CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Modification of chitosan

In order to fulfill the objective of the research, to obtain polymer electrolyte host can dissolve in organic solvents, modification is done via phthaloylation onto nitrogen atom in chitosan.

3.1.1 Chemicals and Solvents

Chitosan, phthalic anhydride, dimethylformamide (DMF), ethanol

3.1.2 Synthesis of N-phthaloylchitosan

The synthesis was carried out similar to that of Yoksan [75]. 1 g of chitosan (Aldrich, 75% deacetylation, viscosity: 800-2000 cps) and 4.39 g of phthalic anhydride (purchased from AC Chemical Co. Ltd.) dissolved in DMF was reacted in a temperature range of 100 ^{o}C to 120 ^{o}C under nitrogen atmosphere for 6 h. The temperature was reduced to 60 ^{o}C, and the mixture was left overnight. The clear yellowish solution was put into ice water to precipitate out the product. The precipitate was collected and washed with distilled ethanol in a soxhlet extractor for 8 h. The product was dried in vacuum.

3.2 Preparation of Polymer Electrolyte

3.2.1 Materials

N-phthaloylchitosan (PhCh), dimethylformamide (DMF) and lithium iodide (LiI)

3.2.2 Preparation of the polymer electrolyte

The polymer electrolyte film was prepared by solvent casting technique. DMF was used as solvent and lithium salt was added in various weight percentages as a doping salt. Various wt.% of LiI from 5% to 50% was introduced into the PhCh based polymer electrolyte as shown in *Table 3.1*. The weight of the salts, *x* was measured according to the equation:

$$wt.\%\ of\ salt\ = \frac{x}{x + wt\ of\ PhCh} \times 100\% \qquad (3.1)$$

The mixture was further stirred for 1 h before casting onto petri dishes. A control film was also prepared without the salt. The cast solution was slowly heated to dryness and the films formed were stored in dessicator before analysis.

Table 3.1: PhCh polymer electrolyte films consisting different LiI concentrations

Wt. % of LiI	Polymer Electrolyte Code
0	PCI 0
10	PCI 10
20	PCI 20
30	PCI 30
40	PCI 40
50	PCI 50

3.3 Characterization

3.3.1 Fourier Transform Infra-Red (FTIR) Spectroscopy

An infrared spectrum can be obtained by passing infrared radiation through a sample of the compound. When a compound is bombarded with radiation of a frequency that exactly matches the frequency of one of its vibrations, the molecule will absorb energy. This allows the bonds to stretch and bend a bit more. Thus, the absorption of energy increases the amplitude of the vibration, but does not change its frequency. By experimentally determining the wavenumbers of the energy absorbed by a particular compound, the kind of bond can be ascertained as each stretching and bending vibration of a bond in a molecule occurs with a characteristic frequency. FTIR spectrometer has several advantages as its sensitivity is better because, instead of scanning through the frequencies, it measures all frequencies simultaneously.

The spectra of all the polymer films were recorded on Spotlight 400 Perkin-Elmer Spectrometer with 15 scanning numbers using attenuated total reflectance (ATR) method. The wavelength was recorded from region 650 to 4000 cm^{-1} at room temperature. FTIR-ATR is a simple, direct, flexible and sensitive in situ IR technique as it requires no sample preparation.

3.3.2 ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy

NMR spectroscopy is another instrumental technique that can be used to determine a structure of a compound. It helps to identify the carbon-hydrogen framework of an organic compound and the functionality at a specific carbon and its neighboring carbons.

Proton nuclear magnetic resonance was taken at 399.65 MHz with JNM–GSX270 Fourier Transform Spectrometer. DMSO-d_6 is used as the solvent with sample concentration of about 20% w/v.

3.3.3 X-ray Diffraction (XRD)

X-ray diffraction is a phenomenon when atomic planes of a crystal cause on incident beam of x-rays to interfere with one another as they leave the crystal. Diffraction effects are observed when electromagnetic radiation impinges on periodic structure with geometrical variations on the length scale of the wavelength of the radiation. XRD is a non-destructive analytical technique which is fast and require easy sample preparation. It assists in identification and quantitative determination of various crystalline phases and orientation. XRD also helps to study crystalline and non-crystalline materials by looking at how they diffract x-rays of a known wavelength.

The XRD profile was recorded at room temperature using Shimadzu D5000 at 2θ angles between 5^o and 80^o with X-ray wavelength of 1.5406 Å. Samples were attached to a glass slide.

3.3.4 Solubility

Solubility test was carried out to find the suitable organic solvent for film forming. 0.05 g of N-phthaloylchitosan was put into the test tubes and tested for its solubility in various solvents at room temperature. For comparison, solubility of chitosan in the various solvents was also carried out. The solubility was observed visually. The solvents used in the solubility test are summarized in *Appendix D*.

i. Solubility Parameter

The solubility parameter is an important quantity for predicting solubility relations. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = (\frac{E}{V})^{1/2} \tag{3.2}$$

where V is the molar volume of the pure solvent and E is its (measurable) energy of vaporization.

Thermodynamics requires that the free energy of the solution (G) must be zero or negative for the solution process to occur spontaneously. The free energy change for the solution process is given by the relation:

$$\Delta G = \Delta H - T\Delta S \tag{3.3}$$

where ΔG is the entropy change of the solution, ΔH is the magnitude of the enthalpy of the solution and T is the absolute temperature of the solution.

Scatchard-Hildebrand equation can be written as

$$\frac{\Delta H}{V}\varphi_{sol}\,\varphi_{Pol} = \left(\delta_{sol} - \delta_{pol}\right)^2 \tag{3.4}$$

Where V is the total volume of the mixture, φ_{sol} and φ_{pol} are the volume fraction of the solvent and polymer, respectively. δ_{sol} and δ_{pol} are the solubility parameter of the solvent and polymer, respectively. For solubility to occur, $| \boldsymbol{\delta_{sol}} - \boldsymbol{\delta_{pol}} | < 1$.

Solvent solubility parameter, δ_{sol} can be calculated from the equation proposed by Hansen which is extension from the Hildebrand parameter method that considers the three intermolecular interactions; dispersion (London) forces, δ_D, dipole moment, δ_P, and hydrogen bonding, δ_H.

$$\delta_{Sol}{}^2 = \delta_D{}^2 + \delta_P{}^2 + \delta_H{}^2 \tag{3.5}$$

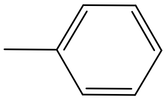
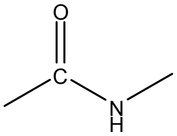
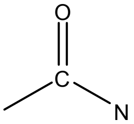
where δ_D is the dispersion solubility parameter, δ_P is the polar solubility parameter and δ_H is the hydrogen bonding solubility parameter.

Polymer solubility parameter, δ_{pol} is obtained from:

$$\delta_{Pol} = \frac{density \times \sum G}{molecular\ mass\ of\ repeating\ unit} \tag{3.6}$$

where $\sum G$ refers to the total molar attraction constant of all the chemical structure groups in the repeating unit of the polymer. Values of the molar attraction constant (Van Krevelen) for the group contribution method are summarized in *Table 3.2*.

Table 3.2: Van Krevelen molar attraction constants

Group	**G ($J^{½}$ cm $^{3/2}$ mol^{-1})**
-CH_3	420
-CH_2	280
-CH	140
-C-	0
-OH	754
-O-	256
-CO	685
-COO	512
-COOH	651
-CH=CH-	444
	1517
	1228
	430

ii. Density

Density is a measure of the “compactness” of matter within a substance and is defined by the *equation 3.7*:

$$Density, \rho = \frac{Mass, g}{Volume, mL} \tag{3.7}$$

0.5 g of PhCh was accurately weighed and submerged in a water (which it is not soluble) in a graduated cylinder. The volume of water displaced was measured and density was calculated using the *equation 3.7.*

Estimation of solubility is done by comparing the solubility parameter of the polymer, δ_{pol} and solubility of the solvents, δ_{sol}. A solvent with δ_{sol} that closely matches to the δ_{pol} of the polymer solute is able to dissolve the polymer.

Solubility parameter of the solvents can also estimated using the Hansen solubility parameter, by considering the three intermolecular interactions; dispersion (London) forces, δ_D, dipole moment, δ_P, and hydrogen bonding, δ_H of the solvents using the following equation;

$$\delta_{Sol}{}^2 = \delta_D{}^2 + \delta_P{}^2 + \delta_H{}^2 \tag{3.8}$$

3.3.5 Electrical Impedance spectroscopy (EIS)

EIS is useful for research and development of new materials and electrode structures, as well as for product verification and quality assurance in manufacturing operations. Impedance is a complex resistance to a current flowing through a circuit made of resistors (R), capacitors (C), inductors (L), or any combination of these, as function of the frequency of the ac source. Resistors represent conductive pathways for ion and electron transfer. As such, they present the bulk resistance of a material to charge transport such as the resistance of the electrolyte to ion transport or the resistance of a conductor to electron transport. Resistors are also used to represent the resistance to the charge-transfer process at the electrode surface. Capacitors and inductors are associated with space-charge polarization regions, such as the electrochemical double layer, and adsorption/desorption processes at an electrode, respectively. The defining relation and impedance for ideal bulk electrical elements are shown in *Table 3.3*

Table 3.3: Relation for ideal bulk electrical elements

	Defining Relation	**Impedance**
Resistor	$V = I \times R$	$Z_R = R$
Capacitor	$I = C\frac{dV}{dt}$	$Z_C = \frac{1}{j\omega C} = -\frac{j}{\omega C}$
Inductor	$V = L\frac{dI}{dt}$	$Z_L = j\omega L$

The ionic conductivities of the films were measured using HIOKI 3531 Z HiTester in the frequency range of 50 Hz to 1 MHz. The films were sandwiched between two stainless steel disc electrodes. The impedance data are mostly presented in Nyquist plots. A complex impedance plot shows the imaginary part, Z_i of impedance, which is indicative of the capacitive and inductive character of the cell, plot against its real part of the cell, Z_r. Nyquist plots have the advantage that activation-controlled process with distinct time-constants show up as unique impedance arcs and the shape of the curve provides insight into possible mechanism or governing phenomena.

The ionic conductivity of the samples can be calculated by using the R_B values in the following *Equation 3.9*:

$$\sigma = \frac{t}{R_B \times A} \tag{3.9}$$

where t is the thickness of the film, R_B is bulk impedance and A is the film-electrode contact area. Thicknesses of the films were measured using the micrometer screw gauge.

3.4 Dye-sensitized solar cell

3.4.1 Preparation of the polymer electrolyte

0.5 g of LiI were added to a solution of 0.5 g of N-phthaloylchitosan in 10 ml DMF to give 50 wt.% LiI-PhCh. 10 wt. % of I_2 crystal to the weight of the LiI salt was dissolved in the polymer solutions.

3.4.2 Preparation of dye-solutions

Dye from the black rice and red cabbage were extracted by dissolving them in 95% ethanol for 24 h at room temperature without exposing to direct sunlight. The solutions were then filtered to remove the solid residues and its pH measured. (Pure dye solution: 5) The pH of the pure dye solutions was varied from pH 1 to pH 3 by adjusting the pH of the solution using 0.02 M hydrochloric acid, HCl solution.

3.4.3 Fabrication of the solar cell

Transparent tin-doped indium oxide or Indium tin oxide (ITO) conductive glass was used for both the working and counter electrodes. ITO glasses were rinsed with distilled water and ethanol successively before used.

The photoactive electrodes were prepared by spin-coating a compact layer, diisopropoxytitanium bis(acetylacetonate) solution at 3000 rpm for 30 s onto ITO glass, followed by heating at 450 ^{o}C for 30 min. Then, the commercialized nanocrystalline TiO_2 paste (STI 18NR-T) was cast onto the glass as shown in the *Figure 3.1*, followed by sintering in air at 450 ^{o}C for 30 min.

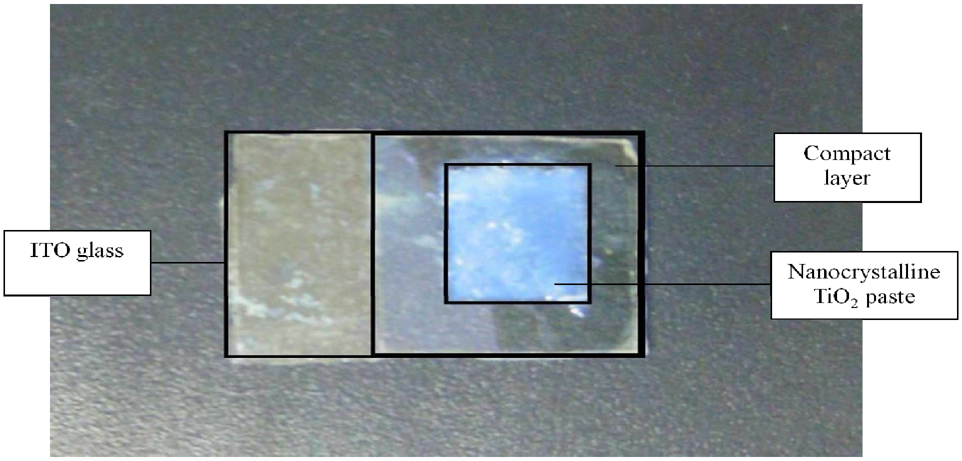


Figure 3.1: Photo of photoelectrode

The TiO_2 layers (thickness of TiO_2 layer: 12–13 m, active area: 0.25cm^2) were then immersed in the prepared dye solutions at room temperature for 24 h under dark. The dye-sensitized TiO_2 film was rinsed with distilled water and acetone and the glasses were then dried in the dark. From *Figure 3.2*, we can observe that dye had attached to the TiO_2 layer as its original white layer become colored.

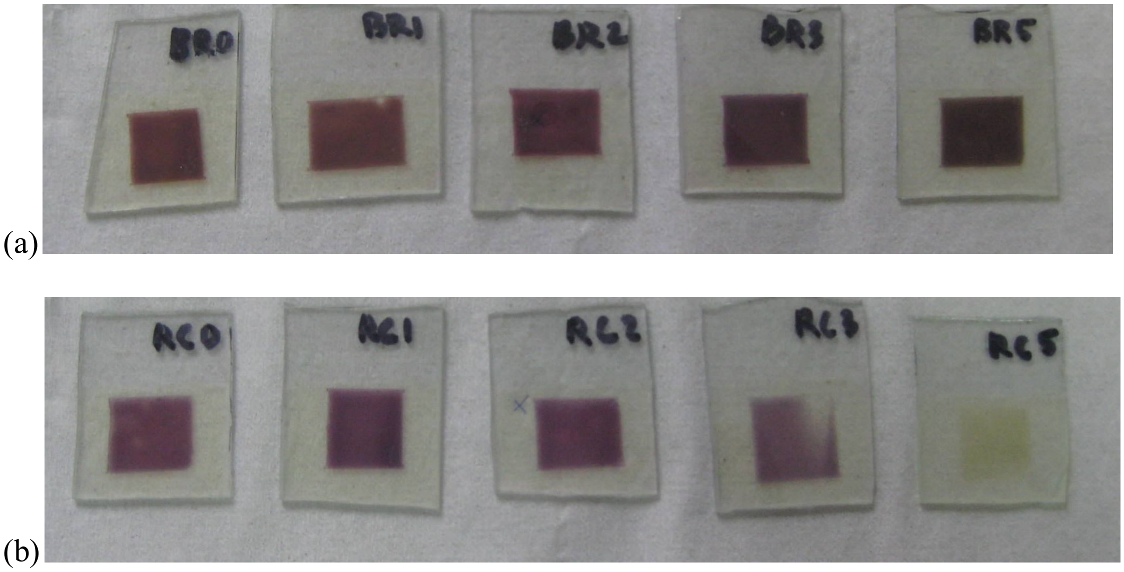


Figure 3.2: Various pH of dye extracted from (a) black rice and (b) red cabbage absorbed into the layer of mesoporous nanocrystalline TiO_2

Counter electrodes as shown in *Figure 3.3* were prepared by spin coating a Pt solution (0.01 M $PtCl_2$ in isopropyl alcohol) at 3000 rpm for 30 s onto ITO glass. The glass was sintered in air at 500 ^{o}C for 40 min.

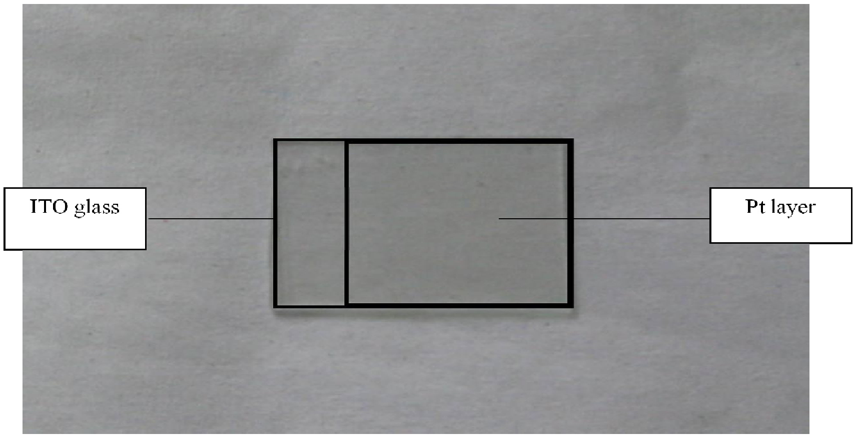


Figure 3.3: Counter Pt electrode

The polymer electrolyte was sandwiched between working photoelectrode and counter electrode. The two electrodes were clipped together for photovoltaic measurement. The photocurrent performances of DSSCs with active area of 0.25 cm^2 were carried using Keithley 2400 electrometer. The cell was illuminated through the active photoelectrode, under a light source of 100 mW as exhibited in *Figure 3.4*.

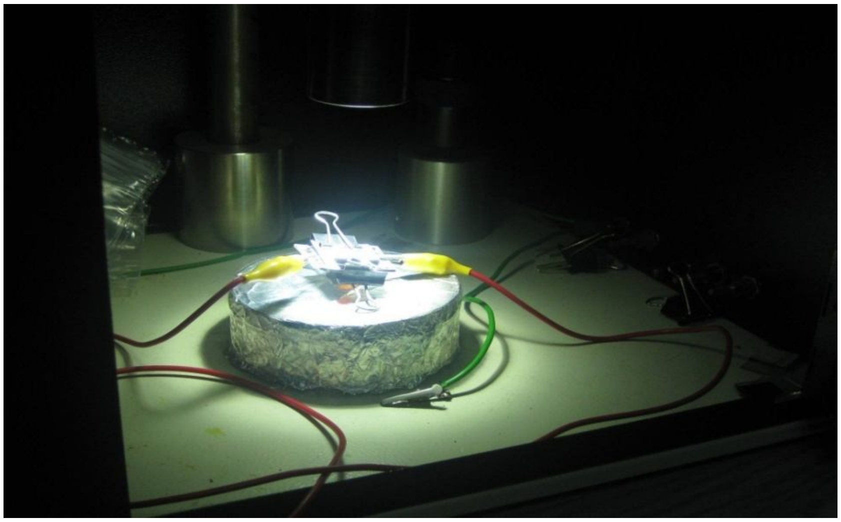


Figure 3.4: Solar cell under illumination of 100 mW lamp

From the I-V characteristic curve, some of the important parameters of solar cell can be calculated. The key performance characteristics of the cells to be considered are as follow:

i. *Short Circuit Current (I_{SC})*

Short circuit current is calculated when the voltage equals to zero.

$$I_{SC} = I \text{ (at } V=0) \qquad (3.10)$$

ii. *Open Circuit Voltage (V_{OC})*

Open circuit voltage is defined as the maximum value of the potential difference when the contacts are isolated. This is equivalent to the condition when dark current and short circuit photocurrent exactly cancel out.

$$V_{OC} = V \text{ (at } I=0) \qquad (3.11)$$

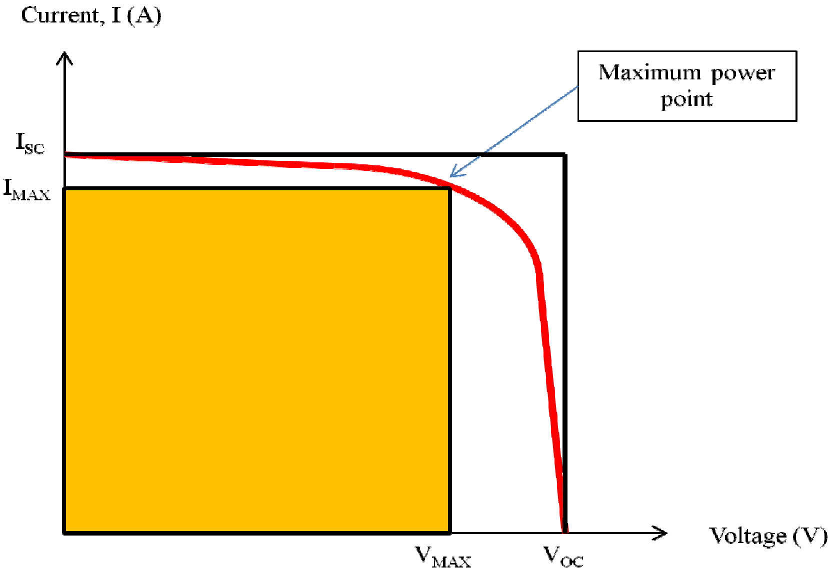


Figure 3.5: Current-voltage curves of DSSCs

From the I-V characteristic curve shown in *Figure 3.5*, some of the important parameter of solar cell can be calculated. These are the key performance characteristics of the cells:

i. *Fill Factor (FF)*

Fill Factor is defined as ratio of the maximum current density, I_{max} x V_{max} given by area of the inner rectangle to the area of I_{SC} x V_{OC} (outer rectangle). This quality measurement of the solar cell is described as the "squareness" of the I-V curve. *FF* can be calculated according to the *Equation 3.12*:

$$FF = \frac{I_{max} \times V_{max}}{I_{SC} \times V_{OC}} \tag{3.12}$$

ii. *Energy Conversion Efficiency (η)*

Efficiency of the cell is the power current delivered at operating point as a fraction of incident light power density, P_{in} as shown in the following *Equation 3.13*:

$$\eta = \frac{P_{out}}{P_{in}} \times 100 = \frac{I_{SC} \times V_{OC} \times FF}{P_{in}} \times 100 \tag{3.13}$$

where P_{in} is the irradiance of incident light.