

FIELD ELECTRON EMISSION PROPERTIES OF VERTICALLY ALIGNED CARBON NANOTUBES SYNTHESIZED FROM PALM OIL PRECURSOR

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ABSTRACT

Vertically aligned carbon nanotubes (VACNT) synthesized at different ferrocene concentration by thermal decomposition of bio-hydrocarbon source namely palm oil were investigated for field electron emission application. The ferrocene concentration ranges from 0.5 to 3.5 wt% and the as-prepared VACNT were characterized using field emission scanning electron *microscopy* and micro-Raman spectroscopy. It was clearly shown that a controlled increase in the mixture of ferrocene and palm oil was important in improving field emission behaviour. The samples synthesized using 2.5 wt% ferrocene concentration proves to be the optimum concentration as for lowest turn-on (corresponding to the current density of 0.1 mAcm⁻²) and threshold field (corresponding to the current density of 1 mAcm⁻²) at 3.17 and 4.07 V μ m⁻¹ respectively in comparison with other concentration. The sample also demonstrates highest peak current of 8.0 mAcm⁻² at a field of 5.5 V μ m⁻¹ as well as less degradation during one hour emission stability testing.

Key words: Carbon Nanotubes, Palm oil, Chemical vapor deposition, Field electron emission, Scanning electron microscopy, Raman spectra, catalytic methods.

ABSTRAK

Karbon nanotube vertikal sejajar (VACNT) disintesis pada konsentrasi ferrocene yang berbeda dengan dekomposisi termal dari sumber bio-hidrokarbon yaitu kelapa sawit untuk diselidiki aplikasi emisi medan elektron. Konsentrasi ferrocene berkisar antara 0,5-3,5% berat dan VACNT tersebut dikarakterisasi menggunakan mikroskop elektron dan spektroskopi mikro-Raman. Hal ini jelas menunjukkan bahwa peningkatan dikendalikan dalam campuran ferrocene dan kelapa sawit sangat penting dalam meningkatkan sifat emisi medan. Sampel yang disintesis menggunakan konsentrasi ferrocene 2,5% berat terbukti menjadi konsentrasi optimal untuk nilai medan *turn-on* (sesuai dengan kerapatan arus 0,1 mAcm⁻²) dan *threshold* terendah (sesuai dengan kerapatan arus 1 mAcm⁻²) yaitu asing-masing 3,17 dan 4,07 V μ m⁻¹ dibandingkan dengan konsentrasi lainnya. Sampel tersebut juga menunjukkan arus puncak tertinggi 8,0 mAcm⁻² pada medan 5,5 V μ m⁻¹ serta degradasi yang rendah selama satu jam pengujian stabilitas emisi.

Kata Kunci: karbon nanotube, minyak kelapa sawit, deposisi uap kimia, emisi medan elektron, mikroskop elektron, spectrum Raman, metode katalitik

INTRODUCTION

One of the prospective applications of vertically aligned carbon nanotubes (VACNT) is that it can be used as field electron emission (FEE) cathodes. VACNT demonstrates excellent properties that are of great interest for FEEs including the potential to operate at low voltages, good emission stability, longer emitter lifetime and also combined with properties such as mechanically strong and chemically inert. The VACNT's FEE performance which has been extensively discussed (Bonard, et al, 1999; Yuge, et al, 2012; Bonard, et al, 2001; Fursey, et al, 2003) depends on several factors such as density of VACNT (Choi, et al, 2003), structural properties of VACNT (Bonard, Salvetat, et al, 1999; Zhang, et al, 2011), adhesion layer (Kumar, et al, 2007) and catalyst concentration (Asli, et al, 2013). As such, the effects of synthesis parameters used for VACNT growth must be well understood and optimized in order to fully take the advantage of VACNT for their FEE potential applications.

In this paper, VACNT with different density, length and crystallinity synthesized using various catalyst concentrations were assessed for its potential as field electron emitters. The potential of palm oil based VACNT as field emitter were investigated by studying the most important parameter for FEE source such as, turn-on and threshold field from current density (J)- electric field (E) plot, field enhancement factor, β value which was estimated from the

slope of the Fowler Nordheim (F-N) plot and current emission stabilities.

MATERIALS AND METHODS

VACNT were synthesized by thermal chemical vapor deposition (TCVD) method using bio-hydrocarbon source palm oil. The following ferrocene concentration of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt% were mixed thoroughly with palm oil precursor. Typical experimental procedures (Suriani, et al, 2009; Suriani, Roslan, et al, 2010; Suriani Mohamad, et al, 2010; Suriani, et al, 2001; Azmina, et al, 2012) were used where 3 ml of palm oil-ferrocene mixture were loaded into the precursor furnace. The ultrasonically cleaned silicon substrates were then loaded into the synthesis furnace. The experiment was done in argon ambient at fixed precursor and synthesis temperature of 450 and 750°C respectively. The synthesis was done for 30 min before the samples were taken out for characterization by field emission scanning electron microscopy (FESEM -ZEISS Supra 40VP) and micro-Raman spectroscopy (Horiba Jobin Yvon -DU420A-OE-325). The FEE measurements were done in a vacuum chamber at working pressure of 10^{-4} Pa in a parallel electrode arrangement. The sample area was 0.25 cm² and the separation between the two electrodes was fixed at 200 μ m. The emission current was measured using Keithly 4210 electrometer with voltage ramping from 0 to 1100 V.

substrate at different ferrocene concentration (0.5- 3.0 wt%). Low magnification image shows uniform growth and vertical alignment of dense

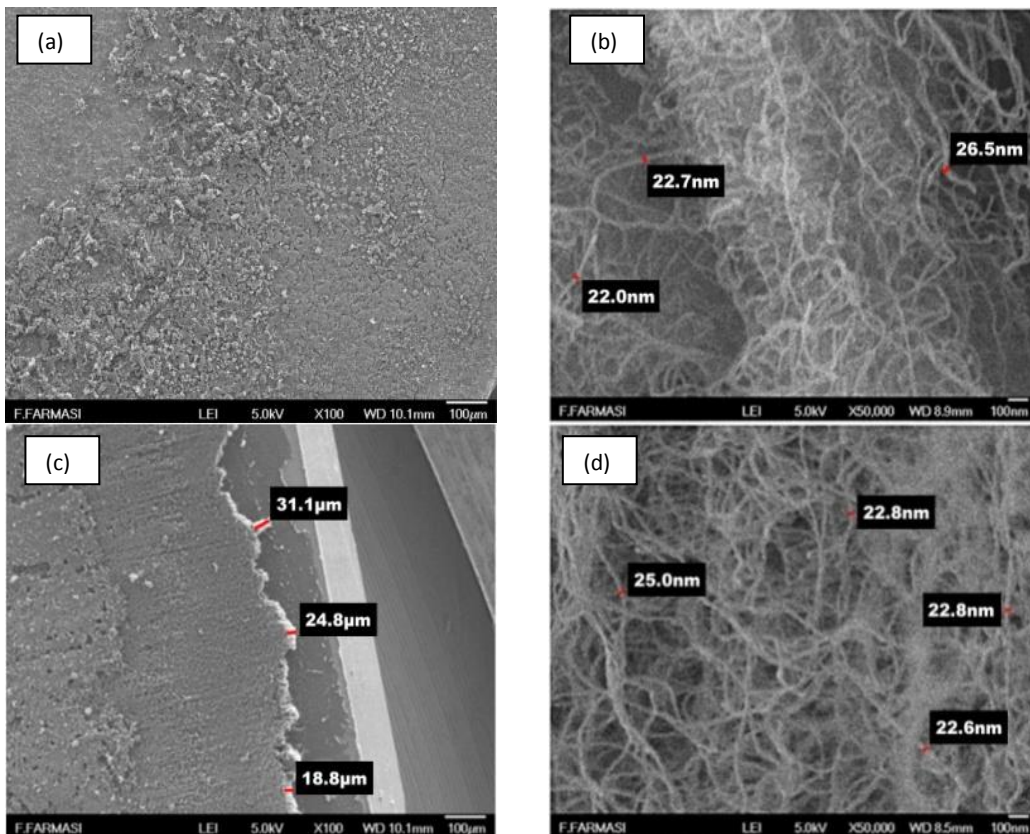
RESULTS AND DISCUSSIONS

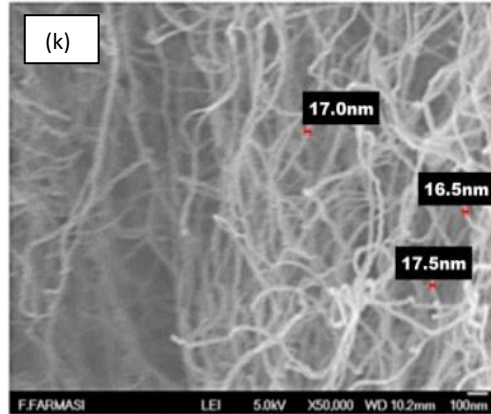
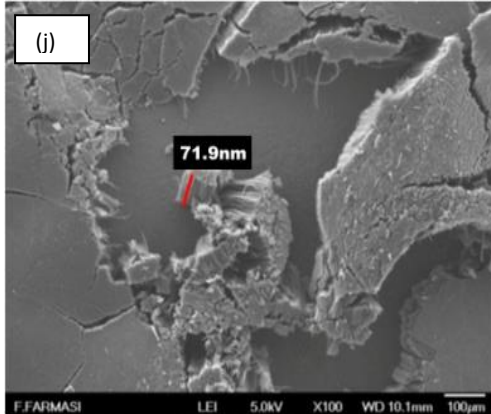
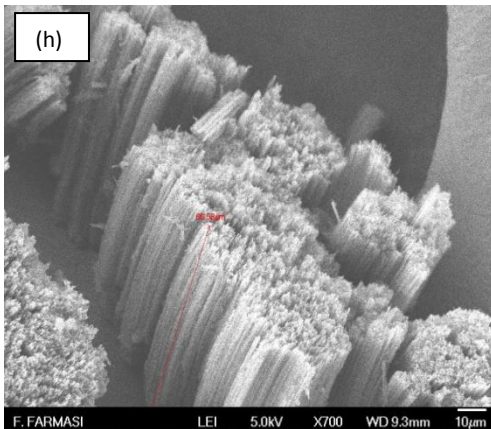
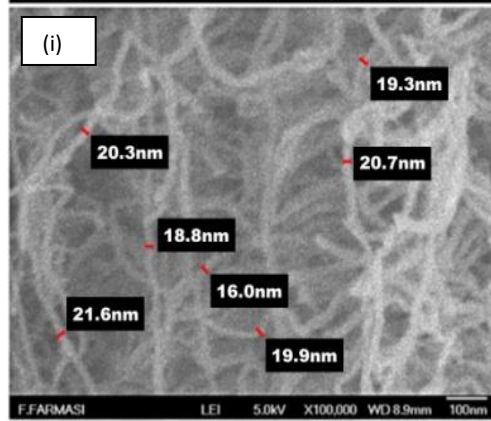
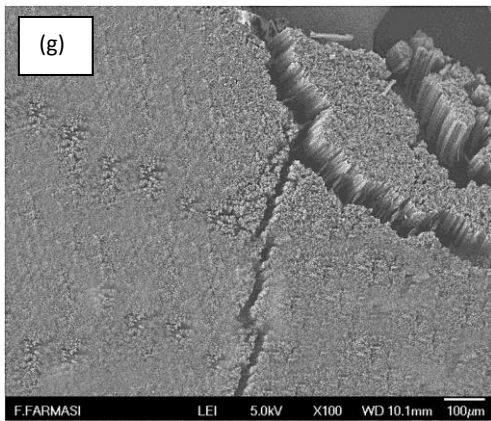
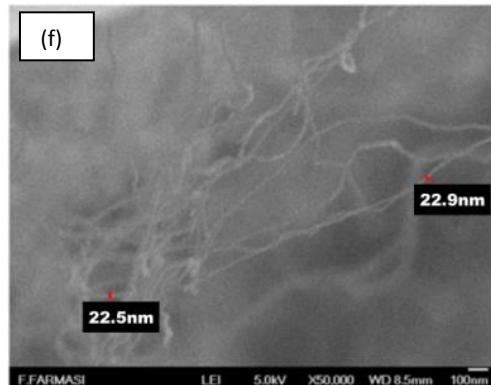
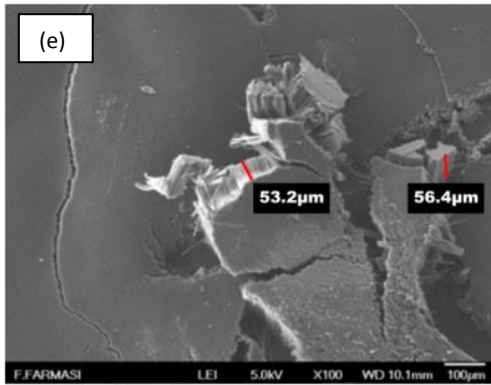
Fig. 1 (a)-(m) show typical FESEM images of CNT deposited on silicon

CNT which measures in the length of 18.8-81.0 nm. This gave a growth rate of about 0.8-2.7 μmin^{-1} for 1.0 to 3.0 wt% samples. At 0.5 wt% of ferrocene concentration, the presence of VACNT was very poor, leading to no side view measurement obtained. High magnification image illustrate that individual CNT were not ideally parallel but somewhat curved and entangled guaranteed a good electrical contact all across (Kumar, et al, 2004). The ferrocene concentration also affected the tubes diameters. The diameter was found to decrease with the increase of ferrocene concentration. The largest diameter of 26.5 nm was detected at 0.5 wt% sample, while 3.0 wt% sample gave smallest average tube diameter of 15.5 nm (see Fig. 1 (a)-(m)). The explanation of the role of

ferrocene concentrations on the tube density, average length and diameter have been discussed into detailed in (Suriani, Mohamad, et al, 2010).

Raman spectra of the CNT are shown in Fig. 2. The figure shows typical twin peaks at 1585.5-1602.3 cm^{-1} for G peak and 1355.8-1362.1 for D peak. An appreciable change in the intensity of the G and D peaks were noticed as the nanotubes quality varies accordingly. The I_D/I_G ratio of CNT produced decreases from 0.84 to 0.66 as ferrocene concentration increases from 0.5 to 3.0 wt%. This gave sign that less defected CNT was grown as Fe amount increases in the precursor. Table 1 shows the summary of Raman scattering data of CNT at various ferrocene concentration.





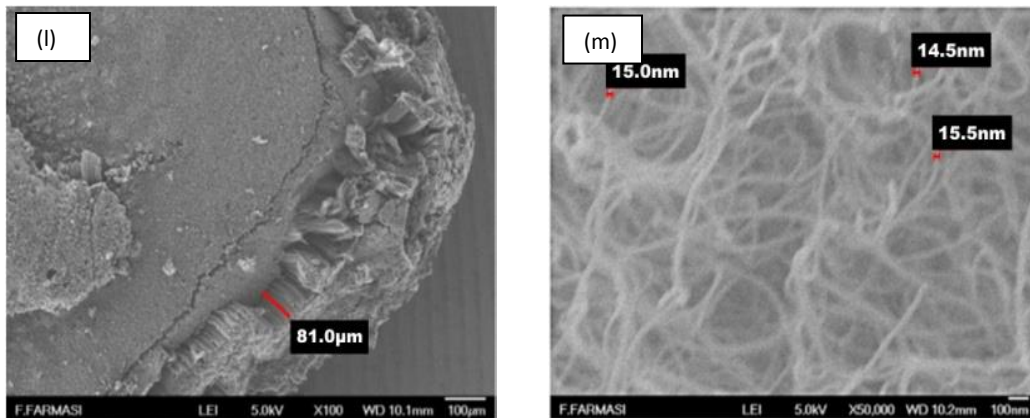


Fig. 1. FESEM images of CNT by thermal CVD method at different Fe concentration; (a)-(b) 0.5, (c)-(d) 1.0, (e)-(f) 1.5, (g)-(i) 2.0, (j)-(k) 2.5 and (l)-(m) 3.0 wt%.

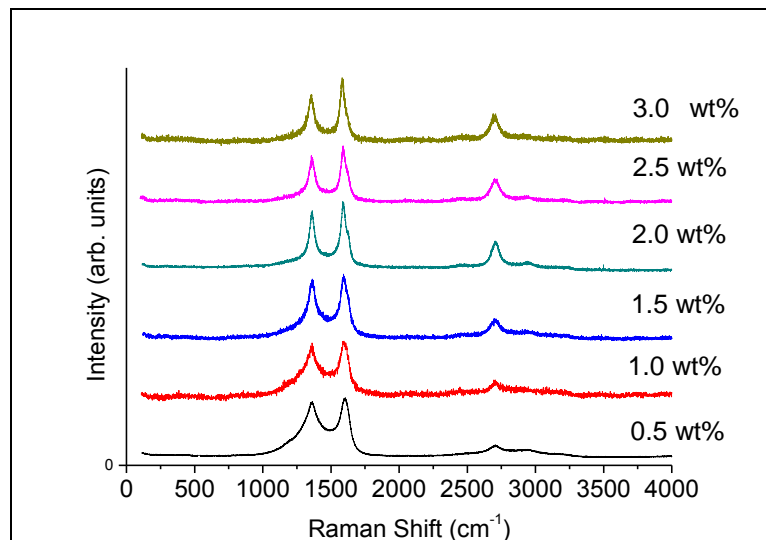


Fig. 2. Raman patterns of CNT synthesized at different ferrocene concentration 0.5-3.0 wt%.

Table 1: Raman peak position and G and D intensity ratios of CNT synthesized at different ferrocene concentration (0.5-3.0 wt%).

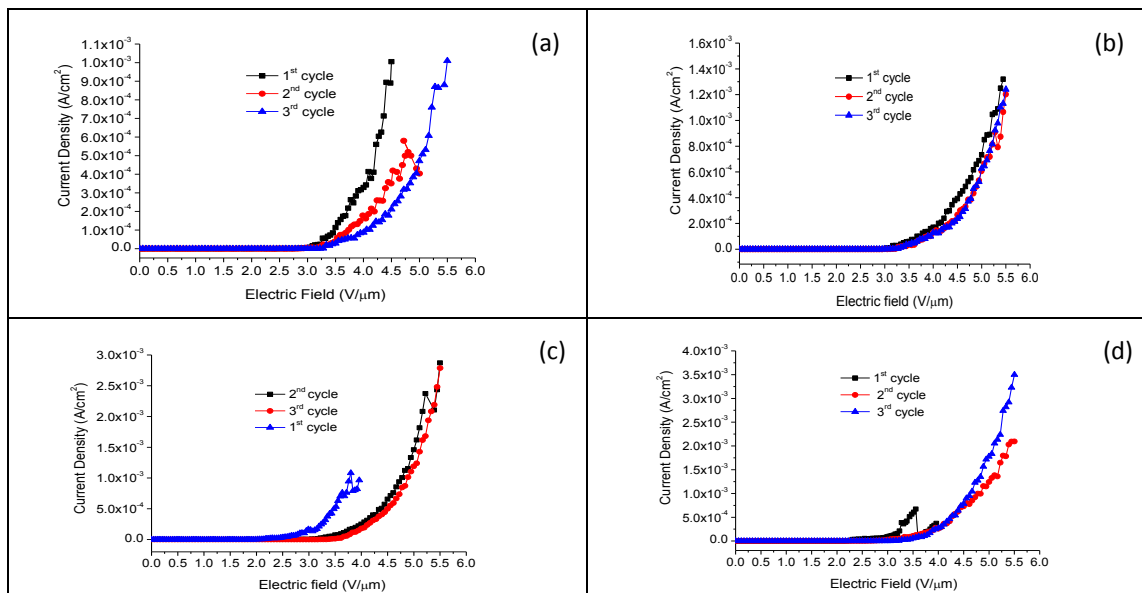
Samples	G peak (cm ⁻¹)	G-Width (cm ⁻¹)	D peak (cm ⁻¹)	D-Width (cm ⁻¹)	I _D /I _G ratio
0.5	1602.3	80.4	1366.1	218.2	0.84
1.0	1598.3	79.9	1362.1	206.1	0.78
1.5	1596.1	79.8	1366.1	155.4	0.74
2.0	1592.6	71.8	1364.1	103.5	0.71
2.5	1593.2	67.2	1362.2	102.3	0.69
3.0	1585.5	59.0	1355.8	88.0	0.66

Fig. 3 (a)-(g) show J-E curves obtained from CNT synthesized at different

ferrocene concentration (0.5-3.0 wt%). For accuracy and reliability of data,

several cycle of measurements were taken for every concentration. The important point of interest was that, all samples yielded a current density range of a few mAcm^{-2} orders at reasonable fields of $3.17 - 5.50 \text{ V}\mu\text{m}^{-1}$. The fluctuation of current in the first cycle were observed, this may be due to non-uniform nanotubes (Ghosh, et al, 2009) and also due to the burnt off amorphous carbon (a-C) material (Zamri, et al, 2009). The unstable current density was observed worst at 0.5 wt% sample (both in low and high electric field region) implying to high quantity of a-C content resulted from inadequate catalytic activity during the synthesis. There were few cases as shown in Fig. 3 (c)-(f) where the first cycle data cannot be replicated, this might be due to the degradation of the

emitter caused by the destruction of exceptional tubes. The exceptional tube normally demonstrates sudden increase in the emission current at lower electrical field. The tube can be destroyed primarily via ion bombardment either by gas phase electron ionization or ion desorption from the electrode, where both were induced by the emitted electron (Bonard, et al 1998). Therefore due to this, in the second and third cycle of measurement, a higher turn-on field were observed. However it did not affect the emitted current, in all conditions the current increases tremendously. For those cases, the first cycle measurements were disregarded and the curve characteristics have been carried out from the third-cycle data.



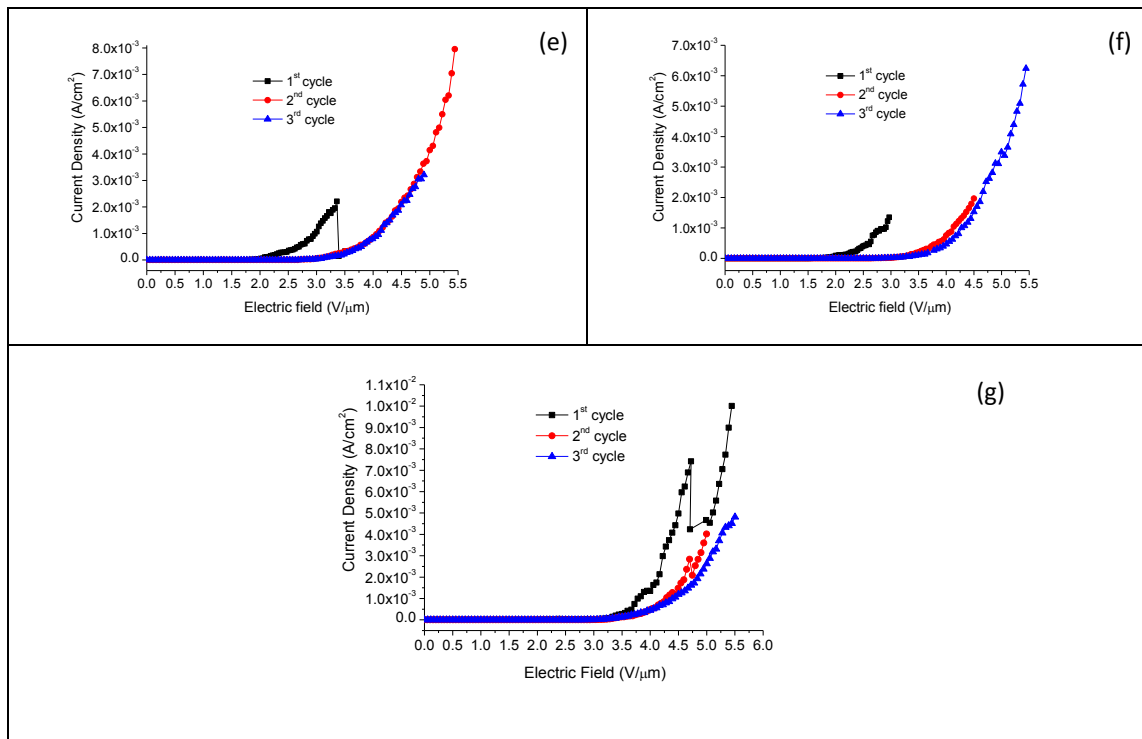


Fig. 3. J-E curves of CNT as a function of ferrocene concentration (a) 0.5 (b) 1.0 (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0 and (g) 3.5 wt%.

The turn-on values which correspond to the current density of 0.1 mAcm^{-2} were found to decrease from $4.06 \text{ V}\mu\text{m}^{-1}$ to a minimum value of $3.17 \text{ V}\mu\text{m}^{-1}$ for CNT samples deposited with 0.5, 1.0, 1.5 and 2.5 wt% ferrocene concentration in the precursor. For sample deposited with higher ferrocene concentration of 3.0 wt% the turn-on value increases to $3.40 \text{ V}\mu\text{m}^{-1}$. In order to verify the increment in turn-on field which was believed due to the increase of ferrocene concentration in CNT produced, the FEE measurement were extended to CNT sample catalyzed by 3.5 wt% ferrocene concentration (see Fig. 3 (g)). This sample shows an increase of turn-on value at around $3.42 \text{ V}\mu\text{m}^{-1}$. As for threshold fields which correspond

to the current density of 1 mAcm^{-2} were also found to decrease from 5.50 to $4.07 \text{ V}\mu\text{m}^{-1}$ as ferrocene increases from 0.5-2.5 wt% in the carbon precursor. Sample 3.0 and 3.5 wt% also showed an increase in threshold field value in the range of 4.27 - $4.39 \text{ V}\mu\text{m}^{-1}$. The maximum current density was found to be 8.0 mAcm^{-2} at a field of $5.5 \text{ V}\mu\text{m}^{-1}$ which was shown by sample synthesized using 2.5 wt% ferrocene concentration. The FEE characteristic for sample prepared using 2.5 wt% ferrocene concentration was reproducible where the turn on and threshold field were consistently detected at lower field of 3.23 and $3.62 \text{ V}\mu\text{m}^{-1}$ respectively corresponding to the current density of 0.1 and 1 mAcm^{-2} (see Fig. 4).

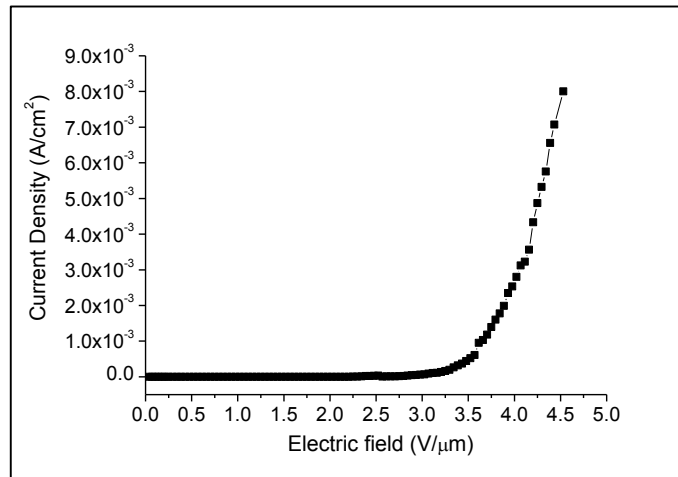
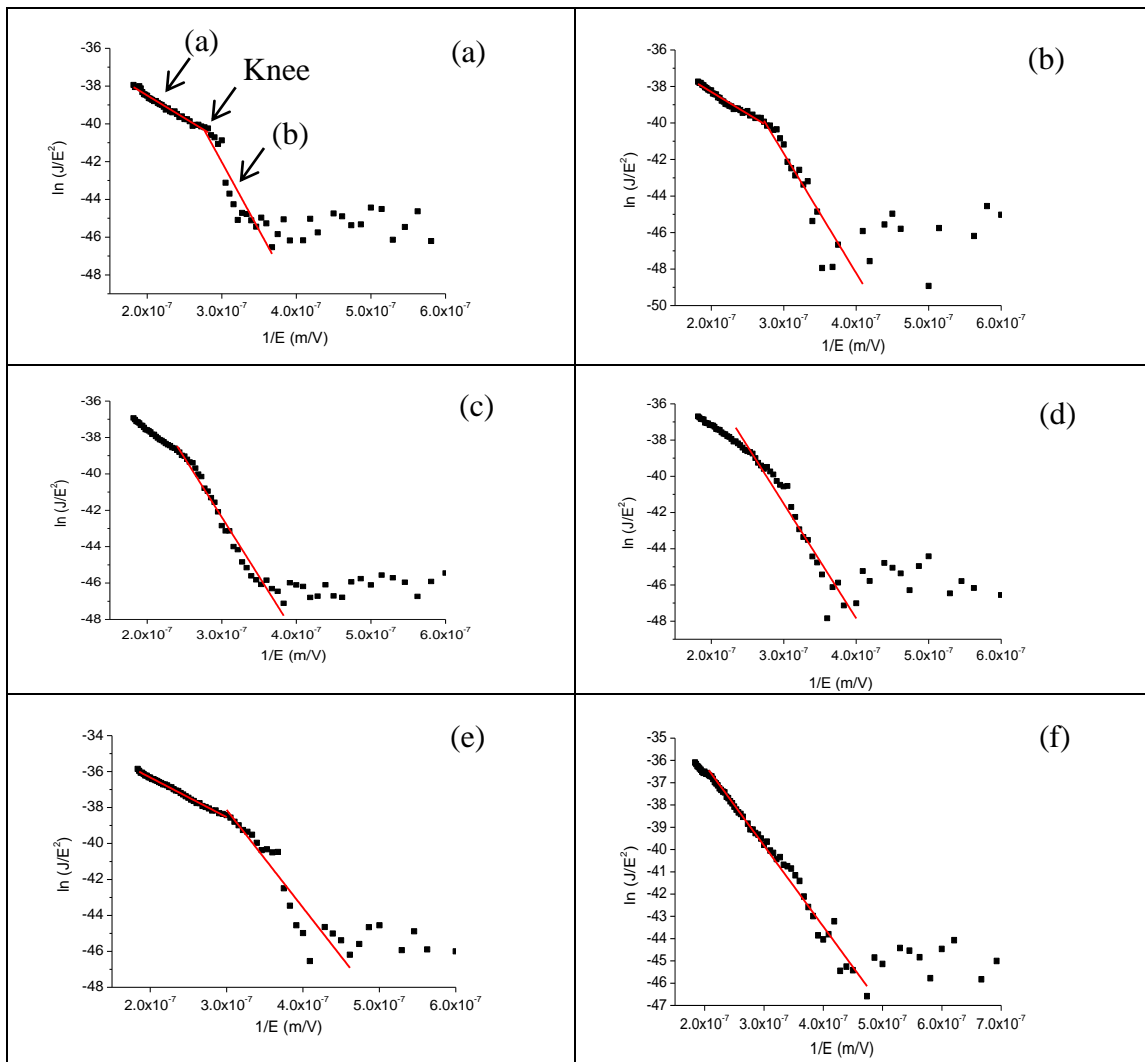


Fig. 4. The reproducibility of FEE performance for sample prepared using 2.5 wt% ferrocene.



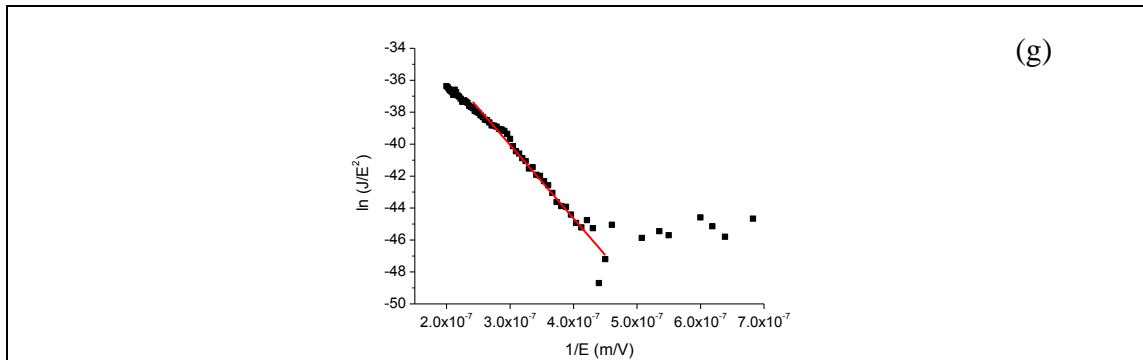


Fig. 5. Corresponding F-N plot as a function of ferrocene concentration (a) 0.5 (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0 and (g) 3.5 wt%.

In-depth field emission characteristic was analyzed using F-N theory (Gadzuk, et al, 1973). According to the F-N relation where $J = A \beta^2 E^2 / \phi \exp(-B\phi^{3/2}/\beta E)$ with $A = 1.54 \times 10^{-6} \text{ AV}^{-2} \text{ eV}$, the emission current density of the tip was dependent on the local field, E_{loc} and work function ϕ of the emitter tip. It was believed that the CNT's current emission occurs from multiple emitters and an average current was measured (Srivastava, et al, 2006). At the same time, due to variation in nanotube geometries, the local field on the CNT emitter varies accordingly. The E_{loc} was related to macroscopic electric field which is external field applied, E that was amplified at the emitter tip by a field enhancement factor, β . Therefore the effective local field $E_{loc} = \beta E$, where β can be determined experimentally from the slope of $\ln(J/E^2)$ vs $1/E$. The β value can be calculated from the equation, $\beta = -B\phi^{3/2} / \text{slope}$ where the CNT ϕ value was $\sim 5 \text{ eV}$ (which was the same as pure graphite) (Kumar, et al, 2004) and $B = 6.83 \times 10^9 \text{ eV}^{-3/2} \text{ Vm}^{-1}$.

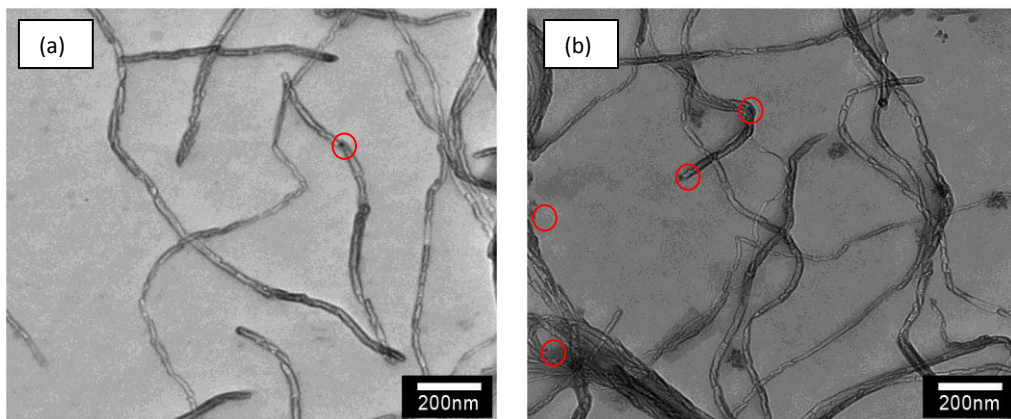
The experimental F-N plots for CNT samples deposited at different ferrocene concentration are shown in Fig. 5 (a)-(g). From the experimental

data, it shows that there was a knee on the F-N plot which were clearly identifiable on samples catalyzed by 0.5, 1.0 and 2.5 wt% ferrocene (see Fig. 5 (a), (b) and (e)). This gave two different slopes at low and high electric field. The slope in high electric field (indicated by arrow (a) on Fig. 5 (a)) was found to be much less as compared to low field region (indicated by arrow (b)). The origin of dual slopes behaviour may be attributed to the space-charge effect, gas absorption and desorption, interaction between the neighbouring CNT tip or the presence of defect which changes the local density of states (Bonard, et al, 1998; Collins, et al, 1997). The calculated β for high (β_H) and low (β_L) field region for CNT samples synthesized by ferrocene concentration from 0.5 - 3.5 wt% were to be in the range of 3185.80-3462.83 and 1058.14-1815.21 respectively. These ranges were acceptable for field emission devices.

Among those, sample synthesized by ferrocene concentration of 2.5 wt% shows the highest calculated β either for β_H or β_L which suggested that the E_{loc} was strongly applied (Choi, et al, 2003). We confirmed that low turn-on and threshold field and an increased in maximum emission current density in

this samples was caused by enhanced local electric fields due to enhanced β on the tip (Asli, et al, 2013) long with other factors. The field emission properties of samples prepared using different ferrocene concentration are compared in Table 2. Other possible explanation that *may* be expected to *contribute* to the total *emission* current was the CNT density. Apparently, there was no marked difference between FESEM images of CNT synthesized using each ferrocene concentration. The effect was obvious on the CNT density obtained from 0.5 wt% ferrocene concentration (see Fig. 1(a)). In this sample, the CNT population was so thin and there were areas with no CNT samples at all. It was suggested that low CNT density catalyzed by 0.5 wt% of ferrocene concentration was the reason for moderate emission behaviour from this sample. The higher the CNT density the higher the emission sites *contribute* to the total *emission* current. Therefore,

it can be said that the CNT density synthesized by this concentration was not suitable for higher FEE performance. At 1.0 wt% of ferrocene concentration, the CNT start to cover the whole substrate, however as ferrocene concentration increases further from 1.5, 2.0, 2.5 and 3.0 wt% the changes on the CNT density were not visibly seen from FESEM images. Significant changes were only detected on the CNT length, where higher ferrocene concentration in the palm oil resulted in higher length. It can be said that the CNT density factor that contributes to FEEs performance can only been at CNT prepared at low catalyst concentration (0.5 wt%) where low CNT density was clearly seen. For sample prepared using high ferrocene concentration which was greater than 1.0 wt% the effects of CNT density cannot be applied because physically it can be seen that the CNT density was similar.



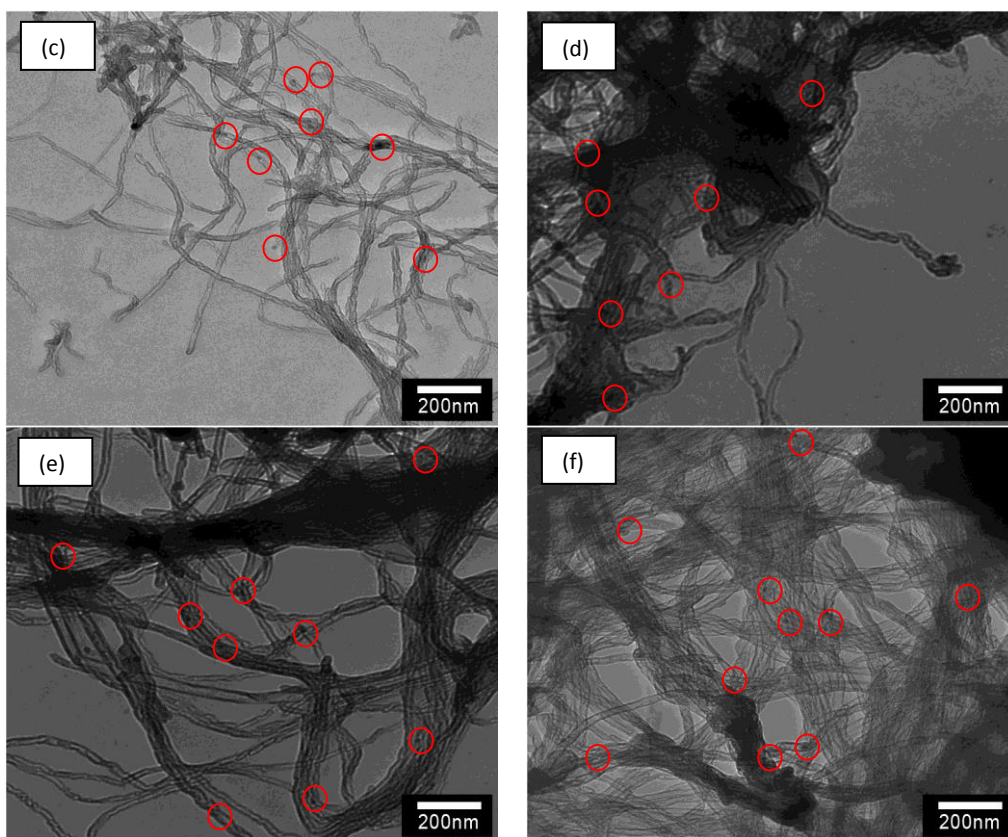


Fig. 6. TEM images indicate the increased of encapsulated Fe catalyst particles within the tubes at different ferrocene concentration; (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, and (f) 3.0 wt%.

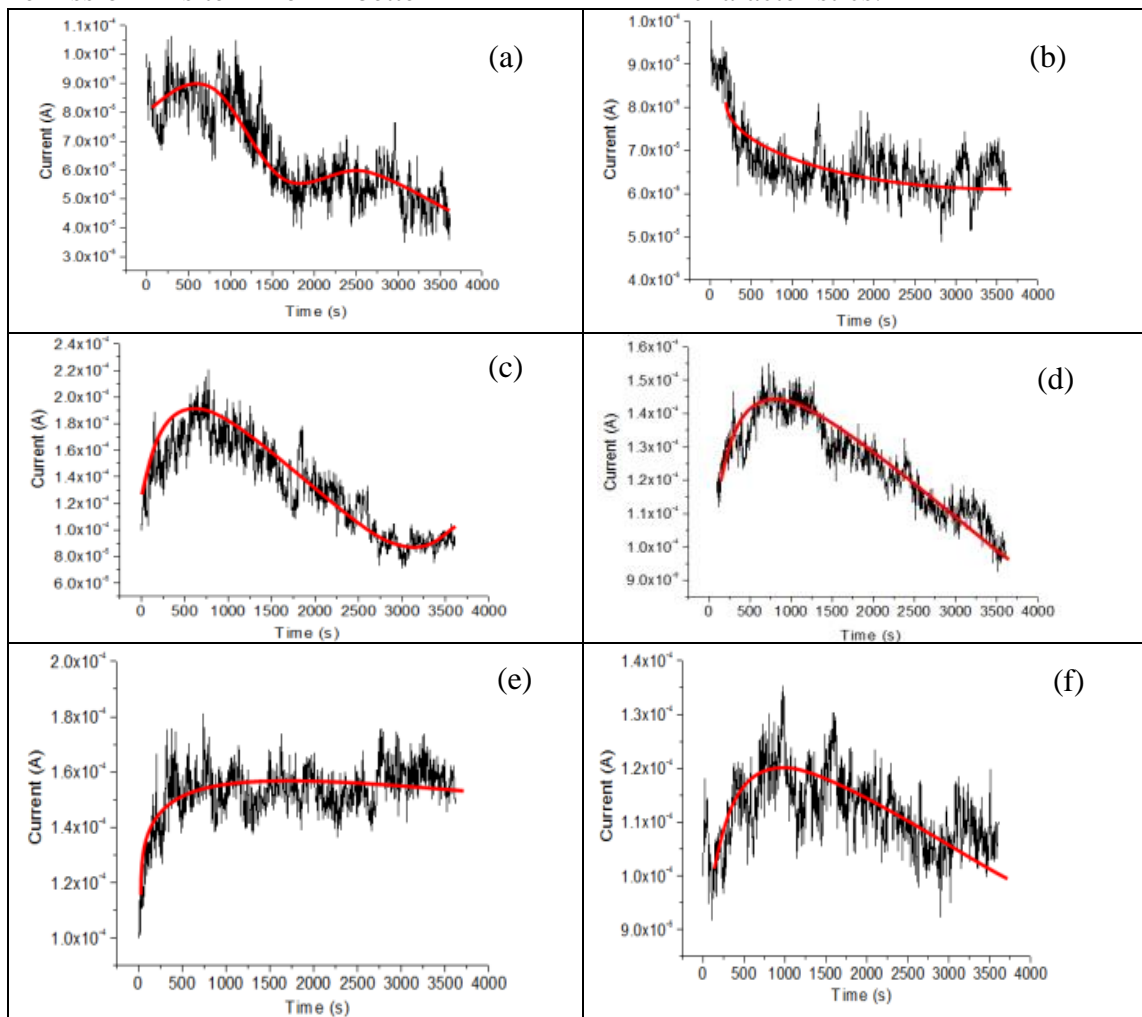
It was also reasonable to attribute the differences of emission properties to the ferrocene concentration in the sample. Fig. 6 (a)-(f) show TEM micrograph that indicate the increased of encapsulated Fe catalyst particles within the tubes at different ferrocene concentration. Here we believed that a controlled increase in Fe catalyst was favourable to improve the emission behaviour of the sample through Fe-assisted emission properties. Tiny Fe particles which may exist in the cavities and surface of VACNT plays an important role to improve FEE characteristics (Kumar, et al, 2007). When it comes to explain the reason why the emission behaviour increases with further increase in ferrocene concentration from 0.5 to 2.5 wt%, it can be related to the structural

modification between Fe and CNT. As the carrier density of Fe was much higher than that of pure graphite cylinder at Fermi level, thus it was highly probable that Fe impurity would provide additional electronic density of state to the CNT under favourable coupling (Bonard, et al, 1999; Kumar, et al, 2007). Furthermore the work function of Fe (4.0-4.7 eV) (Kumar, et al, 2007) lies in the range of work function as that of the CNT which was between 4.0-5.0 eV, this increases the probability of structural modification in CNT material, providing higher electron supply and thus improving the electron emission (Kumar, et al, 2007). However the excess in Fe particles which exceed the critical value did not act as effective dopant in improving

FEE performance (Obraztsov, et al, 1999).

At the same time, the moderate defect level measured from Raman I_D/I_G ratio of 0.69 on this sample (2.5 wt%) might also act as preferential emission site to increase field emission current (Cheng, et al, 2003). The introduction of high catalyst concentration during the synthesis proved to enhance the VACNT quality, however this did not provide additional emission site for better FEE

performance. Higher turn-on and threshold field detected at samples synthesized using 3.0 and 3.5 wt% ferrocene concentration were believed due to field screening effect (Cheng, et al, 2003). This effect causes high electrical barrier on top of the emitter which normally requires higher voltage. In the meantime, the excess in Fe particle in the samples synthesized using 3.0 and 3.5 wt% ferrocene concentration did not seem to assist the FEE characteristics.



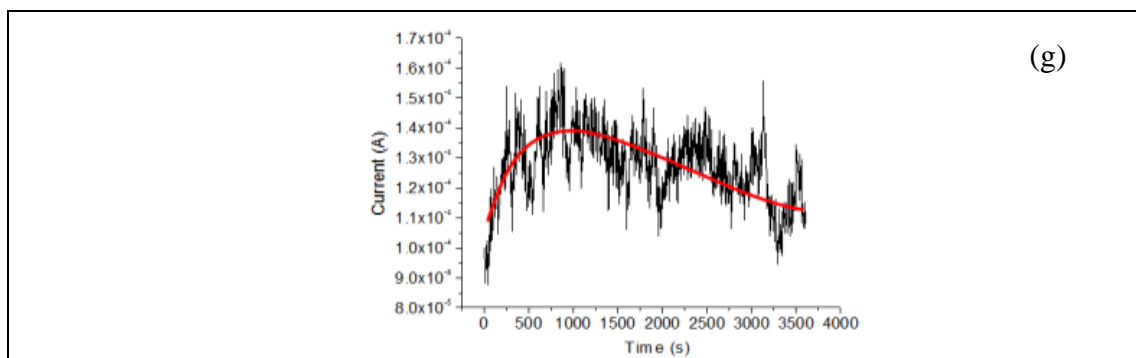


Fig. 7. Current stability measurement done on CNT for one hour as a function of ferrocene concentration (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0 and (g) 3.5 wt% at initial emission current 0.1 mA.

Results of VACNT current stability synthesized at various ferrocene concentration (0.5-3.0 wt%) are presented in Fig. 7 (a)-(g). The display current of 0.1 mA as a function of time with one hour duration was plotted at different applied voltage. As shown in Fig. 7 (a)-(d), for sample catalyzed by 0.5, 1.0, 1.5 and 2.0 wt% ferrocene catalyst, an obvious current emission degradation together with spikes and slight fluctuation in emission were seen. Meanwhile, regardless of ferrocene concentration, it was observed that the current emission curves were quite noisy. This can be associated with the current amplitude fluctuation itself (Kumar, et al, 2007) or this situation may be also attributed to gas discharge which creates plasma between the electrodes. The samples obtained from 0.5 wt% ferrocene concentration shows significant emission dropped after 30 min time in comparison with other samples. In this sample the current was observed to drop from 0.10 to 0.04 mA (Fig. 7 (a)). Such quality was not good

to be adopted in flat panel display technology. On the other hand, as the ferrocene concentration increases from 1.0 to 2.0 wt% in the precursor the emission loss gradually improved. Besides the emission degradation, the drastic increase in the emitted current was seen (particularly for the first 25 min) and this situation was also observed at samples synthesized by 1.5 and 2.0 wt% ferrocene concentration.

In the meantime, it was found that the current hardly dropped for sample synthesized at 2.5, 3.0 and 3.5 wt%, although several current spikes were detected. It can be seen that emission loss of around 0.03 mA was believed due to the current amplitude fluctuation itself. The results indicate that the increment in ferrocene concentration in the CNT synthesized from palm oil precursor helps to improve the stability and lifetime of field emission device effectively. Conditions where more stable current emission and less degradation and spike, lower signal to noise ratio was seen on 2.5 wt% sample.

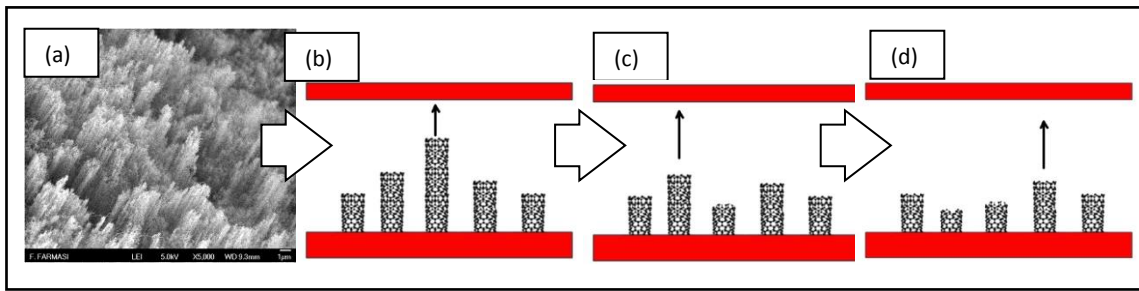
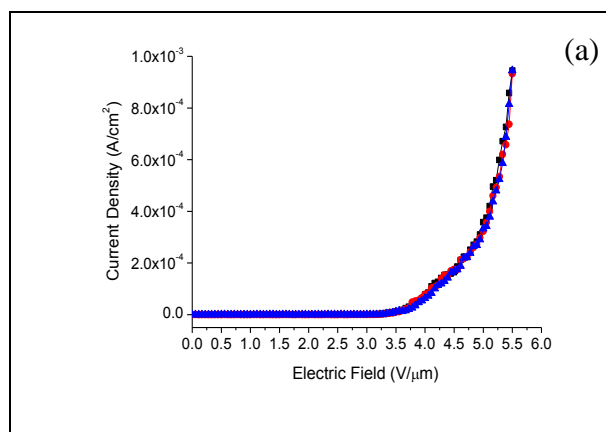


Fig. 8. (a) FESEM image of VACNT showing non-uniformity of CNT height (b) illustration of individual CNT with different height, where the current was contributed by longer tube as pointed by the arrow due to stronger electrical field around the tube (c) due to resistive heating, the tube may become damaged or shorter and the emission of electron was contributed by the other tube (d) the process was continued with the other tube and the process repeated itself.

The reduction in emission was believed due to structural changes during the measurement. At early stage, current was contributed by longer tube due to its closer distance to anode and stronger electrical field around the tube (see Fig. 8). However, after some time, the longer CNT may become short or damaged because of resistive heating. Taking the produced $1 \mu\text{A}$ current as example, temperature at the tip of individual MWCNT could go up to 2000°K (Purcell, et al, 2002; Vincent, et al, 2002). At this temperature CNT

was most likely will become damaged and the process of current emission was taken over by other CNT. We understand that not all CNT was involved in current emission at one time. New CNT may never emit electron at all due to its short geometrical structure. Therefore the same situation repeats itself such as a-C/impurities were initially burnt-off. This situation contributes to current fluctuation or spike as observed on current stability curve.



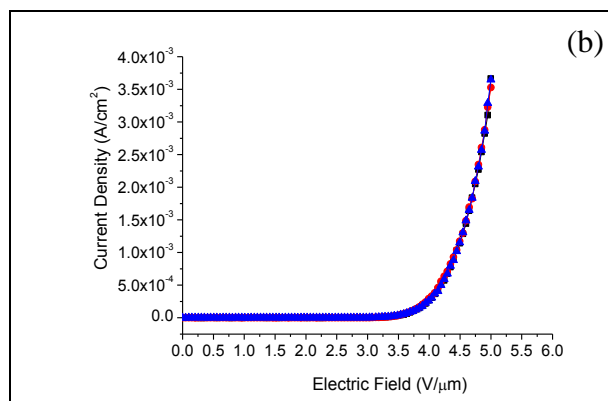


Fig. 9. J-E curves of CNT for (a) 0.5 and (b) 2.5 wt% ferrocene concentration.

After the emission stability testing, the experiment was continued with FEE measurement. It was done once again to see its effect on FEE characteristic as displayed in Fig. 9 (a) and (b). The FEE measurement was only carried out on two samples which were 0.5 and 2.5 wt% of ferrocene concentration. Both samples demonstrated worst and best emission properties respectively. As expected, the unstable current density which was observed worst at 0.5 wt% sample has become more stable both in low and high field region. The curves show excellent emission repeatability as demonstrated in 3 run cycles. Once the sample was scanned over and over again by high electrical field, these causes the a-C/impurities burnt-off and left behind a clean surface of CNT which took part in emission process. However, the value of turn-on field has shifted from 4.06 to a higher value of 4.11 $V\mu m^{-1}$. Same goes for the maximum current achieved which has decreased to less than 1 $mAcm^{-2}$ at 1100 V. Similar condition was also seen at 2.5 wt% sample where the turn-on and threshold field shifted to a higher value of 3.65 and 4.44 $V\mu m^{-1}$ from 3.17 to 4.07 $V\mu m^{-1}$ respectively. The maximum current of only 3.70 $mAcm^{-2}$ was achieved at 5.01 $V\mu m^{-1}$. This shows that after several scan, it

has changed the emitter structure. The stable current emission was caused by the decline of a-C/impurities content on the CNT sample. Here it can be said that FEE measurement can also act as purification process of CNT other than giving high temperature to destroy the by-product in the sample. Raman analyses have been carried out for all samples which have undergone 1 hour stability test, however there were no significant changes on the measured I_D/I_G ratio. This was because we believed that during the FEE measurement, only a single point was involved. This single point was very difficult in determining its location. Even with a sample size of 0.25 cm^2 , (quite large sample area) it was almost impossible to find the point. It was only possible through in situ FEE and Raman characterization. Meanwhile, the decrease of maximum current to a lower value was caused by the declining number of CNT population after a certain period of time, only high quality CNT structure could withstand the applied electric field.

CONCLUSION

In summary, the production of palm oil-VACNT catalyzed using 0.5-3.0 wt% ferrocene concentration has shown appreciable field emission

properties. The samples yielded a current density range of a few mAcm^{-2} order at reasonable fields of $3.17\text{-}5.50 \text{ V}\mu\text{m}^{-1}$. The sample with ferrocene concentration of 2.5 wt% shows the lowest turn-on and threshold field of 3.17 and $4.07 \text{ V}\mu\text{m}^{-1}$ at current densities of 0.1 and 1 mAcm^{-2} respectively. This sample also demonstrated more stable current emission with less degradation and spike, lower signal to noise ratio during one hour current stability testing. The better emission from this concentration was likely due to high local current field and appropriate amount of Fe catalyst which contributed to additional electron density in the sample. The appropriate defect level from micro-Raman analysis was also the reason for good FEE characteristics. The lower density of CNT catalyzed by the ferrocene concentration of 0.5 wt% was the reason for moderate performance of FEE in the sample. Greater turn-on and threshold field demonstrated by samples prepared using more than 2.5 wt% ferrocene concentration were believed due to field screening effect, excessive amounts of Fe catalyst present in the samples and less defect level in the VACNT structure.

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