalyst on carbon fibre also been approved by thermogravimetric analysis (TGA). It is observed that the decomposition of carbon fibre is started at around 450 ºC and completed at around 750 ºC. The left catalyst precursor after carbon burn-off is noted as amount of catalyst precursor loaded on the fibre because the iron metal can only be decomposed at higher temperature more than 1000 ºC. From TGA graph in Figure-7, the amount of catalyst precursor left on the fibre deposited with 1wt% of iron nitrate solution is 3.49%. While the amount of catalyst precursor left on the fibre deposited with 0.1wt% and 0.01wt% of iron nitrate solution are 1.86% and 0.25%. It is obviously seen that the amount of catalyst loading is associated to the concentration of iron nitrate solution. The higher concentration of iron nitrate solution will provide more irons to attach on the fibre surface. Due to the limited area of carbon surface, by increasing the amount of catalyst loading will led to form a thick layer of catalyst precursor on top of carbon surface.

The layer of metal deposited on the surface was transformed to the particle when heat treated or reduced with hydrogen at high temperature [7]. For the thicker layer, after the reduction, the layer is expected to form large particles. Most of them tend to agglomerate and conjunctive with each other and expected led to formation of carbon cluster or amorphous [7].
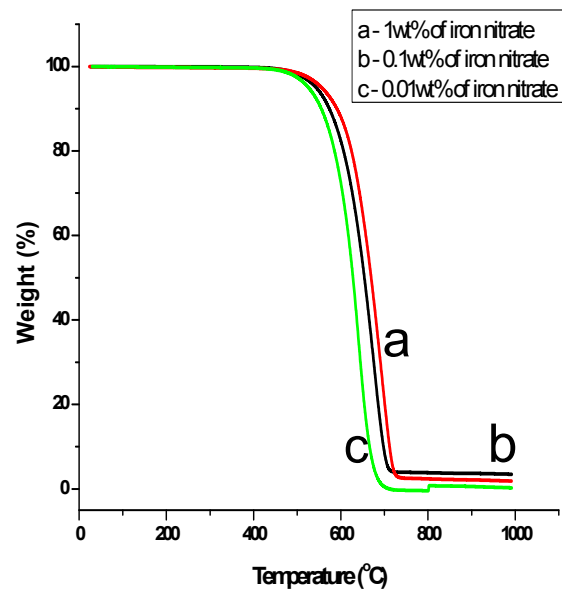

Figure-7. TGA graphs of fibre deposited with a) 1wt%, b) 0.1wt%, c) 0.01wt% of iron nitrate solution.

CONCLUSIONS

Prior to catalyst deposition, the fibre has been treated by hydrogen peroxide in order to improve the catalyst dispersion. The function of treatment has been proved contributes to increase the bond between fibre and catalyst. In this work, it is observed that the different concentration of iron nitrate also has affected the catalyst deposition. High concentration will tend to form a thick layer of catalyst precursor on the fibre surface while low concentration will be formed a thin layer. Since the thickness is influenced the catalyst particle size, then the thickness layer of catalyst precursor need to be optimized in order to get suitable particle size for CNT growth.

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