J Mater Sci: Mater Electron (2016) 27:11599–11605
DOI 10.1007/s10854-016-5291-x

Scaled-up prototype of carbon nanotube production system utilizing waste cooking palm oil precursor and its nanocomposite application as supercapacitor electrodes

A. B. Suriani[1,2] · **J. Norhafizah**[1,2] · **A. Mohamed**[1,3] · **M. H. Mamat**[4] · **M. F. Malek**[4,5] · **M. K. Ahmad**[6]

Received: 20 April 2016 / Accepted: 29 June 2016 / Published online: 4 July 2016

Abstract A simple approach has been introduced for the first time for a scaled-up prototype of a carbon nanotube (CNT) production system by utilizing waste cooking palm oil (WCPO) as carbon feedstock. A modified thermal chemical vapor deposition (TCVD) setup is equipped with a peristaltic sprayer to continuously supply the precursor and catalyst into the system. A total amount of 1000 ml WCPO precursor was sprayed continuously during the experiment with 5.33 wt% ferrocene as catalyst at a flow rate of 30 ml/min. A total of ~433 g CNT were produced with a high carbon conversion rate of 56 %. The produced CNT were then characterized by using electron microscopy, micro-Raman spectroscopy, and thermogravimetric analysis. Growth of dense CNT with a high purity of ~87 % and good crystallinity (I_D/I_G ratio ~0.47) occurred. A CNT/natural rubber-latex (NRL) nanocomposite was also prepared by using latex nanotechnology for supercapacitor application. The nanocomposite exhibited a good capacitance performance with a specific capacitance of 81.82 F/g. This study determined that a high production of CNT using modified TCVD method provided benefits for its utilization as composite material, especially CNT/NRL nanocomposite, for supercapacitor application.

1 Introduction

Carbon nanotubes (CNT) have become the building blocks for the nanoscience and nanotechnology field. They have various potential applications that range from electrical, mechanical, and chemical applications, and are conventionally produced by using fossil fuel-based precursors. To date, one of the companies that successfully produce large-scale CNT is Shenzhen Nano-Technologies Port. Co., Ltd., which is based in China [1]. They produce 40 kg CNT per day using a cycled vertical chemical vapor deposition (CVD) system. Production of ~3 kg/h aligned CNT from ethylene as carbon source via fluidized bed CVD reactor was reported by Fei et al. [2]. However, the use of fossil fuel-based carbon sources is not preferable because these resources will not be renewable in the coming decades. Large-scale production of CNT (1 kg/h) from natural precursor camphor powder using CVD reactor has been successfully achieved by Meijo Nano Carbon Co. Ltd., Japan [3]. However, the use of natural precursors, such as camphor [3, 4], palm [5, 6], olive, corn, sesame, and coconut

---

Electronic supplementary material The online version of this article (doi:10.1007/s10854-016-5291-x) contains supplementary material, which is available to authorized users.

✉ A. B. Suriani
absuriani@yahoo.com

[1] Nanotechnology Research Centre, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

[2] Department of Physics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

[3] Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

[4] NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

[5] NANO-SciTech Centre (NST), Institute of Science (IOS), Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

[6] Microelectronic and Nanotechnology–Shamsuddin Research Centre (MiNT-SRC), Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

oil [7, 8] for large-scale production of CNT is unfavorable because this approach opposes the main usage of the precursors in the food sector and medical industries [9]. This approach may also contribute to environmental damage as the precursors are grown on land converted from rainforests, peatlands, savannas, and grasslands [10]. Therefore, the use of waste material as carbon feedstock for bulk CNT production is a more economical and greener practice.

In this work, we successfully synthesized CNT from waste precursor, namely, waste cooking palm oil (WCPO) [11–13], waste chicken fat (WCF) [14, 15], waste engine oil (WEO) [9], and gutter oil (GO) [16]. The synthesis was carried out in a themal CVD (TCVD) furnace. A wide range of synthesis parameters were optimized [9, 11–17] to synthesize CNT with desired characteristics. The effect of varying synthesis parameters was studied in detail by using electron microscopy, micro-Raman spectroscopy, and thermogravimetric analysis (TGA), among others. The CNT produced from WCPO, WCF, WEO, and GO showed a high purity between 81–89 % with good graphitization of 0.52–0.66 I_D/I_G ratio. The samples also demonstrated good field electron emission (FEE) characteristic [9, 12–16]. The measured FEE properties from the cathodes of the CNT structure achieved a current density range of a few $mAcm^{-2}$ orders at reasonable fields; the attained range is suitable for application in flat panel displays and flat lamps [18, 19]. However the problem of the current TCVD system used for WCPO-based CNT production was low/batch-by-batch CNT production because of non-continuous supply of both catalyst and carbon feedstock. The existing furnace can produce only a maximum of 19.7 g of CNT in a day with a maximum furnace input of 45 ml oil [11–17]. To achieve high-volume CNT production, the growth of CNT needs to be repeated continuously; batch production is discouraged because of difficulty in controlling the quality of CNT.

Here, we report the first scaled-up prototype of a CNT production system by utilizing WCPO as a carbon feedstock. In contrast to existing systems [4–7, 9, 11–17], the modified TCVD system is equipped with a peristaltic sprayer to ensure a continuous supply of oil and catalyst to the furnace; this approach helps to prevent carbon source shortages and poisoning of individual catalysts because the catalyst is replenished constantly during the synthesis. The continuous addition of both oil and catalyst produces a large amount of CNT for use at industrial level with a high carbon conversion rate (56 %). Although the utilization of the sprayer, including medical nebulizer for fossil fuel-based CNT [20], reportedly produces good-quality CNT, the use of a sprayer for highly viscous precursors, such as WCPO, is challenging and requires a special nozzle. Our prototype is the first feeding system that uses a peristaltic sprayer to produce oil-based CNT in bulk, and such CNT are comparable to conventional CNT products, with a high purity, minimal non-tubular carbon structures, and good crystallinity of loose CNT powder. The first scaled-up prototype of a CNT production system by utilizing WCPO as a carbon feedstock is economical and environmentally beneficial. The zero cost of WCPO reduced the price of 1 g of CNT from a range of USD 20–100 [21] to USD 5, and the use of WCPO offers a "green" alternative as a cheap and renewable raw material for industrial volume CNT production. The bulk CNT produced through this work was then used as a nanofiller in natural rubber-latex (NRL) for the fabrication of CNT/NRL nanocomposite, and we demonstrate its potential use as an electrode material for supercapacitor devices.

2 Materials and methods

The initial setup of the WCPO precursor and synthesis of CNT are similar to those given in previous reports [11–17, 22]. A total of 1000 ml of WCPO (mixed with 5.33 wt% ferrocene catalyst) was consumed during the experiment instead of typical precursors with a maximum furnace input of 45 ml [11–17]. The modified TCVD system is attached to (a) the peristaltic sprayer for continuous supply of both catalyst and precursor and (b) the collection container with horizontal rotor at the end of deposition zone for CNT collection, as illustrated in Fig. 1. The peristaltic sprayer consisted of two main components, namely, the peristaltic pump with a precursor flow rate in the range of 1–99 ml/min and a sprayer nozzle with a diameter of 0.50 mm. The sprayer nozzle consisted of four main parts [labeled as (1–4) in Fig. 1]; (1) the inlet tube, which consists of two paths: the path for precursor flow located in the middle of the inlet tube and the Ar gas flow located at the four corners, (2) the outer chamber, which allows the precursor to flow to the inner nozzle and the Ar to flow through four holes directly to the external cap housing (3) the inner nozzle, which acts as an atomizer to break up the precursor into droplets and direct it to the cap housing, and (4) the external cap housing, where the precursor and Ar gas are mixed before the precursor is sprayed into the furnace. The cap housing is attached to the stainless steel tube end, as shown in Fig. 1. The stainless steel tube has an inner and outer diameter of 80 and 100 mm, respectively, and placed in a 1000 mm long electrical furnace. Deposition and precursor furnaces were heated up to 800 and 500 °C, respectively. The precursor was then sprayed into the furnace at a rate of 30 ml/min with a 15 min time interval of sprayers. The synthesis process, including the cooling process, lasted for 10 h. The samples were then annealed at 500 °C for 4 h to remove the

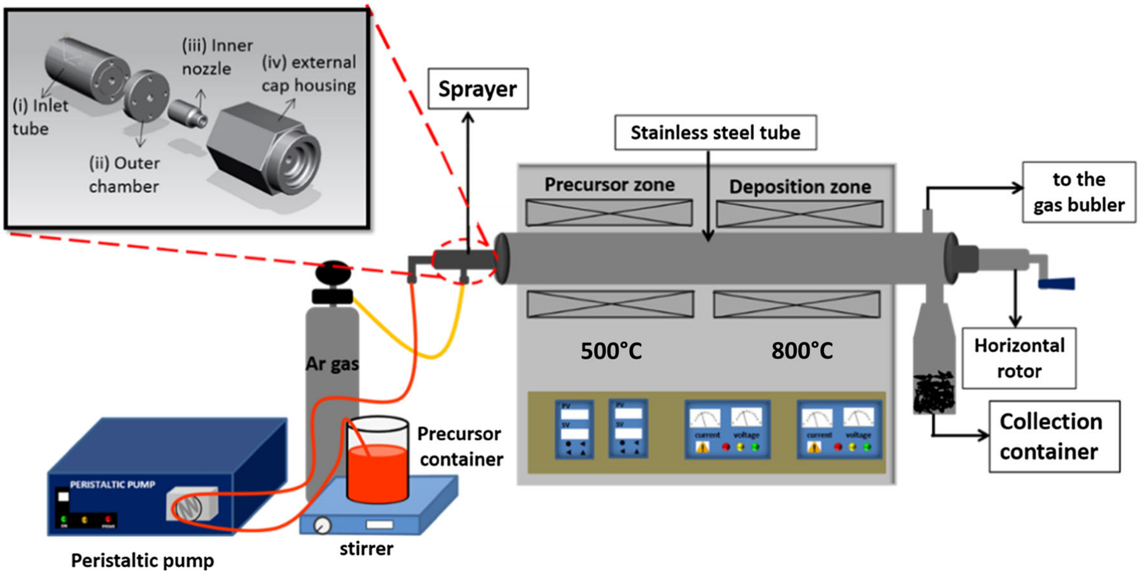

Fig. 1 Schematic diagram of scaled-up CNT production from WCPO using modified TCVD system and sprayer nozzle parts

impurities [23] and characterized using FESEM, HRTEM, micro-Raman, and TGA (see Supplementary Materials). The collected CNT were also used as filler in NRL for supercapacitor application. The dispersion process of CNT/NRL nanocomposite was similar to that in previous reports [24, 25]. The CNT/NRL nanocomposite performance was measured by using four-point probe and cyclic voltammetry (CV) measurement (see Supplementary Materials).

3 Results and discussion

Figure 2b, c present the FESEM image of the synthesized CNT. Dense and uniform CNT were produced with a diameter that ranges from 19.5 to 36.2 nm (Fig. 2c). A total of 433.3 g CNT were collected (Fig. 2a) from 1000 ml (945 g) of precursor, which is much higher than that in the previous report [11–17], which used conventional TCVD method without continuous supply of precursor. The carbon (from WCPO and ferrocene mixture)-to-CNT conversion rate was 56 %. The calculated percentage of carbon conversion was based on [26], and the percentage was comparable to the carbon conversion of camphor oil (61 %) [3], but somewhat higher than the carbon conversion of toluene (31 %), xylene (28 %), and benzene (20 %) [26]. This finding proves that the WCPO is a potential green alternative carbon precursor to replace the fossil fuel precursor for bulk CNT production. The details of the calculation are presented in the Supplementary Materials. HRTEM analysis (Fig. 2d) further revealed that the produced CNT were multi-walled CNT (MWCNT) with an inner and outer diameter of 10.1 and 30.8 nm, respectively, and consisted of approximately 32 layers. The distance between layers was 0.338 nm, which corresponded to the distance of (002) planes of graphite [27]. Micro-Raman and TGA analyses also revealed a good quality of CNT produced by a low I_D/I_G ratio of 0.47 and high purity of 87.16 % (see Supplementary Materials).

The CNT/NRL nanocomposite (Fig. 3a) was also fabricated as electrodes for supercapacitor application. Homogenous distribution of CNT was observed on the surface of NRL (Fig. 3b). Overall CNT (indicated by →) were well dispersed and homogenously distributed on the NRL matrix, as supported by TEM observation (Fig. 3c). Good dispersion mixing of CNT into the NRL solution was assisted by the custom-made surfactant of sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate, which has been reported previously [24]. However, the CNT used in our previous work, which were fossil fuel-based CNT, were obtained commercially. Figure 3d shows the CV curve of nanocomposite electrodes, which store energy during the redox reaction process (charging and discharging). The rectangular shape indicates a good capacitive behavior of reaction. The calculated specific capacitance of CNT/NRL nanocomposite was 81.82 F/g. These results are consistent with I–V analysis (Fig. 3e), which presented a good conductivity value of 2.55×10^{-3} S/cm.

Details of the growth mechanism of CNT from oil-based CNT were discussed thoroughly in our previous study [5, 9, 11, 14, 16]. However, in the current study, the precursors and catalysts were supplied into both precursor and deposition furnaces continuously by using a peristaltic sprayer. Initially after spraying, the precursors and

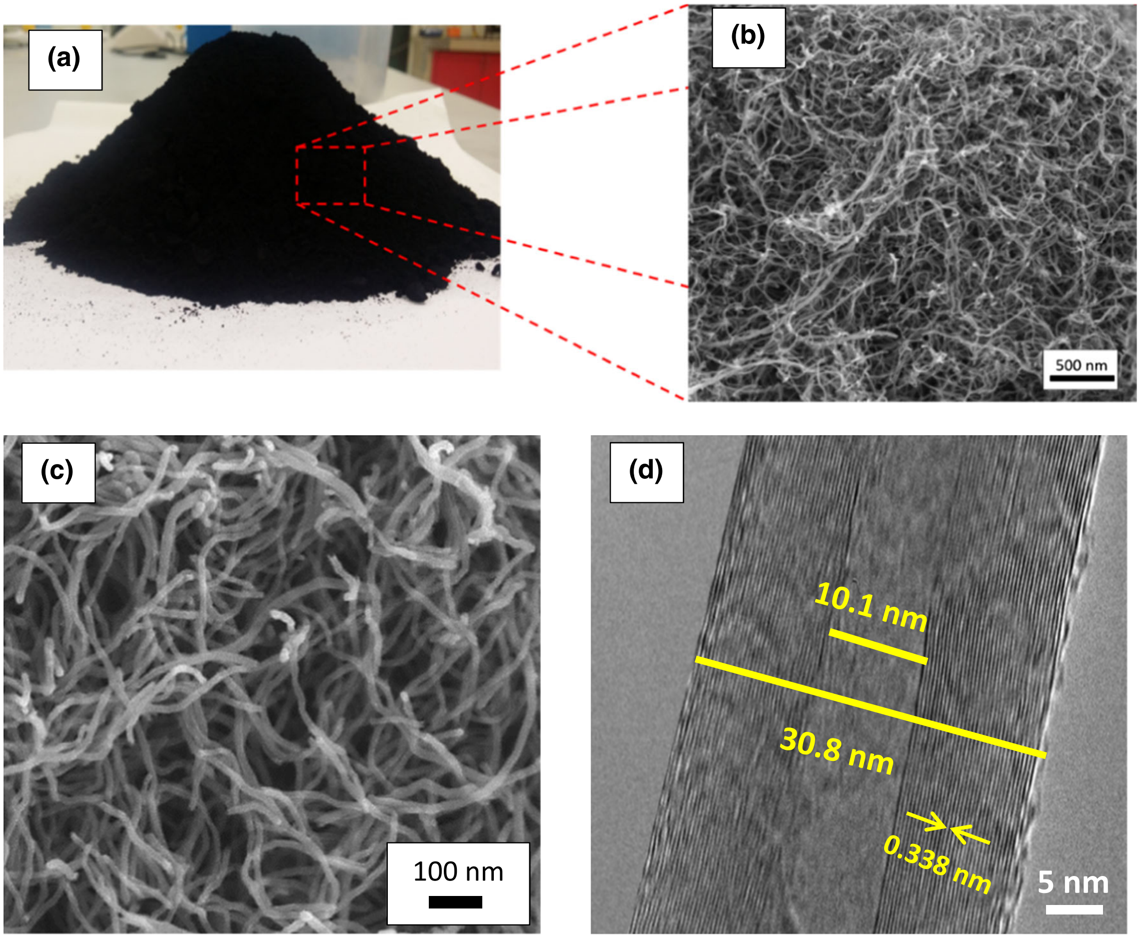

Fig. 2 **a** Total of 433 g collected CNT **b**–**c** FESEM, **d** HRTEM images of CNT production

catalysts were broken up into smaller molecules, namely, Fe particles, hydrocarbons and other vapour elements such ions and radicals. As the Fe particles and hydrocarbon molecules flew through the furnace at 800 °C, both compounds were further broken up to form smaller Fe nanoparticles and hydrocarbon molecules then catalytically decomposed on exposed Fe surfaces, as illustrated in Fig. 4. We suggest that the entire process, including the nucleation and the growth of carbon filament, occurs mostly in the vapor phase, as evidenced by the pile-up of CNT within the effective heating area. CNT growths were also observed along the furnace tube, thereby suggesting that the Fe particles, which served as the basis for CNT growth, also deposited on the deposition wall (Fig. 4a). Then, the precipitation of graphite sheet started via the bottom growth model, as shown in Fig. 4b. Continuous supply of carbon source and catalyst was necessary to maintain the precipitation process, thereby guaranteeing the continuous growth of the CNT. This continuous supply helped to prevent carbon source shortage and catalyst poisoning because the catalyst was replenished continuously during the synthesis process. The HRTEM images shown in Fig. 4b suggest that the upcoming Fe particles filled the open tube end while the carbon elements continued to attach to the catalyst for continuous growth, thereby resulting in more CNT production compared with the conventional growth using a similar carbon source. Growth of bamboo-like CNT structure was also observed in the HRTEM image in Fig. 4c, d, thereby suggesting that the yarmulke nucleation cap also took place during the initial CNT growth. The interval between the spraying process ensured a balance of the decomposition and diffusion rate of hydrocarbon molecules on the catalyst exposed surface with the coming precursors to ensure high-quality production of CNT.

4 Conclusion

A scaled-up prototype of CNT production from WCPO was successfully achieved by using a modified TCVD system. This prototype guarantees large-scale production of CNT

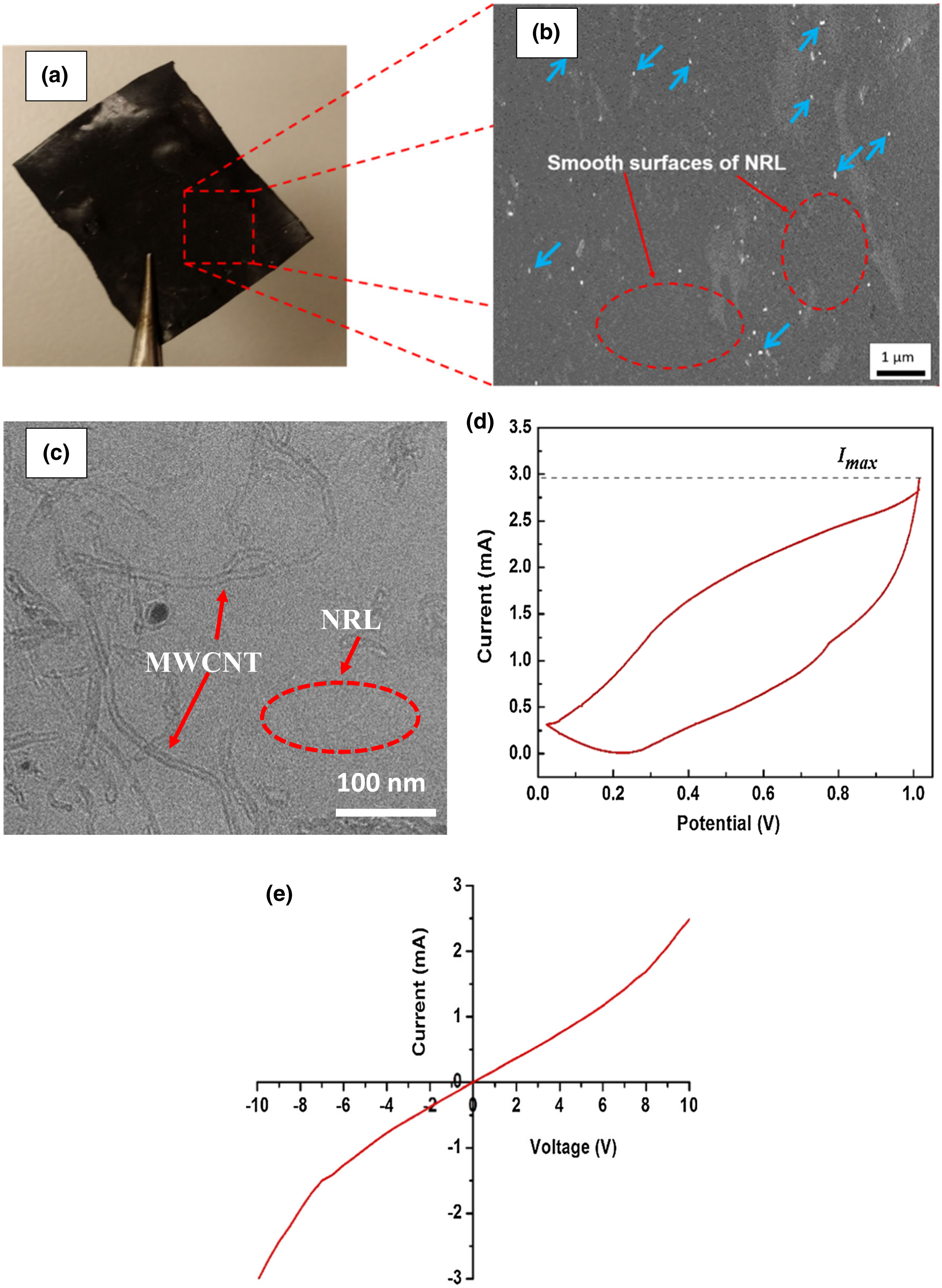

Fig. 3 **a** Sheet of CNT/NRL nanocomposite as electrode **b** FESEM and **c** TEM images **d** CV and **e** I–V characteristics of CNT/NRL nanocomposites

for industrial use. Unlike the existing system, the proposed system incorporates a peristaltic sprayer to ensure a continuous supply of precursor and catalyst. A total of ~433 g CNT were produced with a high carbon conversion rate of 56 %. The quality of the CNT was comparable to that of CNT synthesized by using conventional carbon feedstock.

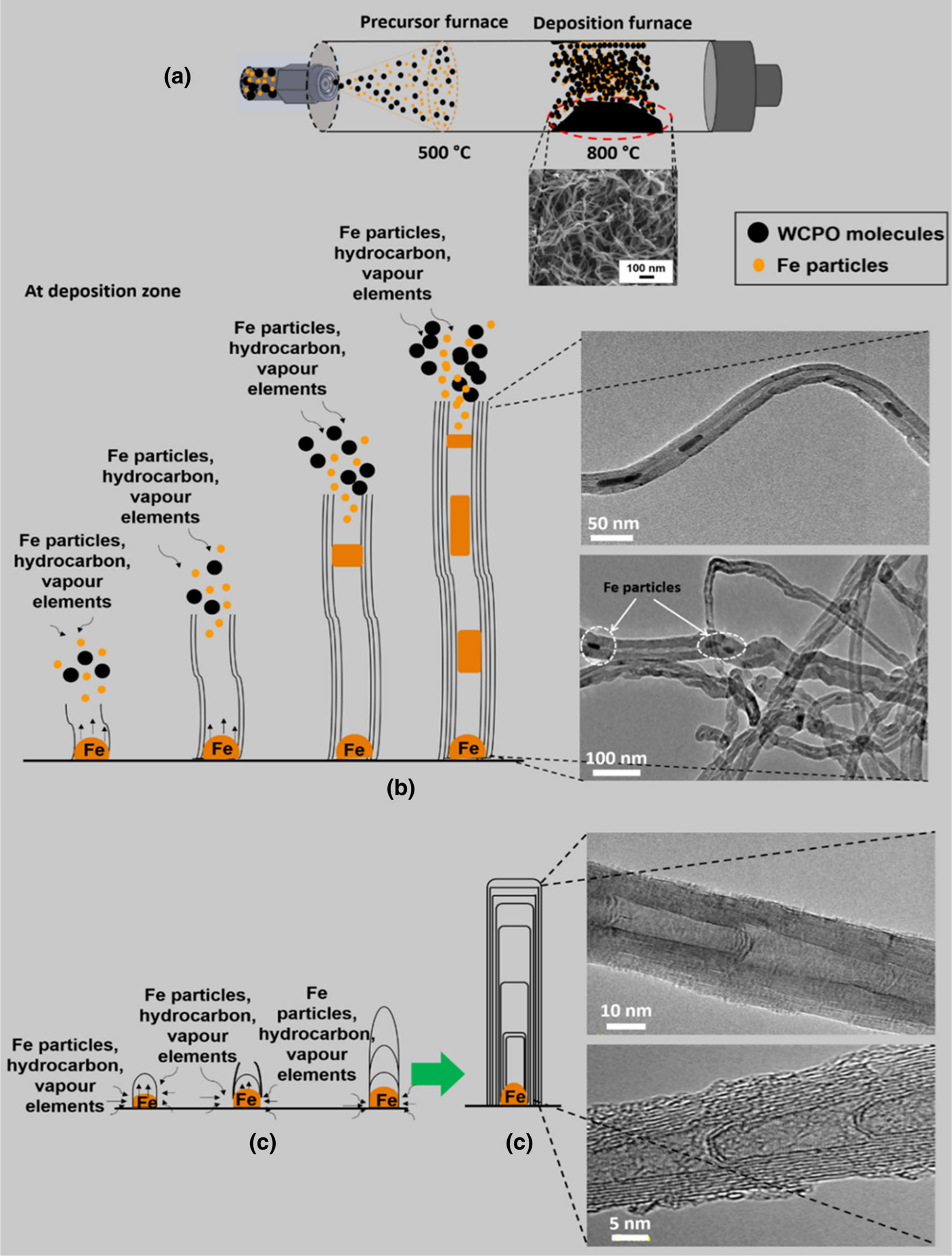

Fig. 4 Possible growth mechanism of CNT production *a* decomposition of precursor into the furnace *b* growth of CNT *c* yarmulke nucleation and *d* bamboo-like CNT structure

A high production of CNT from WCPO is beneficial for both nanotechnology and the environmental. Waste management of WCPO is a threat to the environment. Thus, utilizing this oil as a carbon source for CNT production prevents the oil from being an environmental threat and eliminates dependence on fossil fuel-based carbon sources.

Generally, the prototype development can be concluded to be able to sustain mass production of oil based-CNT in the future. In nanocomposite material, CNT/NRL produced a good capacitance performance ($C_{sp} = 81.82$ F/g), thereby demonstrating its potential as electrode material for supercapacitor application.

Acknowledgments This work was financially supported by the Kurita Water and Environment Foundation Grant, (Grant code: 2015-0151-102-11), the National Nanotechnology Directorate Division Research Grant (Grant code: 2014-0015-102-03), the Fundamental Research Grant Scheme (Grant code: 2015-0154-102-02), the Prototype Development Research Grant Scheme (Grant code: 2013-0097-102-32), and the MARA Innovation and Research Grant Scheme (Grant code: 2016-0006-101-20).

References

1. P. Eklund, P. Ajayan, R. Blackmon, A.J. Hart, J. Kong, et al., World Technology Evaluation Center Inc., USA (2007)
2. Q. Zhang, M.Q. Zhao, J.Q. Huang, J.Q. Nie, W. Fei, Carbon **48**, 1196 (2010)
3. M. Kumar, Y. Ando, J. Nanosci. Nanotechnol. **10**, 3739 (2010)
4. N.A. Asli, M.S. Shamsudin, A.B. Suriani, M. Rusop, A. Saifollah, Int. J. Ind. Chem. **4**, 1 (2013)
5. A.B. Suriani, A.A. Azira, S.F. Nik, R. Md Nor, M. Rusop, Mater. Lett. **63**, 2704 (2009)
6. S.A.M. Zobir, A.B. Suriani, S. Abdullah, Z. Zainal, S.H. Sarijo, M. Rusop, J. Nanomater. **2012**, 11 (2012)
7. M.S. Azmina, A.B. Suriani, M. Salina, A.A. Azira, A.R. Dalila et al., Nano Hybrids **2**, 43 (2012)
8. S. Paul, S.K. Samdarshi, New Carbon Mater. **26**, 85 (2011)
9. A.B. Suriani, S. Alfarisa, A. Mohamed, I.M. Isa, A. Kamari et al., Mater. Lett. **139**, 220 (2015)
10. J. Fargione, J. Hill, D. Tilman, S. Polasky, P. Howthorne, Science **319**, 1235 (2008)
11. A.B. Suriani, R. Md Nor, M. Rusop, J. Ceram. Soc. Jpn. **118**, 963 (2010)
12. A.B. Suriani, R.N. Safitri, A. Mohamed, S. Alfarisa, I.M. Isa et al., Mater. Lett. **149**, 66 (2015)
13. A.B. Suriani, R.N. Safitri, A. Mohamed, S. Alfarisa, M.F. Malek et al., J. Alloys Cmpd. **656**, 368 (2016)
14. A.B. Suriani, A.R. Dalila, A. Mohamed, M.H. Mamat, M. Salina et al., Mater. Lett. **101**, 61 (2013)
15. A.B. Suriani, A.R. Dalila, A. Mohamed, M.H. Mamat, M.F. Malek et al., Mater. Design **90**, 185 (2016)
16. A.B. Suriani, A.R. Dalila, A. Mohamed, T. Soga, M. Tanemura, Mater. Chem. Phys. **165**, 1 (2015)
17. M.S. Azmina, A.B. Suriani, A.N. Falina, M. Salina, M. Rusop, Adv. Mater. Res. **364**, 359 (2012)
18. H. Hu, D. Zhang, Y. Liu, W. Yu, T. Guo, Vacuum **115**, 70 (2015)
19. S.S. Madani, K. Zare, M. Ghoranneviss, A.S. Elahi, J. Alloys Compd. **648**, 1104 (2015)
20. Z. Yang, X. Chen, H. Nie, K. Zhang, W. Li et al., Nanotechnology **19**, 1 (2008)
21. J. Lu, L.T. Drzal, R.M. Worden, I. Lee, Chem. Mater. **19**, 6240 (2007)
22. M.S. Shamsudin, M.F. Achoi, M.N. Asiah, L.N. Ismail, A.B. Suriani et al., J. Nanomater. **2012**, 972126 (2012)
23. M.S. Shamsudin, A.B. Suriani, S. Abdullah, S.Y.S. Yahya, M. Rusop, J. Spectrosc. **2013**, 167357 (2013)
24. A. Mohamed, K.A. Argo, A.B. Suriani, A.A. Aziz, M. Sagisaka et al., Colloid Polym. Sci. **292**, 3013 (2014)
25. A. Mohamed, A.K. Anas, A.B. Suriani, T. Ardyani, W.M.W. Zin et al., J. Colloid Inter. Sci. **455**, 178 (2015)
26. N. Das, A. Dalai, J.S.S. Mohammadzadeh, J. Adjaye, Carbon **44**, 2236 (2006)
27. R. Kumar, R.S. Tiwari, O. Srivastava, Nanoscale Res. Lett. **6**, 92 (2011)