Green Synthesis and Characterization of Carbon Nanotubes from Water Hyacinth Via Chemical Vapor Deposition

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Abstract

Carbon nanotubes (CNTs) were found to have formed during chemical vapor deposition (CVD) process of water hyacinth as green and renewable source without adding catalysts at a relatively low temperature of 700 °C. Acetylene was employed as a carbon source. Scanning electron microscopy (SEM) results showed that the CNTs formed over the bio-char of water hyacinth. The energy dispersive X-Ray fluorescence spectrometer (EDX) showed the silicon and alumina existing elements in water hyacinth, indicating that these elements played a key role as a catalyst for CNTs formation. Transmission electron microscopy (TEM) revealed that the diameter and length of CNTs were ~ 46 nm and 200~300 nm, respectively. Moreover, the microstructure of CNTs synthesized was bamboo-like CNTs structure and a d-spacing of 0.34 nm. The high degree of crystallization and high thermal stabilization were reported by Raman spectroscopy and thermal gravimetric analysis (TGA). Conclusively, this work provides the green and sustainable to synthesis CNTs and add-value of the useless weed into high-value products as CNTs.

Keywords: Carbon nanotubes, Water hyacinth, Chemical vapor deposition, bamboo-like carbon nanotubes, Green synthesis

1. Introduction

Water hyacinth (Eichhornia crassipes) is a native plant in Brazil and Ecuador regions. Nowadays, it's abundantly found in the tropical and subtropical regions. Water hyacinth was presented as an invasive plant due to a higher rate growing even in the worse condition ecology. The serious effect of massive water hyacinths is irrigation, navigation, power generation, and ecology [1]. Recently, various research groups have studied controlling and sustainable disposal routes of water hyacinth such as the production of bioenergy, production of fertilizer, paper production, as well as wastewater treatment aspect [2-6].

Currently, Carbon nanotubes (CNTs) have been increasingly attractive materials due to remarkable properties, for example, lightweight, high thermal stability, high surface area, including high thermal conductivity [7-8]. It was applied in numerous works such as composite materials, energy storage, absorbing pollution, sensors, and catalysts. CNTs were synthesized by well-known methods include arc discharge, laser ablation, and chemical vapor deposition (CVD). Among these methods, CVD is outstanding due to low cost, easy to operate, and low synthesized temperature [9]. Generally, the CVD method is required both the catalyst as a transition metal (i.e. Ni, Co, Fe) and substrates namely quartz and silicon oxide for CNTs formation. However, many researchers have attempted to synthesize CNTs from bio-base materials, which were renewable, sustainable, eco-friendly, as well as low cost.

Yu et al. [10] reported that they synthesized CNTs on bio-char of pine nutshell via microwave-assisted CVD method with Ni catalyst. The results showed that the optimum temperature for CNTs growth was at 600 °C. Nissayan and Artnaseaw [11] demonstrated that the multi-wall carbon nanotubes (MWCNTs) were synthesized using silkworm cocoons as a substrate via the CVD method. Ferrocene and acetylene were used as catalysts and carbon

sources, respectively. Moreover, Araga and Sharma [12] also reported that the MWCNTs were produced by coconut shell derived charcoal pyrolyzed at 900 ^{o}C. Acetylene was used as a carbon source, and plasma-enhanced chemical vapor deposition (PECVD) was conducted to synthesize MWCNTs. It can be seen that bio-based biomass is more attractive to CNTs production because of not only their outstanding properties, but also the green synthesis and sustainable aspect. However, the synthesized CNTs from water hyacinth via the CVD method without adding catalysts have not been reported yet in previous literature. Therefore, the aim of this study was to synthesize of CNTs from water hyacinth via chemical vapor deposition at relatively low temperatures at 700 ^{o}C without adding any external catalyst. A carbon source was acetylene gas. The obtained CNTs were characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM), energy dispersive X-Ray fluorescence spectrometer (EDX), thermogravimetric analysis (TGA), Raman spectroscopy, and X-ray diffraction (XRD) techniques. Moreover, feasible applications of the synthesized CNTs were also described.

2. Materials and Methods

2.1 Preparation of water hyacinth

Water hyacinth (WH) was collected from the pond in Khon Kean University, Khon Kean, Thailand. It was washed by deionized (DI) water to remove the grime and then introduced to hot air oven at 105 ^{o}C for 24 hours to eliminate moisture. Afterward, it was crushed and sieved into powder in the size range of 2-2.36 mm (denoted as DWH) [13]. The element composition of DWH was evaluated by EDX as summarized in Table 1.

2.2 Synthesis of CNTs

The CVD reactor, employed for the synthesis of CNTs, consisted of a horizontal quartz tube furnace with a diameter of 4.5 cm and a length of 62 cm placed in an electric furnace. Acetylene was used as a carbon source. First, the DWH in the ceramic boat was placed in the middle of the furnace. Then, nitrogen (N_2) was purged at flowrate 150 ml/min for 30 min to eradicate oxygen. Suddenly, the furnace was turned on to 450 ^{o}C, together with the feed of hydrogen at a flowrate of 200 ml/min, and maintained for 1 h to remove the moisture. At the same time, lignin, cellulose, and hemicellulose were also eliminated. The bio-char of WH was obtained from this stage. Second, the temperature was increased to 700 ^{o}C, and acetylene was introduced into the system for 15 min with a flow rate of 50 ml/min as a carbon source to promote the CNTs formation. Finally, the CNTs were produced, the furnace was then turned off and cool down to room temperature [14].

2.3 Characterization of CNTs

The surface morphology and micro structure of CNTs were examined by scanning electron microscopy (SEM) transmission electron microscope (TEM). The energy dispersive X-Ray fluorescence spectrometer (EDX) was introduced to investigate the element composition of DWH and synthesized CNTs. The degree of crystallization, thermal stabilization, including purity of CNTs were observed by Raman spectroscopy, and X-ray diffraction (XRD), and thermogravimetric analysis (TGA) instrument.

3. Results and Discussion

3.1 Morphology and microstructure of CNTs

Figure 1 presents the surface of bio-chare water hyacinth after carbonization at temperature 450 ^{o}C. It can be seen that the surface was rough with board porosity. The indented and porosity of the bio-char surface were obtained, implying that the lignin, cellulose, and hemicellulose were eliminated from water hyacinth. After the synthesis process at 700 ^{o}C, the CNTs were distributed over the surface of bio-char of water hyacinth, as shown in Figure 1. (c) and (d). The obtained CNTs were formed dense, entangle, including overlapping noodle-like. Generally, the main element compositions in water hyacinth are silica (Si), alumina (Al), as well as iron (Fe) (Table 1). It could be concluded that these element in water hyacinth can act as catalysts, by postulating the large site for CNTs nucleation, corresponding with previous works by Zhu et al. [12] and Araga and Sharma [15].

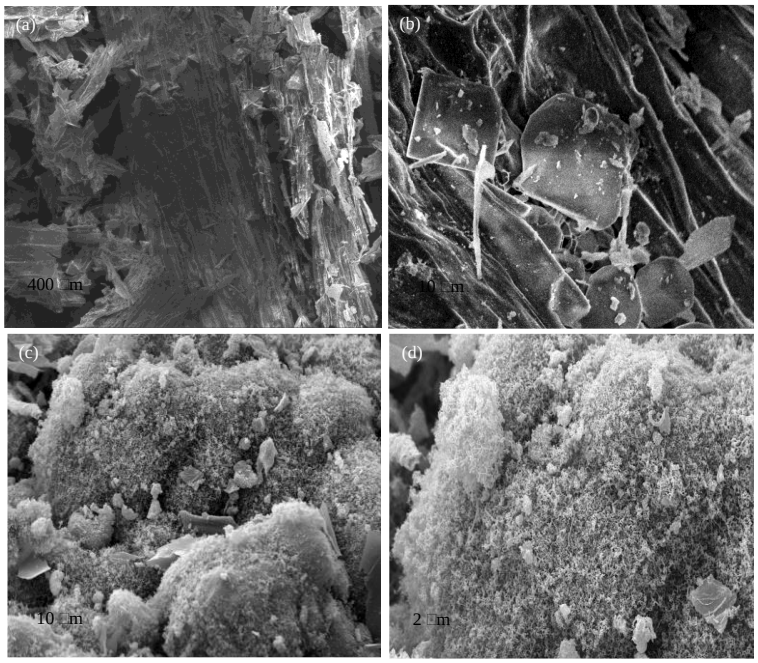

Figure 1. (a) low and (b) high magnification of SEM images of bio-char surface of water hyacinth at temperature 450 ºC, and (c) low and (d) high magnification CNTs formation over the bio-char surface of water hyacinth

TEM images in Figure 2 results reveals that the obtained CNTs were hollow and tubular tubes with open-end. Figure 2 (a) illustrates that the CNTs seemed tangled like noodles, consistent with the SEM results. The average diameter and length of CNTs were 46 nm and 200~300 nm, respectively. Figure 2 (b) shows that the CNTs had a multi-wall structure with the bamboo-like structure, namely the internal structure was hollow and had wrinkles curve that separated hollows like a bamboo structure. It was confirmed by the curvature and compartment inside the CNTs hollow. Besides, the d-spacing of CNTs was approximately 0.34 nm, which was similar to the pure graphite (0.3354 nm). This result indicated that the synthesized CNTs were turbostratic carbon in nature, i.e. the disorderly rearrangement of graphitic carbon order to form tubular CNTs [16].

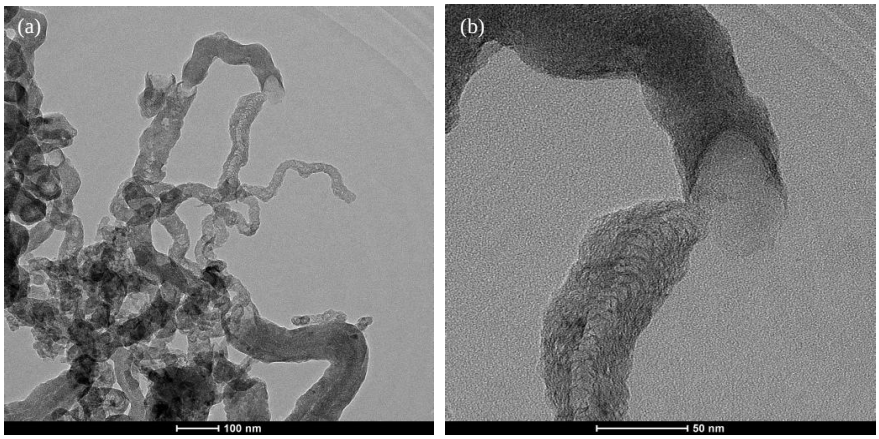

Figure 2. (a) TEM images of CNTs and (b) TEM image of bamboo-like CNTs structure.

Table 1 Element component of DWH and obtained CNTs by EDX (%wt)

	C	Si	Al	O	Fe
DWH	28.72	31.5	18.63	17.2	3.95
CNTs	64.21	14.19	13.47	6.37	1.76

In this case, the growth mechanism of CNTs as bamboo-like structure was proposed in three stages as shown in Figure 3 (d). In the first stage, the carbon source (i.e., C_2H_2) was decomposed to break the bond into a single carbon atom. Second, a single carbon atom was diffused and dissolved into the surface of either catalyst or carbon on bio-char water hyacinth, leading to a saturated stage. Third, it was precipitated as a graphitic cap covering the catalyst. The graphitic cap was eventually lifted off due to the stress accumulation of the driving force, producing the hollow bamboo-like structure. Finally, CNTs were formed by growth direction elongated from the nucleation site [14].

3.2 Structure characterization of CNTs

The structure and the degree of crystallization of CNTs were investigated by XRD and Raman spectroscopy, respectively. The obtained CNTs were characterized by the XRD technique, which was shown in Figure 3 (a). It reveals that the XRD pattern at peaks 2θ= 26.2°, 43°, and 44°, corresponding to graphite plane (002), (100), and (101), respectively [10]. Moreover, the other peaks around 2θ= 28.7°, 30.8°, and 35.6° could be attributed to Si, Al_2O_3, and SiC, respectively, in agreement with previous study by Kim et al. [17]. The presences of Si and Al were vital as a catalyst for CNTs formation, consistent with the EDX result in Table 1. The d-spacing was obtained by Bragg's law about 0.34 nm, corresponding well with d-spacing from TEM results.

Raman spectroscopy has been widely used to characterize the degree of crystallization. Two sharp peaks were observed nearby 1354 cm^{-1} (D-band) and 1605 cm^{-1} (G-band) as shown in Figure 3 (b). The D-band is attributed to the disordered, namely the defect of graphitic plane that formed the CNTs. On the other hand, G-band is the motion of SP^2-carbon atom [18]. Quality of the synthesized CNTs (i.e., carbon order) could be assessed by the ratio of D-band to G-band intensity (I_D/I_G). In this work, the I_D/I_G value of CNTs was approximately 0.885 ± 0.044, comparable to previous studied by Sasrimuang et al. [14] indicating high degree of crystallization. Figure 3 (C) demonstrates the TGA curve of CNTs. It was employed to estimate the thermal stability and purity of CNTs. TGA result shows two stages of degradation; 20-450 °C and 450-900 °C with the weight loss of 5 % and 76.47 %, respectively. The first stage of degradation was moisture evaporation. The second stage was extreme degradation, which was attributed to the degradation of graphitic carbon structure (i.e., CNTs), in agreement with previous research by Nady A. Fathy [19]. This means that the obtained CNTs from water hyacinth using CVD method were high in both thermal stability and quality.

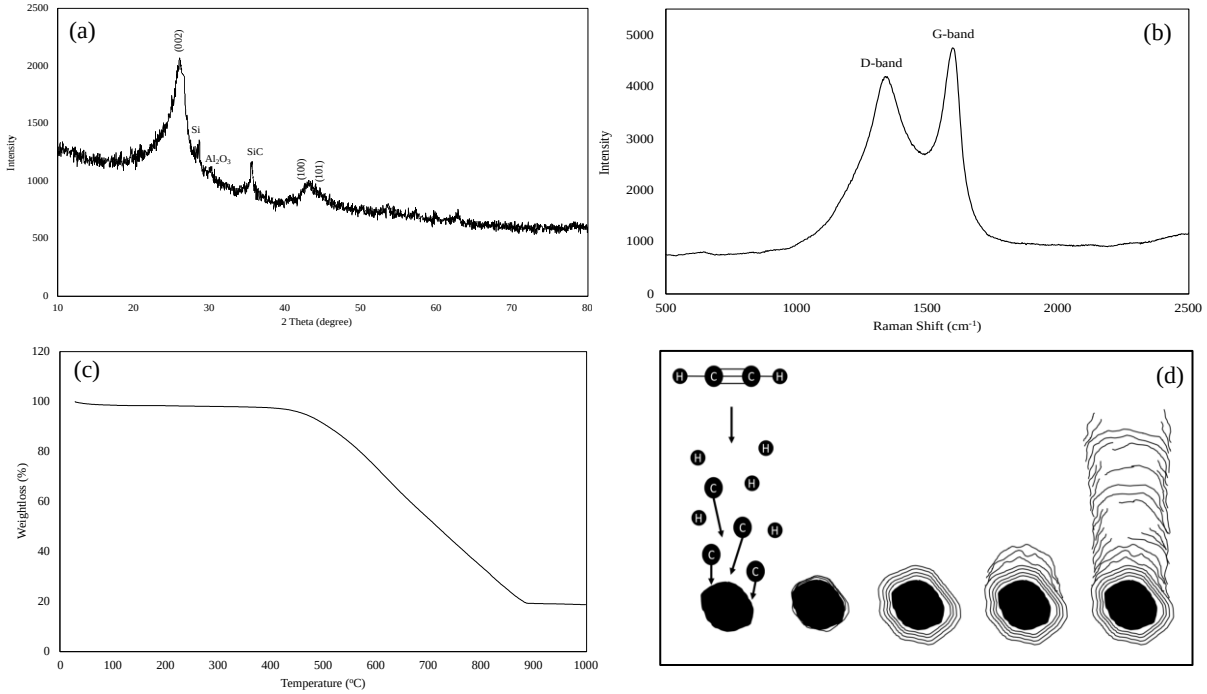

Figure 3 (a) XRD pattern of CNTs, (b) Raman spectroscopy of CNTs, (c) TGA profile of CNTs, and (d) Schematic illustrations the growth mechanism of CNTs start from the left, respectively.

Based on the results, the green synthesized and renewable CNTs from water hyacinth could be a feasible candidate in various applications such as adsorbent of pollutant [20], green material reinforcement [21], and Al-air batteries [14]. However, the CNTs in this study require further characterizations by advanced analysis techniques such as Brunauer-Emmett-Teller (BET) surface area analysis and X-ray photoelectron spectroscopy (XPS) for approach to the practical applications.

4. Conclusions

The CNTs were successfully synthesized from water hyacinth using CVD method without adding any of the external catalysts. The operating temperature was 700 ^{o}C and acetylene was used as a carbon source. The obtained CNTs were in a bamboo-like structure with d-spacing around 0.34 nm, as investigated by both TEM and XRD. The average diameter and length were ~ 46 nm and 200~300 nm, respectively. In addition, Raman spectroscopy presented the high degree of crystallization, and TGA result showed the high thermal stabilization and quality of CNTs. Conclusively, this work presents a green and sustainable synthesis of CNTs for further application. Moreover, it also promotes the alternative way to eliminate and add-value of water hyacinth.

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