

Mono-Dispersed Pt/MWNTs: Growing Directly on Multiwall Carbon Nanotubes (MWNTs) Using NaBH_4 as Reducing Agent for Component of Proton Exchange Membrane Fuel Cell (PEMFC)

Sudirman¹, Wisnu Ari Adi¹, Emil Budianto², Deni Shidqi K.³, Rike Yudianti³

¹Centre for Science and Technology of Advanced Materials – National Nuclear Energy Agency, Kawasan Puspiptek Serpong, Tangerang Selatan, Banten 15314, Indonesia

²Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Indonesia, Depok 16424, West Java, Indonesia

³Research Center for Physics- Indonesian Institute of Science, Kawasan Puspiptek Serpong, Tangerang Selatan, Banten 15314 - Indonesia

Correspondence: Sudirman, Centre for Science and Technology of Advanced Materials – National Nuclear Energy Agency, Kawasan Puspiptek Serpong, Tangerang Selatan, Banten 15314, Indonesia.

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Abstract

Synthesis of mono-dispersed Pt/MWCNTs has been performed. Platinum nanoparticles (Pt NPs) were grown directly on multiwall carbon nanotubes (MWCNTs) through sol-gel method using NaBH_4 as reducing agent. 120 mg of activated MWCNT were weighed and then incorporated into the mixture (1) and sonicated for 2 hours to form the mixture (2). H_2PtCl_6 was weighed as much as 90 mg and dissolved into 45 mL of ethylene glycol until formed mixture (3). Solution (3) was dropwise every 3 seconds into the mixture (2). After that the mixture was distilled for 12 hours at a rate of 450 rpm. Subsequently the mixture was sonicated for 3 hours, then checked its pH, adjusting the desired pH to 4, 7, or 13 using the mixture 2M NaOH-ethylene glycol. The tests include SEM, EDS, XRD, and TEM for the morphologies and microstructures of the mono-dispersed Pt/MWCNT. The result of SEM observation and the analysis of the element using EDS found that the composite sample looked homogenous and contained element of C (MWCNT) and Pt (platinum). From the XRD shows that the composite Pt/MWCNT of the product synthesized without the reducing agent consists of three phases, namely C (MWCNTs), Pt (platinum), and H_2PtH_4 , while the product synthesized using NaBH_4 reducing agent consist of two phases, namely C (MWCNTs) and Pt (platinum). The TEM image shows that the Pt NPs are spherical in size ~ 5 nm. Pt NPs appear to be attached on MWCNTs, either agglomerated or dispersed on the surface of MWCNTs. This paper will be compared between Pt/MWCNTs synthesis results with and without using NaBH_4 reducing agent, as well as dispersed Pt NPs on MWCNTs.

Keywords: synthesis, composite, Pt/MWCNT, mono-dispersed, and morphology

1. Introduction

Platinum-based electrocatalyst with carbon black (Vulcan XC-72) as an electrocatalytic support is widely used as a PEMFC component, in which the reduction of oxygen and hydrogen oxidation will occur (W, Bi et al., 2007; PJ Ferreira et al., 2005; M Umeda et al., 2005, B. Lim et al., 2010). However, this research will be done the development of electrocatalyst support materials to improve the performance of the electrocatalyst. One of them is replacing carbon black with carbon nanotube (CNT) because they have better characteristics than carbon black (S. L. Knupp et al., 2007) as illustrated in Figure 1.

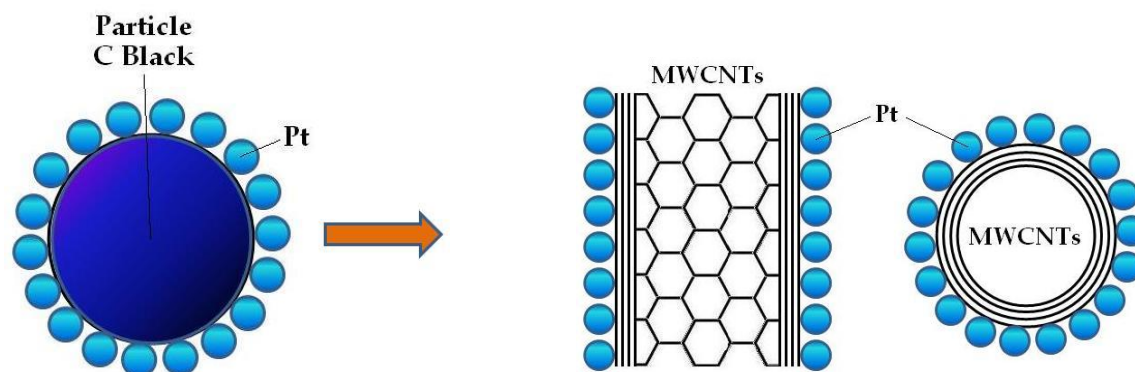


Figure 1. Illustration of the development of monodispersed Pt/C (carbon black) to Pt/MWCNTs

CNT is one of the carbon materials that has characteristics with specific surface area, electronic properties and higher chemical stability than other carbon materials so it has a prospect as a support catalyst that can replace carbon black (Vulcan-XC72) which is currently widely used (JP Singh Et.al., 2008; MH R ümmeli et.al., 2007). The advantages of CNTs as electrocatalytic support compared to carbon black (Vulcan72) are expected to increase electrocatalytic efficiency by increasing power density up to 47% compared to carbon black (S. L. Knupp et.al., 2007).

Based on the advantages of this CNT is expected to reduce the use of platinum which will reduce the cost of commercialization PEMFC up to 60% by using hydrogen-oxygen (J. P. Singh et.al., 2008). This prospect is one of the reasons for using CNTs as an electrocatalyst support in addition to enhancing its functionalization as a nanomaterial. The problem is that CNTs include inert material which is difficult to disperse in solution because of high Van der Waals energy (V. Djordjević et al., 2006). This is due to CNT impurity in the form of metal catalyst, amorphous carbon and graphite nanoparticles. To overcome this, the method of purification, functionalization and the addition of surfactants (surface active agents) is expected to increase the dispersity and hydrophilic properties of CNTs so as to interact with other particles. There are two types of CNTs sold in the market, namely multi wall carbon nan tubes (MWCNTs) and single wall carbon nano tubes (SWCNTs). MWCNTs are much cheaper than SWCNTs.

Development of purification techniques and MWCNT activation can be done by chemical reactions. The purification technique that has been done, succeeded in increasing the purity from 93.4 to ~ 99%. Refined MWCNTs (99%) were functionalized to form active surfaces on the side wall MWCNTs (R. Yudianti et.al., 2010; R. Yudianti et.al., 2010). The study of the effects generated during the functionalization and purification process of the functional density of the formed group and CNT surface defect that has occurred has been carried out (R. Yudianti et.al., 2011).

This research will be carried out the electrocatalytic preparation by depositing platinum on MWCNTs surface with hexachloroplatinic acid as precursors. The platinum deposition on MWCNT wall will be carried out using ethylene glycol as both reducing agent and stabilizer (R. Yudianti et.al., 2010). The integration of membranes as electrolytes and catalysts will be carried out by filtration techniques which will simultaneously orient some CNTs more easily and simpler than chemical vapor deposition (CVD) techniques, electric fields or magnetic fields. During this time, the techniques to orient the CNTs are mostly done by using electric fields (Cheol Park et.al., 2009) and magnetic fields (Ludovico Megalini et.al., 2010). In addition, further development is by using the reducing agent NaBH₄ as a stabilizer in the form of ethylene glycol. In addition, the pH conditions of the solution will also be varied on the addition of the reducing agent.

2. Materials and Methods

The synthesis of Pt/MWNTs was performed by using the sol-gel method. The procedure of making monodispersed Pt/MWNT consists of two stages. The first stage was activation of MWNTs, then proceed second stage was synthesis Pt/MWCNTs with and without using NaBH₄ reducing agent.

Activation of MWNTs

1.2 grams of MWCNTs were inserted into a three-neck flask and mixed with 200 mL solution consisting of 50 mL of H₂SO₄ 96% and 150 mL of HNO₃ 65%. The mixture is then sonicated for 1 hour. After that the mixture is refluxed for 6 hours at a temperature of 100 °C in an oil bath to allow MWCNTs to be activated, then cooled at room temperature and diluted until the pH is not very acidic. After the temperature is stable, it is filtered using a vacuum milipore. The filter used is a 1 micron PTFE. The filtered MWCNTs are neutralized with demineralization water, then dried in a gear oven

at 45-50°C. After drying, MWCNTs are weighed and crushed until they are ready to be used for the synthesis of Pt/MWCNTs composites.

Synthesis of Pt/MWCNTs with pH variation without and using NaBH₄ reducing agent

225 mg of sodium dedocyl sulfate was prepared in 90 mL of ethylene glycol, the mixture was inserted into a three-neck flask and then sonicated for 1 h and mixture (1) was obtained. 120 mg of activated MWCNT were weighed and then incorporated into the mixture (1) and sonicated for 2 hours to form the mixture (2). H₂PtCl₆ was weighed as much as 90 mg and dissolved into 45 mL of ethylene glycol until formed mixture (3). Solution (3) was dropwise every 3 seconds into the mixture (2). After that the mixture was distilled for 12 hours at a rate of 450 rpm. Subsequently the mixture was sonicated for 3 hours, then checked its pH, adjusting the desired pH to 4, 7, or 13 using the mixture 2M NaOH-ethylene glycol. After the pH is adjusted, the mixture is refluxed for 3 hours at 130 °C in an oil bath with N₂ gas to drive O₂ gas. The reflux results are cooled to room temperature and then the pH of the mixture is reduced up to pH of 2. After the pH reaches 2, the mixture is stirred for 12 hours using magnetic stirrer at a rate of 250 rpm. Thereafter, mixtures of reducing agent and ethylene glycol were prepared with the compositions of 120 mg and 30 mL (4: 1), respectively. The reducing agent used is NaBH₄ (varied in each pH condition). The ethylene-glycol reducing agent is dropped into the mixture every 3 seconds. When fully mixed, the mixture is distilled for 4 hours. Subsequently the electrocatalytic mixture formed was filtered using a vacuum millipore. The filter used is also 1 micron PTFE. The stages are continued by neutralization and washing using demineralization water in a vacuum millipore. After neutral, the filtered electrocatalyst is dried in a gear oven at 45-50°C until dry and then weighed and crushed until obtained fine powders.

Characterization of Pt/MWCNTs composite

The surface morphology and element identification of the sample were analyzed by using the JEOL scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), respectively. While the phase identification of the all of samples were characterized using X-ray diffraction (XRD) Pan Analytical brand type PW1710 with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The parameter structure analysis of the sample is calculated based on analysis using the Rietveld method applying GSAS program (general structure analysis system) [17]. The dispersed particle morphology of Pt NPs on MWCNTs from differences in pH of 4, 7 and 13 was observed using a transmission electron microscope (TEM) JEOL brand.

3. Results and Discussion

The synthesis result of Pt/MWCNTs without using this reducing agent was carried out by varying the pH of 4, 7, and 13. Then the all of samples were observed the surface morphology by using SEM to find out the surface homogenization of sample microscopic scale. In addition, the combination with EDS will be obtained by the analysis of each sample element so that the number of mass fractions of the elements contained in the sample is known. Further analysis using X-ray diffraction in order to know the phase composition formed in the sample. Finally we will see disperse Pt on MWCNTs using TEM. Figure 2 shows the surface morphological observations of the sample with variations in pH of 4, 7, and 13.

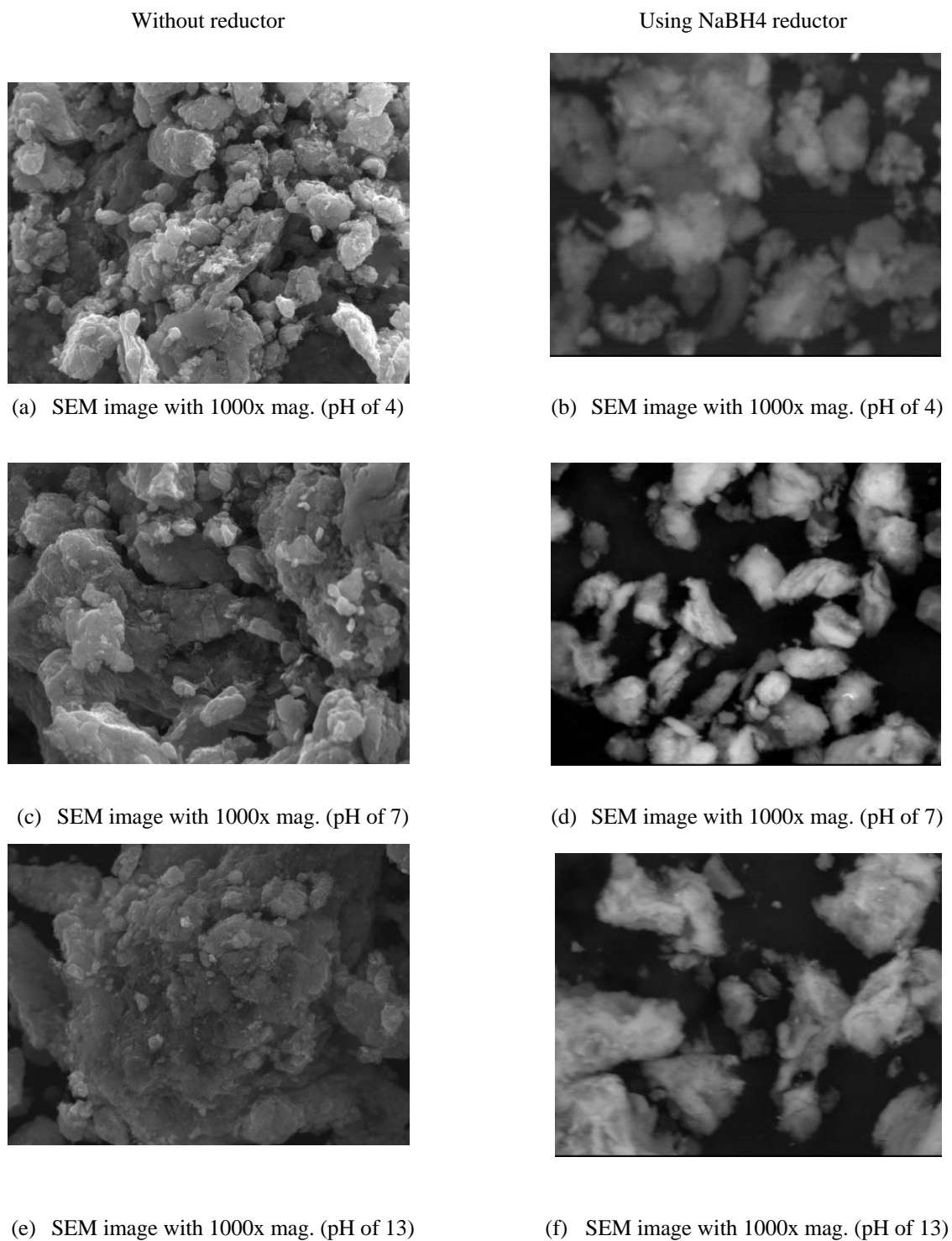
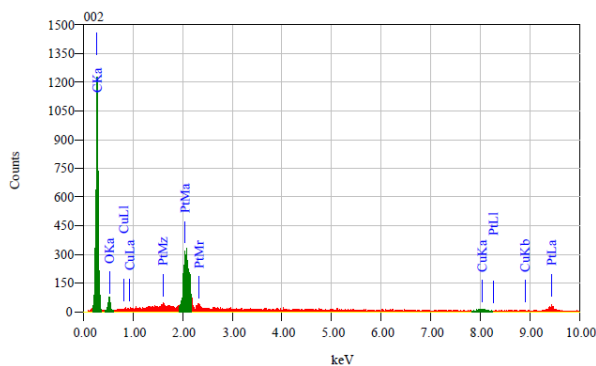
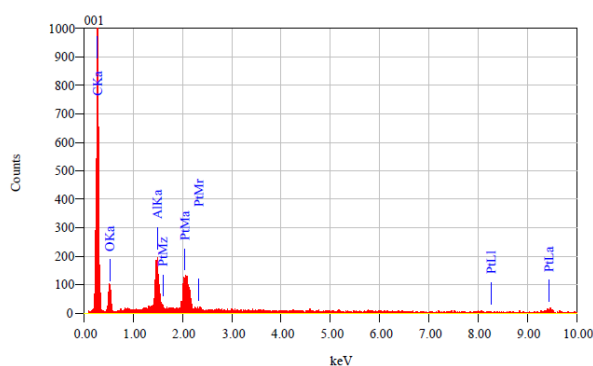


Figure 2. Morphology and EDS analysis of Pt/MWCNTs

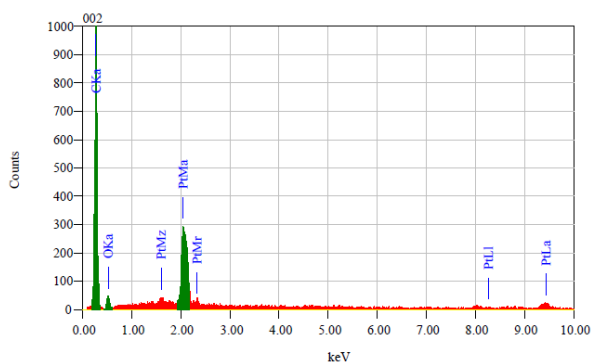
The microstructure analyses shows that the particle shapes was aggregate with the varied particle sizes distributed homogeneously on the surface of the samples. Meanwhile the result of element analysis in detail is shown in Figure 3.



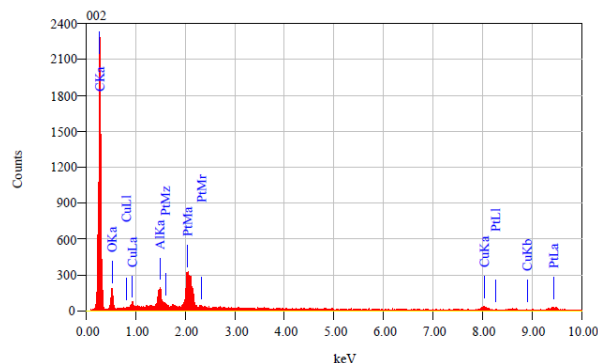
(a) Analysis result of elementer (pH of 4)



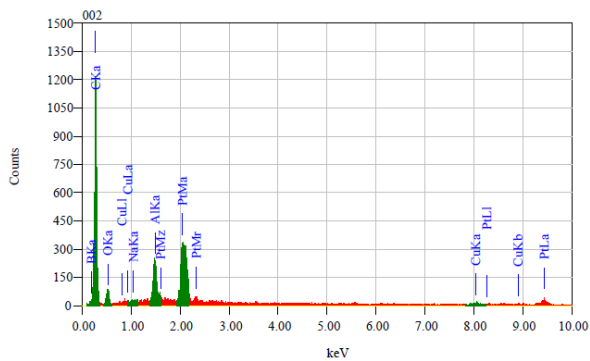
(b) Analysis result of elementer (pH of 4)



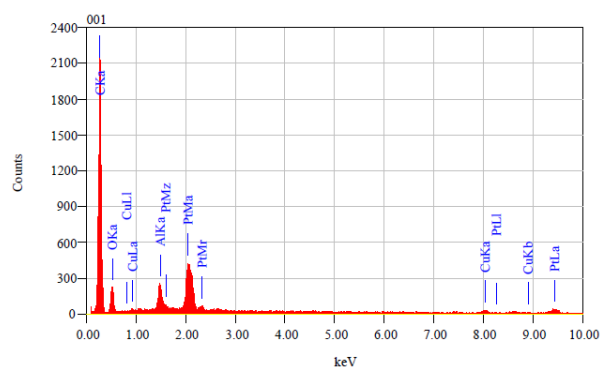
(c) Analysis result of elementer (pH of 7)



(d) Analysis result of elementer (pH of 7)



(e) Analysis result of elementer (pH of 13)



(f) Analysis result of elementer (pH of 13)

Figure 3. EDS analysis of Pt/MWCNTs

In Figure 3 EDS spectra shows electron discharge on dispersive energy of 0.277 keV, 0.525 keV, and 2.048 keV, respectively identified C, O, and Pt elements. Based on the results of the elementary analysis shows that the majority sample contains C (carbon) element of 69-74 wt%, O (oxygen) of 8-10 wt%, and Pt (platinum) of 15-18 wt%. The details are shown in Table 1. However, these results need to be confirmed using XRD data to know that the phase compositions of Pt/MWCNTs composites are well established.

Table 1. Detail of element analysis by using EDS

Element	E (keV)	Mass Fraction (wt %)					
		Without reductor			Using NaBH ₄ reductor		
		pH 4	pH 7	pH 13	pH 4	pH 7	pH 13
C (carbon)	0.277	72.63	73.54	69.02	71.56	66.52	67.16
O (oxygen)	0.525	9.58	8.84	10.27	17.37	17.89	14.17
Pt (platinum)	2.048	17.79	17.62	17.85	11.07	15.59	18.67
Na (sodium)	1.041	ND	ND	2.86	ND	ND	ND

Figure 4 shows the results of the X-ray diffraction pattern of Pt/MWCNTs composite samples with variations in pH of 4, 7, and 13.

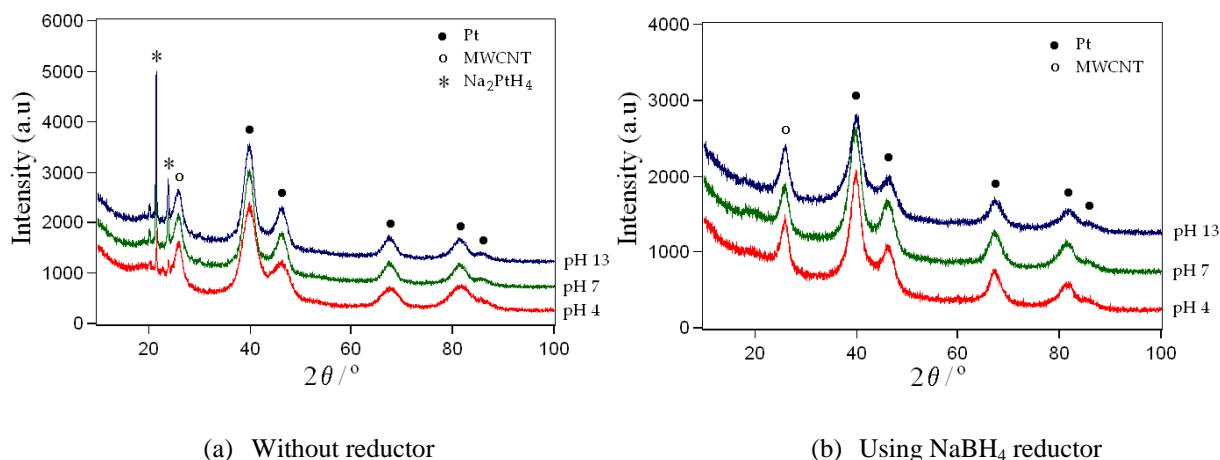


Figure 4. X-ray diffraction pattern of the Pt/MWCNT with variations in pH of 4, 7, and 13

The X-ray diffraction profiles of Pt/MWCNTs composite are shown in Figure 4 in which respective profiles in pH of 4, 7, and 13 are compared. It is shown that the three diffraction patterns exhibit a pattern different between ones each other.

Based on the results of phase identification (Fig. 4) appears that the reaction has been formed three phase namely Pt (platinum), C (multi wall carbon nanotube) and Na₂PtH₄ (sodium platinum hydride). Figure 5 is a qualitative analysis of the X-ray diffraction pattern of Pt/MWCNTs composite samples. It appears that samples of Pt/MWCNTs composite synthesized without using reductors are still found in other phase and the phase is identified as Na₂PtH₄ phase. The peaks of Na₂PtH₄ phase are higher along with the increase in pH. This is thought to be derived from an imperfect reaction at the time of formation of the Pt phase. While qualitative analysis of Pt/MWCNTs composite sample using NaBH₄ reductor obtained X-ray diffraction pattern consisting of two phases, namely C and Pt phase. It's means that the composite sample of Pt/MWCNTs synthesized by using this NaBH₄ reductor has been in accordance with the desired. X-ray diffraction profile both at pH 4, 7, and 13 have the same pattern. However, X-ray diffraction measurement results required quantitative analysis using GSAS software. Thus required further analysis to determine the changes of the crystal structure parameters, the amount of mass fraction formed, and fitting quality as shown Figure 5. Figure 5 shows the results of refinement X-ray diffraction pattern of the Pt/MWCNTs composite with variations in pH of 4, 7, and 13. Qualitative and quantitative analysis refers to the ICDD-JCPDS with the card number (ICDD: 01-0640), (ICDD: 04-0802) and (ICDD: 45-0987) respective for phases of MWCNTs, Pt and Na₂PtH₄.

Figure 5 shows the results of refinement of X-ray diffraction pattern of Pt/MWCNTs composite samples with and without using NaBH₄ reductor in pH of 4, 7, and 13.

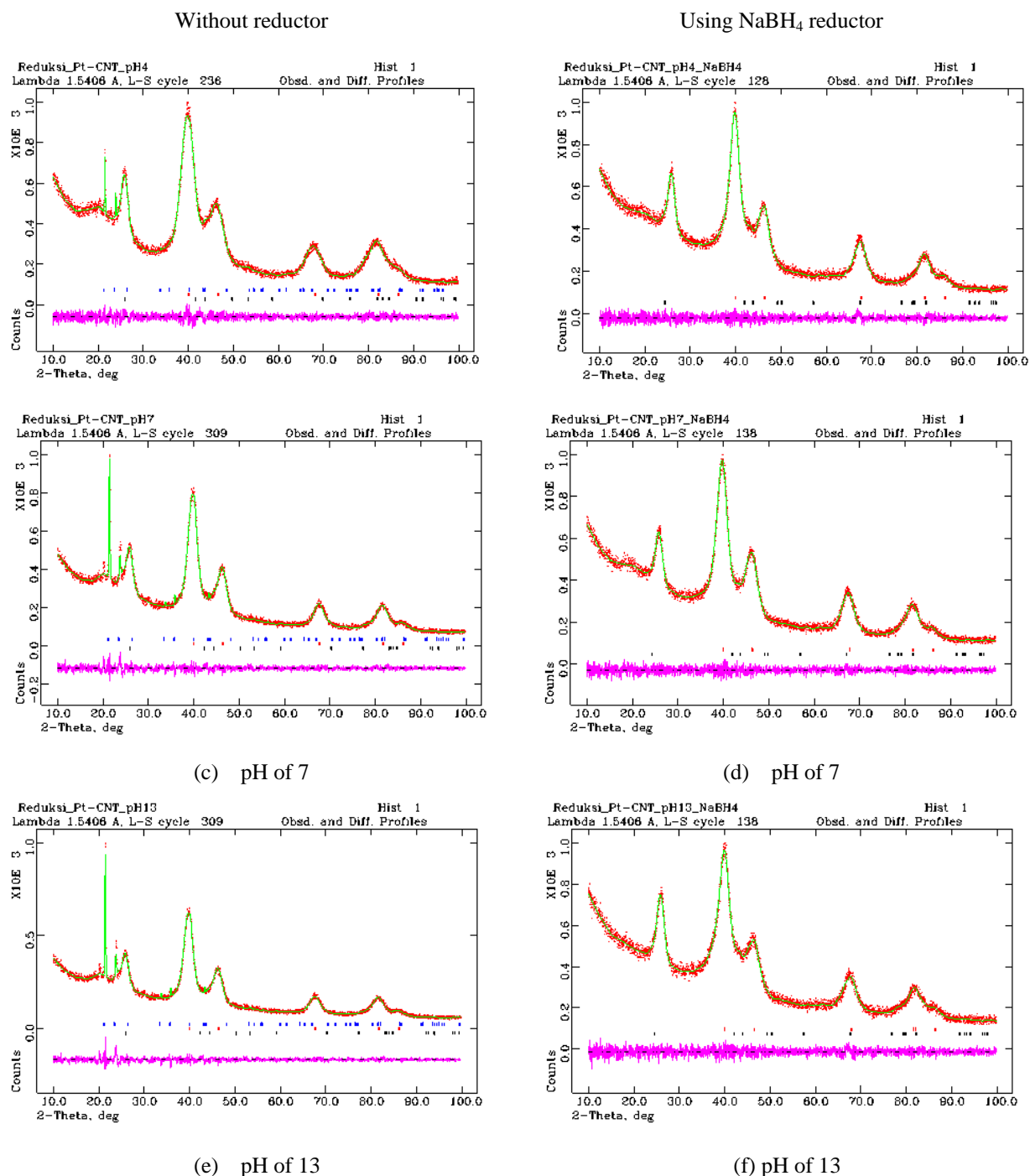


Figure 5. The refinement results of XRD pattern of the Pt/MWCNTs

The refinement of XRD profile for Pt/MWCNTs composite as shown in Figure 5 appears that the fitting X-ray diffraction profile has a very good fitting quality with the criteria of fit (Rwp) and goodness of fit (χ^2) in accordance with the agreement (Toby, 2001). Rwp is the weight ratio of the difference between the XRD pattern of observation and calculation (ideal value of Rwp < 10%). Meanwhile χ^2 (chi-squared) is the ratio of the XRD pattern of observation results comparable with expectations (ideal value of $1 < \chi^2 < 1.3$). The refinement results of x-ray diffraction pattern confirmed that the sample of synthesis without using a reductor consisted of three phases, namely C, Pt, and Na_2PtH_4 phase, while the synthesized sample using NaBH_4 reductor consisted of two phases, namely C and Pt phase. C phase has hexagonal structure with space group of R-3c, Pt phase has cubic with space group Fm3m, and Na_2PtH_4 phase has tetragonal structure with space group I4/mmm. The complete summary of the results of X-ray diffraction pattern of Pt/MWCNTs composite with variations in pH of 4, 7, and 13 for all of samples are shown in Table 2 and 3.

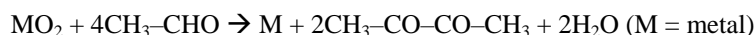
Table 2. The value of structure parameters, criteria of fit (R_{wp}), goodness of fit (χ^2) and the mass fraction of phase formed in the Pt/MWCNTs composite without reductor with variations in pH of 4, 7, and 13

Sample	Phase	Lattice parameter (Å)			V (Å ³)	Density (g/cm ³)	Fraction wt%	R_{wp} (%)	χ^2
		<i>a</i>	<i>b</i>	<i>c</i>					
pH 4	MWCNTs	2.505(1)	2.505(1)	6.874(3)	37.37(4)	4.269	43.07	4.11	1.05
	Pt	3.893(3)	3.893(3)	3.893(3)	59.0(1)	21.947	52.49		
	Na ₂ PtH ₄	5.310(1)	5.310(1)	6.734(3)	189.94(6)	3.883	4.44		
pH 7	MWCNTs	2.469(1)	2.469(1)	6.868(3)	36.26(4)	4.400	39.02	4.66	1.04
	Pt	3.913(1)	3.913(1)	3.913(1)	59.94(6)	21.619	52.25		
	Na ₂ PtH ₄	5.357(2)	5.357(2)	6.766(4)	194.2(2)	3.803	8.74		
pH 13	MWCNTs	2.468(1)	2.468(1)	6.869(3)	36.24(4)	4.405	38.49	4.88	1.04
	Pt	3.912(2)	3.912(2)	3.912(2)	59.94(5)	21.628	50.36		
	Na ₂ PtH ₄	5.346(3)	5.356(3)	6.767(7)	194.1(1)	3.817	11.14		

Table 3. The value of structure parameters, criteria of fit (R_{wp}), goodness of fit (χ^2) and the mass fraction of phase formed in the Pt/MWCNTs composite using NaBH₄ reductor with variations in pH of 4, 7, and 13

Sample	Phase	Lattice parameter (Å)			V (Å ³)	Density (g/cm ³)	Fraction wt%	R_{wp} (%)	χ^2
		<i>a</i>	<i>b</i>	<i>c</i>					
pH 4	MWCNTs	2.487(3)	2.487(3)	7.279(2)	39.0(1)	4.091	59.37	4.36	1.06
	Pt	3.912(1)	3.912(1)	3.912(1)	59.89(6)	21.635	40.63		
	Na ₂ PtH ₄	-	-	-	-	-	ND		
pH 7	MWCNTs	2.488(3)	2.488(3)	7.320(2)	39.2(1)	4.064	50.46	4.20	1.05
	Pt	3.910(1)	3.910(1)	3.910(1)	59.79(6)	21.672	49.54		
	Na ₂ PtH ₄	-	-	-	-	-	ND		
pH 13	MWCNTs	2.479(3)	2.479(3)	7.250(1)	38.6(1)	4.132	43.06	4.29	1.06
	Pt	3.904(1)	3.904(1)	3.904(1)	59.52(7)	21.768	56.94		
	Na ₂ PtH ₄	-	-	-	-	-	ND		

According to Table 2 shows that the refinement results of X-ray diffraction pattern has also a good fitting quality. Appear that based on the refinement of XRD pattern, still found Na₂PtH₄ impurity phase. When the metal salt is completely dissolved in an ethylene glycol alkaline solution, the intermediate metal oxide or hydroxide phase is formed. Then the dehydration reaction of glycerol to acetaldehyde occurs, resulting in a reduction reaction of metal oxide or hydroxide. This reduction reaction has a slow kinetics, particularly the formation of glycolate in the alkaline medium so that its metallic salt grains are reduced (Larcher et al. 2000).



It is mean that the Pt's formation reaction is not yet perfectly formed. In addition, the effect of pH can increase the mass fraction of Na₂PtH₄ formation. While the amount of Pt mass fraction decreases mainly at pH 13 because some Pt interact to form Na₂PtH₄ phase.

In Figure 6 is shown a morphological image of disperse Pt NPs on MWCNTs with particle sizes around ~ 5 nm resulting from Pt/MWCNTs synthesis without using reducing agent.

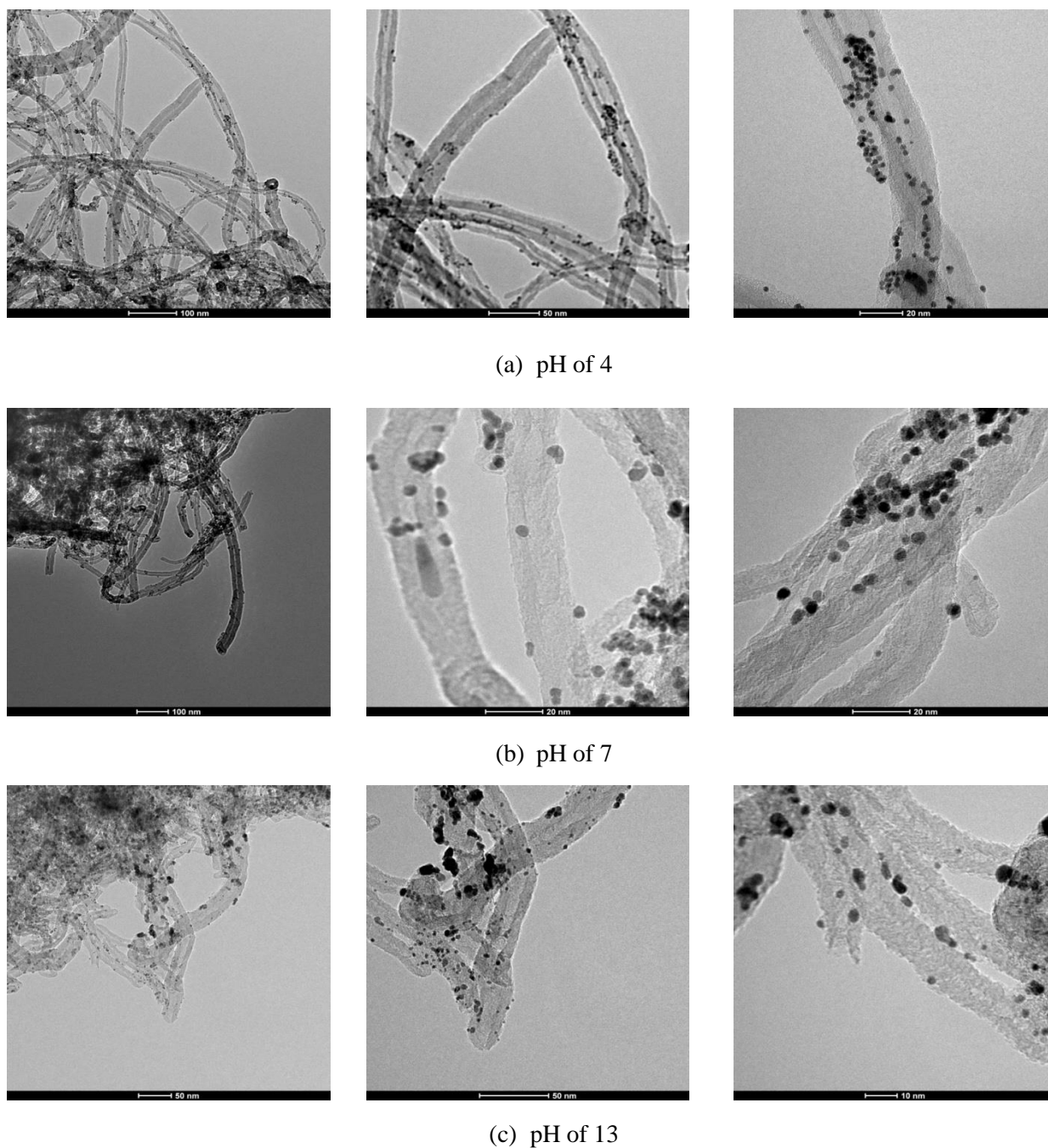
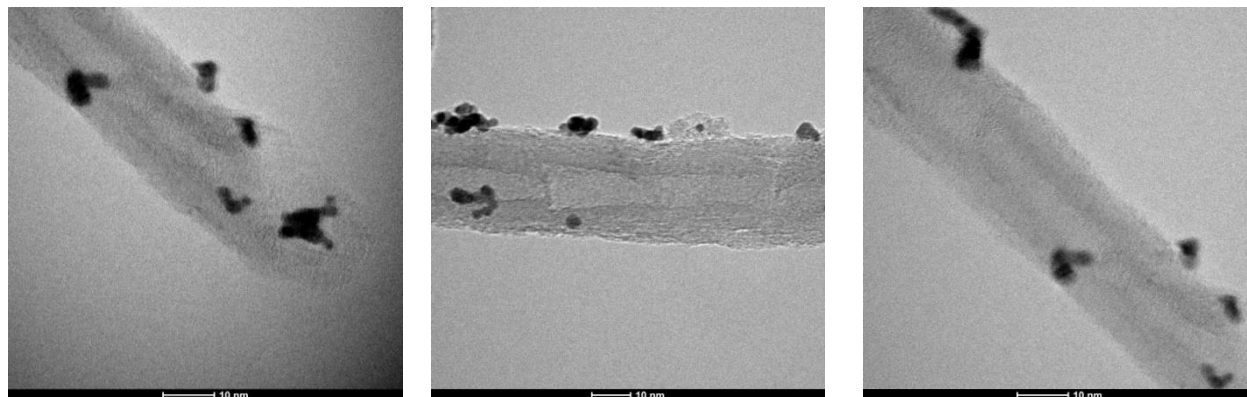


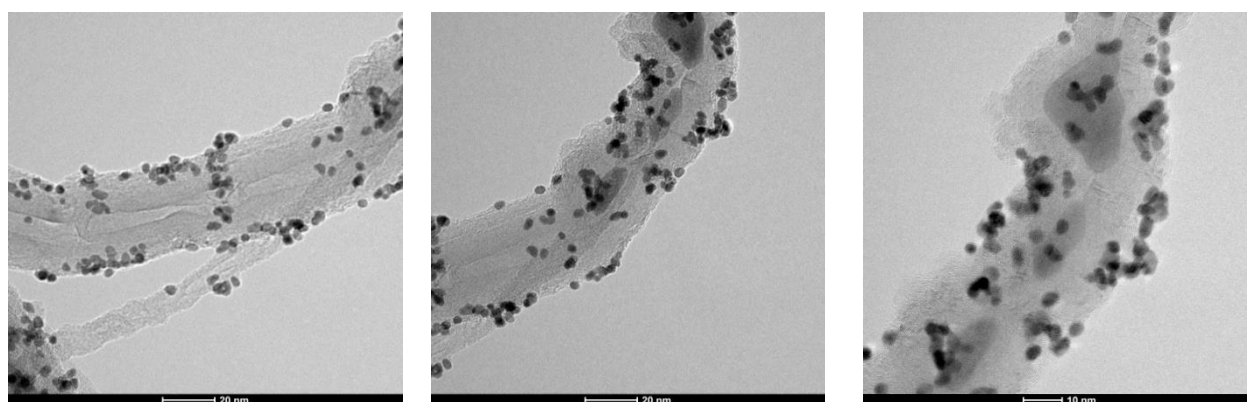
Figure 6. TEM image of morphology Pt/MWCNTs composite without using reductor

In Figure 6 is shown the morphology of Pt/MWCNTs composite without reducing agent according to pH of 4, 7, and 13. Based on the TEM image observations have been obtained the morphology of Pt NPs attached to MWCNTs. It appears that the Pt nanoparticles has been successfully formed. Although still appear there are several Na_2PtH_4 phase according to the analysis phases of X-ray diffraction pattern. Pt NPs formed has a diameter of ~ 5 nm. It's just that Pt NPs have not been well dispersed on the surface of MWCNTs. The result of morphological of Pt/MWCNTs composite with pH of 13 in which Pt NPs is also not well dispersed but slightly better compared with the pH of 4 and 7.

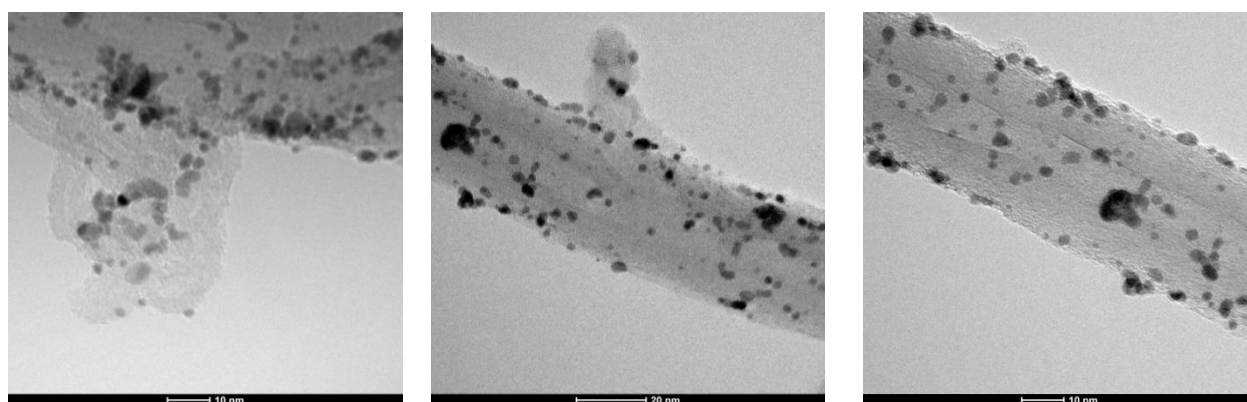
In Figure 7 is shown the morphology image of disperse Pt NPs on MWCNTs with particle sizes around ~ 5 nm resulting from Pt/MWCNTs synthesis using NaBH_4 reducing agent.



(a) pH of 4



(b) pH of 7



(c) pH of 13

Figure 7. TEM image of morphology Pt/MWCNTs composite using NaBH_4 reducing agent

In Figure 7 is shown the morphology of Pt/MWCNTs composite using NaBH_4 reducing agent according to pH 4, 7, and 13. Based on the TEM image observations have been obtained morphology of Pt NPs attached to MWCNTs.

In Figure 76 (a) is a morphology of Pt/MWCNTs composite with pH of 4. Pt NPs formed also has a diameter of ~ 5 nm. Pt NPs are well dispersed on the surface of MWCNTs. Figure 7 (b) is a TEM image to Pt/MWCNTs composite with pH of 7 which dispersed results of its Pt NPs attached to the surface of MWCNTs was much better compared with the results of the pH of 4. While Figure 3(c) is the result of morphological of Pt/MWCNTs composite with pH of 13 in which dispersed results of its Pt NPs attached to the surface of MWCNTs was much better compared with the results of

the pH of 4 and 7. This is due to the ligand glycolate, which acts as a surfactant, interacts weakly and adsorb the surface area of the crystalline platinum particles, so that the nanoparticles with a faceted orientation are easily formed. In addition, ethylene glycol agent is a weak reducer, it usually needs to be activated at 200 °C for 2 hours or heated by microwave, so that the reduction can be accelerated by using 2 reducers, namely ethylene glycol and NaBH₄ (Ingelsten et al., 2001)



In addition to accelerating the metal salt reduction reaction in order to be deposited into the carbon surface, according to Liu et al [1], sodium boron hydrate dissolved into ethylene glycol is used as an alkaline precipitant and forms the basis of macromolecules. Alkaline precipitant also serves as a protector its aggregation transition metal/noble like Pt into powder Pt.

4. Summary

Synthesis of Pt/MWCNTs has been performed both without and with using NaBH₄ reducing agent. Platinum nanoparticles (Pt NPs) were grown directly on multiwall carbon nanotubes (MWCNTs) through sol-gel method without and with using NaBH₄ as reducing agent. The microstructure analyses shows that the particle shapes was aggregate with the varied particle sizes distributed homogeneously on the surface of the samples. EDS spectra shows electron discharge on dispersive energy of 0.277 keV, 0.525 keV, and 2.048 keV, respectively identified C, O, and Pt elements. Based on the results of the elementary analysis shows that the majority sample contains C (carbon) element of 69-74 wt%, O (oxygen) of 8-10 wt%, and Pt (platinum) of 15-18 wt%. Pt/MWCNTs composite synthesized without using reductors appears that the reaction has been formed three phase namely C (multi wall carbon nanotube), Pt (platinum) and Na₂PtH₄ (sodium platinum hydride). Meanwhile Pt/MWCNTs composite synthesized with using NaBH₄ reductors appears that the reaction has been formed two phase namely C (multi wall carbon nanotube), Pt (platinum). The TEM morphological result of Pt/MWCNTs composite with pH of 13 in which dispersed results of its Pt NPs attached to the surface of MWCNTs and homogenous.

Acknowledgments

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Author Contribution

Sudirman and Rike Yudianti are main contributor. Sudirman and Rike Yudianti conceived and directed the project. Sudirman and Rike Yudianti supervised the synthesis of Pt/MWCNTs with pH variation without and using NaBH₄ reducing agent. Wisnu Ari Adi supervised XRD characterization. Deni Shidqi K. prepared and supervised TEM characterization. Sudirman and Emil Budianto prepared and supervised SEM-EDS characterization. Sudirman wrote and edited the manuscript. All authors discussed the data and contributed to the manuscript.

Competing interests

The authors declare no competing interests.

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