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Effect of Ferrocene Concentration on the Carbon Nanotube Cotton Synthesized Via Floating Catalyst CVD Method

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ABSTRACT

Background: Carbon nanotube(CNT) cotton was synthesized via floating catalyst CVD**.** Temperature gradient in the reactor (from hot zone to cold zone) as the CNT was floating causing it to densified at the cold zone forming sock structure and later into cotton. **Objective:** This paper will study the effect of ferrocene concentration mixed with carbon feedstock on the morphological and structure of cnt cotton by FESEM and HRTEM and also the properties of each carbon nanotube cotton by RAMAN, TGA and conductivity test.**Results:** Variation of ferrocene concentration affected the diameter formation of cnt cotton and the properties and quality of the cnt cotton**. Conclusion:** Ferrocene concentration at 1.0 wt% and 1.5 wt% of ferrocene yield good morphology and better properties.

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INTRODUCTION

A great amount of research on CNT has been carried out since the first pioneering report of the discovery of multiwalled carbon nanotube(MWNT) by Iijima(Iijima,1991). Since then, the preparation of high-quality of CNT on a large scale has been the target of many research efforts. Among the reported techniques,(Khavarian, 2013) floating catalyst methods are the best methods for obtaining a continuous process for carbon nanotube production on a commercial scale with the factor of high-purity, high-yield, and low-cost cnt growth (H. M. Cheng, 1998). The floating catalyst method operated as a continuous chemical vapor deposition (CVD) process, and ultra-short filament was made. In the continous CVD process, fiber was collected as a sponge-like strucutre called CNT cotton consisting of CNF with diameter between 0.1-1.5 nm and typical of length about 1mm.Also The diameter and length of the CNT can be controlled by the growth conditions during floating catalyst CVD method(Lim, 2012). This paper will examine the importance of ferrocene as the catalyst to control the diameter of CNT, and influencing the properties of the CNT cotton using horizontal tube furnace for floating catalyst CVD system.

Experimental Details:

In our experiment , ethanol was used as a carbon source, argon as a carrier gas and ferrocene as a catalyst precursor. The synthesis was carried out by injecting a solution mixture of ethanol, ferrocene and thiophene with an argon gas stream into a horizontal heated reactor where the flow rates of the mixed solution and the argon gas could be individually held. CNT sock descended at the end of the reactor due to the temperature gradient from the hot zone to the cold zone sticked to the cold wall and form the cnt cotton(Wang,2014). In this experiment the amount of ferrocene as the catalyst precursor were varied from 0.1 wt% to 2.0 wt%, while other parameters were fixed such as solution mixture injection flow rate and argon gas at 10 ml/h and 150 sccm respectively in a horizontal furnace at 1150^{o}C.

The Raman spectra of the CNT cotton were obtained using a Raman instrument with a radiation wavelength 532 nm. Field Emission Scanning Electron Microscope (FESEM) was used to study the morphology of the cnt cotton obtained. A High Resolution Transmission Electron Microscope (HRTEM) was used to study the structures of the CNT cotton synthesized under each condition. Energy dispersive spectroscopy x-ray (EDX) measurements were collected to analyze the residual iron content in the cnt cotton. The electrical conductivity of the cotton was measured using two-point probe method.

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Australian Journal of Basic and Applied Sciences, 9(12) Special 2015, Pages: 109-113

RESULTS AND DISCUSSIONS

In the CVD gas flow reaction, the growth of CNT and their assembly strongly depend on the alchemy of the carbon source and synthesis condition such as catalyst concentration. In most cases, dispersive phase was formed in the gas flow and deposited on the reactor of the wall as a fluffy film that we called cotton. In this work, a mixture of ferrocene, thiophene and ethanol was mixed at high temperature in a horizontal tube furnace. The iron originated from the dissociation of ferrocene vapour which produced small iron particle that grow in size by coagulation(Conroy, Moisala, Cardoso, Windle, & Davidson, 2010). Iron nanoparticles then acted as the growth site for CNT and carbon from the cracked hydrocarbon became available on the catalyst surface. Individual CNT coagulated into large agglomeration and formed an annular structure or sock(H. M. Cheng, 1998).

A) Surface Morphology:

Equally, FESEM and HRTEM micrographs show variation geometry and size of CNT by increasing the concentration of ferrocene from 0.1 wt %, 0.5 wt %, 1.0 wt%, 1.5 wt% and 2.0 wt%. Figure1 shows CNT produced with ferrocene concentration of 0.1wt%, 0.5 wt%, 1.0wt%, 1.5 wt%, and 2.0wt% having mean diameter 60nm, 120nm, 260nm, 300nm, and 450 nm respectively. The cnt were gradually increased in diameter as the concentration of ferrocene increased due to the increased iron particle size increases because of the higher probability of iron clusters agglomorating in the horizontal reactor(Liu, Ci, Jin-Phillipp, & Rühle, 2007). FESEM micrograph (figure 2), show the effect of iron nanoparticles encapsulated in the carbon structure. Higher amount of iron nanoparticles encapsulated resulted in bigger catalyst sized and causing bigger diameter of CNT (Lanzani *et al*., 2010).

HRTEM (figure2), shows the tip-growth mechanism as the encapsulated catalyst were located at the end of the CNT tube. Ferrocene was first decomposed at 470^{o}C to form small iron clusters or particles by collision in the floating gas. Second, thiophene was adsorbed and decomposed at some sites on the surface of iron particles at a temperature lower than 850^{o}C. Third, ethanol was catalytically decomposed on the surface of the catalysts to start the growth of cnt.(wencai ren, 2006).

Sample with 2.0 wt% shows the branching CNT where Y-junction and T-junction was formed. It is believed that structural variation took place during the growth of the CNT tips which then lead to the branching of CNT. Such variation to form Y-junction and T-junction have been explained from topological point of view and the formation of defects.(Ting & Chang, 2002).

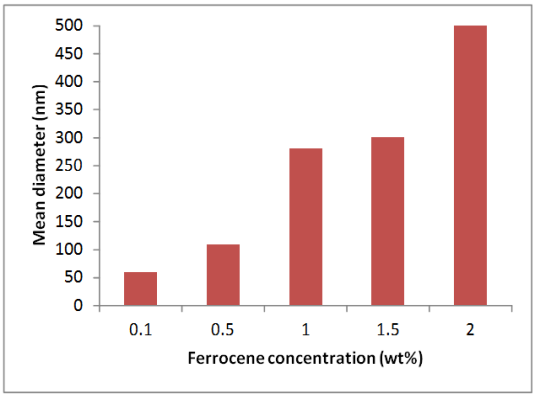

Fig. 1: Mean diameter distribution at different ferrocene concentration.

B) Micro-Raman Analysis:

Raman spectroscopy (figure 3a and 3b) was performed on the CNT cotton prepared with variation amount of ferrocene concentration. The G-band peak were at 1580 cm^{-1} indicated features of graphite and D-band peak which is at 1340 cm^{-1} suggesting that were disordered features of graphite sheet and the constituent peaks are consistent for all concentration without any significant changes of the line position(Kang *et al*., 2006). From figure 3a, there is no RBM signal in the lower wavenumber region at 100-500 cm^{-1} shows that the sample was multiwall nanotubes which in a good agreement with the HRTEM images(figure 2). D-band peak gradually increased in intensity with and increasing in ferrocene concentration. High D-band peak indicating defects form which are needed to bend the long nanostructure (for 1.5 wt% and 2.0 wt% concentration) in order to form sponge-like materials,(Terrones, Lv, Terrones, & Dresselhaus, 2012).

Samples with 1.0 wt%, 1.5 wt%, 2.0 wt% ferrocene concentration show sharp D-band and G-band peaks, suggesting the presence of only sp2 hybridization form in the nanotubes constituting the cotton(Shamsudin, Asli, Abdullah, Yahya, & Rusop,

2012). ID/IG ratio (figure 3b) refers to the quality of nanotubes. The lower ID/IG value close to zero corresponds to a better degree of graphitization(Wepasnick, Smith, Bitter, & Howard Fairbrother, 2010). The ID/IG ratio for sample with 0.1 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt% Ferrocene concentration are 1.00362, 1.0798, 0.63348, 0.9754, and 0.9602 respectively. The higher ID/IG values are influenced by the presence of two factors which are the presence of structural and lattice defect and presence of other carbon materials such as nonuniform nanotubes.

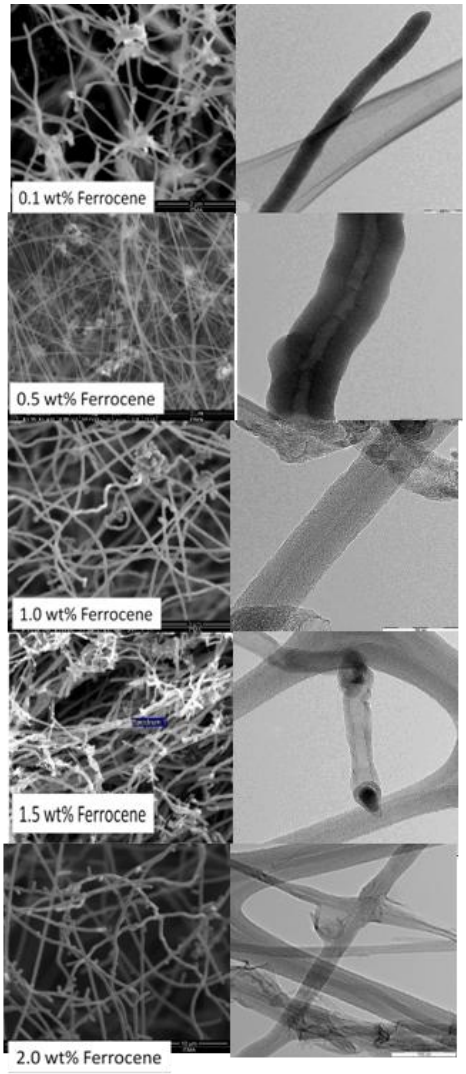

Fig. 2: FESEM and HRTEM micrograph of cnt cotton at different ferrocene concentration.

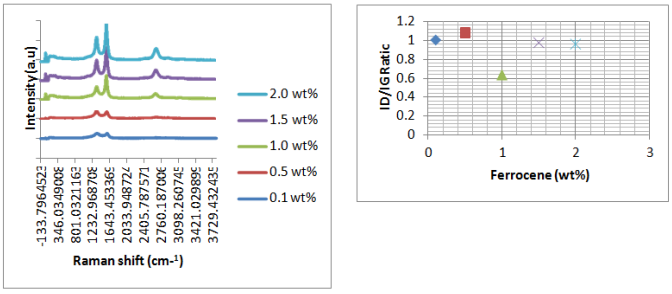

Fig. 3: (a) Micro-Raman analysis of cnt cotton at different ferrocene concentration (b) ID/IG ratio of cnt cotton at different ferrocene concentration.

C) Thermogravanimetric Analysis:

The TGA curves were obtained under an N2 atmosphere and scanned from 30 oC to 1000°C at a heating rate of 10K/min. From figure 4, it can be seen that there is a small amount of weight losses below 100°C due to desorption of the physisorption water.

Australian Journal of Basic and Applied Sciences, 9(12) Special 2015, Pages: 109-113

For the carbon materials, to some extent, the amounts of physisorption water reflect their hydrophilicity and pore structures(Grioui, Halouani, Zoulalian, & Halouani, 2006). CNT cotton with variation of catalyst concentration did not show any obvious thermal degradation, with almost all CNT cotton degraded at 860°C. However,there are an anomaly for sample with 0.5 wt% concentration of ferrocene having additional of weight and the phenomenon is under investigation. From table 1, the residual mass of 82.89% was found after heating up to 1,000°C. This confirmed the high stability of the CNT cotton.

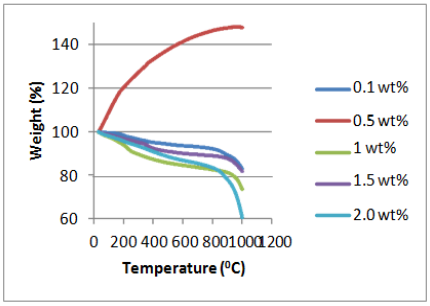

Fig. 4: TG analysis of cnt cotton.

Table 1: Residual mass (%) at different ferrocene concentration.

Concentration (wt%)	Residual mass (%)
0.1	82.8976
0.5	147.965
1.0	73.616
1.5	82.2538
2.0	60.5743

D) I-V Curve and Conductivity:

Electrical measurement was performed for each sample using the two point probe method. In order to perform I-V measurement, our sample CNT cotton samples were cut into 1cm x1cm dimension. Each sample was measured three times to have a statistical average value for the resistance and to see if the behavior observed was repeatable. Conductivity was calculated by fitting the experimental data at high field values, thus neglecting eventual nonlinear effects which appear in the low voltage region(Chen, Wang, & Peng, 2006). From figure 5a, the saturated voltage are 3.6v, it shows that 1.0 wt%, 1.5 wt% and 2.0 wt% samples gave the best linear graph. Linear I–V curves were obtained when Ohmic contacts were established to metallic cnt.

From the literature, straight nanotubes without obvious structural defect exhibit the lowest resistivities and resistivity decreases with increasing diameter(Chen *et al*., 2006). This statement was supported with our FESEM and HRTEM from figure 2, where 1.0 wt%, 1.5wt% and 2.0 wt% samples have almost straight nanotubes and do not have any obviously structural defect as support by RAMAN at figure 3a where G-band is higher than D-band. From figure 5b, as the CNT diameter becoming bigger it exhibited higher conductivity.

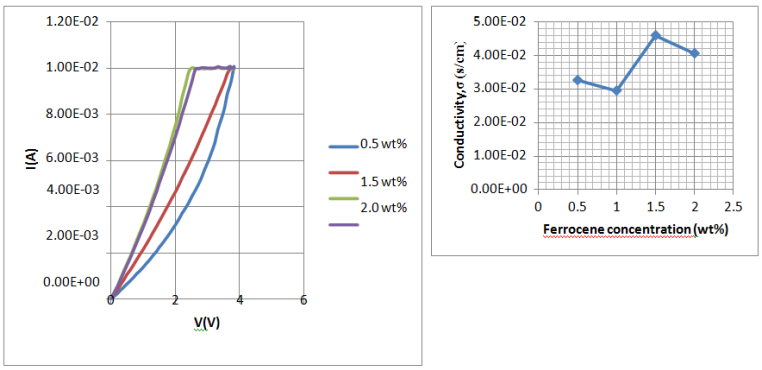

Fig. 5: (a) I-V curve of cnt cotton at different ferrocene concentration (b) conductivity of cnt cotton at different ferrocene concentration.

Strong bonds between carbon atoms also allows CNT to withstand higher electric currents than

copper. Electron transport occurs only along the axis of the tube.

Conclusion:

Generally the morphology of the CNT cotton can be adjusted by changing the experimental condition. By changing the concentration of the ferrocene would resulted in different diameter size of CNT that would also affect the properties in the electron transport in CNT cotton. As the concentration of Ferrocene was increased, causing the iron cluster to become bigger for the nucleation of CNT. Concentration at 1.0 wt% and 1.5 wt% of ferrocene gave good morphology and better properties compared to other weight ratio. .

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