CHAPTER 2

EXPERIMENTAL PROCEDURE

This chapter provides the formation about chemical reagents and instruments which were used in this study. Moreover, experimental procedure of catalyst preparations, characterizations and structure analysis, and electrochemical measurements were explained in detail.

2.1 Chemical reagents and instruments

2.1.1 Chemical reagents

1) Hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) M.W. = 409.82 assay 37.5 % Pt basis, Sigma
2) Tetrachloroauric(III) acid trihydrate ($HAuCl_4{\cdot}3H_2O$) M.W. = 393.83 assay 99.5 % Au, Merck
3) Palladium (II) chloride ($PdCl_2$) M.W. = 177.30 assay 59 % Pd, Merck
4) Multi-Walled Carbon Nanotubes (MWCNTs) BAYTUBES C 150 P, Bayer MaterialScience
5) 10 wt. % Nafion solution, Fuel Cell Store
6) Sulfuric Acid (H_2SO_4) M.W. = 98.08 assay 97.5-98.5 %, Lab Scan
7) Nitric Acid (HNO_3) M.W. = 63.01 assay 65.0 %, Carlo Erba
8) Formic Acid (HCOOH) M.W. = 46.02 assay 99.6 %**,** Fischer Chemical
9) Potassium dihydrogen phosphate (KH_2PO_4) M.W. = 136.08 assay 99.5 %, Merck

10) Di-potassium hydrogen phosphate (K_2HPO_4) M.W. =174.18 assay 98 %, Merck
11) Tetrakis(hydroxymethyl)phosphonium chloride ($C_4H_{12}O_4P{\cdot}Cl$, THPC) M.W. = 190.57, Sigma
12) Sodium L-ascorbate ($C_6H_7O_6Na$) M.W. = 198.11 assay 98 %, Carlo Erba
13) Sodium hydroxide (NaOH) M.W. = 39.997 assay 97.0 %, Carlo Erba

2.1.2 Equipments and instruments

1) Fourier transform infrared spectroscopy (FTIR) 510, Nicolet
2) Powder X-ray diffraction (XRD), Rigaku Mini Fliex II
3) Transmission electron microscopy (TEM) JEM-2010, JEOL
4) Cyclic voltammetry (CV) CV-50W, BAS
5) Centrifuge PLC-012, Harmonic Series

2.2 Experimental procedure

In this research, the binary catalysts loaded multi-walled carbon nanotubes (MWCNTs) supports were prepared in two parts. In the first part, Au and Pt nanoparticles decorated on functionalized MWCNTs surface (PtAu-MWCNTs) were prepared by using THPC reducing reagent method and electrodeposition, respectively. PtAu-MWCNTs were achieved by electrodeposition Pt from Pt salt solution into Au-MWCNTs surface. The second part, preparation of PdPt-MWCNTs were performed with the ratio of palladium to platinum 4:0, 3:1, 1:1, 1:3 and 0:4 by weight denoted as Pd, Pd3Pt1, Pd1Pt1, Pd1Pt3 and Pt. The surface of MWCNTs support used in this research was modified by using mixture of acid oxidation method. THPC and sodium L-ascorbate were used as reducing agent for Pd and Pt catalyst preparations.

The experimental procedure of catalyst preparation is separated into two main parts. The first part explains about the functionalization of the carbon support where the metal loaded MWCNTs preparations are stated in the second part.

2.2.1 Functionalization of MWCNTs

MWCNTs were treated by using mixture of acid oxidation method. In this part, aqueous acid solution of H_2SO_4/HNO_3 mixture was used to modify MWCNTs surface. Firstly, 1 g of MWCNTs was immersed in 40 mL of a 3:1 mixture of concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3), sonicated for 1 h, and vigorously stirred at room temperature for 4 h. The reaction is shown in Figure 2.1. Then, the mixture was washed with a large quantity of deionized (DI) water until the neutral pH value of MWCNTs solution was approximately to pH 7 and then dried in the oven at 90 ˚C for 24 h. Finally, the treated carbon was investigated for functional groups by Fourier transform infrared spectroscopy (FTIR).

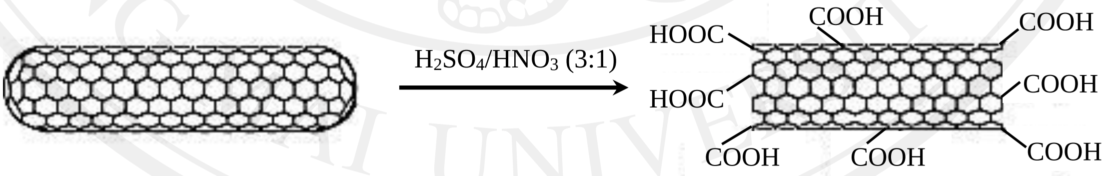

Figure 2.1 Functionalization of MWCNTs by H_2SO_4/HNO_3 mixture [46].

2.2.2 Catalyst preparations

In the first, THPC reduction method and electrodeposition were applied to prepare PtAu binary catalysts supported on functionalized MWCNTs (PtAu-MWCNTs) whereas THPC and sodium L-ascorbate reduction methods were applied to prepare PdPt binary catalysts supported on functionalized MWCNTs (PdPt-MWCNTs).

2.2.2.1 THPC reduction method for prepared Au-MWCNTs [45]

1 mL of a 1 M solution of NaOH, 2 mL of THPC solution (12 µL of 80% THPC in 1 mL of water), and 200 mL of DI water were mixed in a 250 mL flask and vigorously stirred for at least 15 min. A 4 mL of 1% aqueous $HAuCl_4$ was quickly added to the stirred solution, and then stirred further for another 30 min. Afterward, Au-MWCNTs were prepared by mixing 100 mg MWCNTs with 40 mL water and 10 mL THPC Au nanoparticles. The mixture was stirred for 4 h. Then, it was washed by water and dried in the oven. MWCNTs electrode can be prepared similar to above procedure but without Au nanoparticles.

2.2.2.2 Electrodeposition method for prepared Pt-MWCNTs and PtAu-MWCNTs [47]

Pt from the solution of 1 mM $H_2PtCl_6.6H_2O$ was used as a precursor for electrodeposition on MWCNTs and Au-MWCNTs. Voltammetric measurements were carried out with EDAQ potentiostat with a three electrode cell system. The prepared electrodes were employed as the working electrode. Ag/AgCl and Pt wire were used as reference and counter electrodes, respectively. The obtained MWCNTs, Au-MWCNTs, Pt-MWCNTs and PtAu-MWCNTs electrodes were examined for electrochemical and electrocatalytic characteristics.

2.2.2.3 THPC reduction method for prepared Pd-MWCNTs and Pt-MWCNTs

The PdPt-MWCNTs catalyst with 10% w/w overall metallic mass content was prepared by sequential reduction of $PdCl_2$ and then $H_2PtCl_6{\cdot}6H_2O$ precursors in two steps by a modified approach based on a previous report [28,45]. The preparation conditions for THPC reduction method were showed in Table 2.1. First, 90 mg functionalized MWCNTs were firstly dispersed into DI water under sonication for 30 min. Then, 6 mM $PdCl_2$ (0.1064 g of $PdCl_2$ was dissolved in mixture of 88 mL of DI water) and 12 mL of 50 mM of HCl solution (0.41 mL of the 12 M HCl reagent was added into about 50 mL of DI water, and then diluted the solution to 100 mL) was added and vigorously stirred for at least 10 min. A 0.3 M NaOH (50 mL of DI water was added into beaker that containing 1.2 g NaOH, and then diluted the solution to 100 mL) was mixed with 0.067 M THPC (120 µL of 80% w/v THPC in 10 mL of DI water) by sonication. After that, an aqueous mixture solution was quickly added to the stirred solution, which was vigorously stirred further for 24 h. Pt loaded functionalized MWCNTs were prepared using a slightly different procedure [48]. By heating 93 mL of DI water to 90 ˚C containing 90 mg functionalized MWCNTs and 6.40 mL of 3 mM $H_2PtCl_6{\cdot}6H_2O$ (0.1554 g of $H_2PtCl_6{\cdot}6H_2O$ was dissolved in mixture of 50 mL of DI water, and then diluted the solution to 100 mL) in 250 mL flask and vigorously stirred for 10 min. A 0.96 mL of aqueous mixture solution NaOH/THPC was quickly added to the stirred solution and vigorously stirred for at least 10 min. Finally, the solution was vigorously stirred further for 24 h and then cooled to room temperature. The mixtures were centrifuged for 30 min at 4000 rpm to remove unattached nanoparticles. The precipitates were redispersed in 50 mL of DI water, sonicated for 10 min, and then centrifuged again for half an hour. Finally, the precipitates were dried in the oven at 90 ˚C for 24 h.

Table 2.1 Preparation conditions for THPC reduction method.

Pd:Pt ratio	**Volume (mL)**				
	$H_2PtCl_6·6H_2O$ 3 mM	**$PdCl_2$ 6 mM**	**NaOH 0.3 M**	**THPC 0.067 M**	**DI water**
4:0	-	9.40	0.94	1.88	88
3:1	-	7.10	0.71	1.42	91
1:1	-	4.70	0.47	0.94	94
1:3	-	2.40	0.24	0.48	97
0:4	6.40	-	0.32	0.64	93

2.2.2.4 Sodium L-ascorbate reduction method

The Pd3Pt1, Pd1Pt1 and Pd1Pt3 with ratio 3:1, 1:1 and 1:3 were prepared in this method. The Pd-MWCNTs from THPC reduction method were centrifuged for half an hour at 4000 rpm to remove unattached THPC Pd nanoparticles. The precipitate was redispersed in DI water shown in Table 2.2. A 3 mM $H_2PtCl_6·6H_2O$ was added to the stirred solution and vigorously stirred for 20 min, and then a 10 mM sodium L-ascorbate (50 mL of DI water was added into beaker containing 0.1981 g sodium L-ascorbate, and then diluted the solution to 100 mL) was added and vigorously stirred for 24 h. The mixture of Pd3Pt1-MWCNTs, Pd1Pt1-MWCNTs and Pd1Pt3 MWCNTs from Pd:Pt ratio 3:1, 1:1 and 1:3 were centrifuged for half an hour at 4000 rpm to remove unattached Pt nanoparticles, respectively. The precipitates were redispersed in 50 mL of DI water, sonicated for 10 min, and then centrifuged again for half an hour. Finally, the precipitates were dried in the oven at 90 ˚C for 24 h.

Table 2.2 Preparation conditions for sodium L-ascorbate reduction method.

Pd:Pt ratio	**Volume (mL)**		
	$H_2PtCl_6 \cdot 6H_2O$ 3 mM	**Sodium L-ascorbate 10 mM**	**DI water**
3:1	1.60	5.80	93
1:1	3.20	11.60	85
1:3	4.80	17.40	78

2.3 Electrochemical and electrocatalytic measurements of the electrooxidation of small organic molecules on Au-MWCNTs, Pt-MWCNTs, PtAu-MWCNTs and PdPt-MWCNTs electrodes.

2.3.1 Electrode preparation

The 3.0 mm glassy carbon electrode was polished by polishing cloth, and 1.0 and 0.3 µm alumina (Al_2O_3) slurry. Then, it was sonicated in DI water and ethanol.

2.3.2 Preparation of catalysts-MWCNTs-Nafion nanocomposite film-modified glassy carbon electrode

To prepare catalysts-MWCNTs-Nafion nanocomposite film, a 0.5% w/v Nafion solution was prepared by diluting the 10.0% w/v Nafion solution with 0.1 M phosphate buffer solution pH 7, then a 1.30 mL 0.5% w/v Nafion and 1.30 mL phosphate buffer solution were added in 5 mg catalysts-MWCNTs, respectively. Afterward, the suspension was sonicated for 30 min. To prepare a catalysts-

MWCNTs-Nafion film electrode, a 20 µL of suspension was directly dropped on the glassy carbon electrode surface. The solvent was evaporated by the lamp for 30 min which shown in Figure 2.2(a).

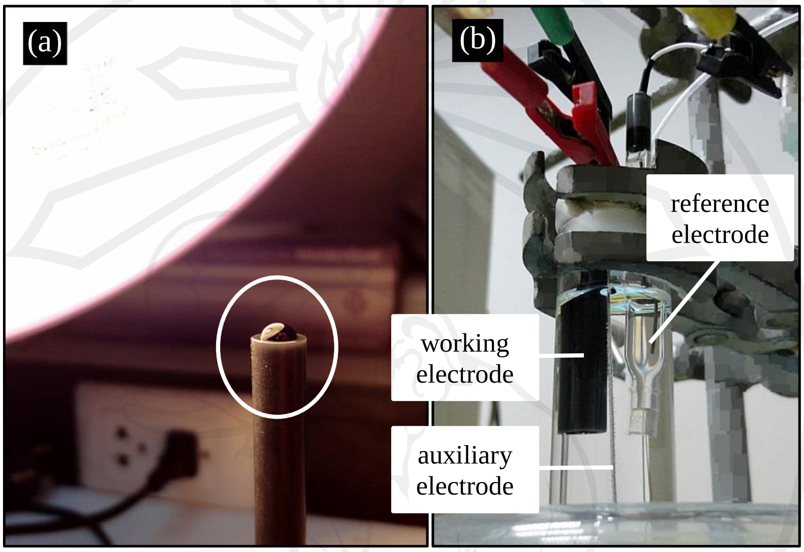

Figure 2.2 Catalysts-MWCNTs-Nafion nanocomposite film-modified glassy carbon electrode (a) and three-electrode system (b).

2.3.3 Electrochemical and electrocatalytic measurements of Au, Pd, Pt, PtAu and PdPt catalysts loaded functionalized MWCNTs surface for the electrooxidation of small organic molecules

The obtained MWCNTs, Au-MWCNTs, Pt-MWCNTs, Pd-MWCNTs, PtAu-MWCNTs and PdPt-MWCNTs electrodes were examined in 1 M H_2SO_4 solution (13.60 mL of the 18.38 M H_2SO_4 reagent was added into about 200 mL of DI water, and then diluted the solution to 250 mL), 2 M CH_3OH in 1 M H_2SO_4 (20 mL CH_3OH reagent was added into about 200 mL of 1 M H_2SO_4, and then diluted the solution to 250 mL), 2 M CH_3CH_2OH in 1 M H_2SO_4 (29 mL CH_3CH_2OH reagent was added into about 200 mL of 1 M H_2SO_4, and then diluted the solution to 250 mL) and

2 M HCOOH in 1 M H_2SO_4 (19 mL HCOOH reagent was added into about 200 mL of 1 M H_2SO_4, and then diluted the solution to 250 mL) by CV at a scan rate of 50 $mV{\cdot}s^{-1}$. The solutions were deaerated by N_2 gas for 20 min and maintained with N_2 atmosphere during the electrochemical experiments. The amperometric current density - time experiments were measured at 0.3 V for 3600 s in 1 M H_2SO_4 containing 2 M HCOOH solutions. The solution was purged with N_2 gas for 20 min before formic oxidation.

2.4 Characterization and structure analysis of Au, Pd, Pt and PdPt catalysts loaded functionalized MWCNTs surface

Both functionalized and nonfunctionalized MWCNTs were characterized by FT-IR technique to confirm functional groups on the MWCNTs surface. The catalysts were characterized their physical properties by using XRD and TEM techniques. The electrocatalytic activities of the prepared catalysts toward the electrooxidation of formic acid were examined by CV technique.

2.4.1 Fourier transform infrared spectroscopy (FT-IR)

Both functionalized and nonfunctionalized MWCNTs were characterized their functional groups by Fourier transform infrared spectroscopy. The samples were diluted by potassium bromide and operated in the wavelength range of 400-4000 cm^{-1} for FT-IR analysis [49].

2.4.2 X-ray diffraction (XRD)

All prepared catalysts were characterized by powder X-ray diffraction for phase identification. The instrument used Cu K_α radiation ($\lambda = 1.5418$ Å) operating at

30 kV – 15 mA, with a scanning rate of 0.2°/s in the 2θ range of 10°- 90° [50]. The sample identification was assisted by X’Pert HighScore Plus Computer Software.

2.4.3 Transmission electron microscopy (TEM)

The morphology and structure of prepared catalysts were also characterized by transmission electron microscope, JEOL model JEM-2010 operating at 20 kV. The prepared catalysts were prepared by dispersing a small amount of sample in DI water and put droplets of the solutions onto copper grids and letting the water to evaporate slowly under a lamp [51].