Utilization of cotton as carbon nanostructure precursor by pyrolysis method

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Abstract. In this study, cotton-based cellulose was used as precursor to developed carbon nanotube–like structures through modified-pyrolysis method with iron (III) chloride hexahydrate as a catalyst. Reflux process with nitric acid was conducted to purify the resultant of carbon material. The resultant of carbon-based nanostructure were characterized systematically. X-ray diffraction spectra shows the presence of C peaks at 2θ of 26.53^o, 42.26^o, 44.49^o, 54.63^o and 77.35^o and Fe peaks at 2θ of 44.1^o and 64.25^o. Scanning electron microscope and transmission electron microscope observation revealed that the resultant of graphitic carbon nanostructures displayed the tube-like structure. Raman spectroscopy results show the presence of D-band and G-band peaks, which confirmed the typical spectrum of carbon-based structures. The D-band peak around 1310-1330 cm^{-1} was assigned to the presence of disorder in graphitic materials whereas the G-band peak around 1580-1590 cm^{-1} was corresponded to the tangential vibrational of the carbon atoms. These condition is a typical spectrum of carbon nanotube-like structures. Eventually, these pyrolysis method could be anticipated as a promising strategy in order to develop the novel carbon nanostructures based on cellulosic material.

1. Introduction

Carbon nanomaterials have received significant attention and development from the scientist and researchers. The excellent propereties make carbon nanomaterial suitable for applications such as optoelectronic, photovoltaic, sensing devices, electron field emission, storage, and production of energy, hydrogen storage, nanocomposites, catalyst support or drug delivery system [1][2][3].

Various techniques have been developed in order to prepare carbon-based nanostructures include electric-arc discharge, laser ablation, or chemical vapor deposition [4]. These techniques are often requires a complex protocol and conducted in high processing temperature which results in expensive and inconvenient procedures. Thus, in order to overcome these challenges, the development of new procedures of which combination with catalyst technology for the easy and low-cost strategies is in needed to develop the carbon-based nanostructures. In this respect, a simple method for preparing graphitic carbon nanostructures is the pyrolisis of carbon precursors in the presence of certain transition metals including Fe, Co, Ni, or Mn that serves as catalyst at moderate temperatures. This

method commonly conducted through the carbonization process of as-impregnated polymeric materials. Several investigation have been conducted through pyrolysis techniques using naphthalene/nickel [5] and tetrahydrofuran/nickelocene [6][7] as precursor/catalyst materials. Transition metals are generally used as catalyst owing to their catalytic decomposition of carbon source, ability to form meta-stable carbides and possibility for carbon to diffuse through and over the metals extremely rapidly [8] and the induce formation of graphitic sheets [9].

Recently, the using of natural renewable precursor is gaining interest for selection of carbon precursor. They are inexpensive and widely available substances around the world. Previous investigation have been conducted by using natural resources as a carbon precursor including saccharose [10], bacterial cellulosa [11], zeamays oil [12], and latex [13]. Cotton (*Gossypium sp.*) is a plant-based fiber composed primarily of cellulose which its utilization is still limited as raw material for textiles.

In these study, carbon nanostructure was developed through pyrolysis method by using cotton as carbon source and iron (III) chloride ($FeCl_3$) used as catalyst. The physicochemical properties of the resultant material were characterized systematically.

2. Experimental
2.1. Materials
Cotton fiber was purchased from Polytechnic Textile Bandung, West Java. Iron (III) chloride was purchased from Merck. Deionized water was used throughout the experiment. All chemicals were used without further purification.

2.2. Methods
Preparation of carbon nanostructures was developed through modified-pyrolysis technique. Briefly, 2 g of cotton fiber was immersed in various concentration of iron (III) chloride hexahydrate (0.16 M (A), 0.32 M (B), and 0.48 M (C)). Sample A, B and C were purified in 7 M of nitric acid. The as-prepared materials were then immobilized into the modified-cotton through the sonication-assisted process (Ultrasonic LC 30 H) for 30 min at 60^oC. The solvent was evaporated in *vacuo* followed by heat treatment process in quartz reactor under a nitrogen flow with a rate 30 ml/min with three steps of heating at 250 and 500^oC for 30 min and 900^oC for 2 hr. The carbon samples obtained consisted of a mixture of amorphous carbon and less-crystalline nanostructures. Afterwards, the samples was subjected to purification processes through an effective purification wet-oxidation techniques [16]. In order to investigate the effect of purification process on carbon structure, refluxing with 7 M (A1), 10.78 M (A2), and 14.5 M (A3) of nitric acid (HNO_3) were studied for the optimization with the catalyst concentration of 0.16 M. X-ray diffraction (XRD) analysis was conducted using a Shimadzu XRD 7000 Maxima X to evaluate the crystallographic characteristics by scanning dried powder with Cu K_α (1.5406 Å) radiation. Scanning electron microscope (SEM) JEOL JSM-T330 A was used to observed the structure and morphology of carbon-based material. Transmission electron microscopy (TEM, FEI-Tecnai, Netherland) at an acceleration voltage of 200 kV was used to evaluate the dimensions and size of the resulted carbon material. Raman spectroscopy was conducted using Raman spectroscopy instrument with operating wavelength at 785 nm laser and supported by OPUS software.

3. Result and Discussion
3.1. Formation of carbon structures
Figure 1. shows the diffraction spectra of cotton-based carbon structures with various concentration of catalyst. Diffraction peaks at $26,53^o$, $26,59^o$ and $26,54^o$ for 0.16, 0.32, and 0.48 M catalyst concentration, respectively, were correspond with the carbon spectra. Table 1 shows particle size of carbon, which was calculated using Scherrer method. According to these method, the as-synthesized carbon were developed in nanometer size with hexagonal crystal system. These results are in

accordance with the previous report of diffraction pattern for carbon nanostructures that showed the presence of C atoms at (002) peak at around 26° [16]. The presence of additional peaks at $44,1^o$, $44,07^o$, $44,22^o$, $64,25^o$, $64,19^o$ and $64,26^o$ might be attributed to the peak of catalyst particles. Carbon nanostructures formation was initiated through the interaction catalyst around the carbon structures. Furthermore, for the growing process of carbon nanostructures, the carbon is incorporated to the end of the growing tube and catalyst particles remains at this end, which is moving away of surface. Afterwards, the catalyst iron nanoparticles diffused the new carbon species that are incorporating to the CNT to radial and axial direction, confirming the development of multi-walled carbon nanotubes (MWCNT) [17].
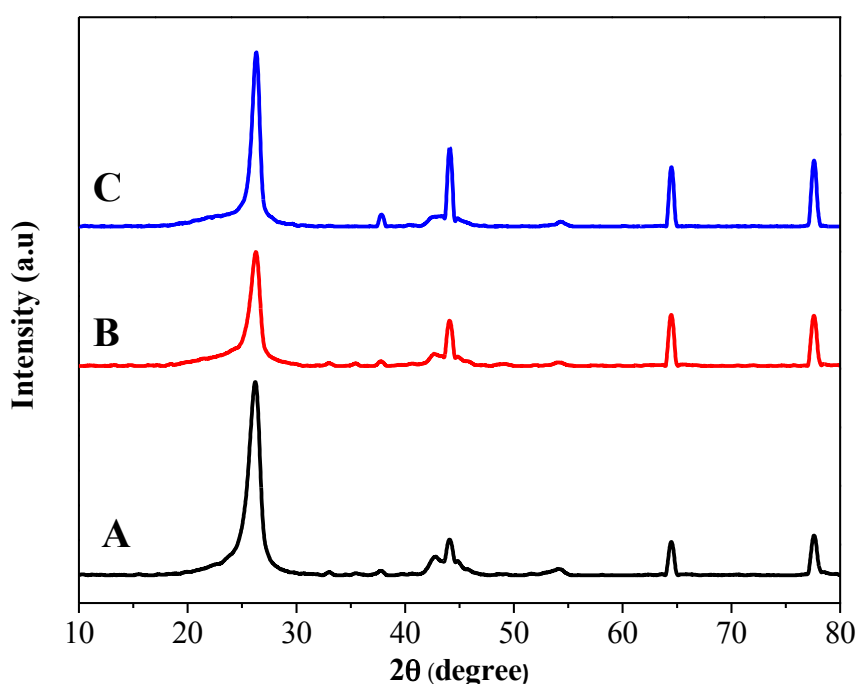

Figure 1. Diffraction spectra of as-prepared carbon structure with catalyst concentration of 0.16 M (A), 0.32 M (B) and 0.48 M (C) and purify with 7 M of nitric acid.

Table 1. Particel size and crystal system of as-prepared carbon structures.

Sample	d (nm)	Element	JCPDS	Crystal System
A	8	C	751621	Hexagonal
B	8	C	751621	Hexagonal
C	10	C	751621	Hexagonal

Figure 2 shows Raman spectra of carbon nanostructure with the presence of D-band and G-band peak, which is in accordance with the well-developed spectrum of carbon nanostructures. The D-band peak was observed around 1350 cm^{-1} which is assigned to the presence of disorder in graphitic materials. Moreover, the G-band peak was observed around 1580 cm^{-1} which is corresponded to the tangential vibrational of the carbon atoms. In parallel with the increasing catalyst concentration, the overall intensity of D-band and G-band peaks was enhanced significantly. These results indicated that iron-based catalyst promoted the growth of carbon nanostructures. Furthermore, Table 2 shows there were no significant different of Raman spectra as increasing catalyst concentration, the ratio of I_D/I_G

was around 1.43-1.49. Theoretically, the quality of the carbon nanostructures, especially carbon nanotubes was depends on the rasio I_D/I_G [18].
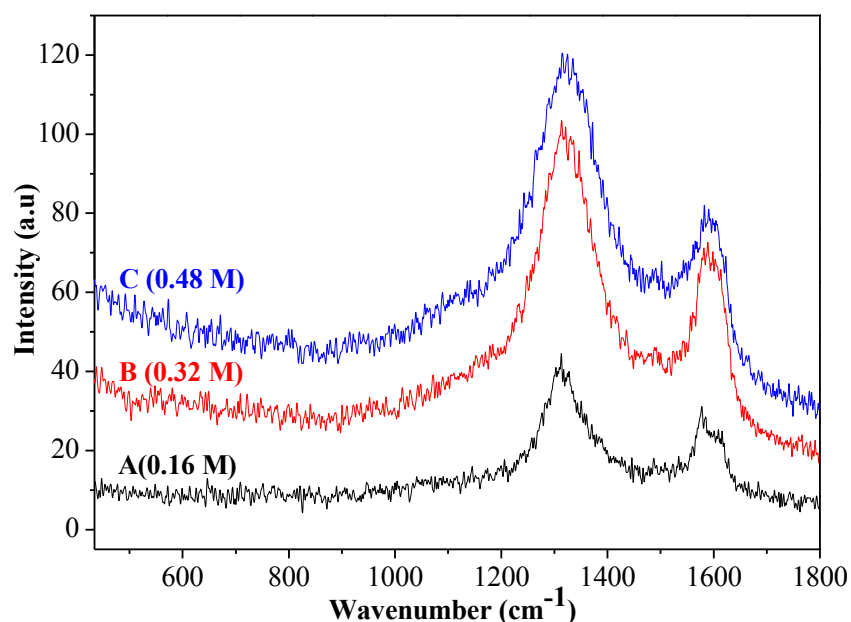

Figure 2. Raman spectra of cotton-based CNT with various catalyst concentration of 0.16 M (A), 0.32 M (B) and 0.48 M (C).

Table 2. Ratio I_D/I_G of cotton-based CNT with catalyst concentration of 0.16 M (A), 0.32 M (B) and 0.48 M (C).

Sample	I_D	I_G	I_D/I_G
A	44.04	30.73	1.43
B	101.2	70.1	1.44
C	117.5	78.,65	1.49

Figure 3. shows the SEM image of CNT samples. All samples showed the morphology of carbon nanotubes with tube-like structures. Sample with the catalyst concentration of 0.16 M pronounced more CNT-like structure. Increasing catalyst concentration led the CNT to be covered by iron particles which is in accordance with XRD and Raman spectra observation.
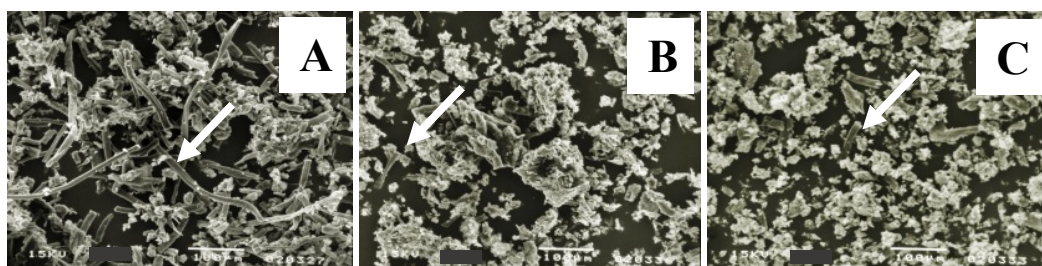

Figure 3. SEM images of cotton-based CNT with catalyst concentration of 0.16 M (A), 0.32 M (B) and 0.48 M (C).

3.2 *Effect of nitric acid to the formation of tube-like structures*

Sample with the catalyst concentration of 0.16 M was used for further purification optimization. Figure 4 shows the typical XRD pattern of C and Fe peak after purification at different concentration of nitric acid whereas Table 3 shows the calculated size. According to the previous report [16], the peak of C (002) was pronounced at $2\theta \approx 26^{o}$ which is in accordance with the XRD pattern of all samples prepared. Generally, there was no obvious changes in the crystal structure of carbon. Moreover, the XRD spectra of sample A2 and A3 peak exhibits less-crystaline in compared with sample A1. This might be due to the increasing concentration of nitric acid tend to disrupted more chemical bonding in carbon structures, thus CNT become less crystalline [19].
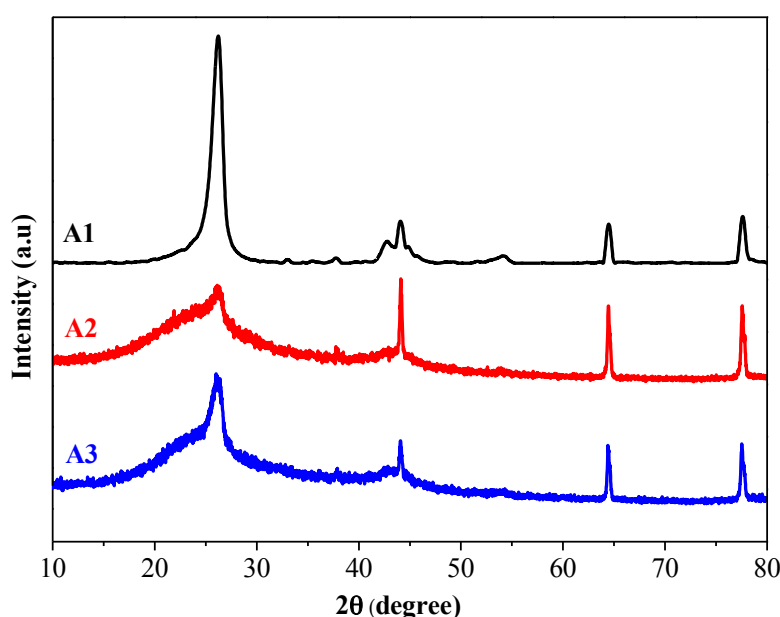

Figure 4. Diffraction pattern of cotton-based CNT with 0.16 M of catalyst purified by nitric acid with concentration of 7 (A1), 10.78 (A2), and 14.56 (A3) M.

Table 3. Particel size (d, nm) and crystal system of as-prepared carbon structures.

Sample	d (nm)	Element	JCPDS	Crystal system
A1	8	C	751621	Hexagonal
A2	28	C	751621	Hexagonal
A3	3	C	751621	Hexagonal

Raman spectra of CNT samples using different concentration of nitric acid are presented in Figure 5. Raman analysis results show the peak of D-band and G-band, which typically spectrum of the CNT. The D-band peak around 1350 cm-^{1} was assigned to the presence of disorder in graphitic materials whereas the G-band peak around 1580 cm^{-1} was corresponded to the tangential vibrational of the carbon atoms. Table 4 shows the ratio of I_D/I_G in the range about 1.22-1.43.
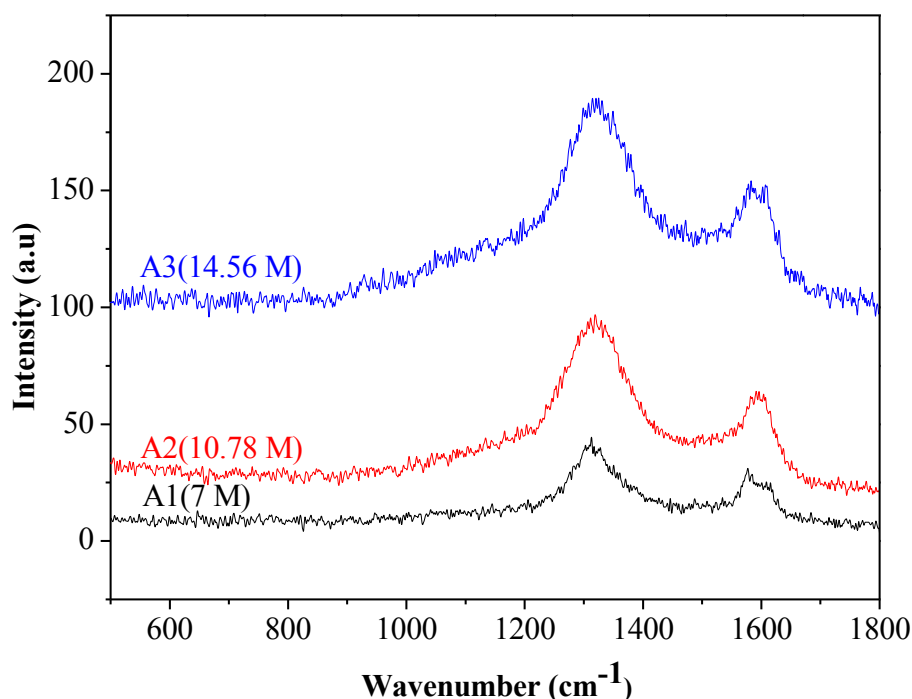
Figure 5. Raman spectra of as-prepared carbon structures with various nitric acid concentration of 7 (A1), 10.78 (A2) and 14.56 (A3) M.

Table 4. Ratio I_D/I_G of as-prepared carbon structures.

Sample	I_D	I_G	I_D/I_G
A1	44.04	30.73	1.43
A2	91.77	64.23	1.42
A3	186.48	151.66	1.22

Figure 6 shows SEM images of cotton-based CNT with various nitric acid concentration of 7 M (A1), 10.78 M (A2) and 14.56 (A3) M. Generally, the samples showed the morphology of carbon nanotubes-like structures. Through purification process, most of the metal catalyst was removed. A portion of remaining catalyst particle surrounded on carbon at sample A2 and A3 might be due to the high concentration of catalyst particles. Interestingly, increasing nitric acidconcentration has affected to length of carbon nanotubes-like structures. Sample A2 and A3 were slightly shorter than sample A1. This is might be due to the high concentration of nitric acid used for the purification process of which distructed chemical bonding in CNT and resulted in less-crystalline structure [19]. This results are in accordance with aforementioned characterization.
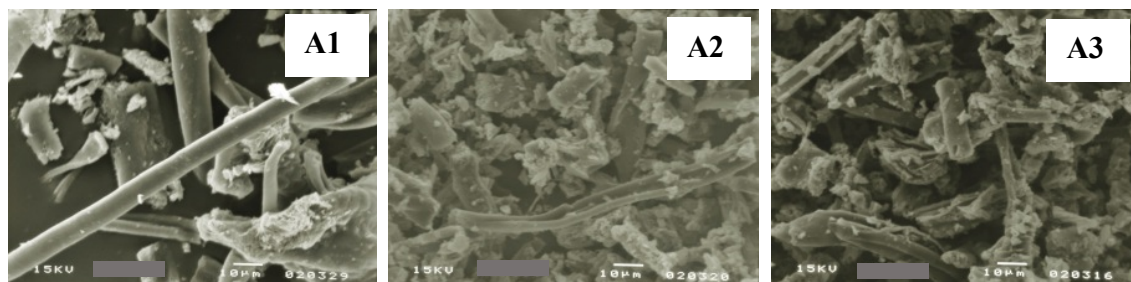
Figure 6. SEM images of as-prepared carbon structures with 0.16 M catalyst with various nitric acid concentration of 7 (A1), 10.78 (A2) and 14.56 (A3) M.

Figure 7 shows the TEM images of sample A1, cotton-based CNT produced by 0.16 M of catalyst and purified by 7 M of nitric acid. Figure 7a shows the tube-like structure of the as prepared carbon-based materials. The sheets of graphite are orderly arranged in concentric cylinders i.e., the tubular structure of nanotubes. Furthermore, Figure 7b shows the formation of multiwalled-like type, and most graphene layers grow perpendicularly to the growth axis of the tubes. The multiwalled carbon nanotube (MWCNT)-like structures was consists of 23 layers and each layer within 2 μm.
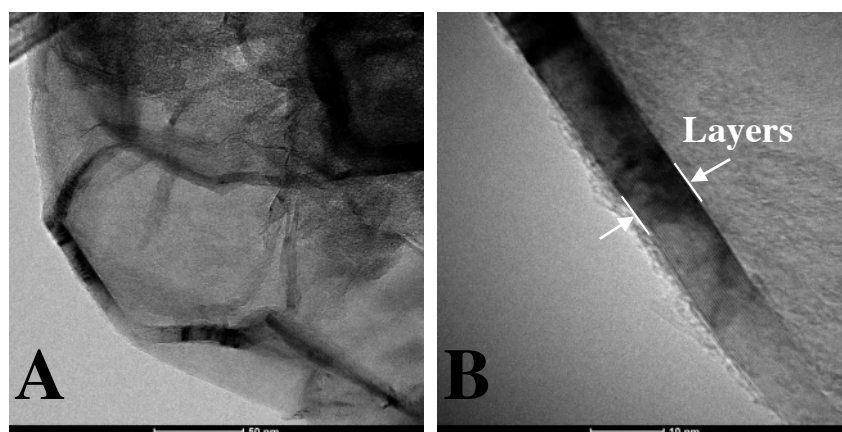

Figure 7. TEM images of as-prepared carbon structures of sample A1 (0.16 M of catalyst and purify with 7 M nitric acid) (A) and its magnified image (B).

4. Conclusion

In summary, multiwalled carbon nanotubes (MWCNT) structures were obtained through modified-pyrolysis process by using cotton as a cellulose-based precursor and iron (III) hexahydrate as catalyst. The formation of MWCNT was optimize at 0.16 M catalystconcentration as in good agreement with XRD, Raman, SEM, and TEM characterizations. The results has obtained I_D/I_G ratio of about 1,43 at 7 M of nitric acid for purification. Eventually, these results show that the utilization of cotton fiber *via* modified-pyrolysis techniques demonstrate a novel strategies to developed carbon-based nanostructure.

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