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Quasi-aligned carbon nanotubes synthesised from waste engine oil

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ABSTRACT

Quasi-aligned carbon nanotubes (CNTs) were successfully synthesised for the first time using waste engine oil (WEO) as the carbon source via thermal chemical vapour deposition (TCVD). The high carbon content of WEO was believed to promote the growth of the quasi-aligned CNTs. The synthesis process was performed at precursor and synthesis temperatures of 500 and 750 °C, respectively, with a ferrocene catalyst concentration of 17.99 wt%. Typical characterisation methods were employed to examine the CNTs: electron microscopy, energy dispersive X-Ray, X-ray diffraction and micro-Raman spectroscopy. The ability of CNT samples to emit electrons was also investigated by field electron emission (FEE) analysis. Electron microscopy and micro-Raman analysis revealed a dense mixture of quasi-aligned single- and multi-walled CNTs with a moderate I_D/I_G ratio of 0.90. The overall diameters of the CNTs ranged from 18.0 to 29.8 nm, with the diameters of the single-walled CNTs estimated to be between 0.6 and 1.1 nm. The FEE results showed that the quasi-aligned CNTs synthesised from WEO exhibited reasonable turn-on and threshold fields of 4.1 and 7.2 V μm^{-1}, which corresponded to current densities of 0.1 and 1.0 μA cm^{-2}, respectively. This study highlights WEO as a new, cheap, abundant and easily available carbon source for quasi-aligned CNTs production with a potential application in electron emission devices.

1. Introduction

Waste engine oil (WEO) is a toxic and harmful waste material. Due to its application for engine combustion and lubrication, WEO contains high concentrations of aromatic compounds, additives and contaminants. In fact, one quart of WEO can pollute 250,000 gallons of water and 40,730 square feet of soil [1]. Widespread use and the fast growth of the automotive industry have made WEO one of the most abundant waste materials available. Conventionally, WEO is recycled as lube oil and processed into diesel fuel. Recently, Datta et al. [2] reported the use of this oil for the production of carbon microspheres using a dry autoclaving method.

The use of WEO to produce carbon nanotubes (CNTs) is promising because this green nanotechnological innovation may not only benefit the field of nanoelectronics but also represent an environmentally conscious approach for the following reasons: (1) WEO serves as a new carbon source for CNTs manufacturing. The oil is an alternative choice that is inexpensive, environmentally friendly and readily available in large quantities. It is believed that a previously reported approach that uses oils from carbon sources such as palm [3], eucalyptus [4], corn, sesame and olive [5] for the production of CNTs may possibly hamper the supply of such natural oils for the industries in which they are normally used, for example, the food and health industry. Therefore, the use of waste material represents a more economical and greener practice. (2) In addition, the core structure of WEO is composed of a large number of carbon atoms, approximately 18–34 atoms [6], compared to natural oils. The results of a CHNS analysis of WEO and natural oils are presented in Table S1 (see Supplementary material). The table shows that WEO has the highest carbon content among the oils, thus making a strong case for WEO as a suitable precursor for mass CNTs production. (3) The methodology presented herein would also directly help reduce WEO pollution in our ecosystem, which would otherwise be very severe to the environment even compared to a petroleum spill. Unlike petroleum spills, WEO discharge is intentional, relentless

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and increasing in frequency every year. Therefore, recycling WEO as a starting material for CNTs production provides a way to help reduce water pollution. (4) This approach could also diversify the use of WEO by producing a material with excellent properties to be applied in nanoelectronics applications.

Accordingly, in this work, we introduced WEO as a new carbon source to synthesise quasi-aligned CNTs by thermal chemical vapour deposition (TCVD). To the best of our knowledge, no report on producing quasi-aligned CNTs from a WEO precursor has been published. The method described herein represents a waste-to-wealth concept that transforms waste into a valuable by-product that offers environmental and economic benefits.

2. Materials and method

WEO was collected from an automobile servicing workshop. To remove dirt and unwanted particles, the oil was initially filtered and centrifuged for 2 h at 5000 rpm before being used. Synthesis conditions similar to those reported in previous studies were

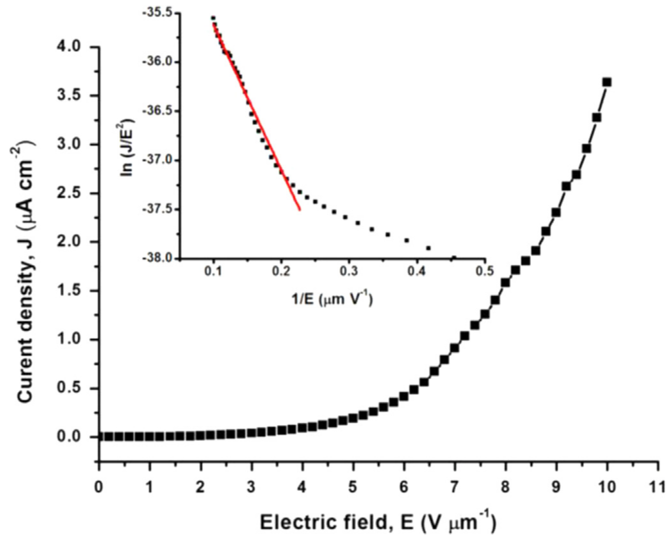

Fig. 2. *J–E* curve and F–N plot (inset figure) of CNTs grown from WEO precursor.

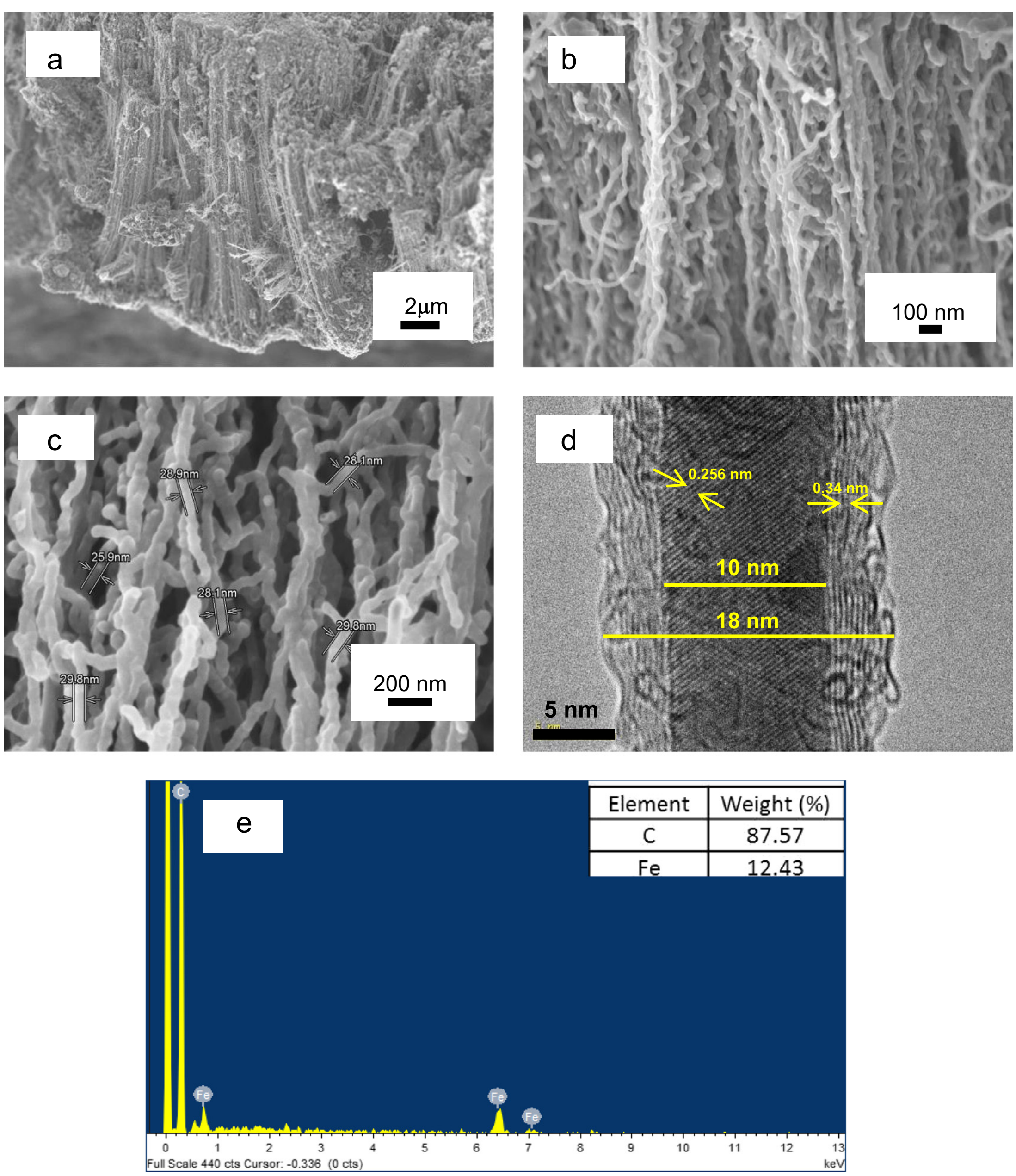

Fig. 1. (a)–(c) FESEM images of CNTs from WEO, (d) HRTEM image of individual nanotube and (e) EDX analysis of CNTs.

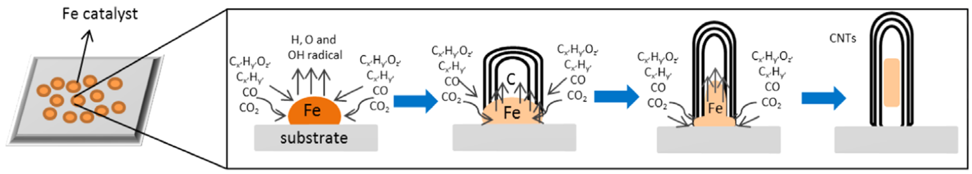

Fig. 3. Growth mechanism of CNTs synthesised from WEO.

applied [3,7,8]. 4 ml of precursor was vaporised at 500 °C and synthesis was carried out at 750 °C using 17.99 wt% ferrocene catalyst. Collected samples were characterised by FESEM (Hitachi SU8020) equipped with EDX spectroscopy, HRTEM (JEOL JEM 2100), XRD (SHIMADZU XRD-6000) and micro-Raman spectroscopy (Horiba Jobin Yvon-DU420A-OE-325). The field emission properties of the samples were measured using field electron emission (FEE) equipment.

3. Results and discussion

FESEM images of quasi-aligned CNTs synthesised from the WEO precursor are shown in Fig. 1(a)–(c). The high density quasi-aligned CNTs produced showed relatively uniform diameters in the range of 18.0–29.8 nm and lengths ranging from 11.8 to 17.1 μm. The average growth rate of the quasi-aligned CNTs was estimated to be 0.48 μm min^{-1}. The HRTEM image shown in Fig. 1 (d) reveals that the CNTs produced were multi-walled CNTs (MWCNTs) consisting of approximately 8 layers with inner and outer diameters of 10.0 and 18.0 nm, respectively. The outermost tube was covered with an amorphous carbon structure, which widened the diameter of the CNTs. The distance between the layers was measured to be 0.34 nm, in agreement with the distance between adjoining graphene sheets, which is reported to be 0.3354 nm [9]. It was also clearly observed that iron (Fe) was encapsulated in and filled the inner tube of the CNTs with an atomic spacing of 0.26 nm, in agreement with the Fe–Fe atom distance reported by Dong et al. [10]. The results of EDX analysis shown in Fig. 1(e) confirmed the presence of elemental C and Fe, with weight percentage of 87.57% and 12.43%, respectively. This result was reinforced by the results of XRD analysis (details of the results are provided in the Supplementary material). Further analysis using micro-Raman spectroscopy revealed the existence of single-walled CNTs (SWCNTs) with estimated diameters between 0.6 and 1.1 nm and moderate I_D/I_G ratio of 0.90 (see Supplementary material). This finding proves that the complex chemical composition structure of WEO with contaminants and additives did not affect the structure or properties, including the graphitisation degree of the quasi-aligned CNTs produced.

The basic theory underlying FEE calculations is based on the Fowler–Nordheim (F–N) model [11]. Fig. 2 shows the current density (J) vs electric field (E) curve of a sample. The turn-on and threshold fields were observed to be 4.1 and 7.2 V μm^{-1}, which corresponded to current densities of 0.1 and 1.0 μA cm^{-2}, respectively. The field emission enhancement factor (β) was calculated to be 5161 from the slope of the F–N plot presented in the inset of Fig. 2. These results indicate that quasi-aligned CNTs produced from WEO have the potential to be used as emitters in electron emission devices.

Fig. 3 shows a schematic of the growth mechanism of quasi-aligned CNTs produced from WEO, which is similar to the mechanisms we have previously described [7,8]. In this study, however, the carbon source used was new. Heating the precursor furnace to 500 °C causes the WEO to dissociate into vapour composed of lighter hydrocarbons and other vapour elements as indicated in Eq. (1). The WEO structure of $C_xH_yO_z$ is based on the results of a previous analysis [12]

$$C_xH_yO_{z(l)} \rightarrow C_{x'}H_{y'}O_{z'(g)} + C_{x'}H_{y'(g)} + CO_{(g)} + CO_{2(g)} + OH^{\bullet}_{(g)} \quad (1)$$

The CNTs grow on Fe nanoparticles that start to vaporise at 185 °C and decompose above 400 °C [13] into Fe particles and hydrocarbon vapour. It is believed that the weak adhesion of Fe particles to the substrate causes them to easily move upward.

The presence of OH$^{\bullet}$ radical gas indicated in Eq. (1) is believed to be useful in enhancing the graphitisation of CNTs, as previously described [7,8]. In this study, we suggested possible reactions through which OH$^{\bullet}$ radicals are formed, as shown in Eqs. (2–4). These reactions are believed to be (i) the termination of C–H bonding in WEO by oxygen (Eq. (2)), (ii) the combination of oxygen with free active H radicals (Eq. (3)) and (iii) C–O bond breaking in WEO by H radicals (Eq. (4))

$$O^{\bullet} + CH \rightarrow C + OH^{\bullet} \quad (2)$$

$$O^{\bullet} + H^{\bullet} \rightarrow OH^{\bullet} \quad (3)$$

$$CO + H^{\bullet} \rightarrow C + OH^{\bullet} \quad (4)$$

The presence of OH$^{\bullet}$ radicals resulted in the stable sp^2 structure of the quasi-aligned CNTs at the growing edge. Therefore, the presence of oxygen in WEO, allowing for the formation of OH radicals, was crucial to enhancing the crystallinity of the quasi-aligned CNTs.

4. Conclusion

We introduced the use of WEO as an efficient, economical and environmentally friendly carbon source for the production of quasi-aligned CNTs. WEO is a new and alternative carbon precursor with a higher carbon content than that of other vegetable-oil sources. Analysis shows that a mixture of SWCNTs and MWCNTs was produced from WEO. The CNTs demonstrated moderate crystallinity (I_D/I_G ratio of 0.90) and quality comparable to that of CNTs produced from conventional sources. The effect of the complex chemical composition of WEO, which features contaminants and additives, on CNTs production was proved to be negligible. FEE measurements indicated a reasonable turn-on field of 4.1 V μm^{-1} at 1.0 μA cm^{-2} with a high β value of 5161. The results of this study suggest that quasi-aligned CNTs synthesised from WEO hold promise for application in field emission devices.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.10.046.

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