

Vertically aligned carbon nanotubes synthesized from waste cooking palm oil

A. B. SURIANI,^{*,**,****,†} Roslan MD NOR^{*****} and M. RUSOP^{*,***}

^{*}NANO-SciTech Centre, Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

^{**}Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

^{***}Solar Cell Laboratory, Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

^{****}Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

^{*****}Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

For the first time, vertically aligned carbon nanotubes (VACNT) were produced using waste cooking palm oil as green starting materials. The synthesis was carried out in a floating-catalyst thermal chemical vapor deposition reactor. Field emission scanning electron microscopy, energy dispersive X-ray, micro-Raman and thermogravimetric analyses, showed that the carbon nanotubes are of excellent quality, comparable to those obtained using conventional carbon sources. Under a typical synthesis condition of 5.33 wt % ferrocene as catalyst and a furnace temperature of 750°C, a mixture of single and multi-walled carbon nanotubes of 85% purity, vertically aligned on a silicon substrate, were produced. Field emission from the VACNT indicated reasonable turn-on field at 2.25 V/ μm which corresponded to the current density of 10 $\mu\text{A}/\text{cm}^2$. The threshold field was observed to be about 3.00 V/ μm at 1 mA/ cm^2 . The maximum current density of 6 mA/ cm^2 measured was obtained for 4 V/ μm . It is concluded that the VACNT from the reuse of waste material are suitable for applications in flat panel displays and flat lamps.

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1. Introduction

The polluting effect of waste cooking oil upon aquatic life can be as severe as petroleum spills. While spills are accidental, the discharge of waste cooking oil to river systems is deliberate, continuous and increasing annually. In efforts to benefit from this waste material, there have been attempts to convert waste cooking oil to biodiesel.^{1)–3)} Another possible beneficial use of waste cooking oil is as the starting material for the synthesis of carbon nanotubes (CNT). Being a material of vast potential applications, industrial scale production of CNT using an abundant waste material will be both economical and environmentally beneficial.

Recently we reported the use of pristine refined palm oil as an efficient, renewable and cheap carbon source for the synthesis of vertically aligned carbon nanotubes (VACNT).⁴⁾ It was demonstrated that refined palm oil was as efficient as, or better than, conventional fossil carbon sources, such as acetylene, methane, ethanol or ethylene. In this paper, we report the use of waste cooking palm oil as the carbon source for VACNT synthesis using a similar technique. The VACNT produced were characterized using field emission scanning electron microscopy (FESEM), micro-Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM). The composition and purity of the samples were determined by energy dispersive X-ray (EDX) and thermogravimetric analyses (TGA). The identification of catalytic cracking reaction of waste cooking palm oil and catalyst mixture were analyzed

using gas chromatography–mass spectrometry (GC–MS). We also assessed the potential of waste cooking palm oil based VACNT as field emitter by measuring its field electron emission (FEE) properties.

2. Materials and methods

VACNT were synthesized using the floating-catalyst thermal chemical vapor deposition technique described previously.⁴⁾ Waste palm oil was obtained from refined domestic cooking palm oil that has been used to fry three loads of fish emulating typical usage in household frying. Each frying cycle lasted about 15 min at temperatures not expected to exceed 180°C. At the end of the three frying cycles, the used oil appeared blackened, probably due to oxidation and carburization of the fried objects. The waste oil was obtained after filtering to remove solid objects. Synthesis of the VACNT was conducted using a two-furnace system utilizing an alumina tube. Typically, 5.33 wt % ferrocene (Sigma Aldrich) was thoroughly mixed with the waste palm oil to act as the catalyst. An alumina boat containing about 3 ml of the mixture was placed in the alumina tube at the centre of furnace 1. A silicon substrate of area 1 cm² was thoroughly cleaned and placed in the alumina tube at the centre of furnace 2. In a typical synthesis run, the alumina tube was initially flushed with argon at 150 sccm for 10 min. Then furnace 2 was set to 750°C, followed by increasing the temperature of furnace 1 to 450°C, all in an argon atmosphere. Normally, the synthesis process took 30 min, after which furnace 1 was switched off. The sample was further annealed at 750°C for 30 min under argon flow to remove any hydrocarbon impurities. Finally, furnace 2 was allowed to cool down to room temperature before the sample was extracted for analysis.

[†] Corresponding author: A. B. Suriani; E-mail: absuriani@yahoo.com

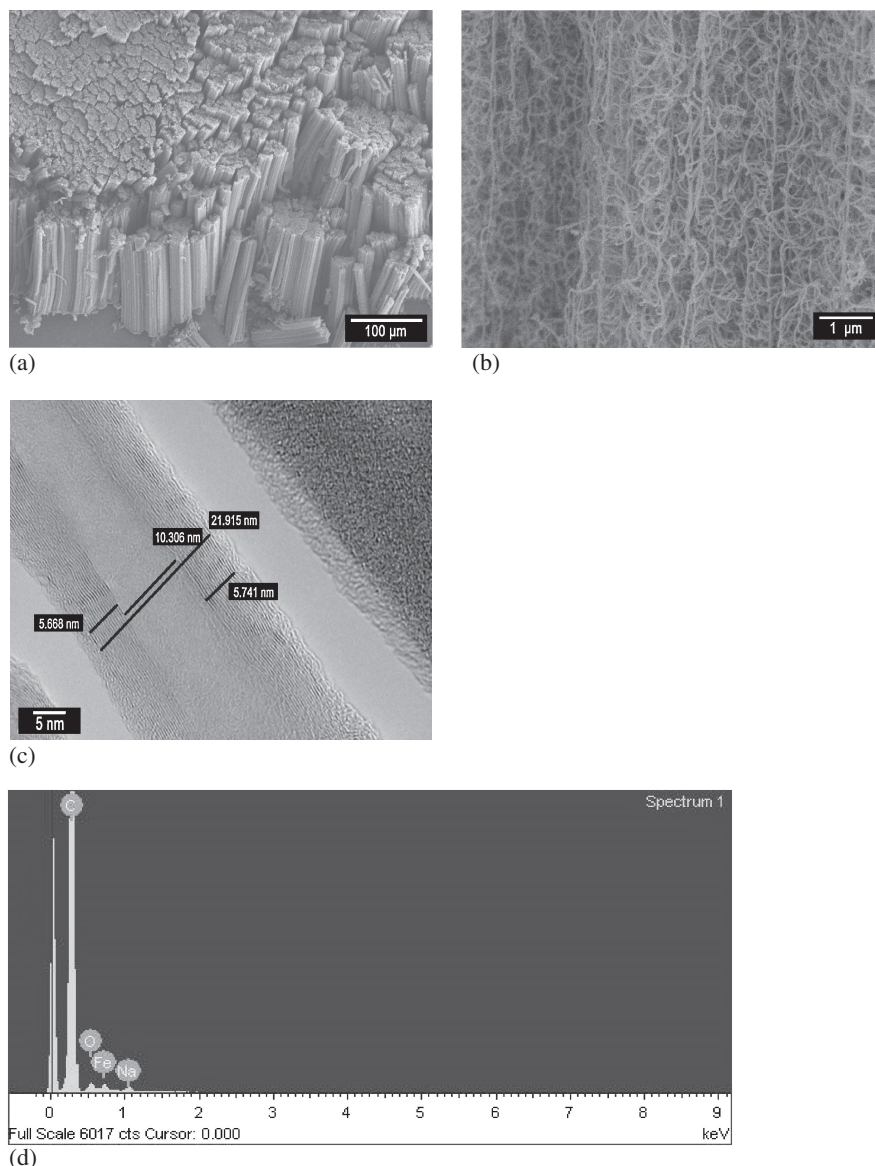


Fig. 1. The electron micrograph of VACNT grown from waste cooking palm oil on a Si substrate, (a) side view of the aligned CNT (b) close up of the side view of the CNT. (c) HRTEM image of MWCNT (d) EDX analysis of the VACNT forest.

FESEM (JEOL JSM 6701F and ZEISS Supra 40VP) operated at 5 kV were used to evaluate the density, alignment, tube diameter and length of the VACNT. Both microscopes are equipped with an EDX for sample composition identification. EDX analysis was based on point analysis and line scanning. The inner structural information was obtained using JEM-2100 HRTEM at 200 kV. Raman scattering study was performed using Horiba Jobin Yvon-DU420A-OE-325 system equipped with an Argon laser at a wavelength of 514.5 nm. The TGA (Perkin-Elmer TGA Pyris 1) was performed to determine the impurities and decomposition temperature of VACNT. The sample was burned with a ramping rate of 10°C/min up to 1000°C under the flow of oxygen gas. The GC-MS system was an Agilent 6890N Network Gas Chromatograph unit with nitrogen as the carrier gas and hexane was used to dissolve catalyst and oil matrix prior to injection into GC-MS. The temperature program consisted of a heating rate of 10°C/min from 45 to 325°C with a hold time of 10 min. The FEE measurements were carried out in a vacuum chamber at working pressure of 10^{-4} Pa in a parallel electrode

arrangement. The distance between the 2 electrodes was 200 μm and the sample area was 0.25 cm². The emission current was measured using an electrometer of Keithly 237 with voltage ramping from 0 to 800 V.

3. Results and discussions

Figure 1 shows the electron micrographs of a typical sample of VACNT obtained from thermal catalytic decomposition of waste cooking palm oil. Figure 1(a) shows a dense VACNT 'forest' of tubes about 120 μm in length following deposition for 30 min, giving an average growth rate of about 4 μm min⁻¹. A higher magnification view of the VACNT (Fig. 1(b)) shows that the tubes have diameters was between 20–50 nm, suggesting that they are multi-walled carbon nanotubes (MWCNT). Individual tubes were found to be twisted with evidence of alignment in bundles. Figure 1(c) shows a high resolution transmission electron micrograph of an individual MWCNT. The tube diameter was ~22 nm consisting of about 15 layers. Quantitative EDX analysis of the tube composition (Fig. 1(d)) yielded 89% C,

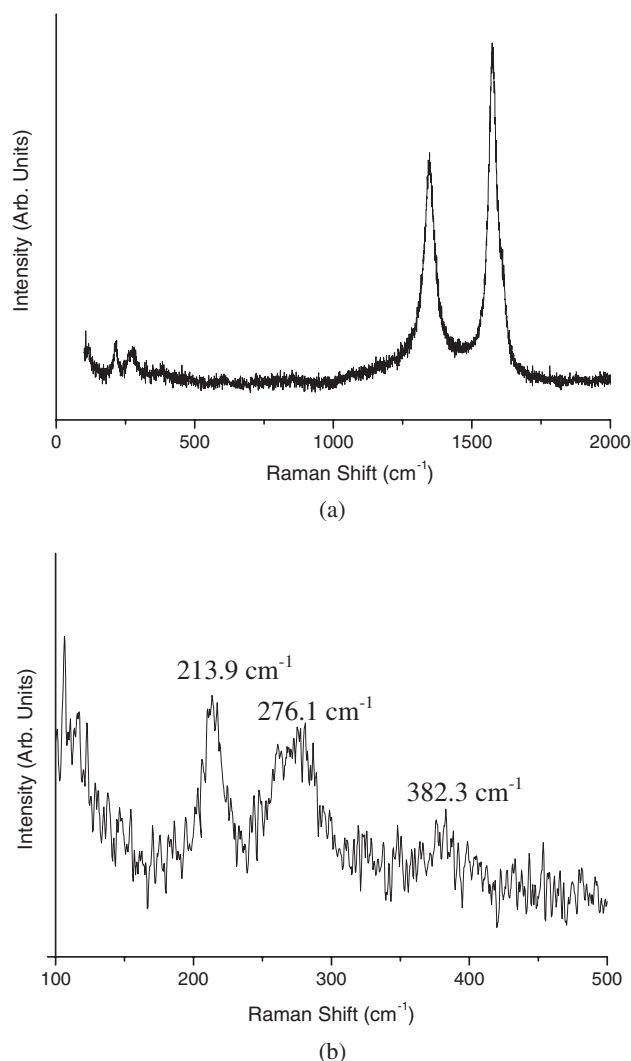


Fig. 2. Micro-Raman spectra of VACNT grown using waste cooking palm oil (a) micro-Raman spectrum showing the RBM modes, the D line and the G line of CNT (b) close up of the micro-Raman spectrum showing the RBM modes of SWCNT.

7% Fe, 3% O and 1% Na. The origin of the Na is suspected to be from cooking salt (NaCl) present during frying.

Results from micro-Raman analysis are shown in Fig. 2, in which several peaks normally attributed to CNT can be identified. Most prominent are the carbon “G” and “D” lines at 1576 and 1347 cm⁻¹, respectively. The ratio of the intensities of these peaks, I_D/I_G was determined to be 0.64 indicating reasonable crystalline quality. Also visible are peaks due to the radial breathing modes (RBM) of single-walled carbon nanotubes (SWCNT) at 213.9, 276.1 and 382.3 cm⁻¹ (Fig. 2(b)). This corresponded to estimated SWCNT diameters, d , of 1.16, 0.90 and 0.65 nm, respectively, obtained from the RBM peak position, ω , and the expression $d = 248 \text{ (cm}^{-1}\text{ nm)}/\omega \text{ (cm}^{-1})$.⁵⁾

The TGA curves shown in Fig. 3 showed a small weight loss from 110–210°C which was thought to be due to the decomposition of residual hydrocarbon impurities. This was about 1% of the total weight. The gradual weight loss from 250–550°C was attributed to the decomposition of amorphous carbon materials.^{6)–8)} This constituted about 4% of the total weight. The dominant weight loss of 85% was due to the decomposition of CNT in the temperature range of 580–740°C. The Fe catalyst and

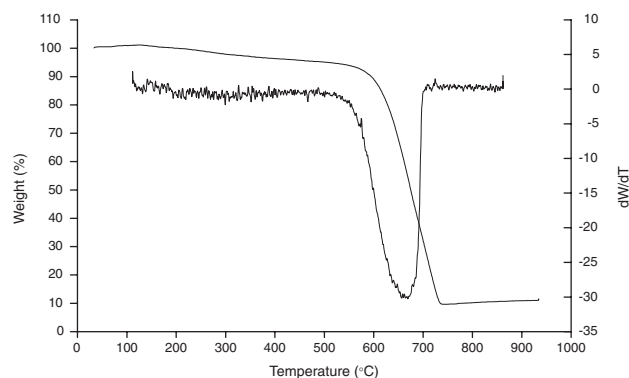


Fig. 3. TGA curves of VACNT synthesized using waste cooking palm oil.

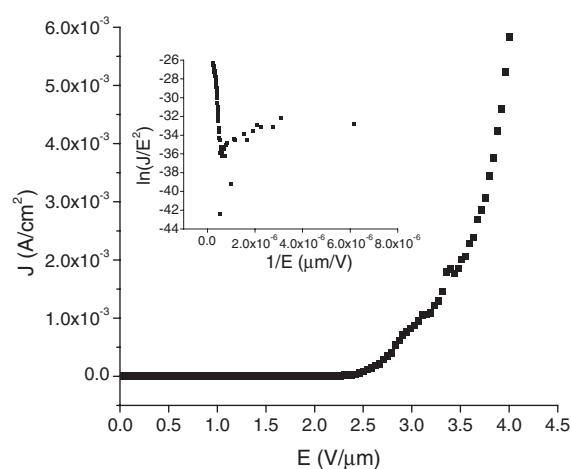


Fig. 4. Current density versus macroscopic electric field for VACNT synthesized from waste cooking palm oil. The inset (top left) is the Fowler–Nordheim plot.

other nonvolatile constituents made up the remaining 10% of the total weight. The Fe catalyst underwent oxidation as indicated by a slight weight gain beyond 800°C. Based on the analysis, the purity of the VACNT produced was about 85%, and so it can be regarded as high quality.

Typical emission current density versus applied field (J – E) curve obtained from VACNT cathode from waste cooking palm oil is shown in Fig. 4. From the curve it was obtained that the turn-on electric field was 2.25 V/μm which corresponded to the current density of 10 μA/cm². The threshold field was about 3.00 V/μm at 1 mA/cm². The maximum current density was found to be 6 mA/cm² at 4 V/μm. The as-prepared waste palm oil based VACNT shows high current density at reasonable electric field which suits FEE future application. The theoretical model for field electron emission from cold cathodes are normally based on the Fowler Nordheim model⁹⁾ which gives the relationship of the current density, J (A/cm²) and the electric field, E (V/μm) as;

$$J = A\beta^2 E^2 / \varphi \exp(-B\varphi^{3/2} / \beta E) \quad (1)$$

where φ is work function with value of ~ 5 eV for carbon, E is the electric field, A and B are constants ($A = 1.54 \times 10^{-6} \text{ A V}^{-2} \text{ eV}$ and $B = 6.83 \times 10^9 \text{ eV}^{-3/2} \text{ V m}^{-1}$).

The Fowler–Nordheim (F–N) plot was obtained by plotting $\ln J/E^2$ as a function of $1/E$ to yield a linear curve as shown in the inset of Fig. 4. The value of β can be obtained from the slope

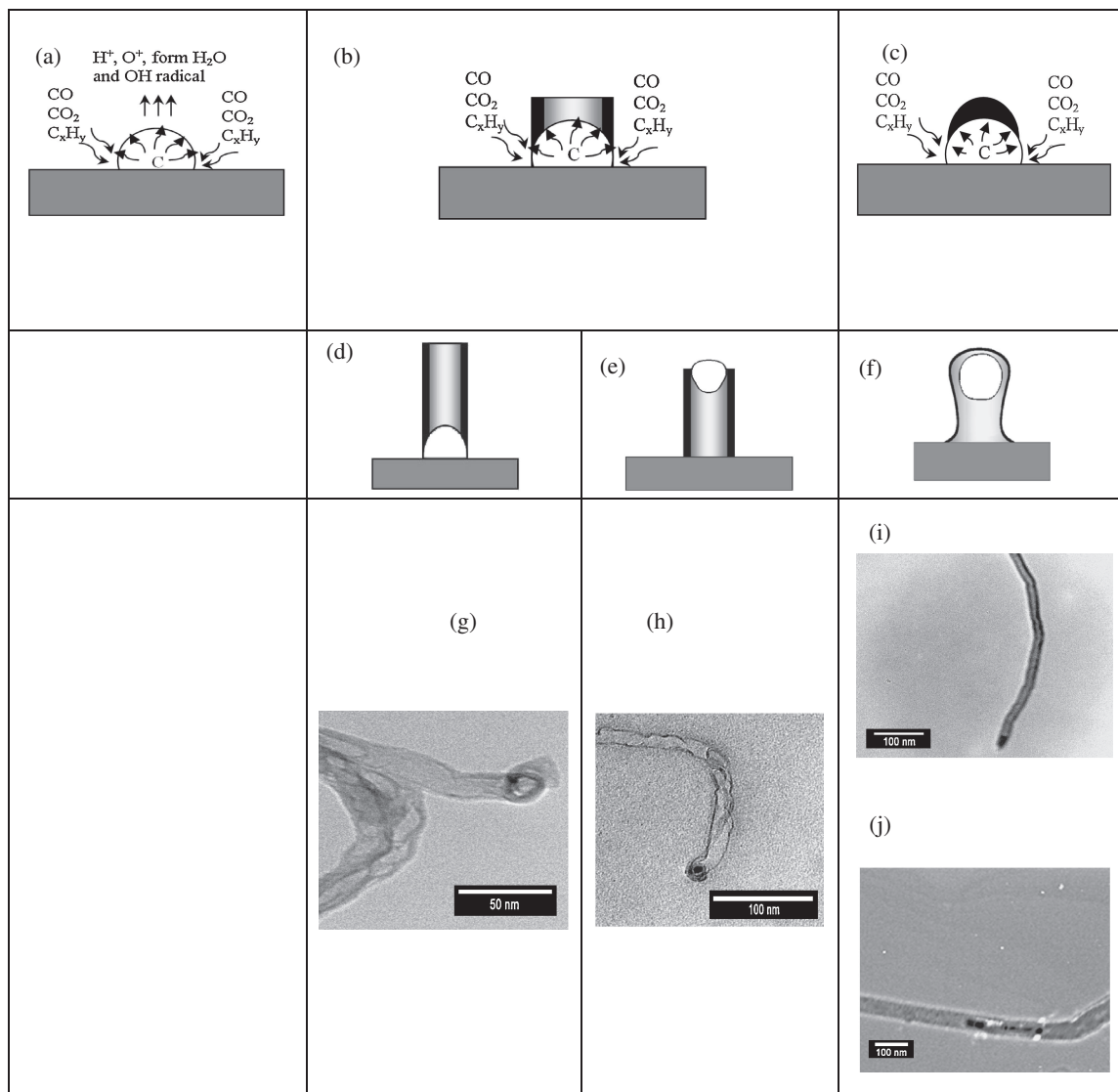


Fig. 5. (a) The coming C_xH_y , $C_xH_yO_2$, CO and CO_2 vapors were catalytic decomposed on the upper exposed surface of Fe particles to release hydrogen and oxygen. The illustration of initial growth of the nanotubes which took place via (b) bottom growth model and (c) yarmulke cap. The illustration of (d) bottom (e) tip and (f) yarmulke growth. The HRTEM images of (g) open-ended, (h) Fe catalyst in the tip (i) Fe catalyst in the tip (yarmulke cap) and (j) Fe catalyst encased in tube.

linear part of the F–N plot, normally associated with emission due to high electric field. For our sample, a value of 2740 was obtained which was typical of vertically aligned MWCNT cathodes.

The growth process of VACNT by thermal catalytic decomposition of waste cooking palm oil can be explained based on known mechanisms of catalytic CVD process. Based on the observation of catalyst location from HRTEM images the growth was by the established bottom growth mechanisms of CNT as illustrated in Fig. 5(d) or tip growth model as illustrated in Fig. 5(e) depending on whether the catalyst remain on the substrate due to strong catalyst-support interaction or weak interaction which causes the catalyst easily lift off during the synthesis process.^{10)–12)} Figures 5(g), 5(h) and 5(i) show HRTEM images of catalyst in the tubes which located in the bottom as seen on open-ended tube and the tip of the tubes.

Although the mechanism seems to be similar in CVD processes involving methane or acetylene, here the carbon source was different. We have used GC–MS to investigate the

cracking pattern of waste palm oil–ferrocene mixture. The spectrum shown in Fig. 6 gave the results of the GC–MS analysis of waste palm oil, ferrocene only and the mixture of waste palm oil and ferrocene at 5.33 wt%. The chromatograph obtained from each samples were analyzed using the ChemStation® Data Analysis software included on the Agilent GC–MS unit to identify any differences obtained between the curves. Obviously, the peak at retention time of around 10 and 11 min shifted to a lower value with the presence of ferrocene in waste palm oil. This indicated that, there was an immediate catalytic reaction occurring between waste palm oil and ferrocene which changed the heavy molecules into lighter hydrocarbon. The reaction was believed to occur without the assistance of heat. The details of catalyst and hydrocarbon content from GC–MS analysis at certain retention time were tabulated in Table 1.

During the synthesis process ferrocene were thermally decomposed to form many Fe atoms at a lower temperature of 190°C as follows;

Table 1. Result of GC-MS analysis of the waste palm oil, ferrocene and 5.33 wt % ferrocene in palm oil mixture

Samples	Peak No.	Retention time (min)	Compound and chemical structure	Area (%)
Waste cooking palm oil	1	10.3	2,3-Dihydroxypropyl elaidate-C ₂₁ H ₄₀ O ₄	13.7
	2	10.9	11-Tricosene-C ₂₃ H ₄₆	12.8
	3	11.2	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester-C ₂₁ H ₄₀ O ₄	4.5
	4	11.8	2,3-Dihydroxypropyl elaidate-C ₂₁ H ₄₀ O ₄	26.8
Ferrocene	1	6.5	Ferrocene-C ₁₀ H ₁₀ Fe	35.8
	2	10.9	16-Nitrobicyclo[10.4.0]hexadecan-1-ol-13-one-C ₁₆ H ₂₇ NO ₄	24.1
	3	11.2	1,8,15,22-Tetraaza-2,7,16,21-cyclooctacosanetetron-C ₂₄ H ₄₄ N ₄ O ₄	7.8
	4	11.8	2,3-Dihydroxypropyl elaidate-C ₂₁ H ₄₀ O ₄	32.3
Palm oil-ferrocene mixture at 5.33 wt %	1	6.3	Ferrocene-C ₁₀ H ₁₀ Fe	6.5
	2	10.1	9-Octadecenoic acid (Z)-, 2-hydroxyethyl ester-C ₂₀ H ₃₈ O ₃	8.2
	3	10.7	Palmitic anhydride-C ₃₂ H ₆₂ O ₃	9.1
	4	11.0	Oleic acid-C ₁₈ H ₃₄ O ₂	2.9
	5	11.3	9-Octadecenoic acid (Z)-2,3-dihydroxypropyl ester-C ₂₁ H ₄₀ O ₄	3.5
	6	11.5	9-Octadecenal, (Z)-C ₁₈ H ₃₄ O	10.6
	7	11.9	Oleic acid-C ₁₈ H ₃₄ O ₂	7.6

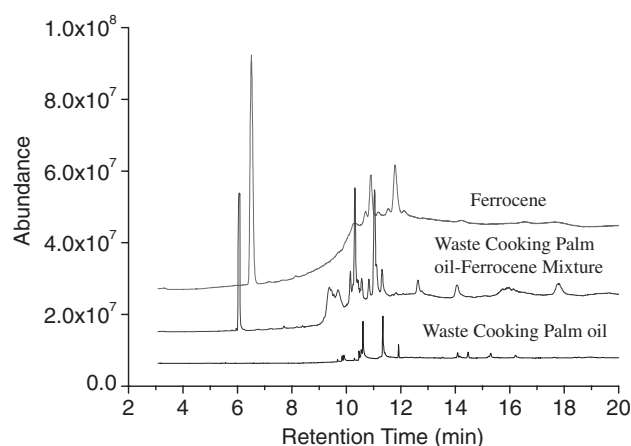
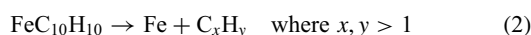


Fig. 6. GC-MS spectra of waste palm oil, ferrocene only and palm oil-ferrocene mixture at 5.33 wt %.



Free Fe atoms then aggregated into nanoparticle or nanoscaled liquid cluster and were initially deposited on the substrate.¹³⁾ This provides the basis for proposing the bottom growth in this study.

Simultaneously, hydrocarbon chain of waste cooking palm oil molecules decomposed into lighter hydrocarbon where the entire decomposition occurred at 450°C. The suggested reaction for waste cooking palm oil cracking is shown in Eq. (3):

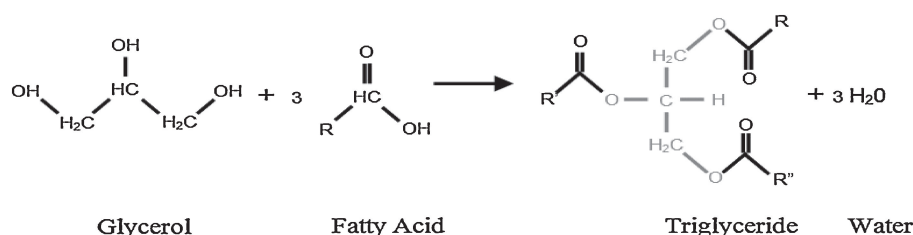
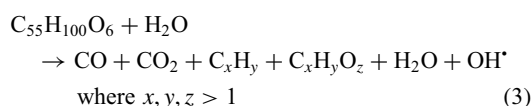


Fig. 7. The possible scheme for the formation of triglyceride and its chemical structure.

Table 2. Fatty acid composition in palm oil

Fatty acid	Number of carbon atoms	Wt (%)
Oleic acid (C ₁₈ H ₃₄ O ₂)	18	42.5
Palmitic acid (C ₁₆ H ₃₂ O ₂)	16	40.0
Linoleic acid (C ₁₈ H ₃₂ O ₂)	16	11.2
Lauric acid (C ₁₂ H ₂₄ O ₂)	12	6.3
Other	—	—

Here, we assumed that the triglyceride was formed when oleic (RCOOH), palmitic (R'COOH) and linoleic (R''COOH) acids were bonded to give the chemical composition; C₅₅H₁₀₀O₆. The possible scheme for the formation of triglyceride and its chemical structure is shown in Fig. 7.¹⁴⁾ The weight % of fatty acid in palm oil is given in Table 2.¹⁵⁾

The C_xH_y, C_xH_yO_z, CO and CO₂ vapors from waste palm oil were then catalytically decomposed on the exposed surface of Fe particles to release hydrogen and oxygen as illustrated in Fig. 5(a). The release of hydrogen and oxygen were expected to form H₂O and OH* radical which both help for better nanotubes graphitization.¹⁶⁾ Meanwhile, the dissolved carbon then diffused through the particles either via surface¹⁷⁻¹⁹⁾ or bulk diffusion.¹⁰⁾ This continued until saturation and once saturation was achieved additional carbon will condensed out of the Fe particle with the filamentous structure as illustrated in Figs. 5(b) and 5(c).

However due to weak Fe substrate interaction some Fe catalyst particles were moved to the tip possibly by capillary force. The yarmulke cap formed on the Fe surface as illustrated in Figs. 5(c) and 5(e) may also cause the catalyst to be lifted to the tip or the middle of the nanotubes. The HRTEM image in Fig. 5(j) shows the Fe catalyst which encased in the middle of the tubes. It can be

concluded that direct mixed between catalyst and precursor show no exact growth pattern where the growth pattern is the combination of bottom and tip growth.

4. Conclusion

We have demonstrated that waste cooking palm oil from domestic frying can be utilized as an efficient, economical and environmentally friendly carbon source for CNT synthesis. Electron microscopy and micro-Raman analysis showed that the CNT obtained were a mixture of MWCNT and SWCNT. The complex composition of the waste oil, mainly due to leaching of fats and other hydrocarbons from the fried objects did not affect the synthesis process. Significantly, this implies that other waste cooking oils from other vegetable or animal sources are also feasible carbon sources for the synthesis of CNT, possibly for scaled-up industrial production of vertically aligned or bulk CNT. EDX and TGA analysis showed that the purity of the VACNT was high at about 85%. Based on GC-MS analysis, thermal decomposition of the hydrocarbon molecules present in the waste palm oil was aided by the presence of ferrocene, which also served as the Fe catalyst source for CNT growth. The measured field electron emission properties from cathodes of VACNT synthesized using waste palm oil yield field enhancement, β , of 2740, turn on electric field of 2.25 V/ μ m, threshold electric field of 3.00 V/ μ m and maximum current densities of a few mA/cm², which are useful for applications in flat panel displays and flat lamps.

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