

MULTI-WALLED CARBON NANOTUBE SYNTHESIS BY MICROWAVE-INITIATED CATALYTIC OF PLASTIC WASTE POLYETHYLENE PRODUCTS

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Abstract

The multi-walled carbon nanotube (MWCNT) was synthesized by microwave radiation composed of 3 steps. First, the high-density polyethylene (HDPE) plastic was washed with water. Second, the plastic was mixed with a catalyst ($FeAlO_x$). Finally, the mixer was input into a microwave to generate MWCNT under 1,200 W. It was found that MWCNT outer and inner diameter of ~8-29 nm and ~4-12 nm by TEM, saving time 20% and confirmed successfully crystalline structure, and microstructure by SEM, and XAS. The XRD patterns of the sample corresponded with the MWCNT standard at 44° .

Keywords: $FeAlO_x$ catalyst; plastic, multiwall carbon nanotube; microwave

Introduction

Plastics are growing faster than any other man-made materials and the scourge of our time. Although there is a campaign to refrain from using plastic of single-use plastics in 2022, up to 250,000 tons of imported plastic waste from other nations continues to flow into the country annually through the international plastic waste trade. Currently, the majority of 4.9 billion tons plastic which accumulates in landfills or in the natural environment will increase to ~12 billion tons by 2050 and then it became to plastic pollution (Geyer *et al.*, 2017; Rujivanarom, 2021). Plastics includes materials composed of various elements such as

carbon, hydrogen, oxygen, nitrogen, chlorine, and sulfur. Plastics typically have high molecular weight, meaning each molecule can have thousands of atoms bound together.

Recently, researchers have been working on extracting carbon and hydrogen that the main product of plastics to synthesize rich material carbon nanotube (CNT). There have variety method for synthesis CNT such as arc discharge with simple method but the products need to be purified later, non-uniform, possible high yield of nanotubes and careful control (Mohammad *et al.*, 2013), laser ablation method with relatively low metallic

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impurities, relatively high yield but not be regularly straight and have some degree of branching (Das *et al.*, 2016), chemical vapor deposition (CVD) that the typical method usually used with the purity and yield is very high, alignment is regular, having low cost, being suitable for large scale fabrication but defect and bend (Kazemizadeh *et al.*, 2017; Tripathi *et al.*, 2017), pyrolysis with high temperature and gasification temperature around 600°C (Wu *et al.*, 2013; Harussani *et al.*, 2022).

In this study, synthesis MWCNT from plastic waste by microwave-driven destruction method is presented. This is a fast synthesis of MWCNT by microwave irradiation, washed plastic HDPE, mixed with catalyst ($FeAlO_x$), and then use microwave generate MWCNT to very short synthesis time, separation and purification are also very simple and time saving (Jie *et al.*, 2020). Moreover, the trace evidence of $FeAlO_x$ catalysts used in this MWCNT synthesis is also studied by Fe K-edge X-ray absorption spectroscopy (XAS).

Materials and Methods

Preparation of $FeAlO_x$ Catalyst

The $FeAlO_x$ catalyst was prepared by using analytical grade Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9(H_2O)$, Carlo, Erba, France), Aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9(H_2O)$, Panreac, Spain), Citric acid ($C_6H_8O_7$, Loba, India) and a minimum amount of distilled water were mixed in a desirable molar ratio produce a viscous orange gel with magnetic stirrer at 90°C for 2 h. The gel was burnt and calcined by kilns and furnaces in air at 500°C for 3 h in self propagation combustion manner and formed loose powder.

Experiment Set-Up and Microwave Reactor

The microwave reactor set-up is consisting of microwave generator, tube, rubber stopper for bringing the combustion gas to cylinder for measure the volume of gas, metal cabinet to prevent microwave transmission, heating and temperature as shown in Figure 1.

Microwave electromagnetic spectrum has frequencies ranging from 300 MHz to 300 GHz.

Microwave heating represent the transfer of electromagnetic energy to thermal energy (Fernández *et al.*, 2011). The mechanistic model's catalytic methane decomposition over Fe-Al catalyst and claimed the important role of Fe_3C transformed to hydrogen and MWCNT (Enakonda *et al.*, 2016; Lopez *et al.*, 2017; Zhou *et al.*, 2017; Jie *et al.*, 2020).

Experimental Procedure

The plastic waste of HDPE was washed and pretreated by crushing into small pieces using a blender. These pieces of plastic were then mixed with $FeAlO_x$ catalyst in a typical weight ratio of 1:1 used 1.5 g of plastic for test. The sample ($HDPE+FeAlO_x$) was place in a quartz tube with inner diameter 1.9 cm, outer diameter 2.2 cm. The filled tube was placed in refractory brick and then was placed axially in the center of R-390I microwave cavity to minimize depolarization effects under microwave radiation. The clean HDPE was irradiated microwave under 1,200 W for 20, 30, 40, and 45 min get the samples.

Mechanism of synthesis CNTs from Plastic Waste

Mechanism of synthesis CNTs from plastic waste by microwave-driven destruction method are shown in Figure 2. Figure 2(a) Mixing plastic with $FeAlO_x$ catalyst which the catalyst particles attached to the surface of the plastic and through microwave radiation. Figure 2(b) there are two different roles in the process. On the one hand, the transfer of incoming microwave energy to initiate the physical heating process of the catalyst particles, on the other, the reaction on the surface of the plastic particles. Figure 2(c, e) the area where the catalytic interface is formed between the catalyst particles and the plastic for hydrocarbon intermediate degradation. Subsequently, the intermediates were radiated by microwave radiation and then diffused to Fe_3C . Figure 2(d, f) Mechanism of methane decomposition catalysts on Fe-Al catalysts and converted to hydrogen and CNTs (Enakonda *et al.*, 2016; Lopez *et al.*, 2017; Jie *et al.*, 2020).

Destruction Method. (a) plastic HDPE mix with $FeAlO_x$ on microwave (b) Microwave radiation expose to HDPE mix with $FeAlO_x$ (c, e)

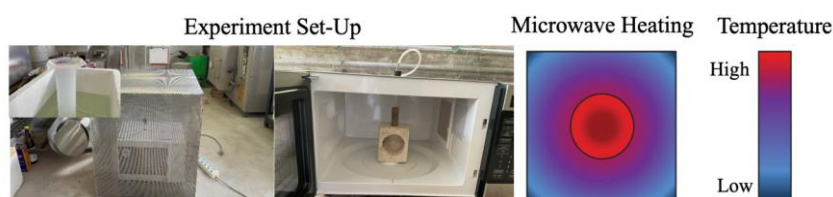


Figure 1. Experiment set-up and microwave reactor, heating, and temperature

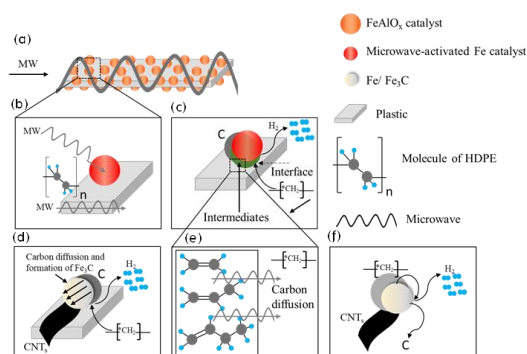


Figure 2. Mechanism of synthesis CNTs from plastic waste by microwave-driven

Table 1. Mass fraction of MWCNT standard and the sample (HDPE+FeAlO_x) in 20, 30, 40, and 45 min

Time	Mass fraction %			
	C	O	Al	Fe
20	69.88	14.67	10.31	5.14
30	76.47	6.69	4.31	12.22
40	88.54	3.89	2.26	4.80
45	62.74	17.39	13.62	5.87
MWCNT standard	94.25	3.35	0.70	0.84

collisions in interface and intermediates (d) Diffusion and formation of Fe₃C and carbon (f) Growth of CNTs (Enakonda *et al.*, 2016; Lopez *et al.*, 2017; Jie *et al.*, 2020).

Characterization and Analysis of Samples

The crystal structure of samples was measured by power X-ray Diffraction (XRD). The morphology and the element analysis of samples was observed by Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDX). The characteristically MWCNT of samples and diameter were analyzed by Transmission Electron Microscope (TEM). Additionally, The Fe K-edge at the BL5.2 was measured by X-ray absorption Spectroscopy (XAS, SUT-Nanotec-SLPI XAS Beamline, Thailand) at Synchrotron Light Research Institute (Public Organization), Thailand.

Results and Discussion

The TEM images of images (a) MWCNT standard (b-e) the sample (HDPE+ FeAlO_x) in 20, 30, 40, and 45 min as shown in Figure 3. It showed outer and inner diameter of ~8-29 nm and ~4-12 nm, respectively.

The SEM and EDX images of MWCNT standard and the sample (HDPE + FeAlO_x) in 20, 30, 40, and 45 min are shown in Figure 4. It appears that

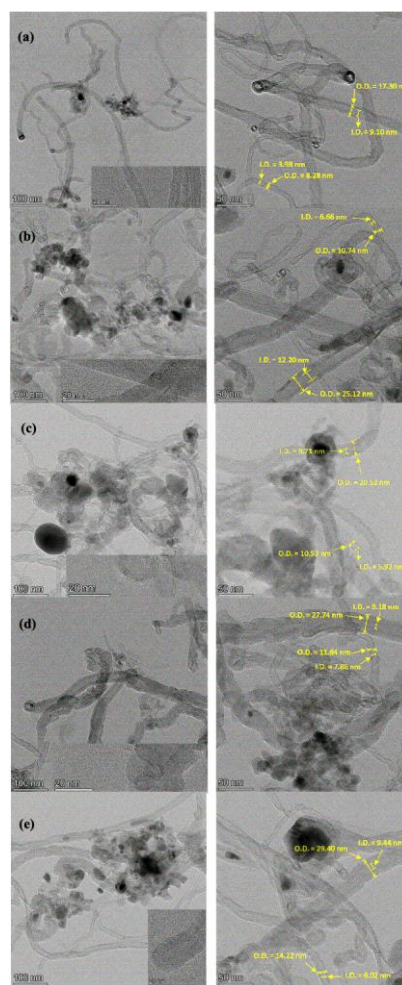


Figure 3. TEM images (a) MWCNT standard (b-e) the sample (HDPE+FeAlO_x) in 20, 30, 40, and 45 min respectively

many particles and shows EDX spectra of the metal particles presented, suggesting that Al, Fe, and O which part of with catalyst (FeAlO_x) and in Table 1 is shown mass fraction of MWCNT standard and the sample.

The XRD pattern of FeAlO_x catalyst is shown in Figure 5(a), which scanning range in 2θ of 20° to 80° which main peak at 36.0° (311) correspond with FeAl₂O₄ ICDD data 30.5° (220), 35.8° (311), 43.6° (400), 58.0° (511) and 63.7° (440) in cubic structure (Enhessari, 2017). The XRD patterns of the MWCNTs standard, irradiated microwave for 20, 30, 40, and 45 min respectively as shown in Figure 5(b). The main peak of XRD patterns the sample (HDPE+FeAlO_x) in 20, 30, 40, and 45 min were corresponded with MWCNT standard at the angle about 2θ = 26°, 44°, 64°, and 77.5° together with Saravanan *et al.* (2014) and Zahra *et al.* (2017) at the angle about 26.05 (002), and 43.53 (100).

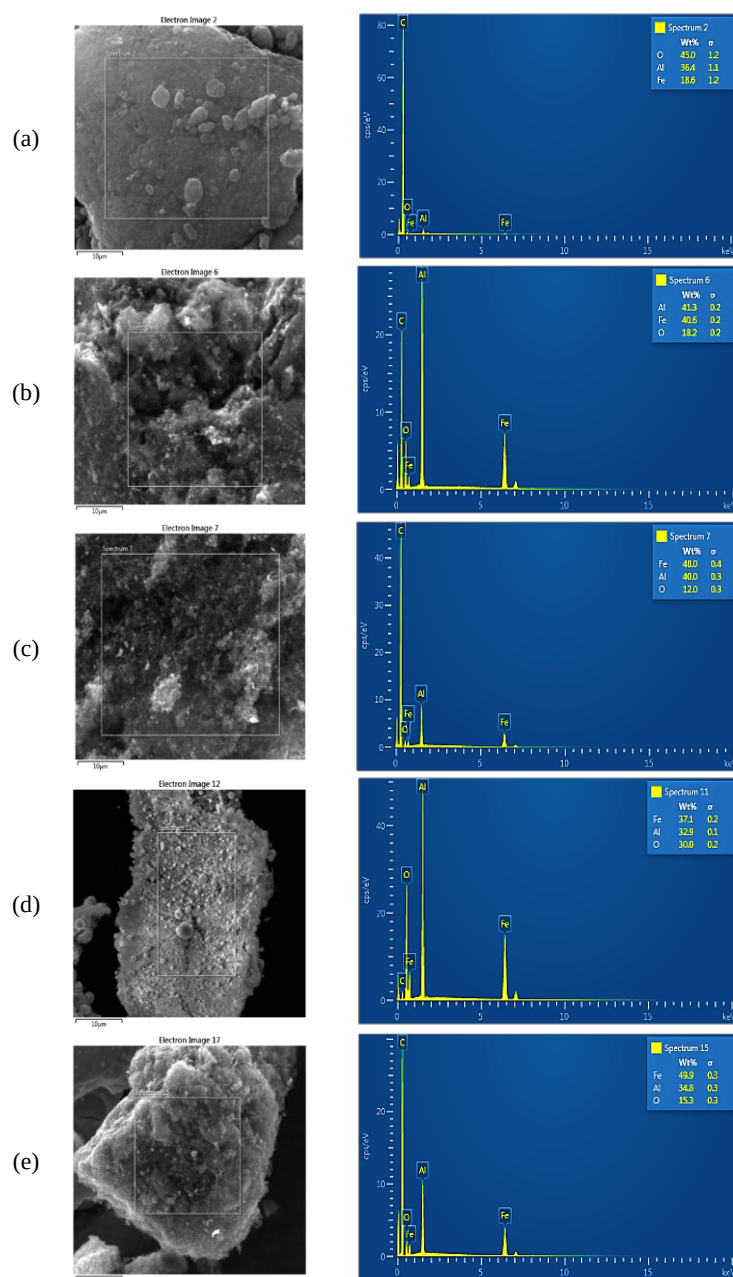


Figure 4. SEM and EDX images (a) MWCNT standard (b-e) the sample (HDPE+FeAlO_x) in 20, 30, 40, and 45 min respectively

The local geometric and absorption of atoms in the sample as a function of electronic structure were measured by X-ray absorption spectroscopy (XAS) technique. The XAS has tunable monochromatic X-rays and energy in their absorption energy range or close to the binding energy of electrons in atom (Klysubun, 2002). The absorption edge energy was corresponded with the energy required to eject an electron from an electron shell of an element of interest. Small changes in how X-rays are absorbed near an atom's absorption edge provide insight into

the state of the electrons (Sigray, 2020). The transitions from core electronic states of the metal to the excited electronic states lowest unoccupied molecular orbital (LUMO) is measured by XAS known as X-ray absorption near-edge structure (XANES). The fine structure in the absorption at energies greater than the threshold for electron release latter was studies by extended X-ray absorption fine structure (EXAFS) to give complementary structural information. The XANES spectra reporting electronic structure and symmetry

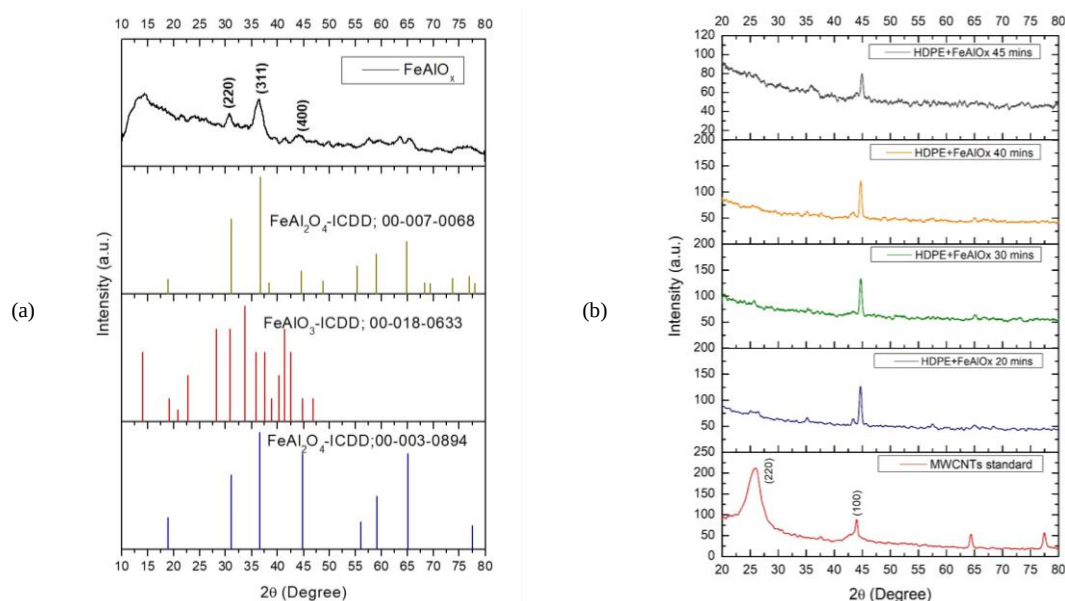


Figure 5. XRD pattern of (a) FeAlO_x catalyst and (b) the sample MWCNTs standard, irradiated microwave for 20, 30, 40, and 45 min respectively

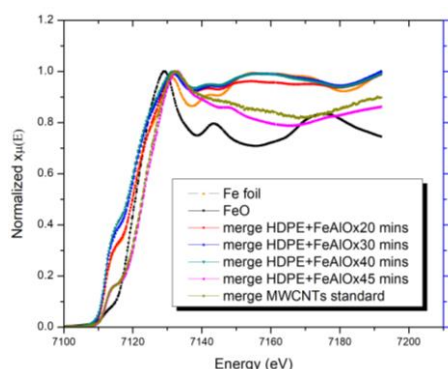


Figure 6. Fe K-edge XANES spectra of MWCNT standard, the sample ($\text{HDPE}+\text{FeAlO}_x$) in 20, 30, 40, and 45 min respectively

of the metal site, and the EXAFS reporting numbers, types, and distances to ligands and neighboring atoms from the absorbing element (Koningsberger and Prins, 1988). The Fe K-edge XANES spectra of MWCNT standard was found for the peak at $\sim 7,132$ eV as shown in Figure 6. However, the Fe K-edge XANES spectra of the sample ($\text{HDPE} + \text{FeAlO}_x$) in 20, 30, 40, and 45 min was found for the peak at $\sim 7,132$ eV which are consistent with Sa *et al.* (2016); Woo *et al.* (2018) and Li *et al.* (2019). The strong peak at $\sim 7,132$ eV in the energy position of the main absorption edge for the sample and FeO reference can be seen for Fe^{2+} compound.

Conclusions

We can value added of the plastic waste by general microwave irradiated to obtain the MWCNT and very simple to save time. The FeAlO_x can catalytically process with small plastic wastes by the microwave irradiated. The crystallographic of the sample ($\text{HDPE}+\text{FeAlO}_x$) in 20, 30, 40, and 45 min were corresponded MWCNT structure. The morphology of sample confirmed MWCNT and corresponded with MWCNT standard at $\sim 7,132$ eV by XANES. Moreover, the outer and inner tube diameter of MWCNT of $\sim 8\text{-}29$ nm and $\sim 4\text{-}12$ nm.

The authors declare that they have no conflict of interest.

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