CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

1) Ammoniumpersulfate, $(NH_4)_2S_2O_8$, ALDRICH
2) Aniline monomer, ALDRICH, 99%
3) Graphite powder, ALDRICH
4) Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-((2ethylhexyl) carbonyl] thieno[3,4-b] thiophenediyl]] , PTB7
5) $PC_{60}BM$ - [6,6]-phenyl-C61-butyric acid methylester , $PC_{61}BM$
6) Poly(diallydimethylammonium chloride), PDADMAC, medium molecular weight, 20 wt.% in water, Mw=200,000-350,000, ALDRICH
7) Poly(sodium 4-styrene-sulfonate), PSS, ALDRICH, Mw=70,000
8) Potassium permanganate, $KMnO_4$, ALDRICH, U.S.A
9) Sodium Chloride, NaCl, CALRO ERBA, 99.5%
10) Sodium Hydroxide, NaOH, CALRO ERBA

3.1.2 Solvents

1) Ammonia, APPLICHEM PANREAC, 30%
2) Dichlorobenzene
3) Diodoctan
4) Ethanol, VRBIOSCIENCE, 99%
5) Hydrochloric acid, HCl, LAB SCAN, 37%
6) Hydrogenperoxide, H_2O_2, ALDRICH, 30%
7) Sulfuric acid, H_2SO_4 , CARLO ERBA, 96 %
8) Water, H_2O, ALDRICH

3.2 Equipment

1) Contact angle measurement
2) Fourier Transform Infared spectroscopy (FT-IR)
3) Thermogravimetric analysis (TGA)
4) Transmission electron microscopy (TEM)
5) UV-Vis spectrophotometer (UV-Vis)
6) X-ray diffraction (XRD)

3.3 Experiment Procedures

3.3.1 Preparation of Substrate

3.3.1.1 Primer Substrate for LbL Technique.

Glass sides are used as substrate to do layer-by-layer. Glass slides were cleaned by soaking in hot ammonia of which ratio is 5:3:1 of DI water: NH_3:H_2O_2 for 20 minutes after that rinsed with ethanol and dried. To improve the adhesion of the RGO/PDADMAC nanocomposite on the substrate, a primer coating composed of 5 PDADMAC/PSS layers to generate positive charges on top. PDADMAC and PSS solutions contain 10 mM and 1 M NaCl. Each layer used 1 min. dipping and rinse 2 times with water.

3.3.1.2 ITO-coated Glass Substrate for Inverted PSCs

ITO-coated glass substrates were first cleaned with acetone, water, isopropyl alcohol and ethanol by ultrasonication and keep under UV ozone radiation at 80° C for 15 min.

3.3.2 Part A : Synthesis of Graphene Oxide (GO), Reduced Graphene Oxide (RGO) and Polyaniline (PANi-PSS)

3.3.2.1 Synthesis of GO

Graphene oxide was synthesized from commercial graphite powder by modified Hummers-Offeman method. Graphite powder was added into the 50 mL of concentrated sulfuric acid (H_2SO_4) with in ice bath and kept for 1 h. Then potassium permanganate ($KMnO_4$) was mixed at below 20 °C for 2 h in order to control the reaction.

After that put into oil bath at 45° C for 2 h. Distilled water was slowly dropped into the mixture and kept temperature at 45 °C for 1 h. The oil bath was removed, add H_2O_2 and keep stirring overnight. The mixture was centrifuged and rinsed with 1M HCl and deionized water 3 times. The graphene oxide was kept in moist. GO was synthesized follow the ratio in Table 3.1.

Table 3.1 The ratio used for synthesis of graphene oxide, GO 1:1, 1:3, 1:5, 1:7 and 1:9

Ratio	Graphite Powder (g)	$KMnO_4$ (g)	Conc.H_2SO_4 (ml)	30%H_2O_2 (ml)	Water (ml)
1:1	1	1	50	2	50
1:3	1	3	50	2	50
1:5	1	5	50	2	50
1:7	1	7	50	2	50
1:9	1	9	50	2	50

3.3.2.2 Synthesis of Reduced Graphene Oxide under Alkaline Condition

The GO was sonicated with sodium hydroxide solution for 1 h by varying the concentration of NaOH , 0.01, 0.05, 0.1 and 0.5 M. This RGO was used for application part a, flexible electrode by LbL technique.

3.3.2.3 Synthesis of Reduced Graphene Oxide by p-toluenesulfonyl Hyhrazide (p-TSH)

Table 3.2 The ratios use for preparation of RGO by p-TSH reductant

RGO	Graphene oxide (mg/ml) 50 ml	PSS (g)	p-TSH (g)
RGO 3 h	1	-	0.5
RGO 24 h	1	-	0.5
RGO-PSS 24 h	1	0.05	0.5

p-TSH was added into aqueous GO solution, and then the mixture was heated and stirred at 60°C following time condition in table 3.2. After the reduction, the mixture was centrifuged and washed with water, ethanol and water.

3.3.2.4 Synthesis of PANi-PSS by in situ Polymerization.

The PANi-PSS composite were prepared via the interfacial polymerization with various molar ratios of APS:ANi (4:1, 2:1, 1:1, 1:1.5, 1:2 and1:4) and ANi:PSS (2:1, 1:1, 1:2, 1:4 and1:8). Before varying the molar ratio, The effect of acid concentration was studied by using 0.1 and 1 M HCl acid. The interfacial polymerization reaction was performed in 100 mL beaker.

A solution of aniline (10 mM) was prepared in chloroform. Various molar moles of APS were prepared by dissolving calculated amount of APS in an aqueous 0.1 M HCl acid solution of PSS (10 mM) as shown in Table 3.3.

Table 3.3 The molar ratios of ANi : APS

Molar Ratio ANi : APS	**Concentration of APS (mM)**	**Weight (g)**
1:0	0	0
4:1	2.5	0.0228
2:1	5	0.0456
1:1	10	0.0913
1:1.5	15	0.1369
1:2	20	0.1826
1:4	40	0.3651
2:1 (in 1 M HCl)	5	0.0456

Various molar moles of PSS were prepared by dissolving calculated amount of PSS in an aqueous 0.1 M HCl acid solution of APS (5 mM).The aqueous solutions (PSS/APS mixture) were carefully poured into aniline in chloroform solution. The aqueous was collected after 24 h of reaction in fridge.

Table 3.4 The molar ratios of ANi : PSS

Molar ratio ANi : PSS	Concentration of PSS (mM)	Weight (g)
1:0	0	0
2:1	5	0.0412
1:1	10	0.0825
1:2	20	0.1650
1:4	40	0.3300
1:8	80	0.6598

3.3.4 Part B : Applications of Graphene Oxide

3.3.4.1 Flexible Thin Film Electrode of RGO/PDADMAC by LbL Assembly Technique.

The primer substrates were dipped in RGO prepared in 3.3.2.2 and PDADMAC solution by repeating this process until the desired number of layers. After that, RGO/PDADMAC nanocomposite film was dried at 60 °C for 12 hours and immersed in 40 %HBr acid for 60 seconds then rinsed with ethanol. The parameters of LbL studied was shown in Table 3.5.

Table 3.5 Parameter studied in flexible thin film electrode of RGO/PDADMAC by LbL assembly technique.

Parameter (Unit)	Condition
GO in different ratio	1:1, 1:3, 1:5, 1:7 and 1:9
Dipping time (minutes)	1, 3, 5, 10, 15 and 20
Concentration of NaCl (M)	0, 0.025, 0.050, 0.075 and 0.10
Effect of pH	2, 4, 6, 8, 9, 10, 11, 12, 13 and 14
Concentration of NaOH (M)	0, 0.01, 0.05, 0.10 and 0.50
Concentration of GO (mg/ml)	0.25, 0.50, 1, 2, 4, 5 and 6

3.3.4.2 RGO/PANi Composite as Interfacial Hole Transport Layers for Inverted PSCs.

RGO/PANi was prepared by physical mixing solution. RGO-PSS was dispersed in water solution after that add PANI-PSS into the solution. The mixture was sonicated for 1 h and used to do spin-coating.