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Synthesis and characterization carboxyl functionalized Multi-Walled Carbon Nanotubes (MWCNT-COOH) and NH₂ functionalized Multi-Walled Carbon Nanotubes (MWCNT-NH₂)

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Abstract. A making of MWCNTs-COOH has been conducted to improve the compatibility of carbon nanotubes and MWCNTs-NH₂, in order to have conductive properties. The MWCNTs-COOH study was performed, using the first reflux method using HNO₃ for 6 hours heated with 60°C (concentrated HNO₃ ratio with MWCNTs is 1: 5), followed by the second reflux using SOCl₂ for 5 hours heated to 70°C (concentrated HNO₃ ratio with MWCNTs is 1: 3). Meanwhile, the making of MWCNTs-NH₂ used homogenization process, used magnetic stirrer, with comparison between MWCNTs-COOH with Etanadamine 1: 2000, for 8 hours at 40°C. Both products were analyzed using Fourier transform infrared (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). The C-O bond on MWCNTs-COOH is indicated by absorption at wavelength 1672.28 cm⁻¹ and O-H bond at 3431.36 cm⁻¹ N-H bond on MWCNTs-NH₂ shown at wavelength 1440.83. The SEM analysis indicates that both products have a tubular surface morphology.

Keywords: MWCNTs, MWCNTs-COOH and MWCNTs-NH₂, SEM

1. Introduction

Electronic nose (e-nose) is an instrument that mimics the workings of human panel systems using a trained sense of human sense or expert. The main part of the e-nose consists of gas sensor array, data acquisition system and pattern recognition system. In its development, e-nose was used in the field of tracking robot (e dog nose). The existing gas sensor in the market uses MO_x (Metal Oxide) in its manufacture, requiring a large current for each sensor (more than 0.8 A per sensor). It means the robot is less flexible in moving because it carries a heavy load. But unfortunately, although MO_x has a fast sensor response, cheap and high maximum value, but it can only be used for a week, for outdoor use. After that, the sensor response is pure white noise, so it cannot be used as material analysis. TGS sensor resistance is much better than MO_x. Any sophisticated model of PARC (Pattern Recognition) that built, will still experience constraints, when the input signal from the sensor array is bad. In addition, the existing gas sensors in the market use a heater because the used polymer material requires high temperature, it affects the needs of a large current, between 0.8-1A per sensor.

A new hope for mobile robots is the nano array of electronic nose sensors, which apply nanosensor technology to electronic noses. Unlike other gas sensors that have to be imported from other countries, CNTs can already be localized (in Indonesia manufactured), so nanosensor components can be developed with local resources. Nano sensors work at room temperature, so it does not require heater and small current requirements. The advantage of nano sensor is it has a small size, nano-based material, requires little power, and more compact. The metal oxide sensor is usually based on only one



material, ie. tin oxide (SnO_2). In contrast, nanomaterials use a variety of nano-sized ceramics, coupled with special polymers and metals, and their performance will be measured based on the composition and nanostructure of the sensor. The effect of particle size is shown in Figure 1.

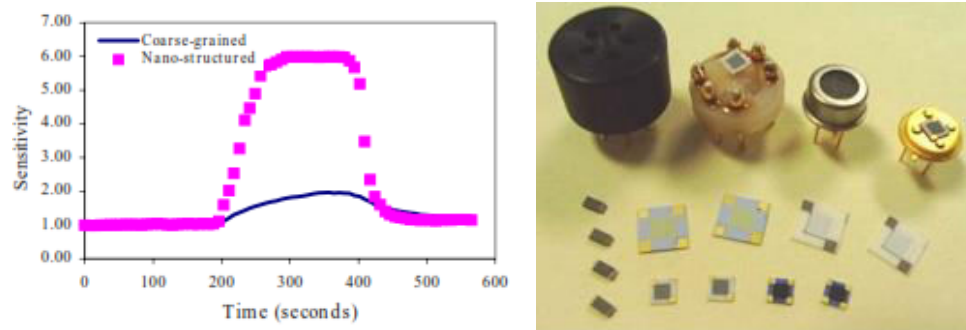


Figure 1. Effects of Particle Size of Gas Sensors [1]

The role of the grain size on the sensor response, for example, Fig. 1, shows the effect of the initial size of the particles on the NO_x sensor, in the form of a milligrams powder ($> 1 \mu\text{m}$), and one being a nano powder ($< 100 \text{nm}$). The increasing of the sensor sensitivity is shown by nanostructured sensors, in addition to the nano sensors are able to respond more quickly. In this paper will be discussed about the process of nano material synthesis using the base material MWCNTs (Multiwall Carbon Nanotubes). Each stage of the manufacturing process, tested to determine the detection potential sensitivity.

Some forms of CNTs that are often used as feedstocks for the manufacture of nano sensors consist of 2, namely Singlewall Carbon Nanotubes (SWCNT) [2-6] and Multiwall Carbon Nanotubes (MWCNTs) [7-17]. The use of these nano sensors also varies, some nano sensors are used for the detection of microbial contaminants [18], gas detection such as hydrogen [1,19], air humidity [7,9,20], formalin [2,16,21,22,23]. Nanomaterials have a high surface area so that if used as a sensor will have a better response. However, the nanotubes in the CNT material have not been able to respond well if they have not been activated by breaking the carbon bonds on the tube wall and attached to the amino group as material functionalization so it is easy to interact with the gas. Although this material provide safe detection of gas, it still have some limitations and challenges such as low relative resistance changes and selectivity, long-term instability and so on. In this paper functionalization of MWCNTs with amino groups is conducted and characterized.

2. Experiment

Nano sensor raw materials, which are pure MWCNTs are treated using concentrated acid solution [7]. MWCNTs is produced from the process of spray pyrolysis between iron (Fe) and Carbon (C), where carbon produced by 80%, has a diameter of 20-30 nm used in our experiments. MWCNTs are then refluxed for 2 stages, followed by filtration of the acid mixture. The residue is again suspended in deionized water. This process is repeated for several times until the pH of the solution reaches neutral. The acid treatment can greatly increase the solubility of MWCNTs by introducing the carboxylic functional group ($-\text{COOH}$) to the side wall and the tip of MWCNTs [9]. In this experiment, a multiwalled carbon nanotubes (MWCNTs) functionality process with an amino group (MWCNTs- NH_2) was performed under one reaction. Some of the NH_2 group functionalization procedures in MWCNTs, carried out by some researchers, are using AlCl_3 and CHCl_3 [13], using SOCl_2 [24] or variations between HNO_3 and SOCl_2 [16] as shown on figure 2 and figure 3.

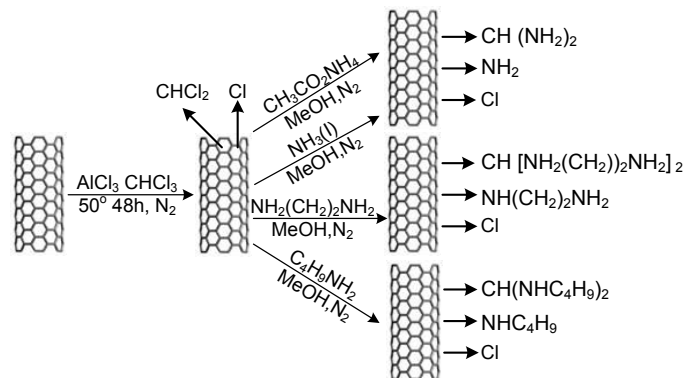


Figure 2. Functionalize procedure for chemically attachment of NH_2 and amino groups on MWCNTs with AlCl_3 and CHCl_3 [13].

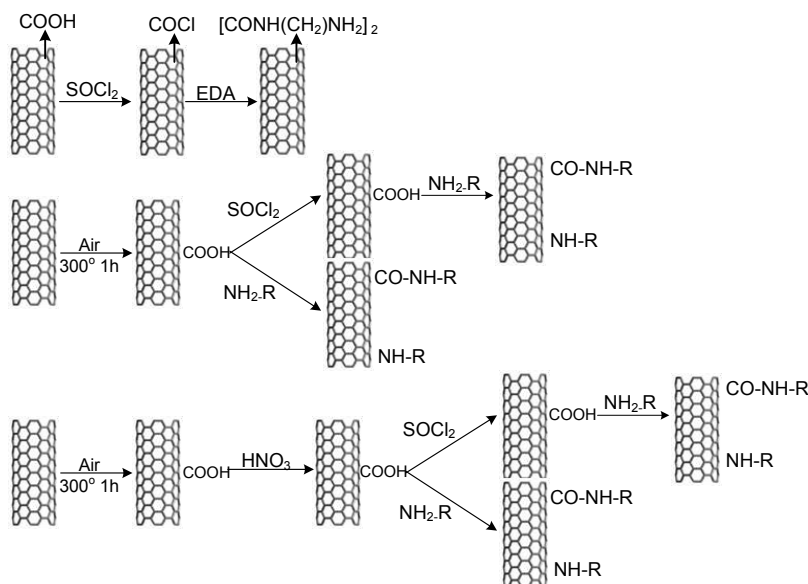


Figure 3. Functionalize procedure for chemically attachment of NH_2 and amino groups on MWCNTs with HNO_3 and SOCl_2

Shen et.al studied the functionalization of MWCNTs with amino groups carried out through the experimental steps, ie carboxylation (MWCNTs), acylation (MWCNTs-COOH) and amidation (MWCNTs-NH₂) [25]. Figure 4 shows the steps of the experiment.

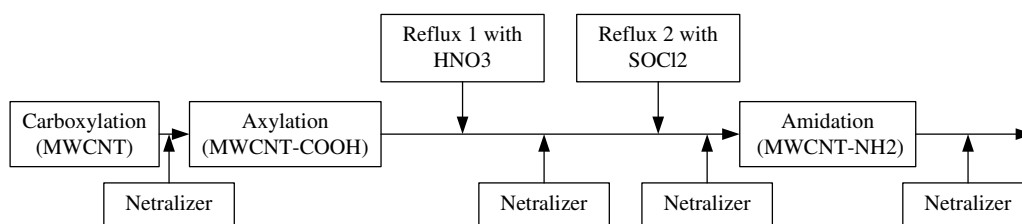


Figure 4. Research steps

1. Carboxylation

Composition: Ferrosine / Benzene (1:17).

Process: Mixing ferrosine and benzene as precursor by using a magnetic stirrer to form a homogeneous mixture, then injected into a pyrolysis spray tube by using a temperature of 900°C with flows of argon gas up to 30 minutes. The argon gas serves as a gas for the reduction of oxygen. In the reaction using the spray pyrolysis method, it is performed in the absence of oxygen (anaerobe), because the oxygen that enters the reaction at high temperatures will burn precursor and MWCNTs is not formed. Neutralization process is used to neutralize PH from MWCNTs to 7 by washed with water and filtered using filter paper and vacuum pump, then dried by oven at 60°C for 24 hours.

2. Acylation

The manufacture of MWCNTs-COOH is carried out through a reflux process between MWCNTs and HNO₃.

1. Composition: MWCNTs / HNO₃ (1:200).

Process: HNO₃ and MWCNTs are placed on Erlenmeyer tube, heated by hot-plate for 6 hours with temperature of 60°C. This process is used to create defects in MWCNTs walls. The defect that is used to attach a cluster that serves to provide response and reaction to interference from outside. The wall will be plastered with NH₂ for the sensors, where NH₂ reacts with formalin. The neutralization process is used to neutralize pH from MWCNTs-COOH to pH 7, ie. by means of abrasives, then filtered using filter paper and vacuum pump, then dried by oven at 60°C for 24 hours. Next step is followed by chlorination by reflux with SOCl₂.

2. Composition: MWCNTs-COOH / SOCl₂ (1:320).

Process: SOCl₂ and MWCNTs-COOH are placed on Erlenmeyer tube by heating using hotplate for 5 hours with temperature 70°C. SOCl₂ is metal. This process is used to coat the defective surface of MWCNTs-COOH by forming a Cl bond which will be replaced by NH₂. The neutralization process can be carried out by means of water, because SOCl₂ reacts to water, so the neutralization process is carried out using desiccators already filled with silica gel. The silica gel is placed until the colour is change, ie. for 24 hours, which is then filtered by means of a vacuum pump to separate the SOCl₂ that has been attached to MWCNTs-COOH and SOCl₂ which are non-bonded (residue). Next MWCNTs-COOH neutralized it's pH until pH 7, that is filtered by using filter paper and vacuum pump, then dried by using oven at 60°C for 24 hours, by filtering using filter paper and vacuum pump, and then dried using oven at 60°C for 24 hours.

3. Amidation

In the NH₂ attachment process to MWCNTs-COOH coated with metal from the SOCl₂ reflux process.

1. Composition 1: MWCNTs-COOH / Ethanadamine (1:50). Both are mixed and stirred using a magnetic stirrer and heated using a hot-plate for 4 hours at 40°C.
2. Composition 2: MWCNTs-COOH / Ethanadamine (1:50). Both were mixed and stirred using a magnetic stirrer and heated using hot-plate for 8 hours at 40°C.
3. Composition 3: MWCNTs-COOH / Ethanadamine (1:50). Both are mixed and stirred using a magnetic stirrer and heated using a hot-plate for 12 hours at 40°C.
4. Composition 4: MWCNTs-COOH / Ethanadamine (1:50). Both are mixed and stirred using a magnetic stirrer and heated using a hot-plate for 24 hours at 40°C.

From these compositions are expected to see the optimal time used to increase the number of NH₂ attached to MWCNTs-COOH. The neutralization process is used to neutralize PH from MWCNTs-COOH-NH₂ to PH 7, ie, by abrasives, then filtered using filter paper and vacuum pump and then dried by oven at 60°C for 24 hours.

3. Results and Discussions

Characterization using FTIR Spectroscopy aims to know the occurrence of bonds that occur before and after modification of carbon nanotubes. This characterization is performed on medium infrared between 400–4000 cm^{-1} . Test with FTIR result is in a comparison graph between waves (cm^{-1}) against the percentage of infrared ray transmittance. The graph provides information about the absorption of waves by the functional groups in the sample to excite the vibrations.

The results of FTIR CNTs analysis with CNTs oxidized nitric acid and CNTs oxidized by SOCl_2 show Fig. 4. In figure a, b, c show that the absorption of C=C groups in wavelength regions 2318.39, 2353.16 and 2351.23 cm^{-1} . The presence of absorption of C=C groups was formed from benzene by spray pyrolysis process. The reaction between benzene and ferrocene as a cathalis with high temperatures will occur covalent bonds C-C or C=C and produce carbides (carbon-carbon). The unstable carbides that are formed will tend to bind themselves in chains or rings, not only with a single bond (C-C) but also containing double bonds (C=C). This proves that CNT synthesis with this method has been successfully performed.

The results of the analysis of CNTs modified with oxidation of nitric acid (HNO_3) and thionyl chloride (SOCl_2) of the images (b and c) show the carboxylic acid characteristic bands C=O at peak regions 1672.28 and 1595.13 cm^{-1} , that identify carbonyl specific absorbance bands of CNTs. The bands are rather strongly shown in peaks between 1595.13 and 1672.28 cm^{-1} indicate the presence of aromatic compounds²⁶. In regions 3431.36 and 3427.51 cm^{-1} , there is a sharp band that indicate the CNTs shows the presence of the (-OH) group. The emergence of 1672.28 cm^{-1} wave absorption in C=O and at wave number 3431.36 cm^{-1} identifies the (-OH) bond, strongly suspected that carbon nanotubes contains a carboxyl functional (-COOH) groups.

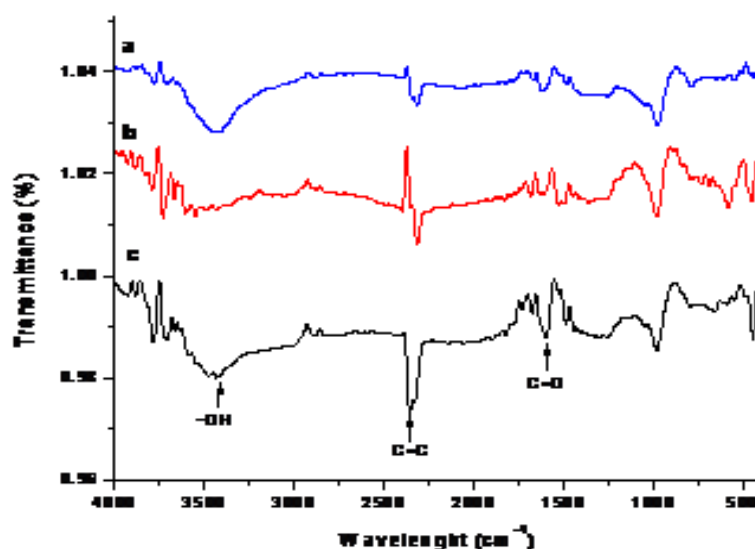


Figure 5. FTIR spectra of: (a) MWCNTs; (b) MWNTs-COOH; (c) MWCNTs-COCl

The analytical results with FTIR spectroscopy on CNTs before and after modified using ethanediamine showed different peaks (figure 6). Carbon nanotubes before modification do not show a clear peak whereas after modification (addition of ethanediamine) a peak that is not too sharp and has different wave numbers.

The result of the modified carbon nanotubes that have amine (CNTs-NH₂) group will be showed in presence of NH bonds at wave numbers 1597.06–1672.28 cm^{-1} . At the breeze of the (-OH) group is showed with 3427–3466 cm^{-1} which almost all of the samples possess. The presence of the (-OH) group formed due to CNT Oxidation functionalization using a strong acid (HNO_3) [27]. This assumption is strengthened in the presence of C=O groups at a wave shift of about 1672.28 cm^{-1} , that indicate an uptake of wave carboxylate groups.. The presence of the C=O group indicates that the sample has a

carbonyl group due to the oxidation treatment. In addition, there is a C-N bond showing that the sample contains an amine group, in a tune at a wave shift of about 975-1440.83 cm^{-1} .

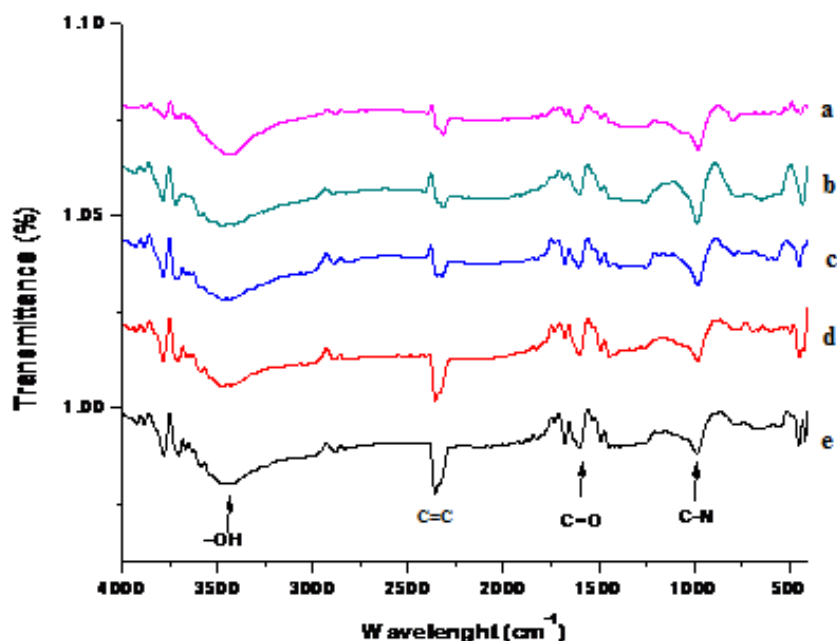


Figure 6. FTIR spectras of (a) pure MWCNTs; (b) MWCNTs-NH₂ 4 hours (c) MWCNTs-NH₂ 8 hours (c) MWCNTs-NH₂ 12 hours (d) MWCNTs-NH₂ 24 hours.

The result of characterization of modified Carbon Nanotubes (CNTs) using Scanning Electron Microscopy (SEM) is used to obtain images morphological of modified carbon nanotubes. Figure 7 show CNTs image results without modification, CNTs with nitric acid oxidation, CNTs with SOCl₂ oxidation and CNTs after modification with addition of ethanediamine.

In figures (7a), (7b), and (7c) we can see some yarns that just like fibers which indicate that CNTs have been formed. The morphological form of the tube is not uniform, the presence of clots also contain white spots. The white patches and dots are not representative of carbon nanotubes, but other materials of carbon nanotubes synthesis process are ferrocene metal catalysts. It shows that in carbon nanotubes there are still impurities, especially impurities from ferrocene catalyst. The size of CNTs diameter is estimated from SEM image with 10,000 times magnification that is between 20 - 60 nm. Based on the size of the diameter, the CNTs produced from the spray pyrolysis process is a type of Multi-walled Carbon Nanotubes (MWCNTs) instead of Single-walled Carbon Nanotubes because the difference between them can be determined by looking at the diameter size. SWCNTs typically has a diameter between 0.4 to 3 nm, whereas MWNT is between ~1.4 to 100 nm [28]. In figure (d) the modified oxidation CNTs with ethylenediamine for amine group formation exhibit a morphological form resembling a long tube which is more visible than before. The diameter of the CNTs is about 20-60 nm. In addition to the modified CNTs, there are still clumps around the tube that are slightly less regular than before. This shows that CNTs after added ethylenediamine are not from pure CNTs, but from CNTs that still contain impurities.

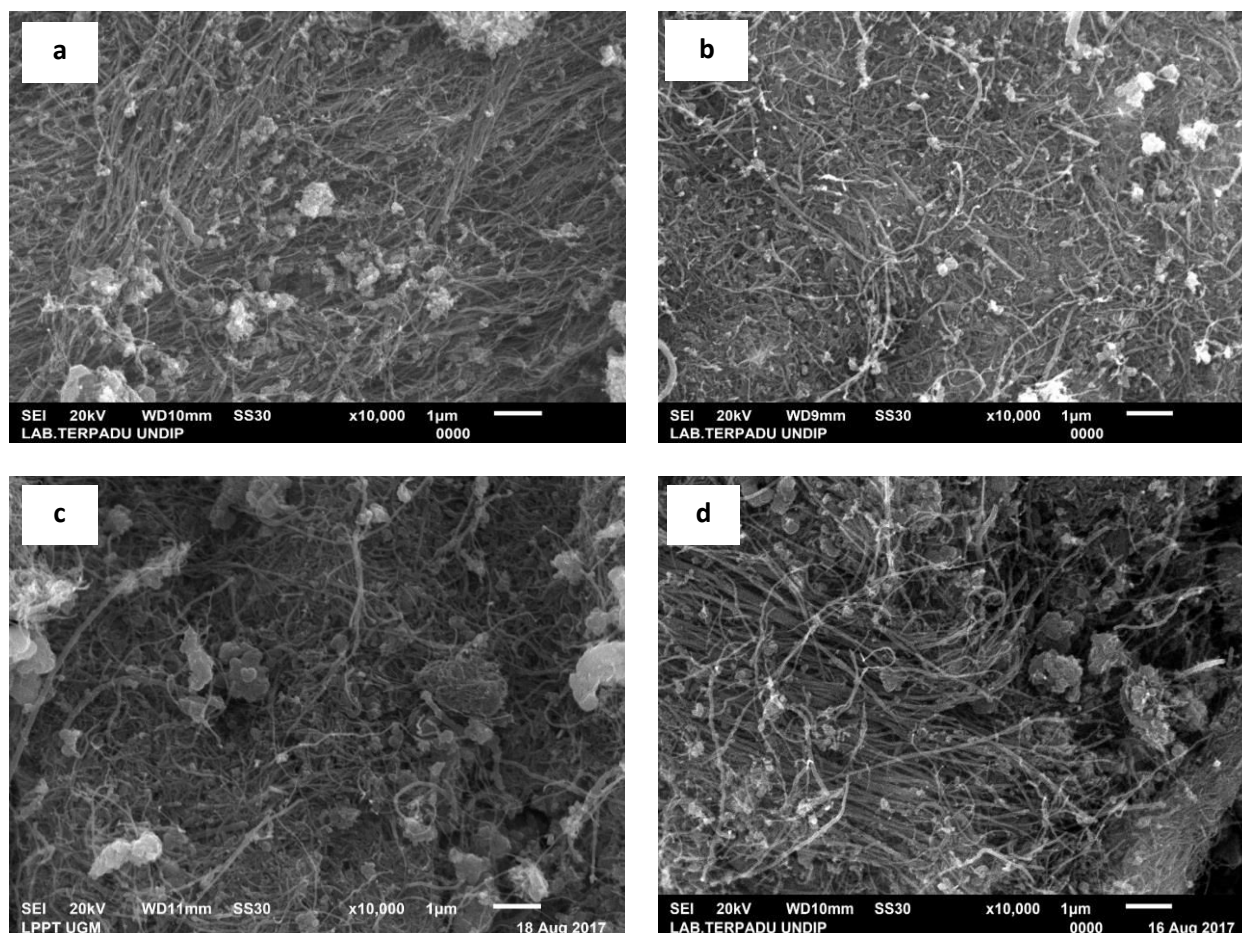


Figure 7. SEM images of (a) MWCNTs; (b) MWCNTs-COOH; (c) MWCNTs-COCl and (d) MWCNTs-NH₂

Table 1 shows element content on CNTs without modification and CNTs oxidation obtained some elements contained in the sample. The results of the analysis indicate the presence of elements contained in samples such as carbon (C), Oxygen (O) and iron (Fe). The elements of C and Fe are derived from the synthesis of pyrolysis spray from benzene and ferrocene catalyst, while O is derived from the outside air entering the quartz tube at the time of the injection of the precursor. The elements contained in the CNTs include C, O and Fe with different percentages. The result of the table showed that MWCNTs without modification did not decrease of the Fe which is 2.36% and after oxidation to 2.66%, after oxidized by SOCl₂ the percentage of atom decreased sharply to 0.99% and after added with ethylenediamine the percentage of Fe to 1.83%.

Table: EDS Data MWCNTs, MWCNTs-COOH, MWCNTs-COCl and MWCNT-NH₂ (t = 4 hours).

Perlakuan MWCNT	Unsur	Massa (%)	Mol (%)	Prosentase Atom (%)
MWCNT murni	C	87.54	97.68	97.64
	O	2.77	-	-
	Fe	9.68	2.32	2.36
MWCNT-COOH	C	86.15	97.38	97.34
	O	3.08	-	-
	Fe	10.77	2.62	2.66
MWCNT-COCl	C	82.44	97.38	89.50
	O	10.71	-	8.73
	Fe	4.24	2.62	0.99

MWCNT-NH ₂ (t =4 Jam)	C	88.32	96.89	93.78
	O	2.32	-	3.27
	Fe	8.09	1.91	1.83
	N	1.28	1.2	1.12

4. Conclusion

In this study MWCNTs materials have been functionalized by some chemical treatments to break bonds on CNT walls and form bonds with amino groups. The C=O bond at MWCNTs-COOH indicated by absorption at a wavelength of 1672.28cm^{-1} and O-H bond at 3431.36cm^{-1} . We found N-H groups at MWCNTs-NH₂ on the wavelength 1440.83cm^{-1} . In addition to the MWCNTs functionalization process, it can also automatically reduce Fe as an impurity derived from ferrocene sources during its fabrication. The SEM analysis indicates that products have a tubular surface morphology.

Acknowledgments

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