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Preparation and Characterization Carbon Nanotubes – Chitosan Nanocomposite by Using Oil Palm Shell and Horseshoe Crab Shell

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Abstract: *Preparation of carbon nanotubes (CNTs) nanocomposite-chitosan can be made by using oil palm shell and horseshoe crab shell (Tachypleus gigas). For the preparation of CNTs are made by changing the oil palm shells into activated carbon, then impregnated with Fe catalyst, and then made the process of growing CNTs by pyrolysis CVD method at calcination temperature of 950 ° C with a gas flow of methane and nitrogen. For the preparation of chitosan is made by changing the horseshoe crab shell to chitin through deproteinization and demineralization process, and then in deasitilasi into chitosan. Preparation of CNT-chitosan nanocomposite made by mixing CNTs with chitosan with ratio (1: 3) through the process of sonication for 4 hours, and 2.5% glutaraldehyde was added during sonication process takes place resulting in physical and chemical bonding in the nanocomposite. The results of CNT-chitosan nanocomposite preparation is characterized using XRD and FTIR. Based on test results of XRD showed that the CNTs are made of nano-sized, and the appearance of peak at 25,79^o and 43,54^o which means CNT has been formed, and based on test results of FT-IR show that the presence of the C=C absorption at the wave number 2344 cm^{-1}, and based on test results of SEM showed that the morphology of CNTs were obtained in the form of small tubes of a length.*

Keywords: *CNT, chitosan, nanocomposite, glutaraldehyde, sonication.*

1. INTRODUCTION

Mining business in Indonesia until today is still regarded by most people as one of the causes of environmental degradation and pollution, such as one liquid waste from a gold mine. Liquid waste from gold mines contain highly hazardous metals such as mercury. Generally mining often dispose of their waste directly into the river without any prior screening process so that's it is triggering environmental pollution. There are many ways that can be done to overcome the liquid waste from gold mines, namely the use of absorbent material to reduce levels of metals contained in the wastewater, such as activated carbon, chitosan, including modification of the adsorbents have also been made in improving the quality of the adsorbent. Modifications can be done to make a better adsorbent is by using oil palm shell and turn it into activated carbon, and then used as a support medium for growing carbon nano tubes (CNTs). CNT is a carbon nano-sized and shaped long tubes, which serves as the adsorbent with absorbency considered quite good.

Use of oil palm shell is based on research Najma (2012) which utilizes waste banana peel to be converted into activated carbon as a support medium, then grown into CNTs using methane gas by pyrolysis-CVD method, the results obtained are MWCNTs.

Some research on the manufacture of CNTs have also been carried out, among others : Atyaforza (2012) which makes MWCNT by CCVD method using acetylene gas and compare the characteristics and morphology of CNTs using Fe and Co catalysts. Nur (2007) synthesize CNTs from ethanol by the CVD method using Fe and Co catalyst at a temperature of 900 ° C, the results show that the structure of CNTs Grafite crystallinity using Fe catalyst is much better than the Co catalyst. Gang-Yu (2014) compared two types of CNTs, namely SWCNT and MWCNT to absorb organic materials in the wastewater, where it is known that the use of SWCNT has its advantages can absorb many organic materials, but expensive in the manufacturing process, while the use of MWCNT is opposite cheaper in the making, but it has the capability of smaller absorption, and he thinks it can be overcome by modifying the MWCNT into composite materials.

To modify MWCNT composite then becomes necessary materials such as chitosan. Chemically functionalized MWCNT in order to produce a strong bond with the polymer interface, such as chitosan that enables became CNT-based nanocomposite which has mechanical and functional properties better.

Research on CNT-chitosan have been carried out, such as Salam et al (2011) which makes MWCNT-chitosan nanocomposite using glutaraldehyde as a cross linking, and characterize and applied to absorb heavy metals such as Co, Cd, Zn and Ni. Carson et al (2009) which makes chitosan-CNT Composites, the way to first oxidize CNTs with aqua regia to form CNT-COOH, and COOH groups are converted into chlorides, and subsequent grafting with chitosan, so that the results obtained in the form of CNT-g-chitosan. Furthermore Shieh et al (2013) which makes CNT-chitosan nanocomposite with different acid solution used to dissolve chitosan include acetic acid, hydrochloric acid, and citric acid, then from these variations mixed with CNT and fCNT (CNT-COOH).

To further maximize the absorption of the metals in the wastewater, then used MWCNT-chitosan nanocomposite adsorbent with glutaraldehyde as a cross-linking enable the strong bond between chitosan and chitosan, resulting MWCNT will be trapped in a series of existing bonds, and the resulting CNT-chitosan nanocomposite better and effective when used to absorb metals in particular gold mine wastewater mercury (Hg) .

This is the reason for doing the research on the preparation and characterization of CNTs-chitosan nanocomposite. For the preparation of CNTs in this study by the CVD method using methane gas and Fe catalysts at 950^{o}C calcination temperature and support medium used is oil palm shell which has been converted into activated carbon. For the preparation of chitosan using horseshoe crab shells. Modification of CNTs-chitosan nanocomposite was prepared by mixing directly CNTs, chitosan, and gutaraldehid as a cross-linking agent

Purpose of this study was to determine that carbon nanotubes (CNTs) can be made from methane gas and catalyst Fe with media support is activated carbon from oil palm shell and modified with a chitosan from horseshoe crab shell based nanocomposite materials.

2. METHODS

2.1. Preparation of Activated Carbon from Oil Palm Shells

300 g of palm oil shells are cleaned, put into a porcelain dish, and put in the oven (t = 2h, T = 110 °C) to remove the water content. Furthermore carbonized in a furnace (t = 2,5h, T = 400 °C). Carbon then activated with H_3PO_4 7% with a ratio of 1:10 (w/w), stirring (t = 0.5 h), soaked (t = 24 h), then filtered and dried in an oven (t = 24 h, T = 120-150 °C). Carbon is heated in the furnace (t = 2.5 h, T = 600 °C), washed with 5N HCl to remove the chloride content, washed with hot distilled water until neutral pH, and washing with cold distilled water to remove phosphorus, dried in an oven (T = 120-150 °C), until finely crushed, filtered with a 400 mesh sieve. The results were characterized by FTIR, XRD, and SEM.

2.2. Growth of Carbon Nanotubes (CNTs) with Calcination Process

50 g of activated carbon in the calcination (t = 4h, T = 400 °C). The catalyst $Fe(NO_3)_3.9H_2O$ was dissolved with 0,09M acetone. Fe catalyst and activated carbon that has been calcined impregnated by mixing 500 mL of Fe solution into 50 g of activated carbon, and then sonicated (t = 1h, T = 60-70 °C) until the solvent evaporated. After it is dried in an oven (t = 12h, T = 60-70

°C). Results impregnating calcined in a quartz reactor which has been assembled by some of the gas tube. Furthermore, the nitrogen gas flows (υ = 50 mL/min, t = 4h, T = 500 °C), reduced by flowing hydrogen gas (υ = 70 mL/min, t = 4h, T = 700 °C) to remove metal oxides which is formed when calcined. Then the temperature is raised up to 950 °C while nitrogen gas flowed slowly to remove oxygen gas, after the temperature reached a nitrogen gas flow was increased to 200 mL/min, and methane gas flowed with a flow rate of 100 mL/min simultaneously follow the best flow decomposition of methane on activated carbon. The results obtained were characterized by FTIR, XRD, and SEM.

2.3. Preparation of Chitin from Horseshoe Crab Shells

Horseshoe crab shells washed with water, and dried at room temperature. The dried shell in deproteinization with 5% NaOH solution with a composition of 1:8 (w/w) for 24 hours, washed with water until neutral pH, and dried at room temperature. Furthermore, in demineralized with 5% HCl solution with a composition of 1:8 (w/w) for 24 hours, washed with water until neutral pH, and dried at room temperature, pulverized, and dried chitin obtained. Results obtained are tested solubility of chitin using 98% formic acid with a composition of 1: 100 (v / v).

2.4. Deacetylation Process of Chitin from Horseshoe Crab Shells Being Chitosan

Chitin soaked in 50% NaOH solution with the composition of 1:14 (w/w) for 6 days while stirring every day to immersion homogeneous, filtered to obtain chitosan wet. Wet chitosan obtained was washed with water until neutral pH, dried at room temperature and pulverized. The results obtained, further tested the solubility of chitosan using 1% acetic acid with a composition of 1:100 (v/v). The results obtained were also characterized by FTIR, XRD, and SEM.

2.5. Preparation and Characterization of CNT-Chitosan Nanocomposite

3 g chitosan was poured into 100 mL of 1% acetic acid solution, sonicated (t = 2 h) to the chitosan solution is homogeneous. 1 g of CNTs was poured into 100 mL of distilled water, sonicated (t = 2 h) until the mixture became homogeneous. The chitosan solution was mixed with CNTs, and sonicated for 4 hours to improve the homogeneity of the mixture, then add 3,5 mL of 2,5% glutaraldehyde solution into the mixture while the process is still running sonication, the mixture was dried in an oven (T = 24 h, T = 60 ° C). The results obtained, were characterized using FTIR, XRD, and SEM.

3. RESULTS AND DISCUSSION

3.1. Characterization of CNTs Using FT-IR

The results of FT-IR CNTs as shown in Figure 1 is a carbon graphite, which is visible in the presence of shift the wave number of 2311,04 cm^{-1} which indicates the presence of alkyne absorption reinforced with the appearance of a weak absorption around the wave number of 2056,15 cm^{-1} and 1999,81 cm^{-1}.

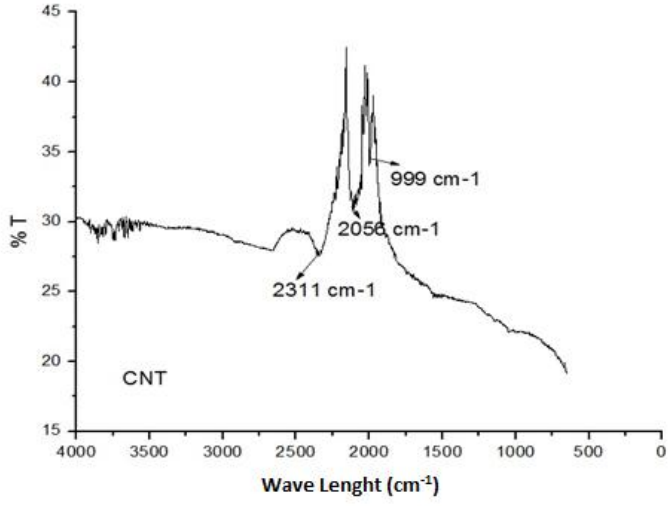


Fig1. *FT-IR CNTs*

3.2. Characterization of Chitosan Using the FT-IR

The results of FT-IR Chitosan as shown in Figure 2 shows that OH stretching vibration of the shift is located in the area of the spectrum at wave number 3358.36 cm^{-1} which is reinforced by the appearance of NH2 stretching vibration on the strain 3208.16 cm^{-1}. Spectrum shows the presence of dilated and weak absorption at wave number at the wave number 2900 cm^{-1} indicate the presence of symmetric CH stretch. In the spectrum of 1590.83 cm^{-1} indicates the presence of the C = C stretch. The presence of C-N which are in the wave number region 1200 -1020 cm^{-1} are indicated by the appearance of the spectrum at wave numbers 1210.8 cm^{-1}. The presence of CH_2 and CH_3 groups at wave number 1420 cm^{-1} and 1370 cm^{-1}. The existence of the spectrum are the wave number 1022.96 cm^{-1} which shows the C-O symmetric. = C-H bending out the field are the wave numbers 800-740 cm^{-1}, and this is seen by the wave number spectrum at 766.01 cm^{-1}.

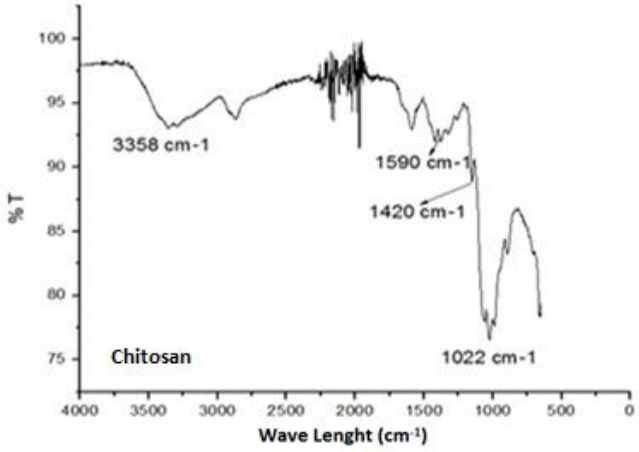


Fig2. *FT-IR Chitosan*

3.3. Characterization of CNT-Chitosan Nanocomposites Using FT-IR

The result of FT-IR CNT-Chitosan nanocomposite as shown in Figure 3 shows that OH stretching vibration is experiencing a shift in the spectrum of 3228.50 cm^{-1} and reinforced by the appearance of a sharp absorption at wave number of 1019.21 cm^{-1} indicating the presence of carbonyl group CO. The presence of sharp absorption and medium intensity shifting wave number 2917.96 cm^{-1} which shows the aliphatic -CH reinforced by the appearance of a sharp absorption at 1404.09 cm^{-1} and 1323.50 cm^{-1} indicating the presence of CH_2 and CH_3. The shift also occurs on the C=C bond with the appearance of the spectrum at 1633.69 cm^{-1} and 1542.28 cm^{-1}.

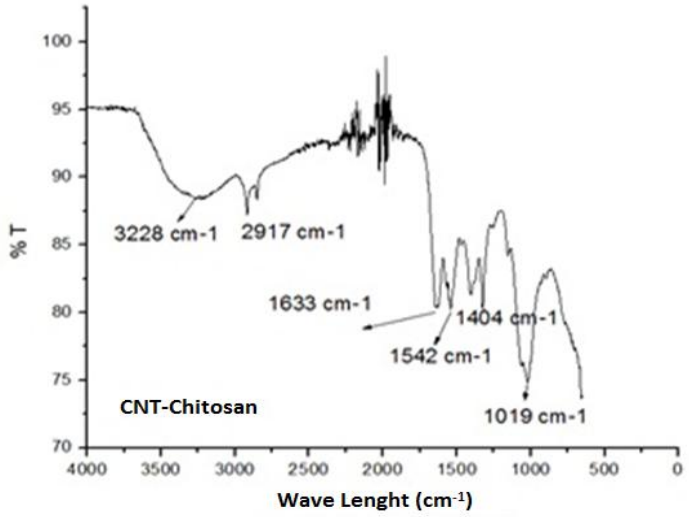


Fig3. *FT-IR CNTs–Chitosan Nanocomposites*

3.4. Characterization of CNTs Using XRD

This characterization shows the crystal structure contained in the CNT which occurred strengthening crystalline structure of activated carbon in the range that has strengthened

crystalline activated carbon. This happens because the heating temperature increases up to 950oC which causes a low-grade carbon amorphs began to change into a graphite structure.

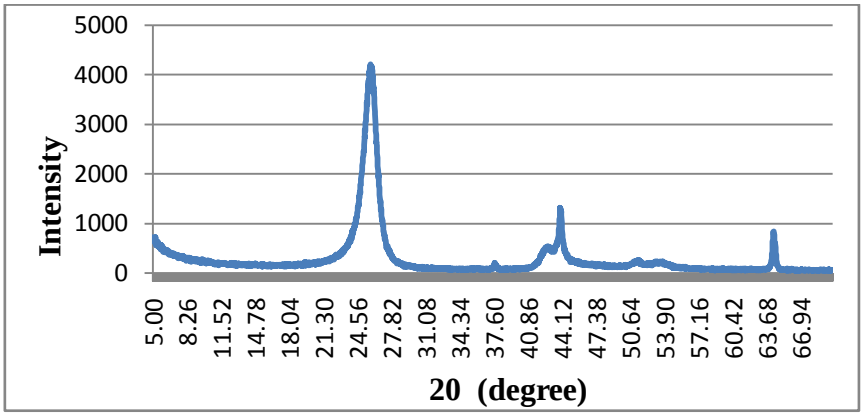


Fig4. *XRD Patterns of CNT*

In Figure 4 it can be seen in the presence of the highest peaks on 25,79^{o}, 43,54^{o}, 42,68^{o}. Maximum peak at an angle 25,79^{o}. That the research Mopoung (2011) reported that the CNT peak detected at 26^{o}, 28,5^{o}, 43^{o} and 54,5^{o}. Fullerene peak appears at 11^{o}, 19^{o}, 21,5^{o}, 31,5^{o}, 41,5^{o} and 56,5^{o}. If the observed results obtained in this study that CNTs are at peak 43,54^{o} and including the maximum peak. It can be concluded that CNTs have been successfully formed on the activated carbon support materials from oil palm shell. This is supported by SEM characterization of CNTs obtained which produces pipes that are characteristic of the CNT.

CNT growth on the research described Hang et al (2002), that the growth of CNTs by catalytic Fe will be able to grow at the time of the open ends during the growth process. At the time of Fe catalyst on the edges then began the process of rapid growth of the nanotubes with the entry of Fe particles into the sleeve so that growth is stalled and Fe catalysts come and go again to the ends of the nanotubes, the re-growth will continue so that it will form a long tube. Growth process actually stops when the active core of the catalyst has been exhausted, the concentration of methane gas cannot be used as the basis for the growth of CNTs because if the Fe catalysts encapsulated in activated carbon that methane gas would be difficult to get into shape CNTs.

The results of the study Sivakumar (2011) who reported that CNTs are not formed at a temperature of 750oC and will be formed at temperatures above 850^{o}C. In this study, the temperature used was 950^{o}C, so it will support the success of the CNTs formed with homogeneous results. Based on the above calculation, obtained CNTs have a particle size minimum of 11.04784 nm and maximum of 33.11062 nm with an average of 15.65011 nm. CNTs with a particle size such as this can be referred to as nanoparticles.

3.5. Characterization of Chitosan Using XRD

The results of X-ray diffraction pattern for chitosan particles as follows:

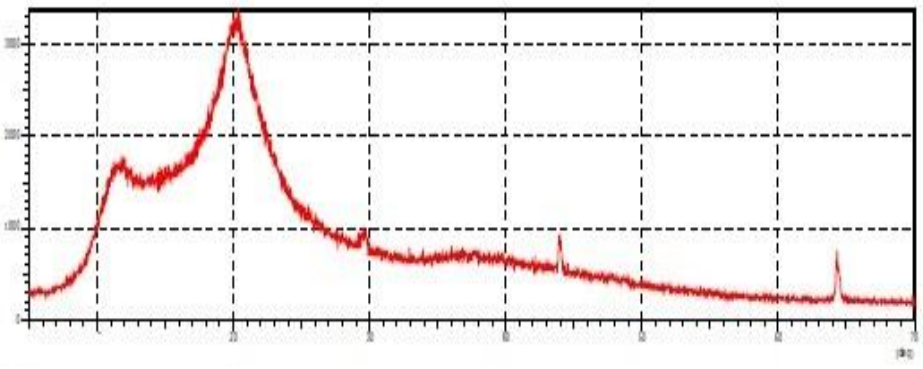


Fig5. *XRD Patterns of Chitosan*

In Figure 5, it seems that the presence of the highest peaks on 20,28^{o}; 21,64^{o}; 18,64^{o}. Maximum peak at 20, 28^{o}. Based on the above calculation, Chitosan is obtained which has a minimum

particle size of 6.0326 nm and a maximum of 33.9043 nm with an average of 8.5178 nm. With this size of particles can be considered as chitosan nanoparticles.

3.6. Characterization of CNT-Chitosan Nanocomposite Using XRD

Based on the results of characterization using XRD that the CNT-chitosan nanocomposite obtained peak which indicates 26, 29°; 43,86° and 14,18°. The addition of chitosan is much more than the CNT, there will be a shift of intensity towards lower. CNT-chitosan nanocomposite showed that there was no peak at 28° - 41,5° which indicates that no fullerene (Mopoung, 2011), also there is no peak appeared in 54,5°, but the CNT-chitosan nanocomposite peak appeared in 54,72°.

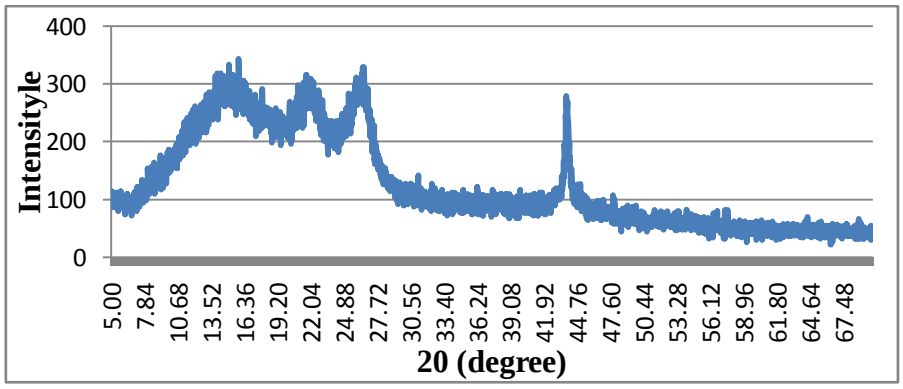


Fig6. *XRD Patterns of CNTs-Chitosan Nanocomposites*

The presence of chitosan on weight gain CNTs to form CNT-chitosan nano-composite produces a smaller peak intensity. Boar, reported a decrease in peak intensity is proportional to the number of straight CNTs. Based on these references can be concluded that without the addition of weight chitosan, then the resulting CNTs are not so straight. Diffraction patterns of chitosan on weight gain in the CNT showed a decrease in peak intensity, peak intensity decreases produces a straight-shaped CNTs it is becoming very well (Sadeghian, 2008). It can be concluded that the CNT-chitosan nanocomposite with a composition of 1:3 is the best.

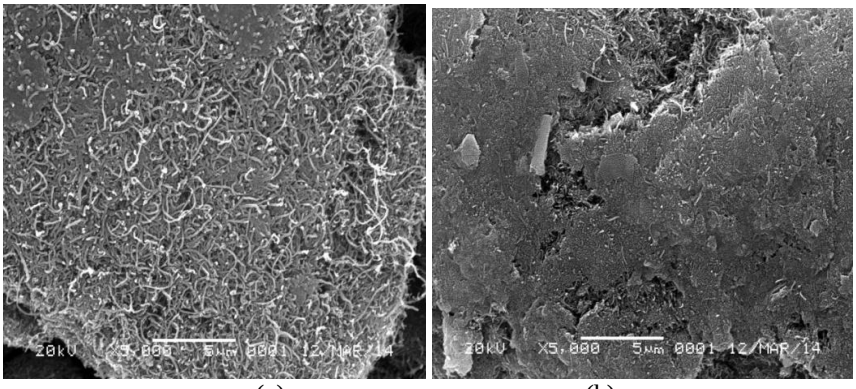
CNT-chitosan nanocomposite produces peak 26,5°, 43,67°, and 54,99° which is the peak of CNT (Mopoung, 2010). It can be concluded with the addition of the weight of the chitosan impurities on the CNT is getting smaller. To determine the particle size CNT- chitosan nanocomposite can be calculated using the Scherrer equation:

$$D = \frac{k\ \lambda}{B \cos \theta_B}$$

The results of the calculation for CNT-chitosan nanocomposite particle size is known to have a minimum of 96.20007 nm and a maximum of 229.5385 with an average of 131.0585 nm.

3.7. Characterization Using SEM

Characterization by SEM performed to show the structure of the surface CNTs, Chitosan-CNT Nanocomposite with the size of the magnification is 5000 times.



(a) (b)

Fig7. *SEM of (a) CNTs; (b) CNTs-Chitosan Nanokomposit*

In Figure 7 (a) and (b) were taken at different points in the sample. SEM results of CNTs as shown in Figure 7 (a) shows that the CNT tubular nano-sized tubes, where long pipes that form has not homogeneous, there is a straight and bent. SEM results of CNT-chitosan nanocomposite as shown in Figure 7 (b), it appears that the surface structure and pore clear, and visible pipes are coated with chitosan.

4. CONCLUSION

Based on the results of this study, it can be concluded that CNTs can be made by using oil palm shell that has been processed into activated carbon, then impregnated with Fe catalyst, calcined at a temperature of 950 °C while the gas flows of nitrogen and methane (2: 1). CNT-chitosan nanocomposite can be prepared by modifying chitosan derived from horseshoe crab shell waste and CNT, and both of them mixed with sonication process with CNT-chitosan composition ratio (1:3), accompanied by the addition of 2.5% glutaraldehyde as cross-linker agent to the mixture, and dried at 60 ° C for one day. Based on the test results of XRD showed that the CNTs are made of nano-sized, and the presence and appearance of the peak at $25{,}79^{o}$ $43{,}54^{o}$, indicating that the CNT was formed. FT-IR results indicate the presence of the C=C absorption at wave length 2344 cm^{-1}. SEM results showed that the morphology of the resulting CNT tubular length.

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