MATERIALS AND METHOD

Materials

1. Apparatus

1.1 Cyclic Voltammograms were recorded with potentiostat PGSTAT20 (Autolab), interfaced to IME663 (Eco chemie), 663 VA stand (Metrohm) and Socos computer.

1.2 The electrochemical cell consists of a platinum electrode or a glassy carbon as working electrode, Ag/AgCl with saturated KCl or Ag/AgCl with 0.1 M LiCl in methanol as reference electrode and a platinum wire as an auxiliary electrode (all of them from Metrohm).

1.3 UV-Visible spectra were recorded using a Perkin-Elmer lambda 35 spectrophotometer.

1.4 Fluorescence spectra were recorded using a Perkin-Elmer LS55 Luminescence spectrometer.

1.5 The photocurrent and photovoltage characteristics were measured using a Keithley 4200 semiconductor characterization system.

1.6 An illuminator (3,000 K) light intensity 18,000 footcandle at 2 inches was used as light source.

1.7 A UEI DM384 digital multimeter was used as a voltmeter and a ammeter.

1.8 A variable resistance

1.9 The pH was measured using a Metrohm 744 pH meter

1.10 An analytical balance, Bp 2215

1.11 An electronic balance, AND GF 2000

1.12 A hot plate stirrer

1.13 An ultrasonic bath

1.14 A rotatory evaporator

1.15 A furnace

1.16 Indium tin oxide (ITO) glass of sheet resistance 25 Ωcm^{-2} purchased from Merck was used as conducting glass.

2. Reagents

All chemicals used in this work were listed in Appendix A. All chemicals are analytical grade, except 95% ethanol is commercial grade.

2.1 Reagent for cyclic voltammetry technique

- 1 M potassium nitrate (KNO_3) solution was prepared by dissolving 10.1102 g of potassium nitrate in 100 mL of deionized water.

- 0.1 M lithium perchlorate solution was prepared by dissolving 1.1244 g of lithium perchlorate hydrate ($LiClO_4 \cdot 3H_2O$) in 100 mL of 95% ethanol.

- 0.1M lithium chloride (LiCl) solution was prepared by dissolving 0.4244 g of lithium chloride in 100 mL of methanol.

- 0.1 M sodium sulphate (Na_2SO_4) solution was prepared by dissolving 1.4204 g of sodium sulphate in 100 mL of deionized water.

- 0.04 M phosphoric acid (H_3PO_4) solution was prepared by adding 5 mL of conc. phosphoric acid in 100 mL of deionized water.

- 0.04 M acetic acid (CH_3COOH) solution prepared by adding 0.23 mL of conc. acetic acid in 100 mL of deionized water.

- 0.2 M acetic acid (CH_3COOH) solution prepared by adding 1.20 mL of conc. acetic acid in 100 mL of deionized water.

- 0.2 M sodium acetate (CH_3COONa) solution was prepared by dissolving 1.6407 g of sodium acetate in 100 mL of deionized water.

- 0.04 M boric acid solution was prepared by dissolving 2.4732 g of boric acid in 100 mL of deionized water.

- 0.2 M sodium hydroxide (NaOH) was prepared by dissolving 2.00 g of sodium hydroxide in 250 mL of deionized water.

- 0.01 M sodium hydrogen phosphate (NaH_2PO_4) solution was prepared by dissolving 1.4196 g of sodium phosphate in 100 mL of deionized water.

- Britton-Robinson (B-R) buffer pH 4 was prepared by mixing a solution containing 0.04 M orthophosphoric acid, 0.04 M acetic acid and 0.04 M boric acid with the appropriate volume of 0.2 M sodium hydroxide (NaOH) solution. (in this work, 0.04 M orthophosphoric acid was replaced with 0.04 M phosphoric acid.)

- Acetate buffer pH 4 was prepared by mixing a solution containing 0.2 M acetic acid and 0.2 M sodium acetate and made up pH to pH 4 with 0.2 M acetic acid and 0.2 M sodium acetate solution.

- Phosphate buffer (pH 3) was prepared by mixing a solution containing 0.05 M phosphoric acid and 0.01 M sodium hydrogen phosphate and made up pH to pH 3 with 0.05 M phosphoric acid and 0.01 M sodium hydrogen phosphate solution.

2.2 Reagent for cleaning conducting glass

- 0.1 M sodium hydroxide (NaOH) solution was prepared by dissolving 1.00 g of sodium hydroxide in 250 mL of deionized water.

2.3 Reagent for preparation of nanocrystalline TiO_2 film electrode

- Nitric acid (HNO_3) solution (pH 3-4) was prepared by adding 3-4 drops of conc. nitric acid in 125 mL of deionized water and made up pH to 3-4 with deionized water.

- Acetylacetone solution was prepared by adding 4 mL of acetylacetone in 20 mL of deionized water.

2.4 Reagent for preparation of platinum coated counter electrode

- 10 mM hydrogen hexachloroplatinate solution was prepared by dissolving 0.0410 g of hydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot xH_2O$) in 10 mL of 2-propanol.

3. Preparation of stock solutions of dye

3.1 Preparation of stock solution of dye from roselle

The 15.694 g/l stock solution of dye from roselle was prepared by soaking 25.00 g of dry roselle in 400 mL of 95% ethanol. The dry roselle in 95% ethanol solution was kept in ambient temperature. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of roselle dye solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 3.9235 g was received and dissolved in 250 mL of 95% ethanol.

The 14.7030 g/l stock solution of dye from roselle was prepared by soaking 72.22 g of dry roselle in 1,200 mL of 95% ethanol. The dry roselle in 95% ethanol solution was kept in ambient temperature. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of roselle dye solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 14.7030 g was received and dissolved in 1,000 mL of 95% ethanol.

The 30 g/l stock solution of dye from roselle was prepared by evaporating 14.7030 g/l dye stock solution from 510 mL to 250 mL

3.2 Preparation of stock solution of dye from turmeric

The 4.4323 g/l stock solution of dye from turmeric was prepared by soaking 15 g of dry turmeric in 800 mL of 95% ethanol. The dry turmeric in 95% ethanol solution was kept in ambient temperature. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of turmeric dye solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 4.4323 g was received and dissolved in 1,000 mL of 95% ethanol.

The 12 g/l stock solution of dye from turmeric was prepared by soaking 20.00 g of dry turmeric in 800 mL of 95% ethanol. The dry turmeric in 95% ethanol solution was kept in ambient temperature. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of turmeric dye solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 5.9097 g was received and dissolved in 500 mL of 95% ethanol.

3.3 Preparation of stock solution of dye from *Monascus* red rice culture

The 4.0792 g/l stock solution of dye from *Monascus* red rice culture was prepared by soaking 12.00 g of *Monascus* red rice culture in 210 mL of 95% ethanol. The *Monascus* red rice culture in 95% ethanol solution was kept in a refrigerator. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of *Monascus* red solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 1.0198 g was received and dissolved in 250 mL of 95% ethanol.

The 4.6312 g/l stock solution of dye from *Monascus* red rice culture was prepared by soaking 20.00 g of *Monascus* red rice culture in 400 mL of 95% ethanol. The *Monascus* red rice culture in 95% ethanol solution was kept in a refrigerator. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of *Monascus* red solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 2.3156 g was received and dissolved in 500 mL of 95% ethanol.

The 1.7021 g/l stock solution of dye from *Monascus* red rice culture was prepared by soaking 20.00 g of *Monascus* red rice culture in 400 mL of 95% ethanol. The *Monascus* red rice culture in 95% ethanol solution was kept in a refrigerator. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of *Monascus* red solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 1.7021 g was received and dissolved in 1,000 mL of 95% ethanol.

The 8.1866 g/l stock solution of dye from *Monascus* red rice culture was prepared by soaking 60.00 g of *Monascus* red rice culture in 1,200 mL of 95% ethanol. The *Monascus* red rice culture in 95% ethanol solution was kept in a refrigerator. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of *Monascus* red solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 4.0933 g was received and dissolved in 500 mL of 95% ethanol.

The 16 g/l stock solution of dye from *Monascus* red rice culture was prepared by evaporating 8.1866 g/l dye stock solution from 391 mL to 200 mL

3.4 Preparation of stock solution of dye from *Monascus* yellow rice culture

The 5.2748 g/l stock solution of dye from *Monascus* yellow rice culture was prepared by soaking 12.00 g of *Monascus* yellow rice culture in 210 mL of 95% ethanol. The *Monascus* yellow rice culture in 95% ethanol solution was kept in a refrigerator. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of *Monascus* yellow solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 1.3187 g was received and dissolved in 250 mL of 95% ethanol.

The 4.900 g/l stock solution of dye from *Monascus* yellow rice culture was prepared by soaking 20.00 g of *Monascus* yellow rice culture in 400 mL of 95% ethanol. The *Monascus* yellow rice culture in 95% ethanol solution was kept in a refrigerator. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of *Monascus* yellow solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 2.4800 g was received and dissolved in 500 mL of 95% ethanol.

The 5.2997 g/l stock solution of dye from *Monascus* yellow rice culture was prepared by soaking 40.00 g of *Monascus* yellow rice culture in 800 mL of 95% ethanol. The *Monascus* yellow rice culture in 95% ethanol solution was kept in a refrigerator. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of *Monascus* yellow solution was removed on a rotatory evaporator at 50-55 °C. The viscous liquid as crude dye extract of 5.2997 g was received and dissolved in 1,000 mL of 95% ethanol.

The 15.7734 g/l stock solution of dye from *Monascus* yellow rice culture was prepared by soaking 60.00 g of *Monascus* yellow rice culture in 1,200 mL of 95% ethanol. The *Monascus* yellow rice culture in 95% ethanol solution was kept in a refrigerator. The solution was protected from direct light exposure for one week to extract natural dye in the solution adequately. After one week, the solid residues in solution were filtrated out and the solvent of *Monascus* yellow solution was removed on a rotatory evaporator at 50-55 °C.

The viscous liquid as crude dye extract of 7.8867 g was received and dissolved in 500 mL of 95% ethanol.

The 20 g/l stock solution of dye from *Monascus* yellow rice culture was prepared by evaporating 15.7734 g/l dye stock solution from 317 mL to 250 mL

3.5 Preparation of 0.3 mM [Ru(4,4'-dicarboxylic bipyridyl)$_2$(NCS)$_2$] or N3 dye solution

0.3 mM [Ru(4,4'-dicarboxylic bipyridyl)$_2$(NCS)$_2$] or N3 dye solution was prepared by dissolving 0.0012 g of N3 dye in 5 mL of 95% ethanol.

Methods

1. Spectroscopic measurement of dye extracts

1.1 UV-visible spectroscopic measurements

1.1.1 UV-visible absorption spectrum of roselle dye solution

UV-visible absorption spectrum of roselle was recorded using a UV-visible spectrophotometer. The dye solution of roselle was prepared from 30 g/l stock solution of dye. The concentration of roselle dye solution was 7.2 g/l.

1.1.2 UV-visible absorption spectrum of turmeric dye solution

UV-visible absorption spectrum of turmeric was recorded using a UV-visible spectrophotometer. The dye solution of turmeric was prepared from 12 g/l stock solution of dye. The concentration of turmeric dye solution was 0.011 g/l.

1.1.3 UV-visible absorption spectrum of *Monascus* red rice culture dye solution

UV-visible absorption spectrum of *Monascus* red rice culture was recorded using a UV-visible spectrophotometer. The dye solution of *Monascus* red rice culture was prepared from 16 g/l stock solution of dye. The concentration of *Monascus* red rice culture dye solution was 0.064 g/l.

1.1.4 UV-visible absorption spectrum of *Monascus* yellow rice culture dye solution

UV-visible absorption spectrum of *Monascus* yellow rice culture was recorded using a UV-visible spectrophotometer. The dye solution of *Monascus* yellow rice culture was prepared from 20 g/l stock solution of dye. The concentration of *Monascus* yellow rice culture dye solution was 0.13 g/l.

1.1.5 UV-visible absorption spectrum of N3 dye solution

UV-visible absorption spectrum of N3 dye solution was recorded using a UV-visible spectrophotometer. The concentration of N3 dye solution was 0.012 mM. The 0.012 mM N3 dye solution was prepared by pipeting 1 mL of 0.3 mM of N3 dye solution and the solution was made up to 25 mL with 95% ethanol in a volumetric flask.

1.1.6 UV-visible absorption spectrum of the mixture of roselle and turmeric dye solutions

UV-visible absorption spectrum of the mixture of roselle and turmeric dye solution was recorded using a UV-visible spectrophotometer. The mixed solution of roselle and turmeric was prepared from 30 and 12 g/l of roselle and turmeric stock solution of dyes, respectively. The concentrations of roselle and turmeric dyes in mixture of roselle and turmeric dye solutions were 7.2 and 0.011 g/l, respectively.

1.1.7 UV-visible absorption spectrum of the mixture of roselle and *Monascus* red dye solutions

UV-visible absorption spectrum of the mixture of roselle and *Monascus* red dye solutions was recorded using a UV-visible spectrophotometer. The mixed solution of roselle and *Monascus* red was prepared from 30 and 16 g/l of roselle and *Monascus* red stock solution of dyes, respectively. The concentrations of roselle and *Monascus* red dyes in mixture of roselle and *Monascus* red dye solutions were 7.2 and 0.064 g/l, respectively.

1.1.8 UV-visible absorption spectrum of the mixture of roselle and *Monascus* yellow dye solution

UV-visible absorption spectrum of the mixture of roselle and *Monascus* yellow dye solutions was recorded using a UV-visible spectrophotometer. The mixed solution of roselle and *Monascus* yellow was prepared from 30 and 20 g/l of roselle and *Monascus* yellow stock solution of dyes, respectively. The concentrations of roselle and *Monascus* yellow dyes in mixture of roselle and *Monascus* yellow dye solutions were 7.2 and 0.13 g/l, respectively.

1.1.9 UV-visible absorption spectrum of the mixture of turmeric and *Monascus* red dye solutions

UV-visible absorption spectrum of the mixture of turmeric and *Monascus* red dye solutions was recorded using a UV-visible spectrophotometer. The mixed solution of turmeric and *Monascus* red was prepared from 12 and 16 g/l of turmeric and *Monascus* red stock solution of dyes, respectively. The concentrations of turmeric and *Monascus* red dyes in mixture of turmeric and *Monascus* red dye solutions were 0.011 and 0.064 g/l, respectively.

1.1.10 UV-visible absorption spectrum of the mixture of turmeric and *Monascus* yellow dye solutions

UV-visible absorption spectrum of the mixture of turmeric and *Monascus* yellow dye solutions was recorded using a UV-visible spectrophotometer. The mixed solution of turmeric and *Monascus* yellow was prepared from 12 and 20 g/l of turmeric and *Monascus* yellow dye solutions, respectively. The concentrations of turmeric and *Monascus* yellow dyes in mixture of turmeric and *Monascus* yellow dye solutions were 0.011 and 0.13 g/l, respectively.

1.1.11 UV-visible absorption spectrum of the mixture of *Monascus* red and *Monascus* yellow dye solutions

UV-visible absorption spectrum of the mixture of *Monascus* red and *Monascus* yellow dye solutions was recorded using a UV-visible spectrophotometer. The mixed solution of *Monascus* red and *Monascus* yellow was prepared from 16 and 20 g/l of *Monascus* red and *Monascus* yellow stock solution of dyes, respectively. The concentrations of *Monascus* red and *Monascus* yellow dyes in mixture of *Monascus* red and *Monascus* yellow dye solution were 0.064 and 0.13 g/l.

1.2 Fluorescence spectroscopic measurements

1.2.1 Fluorescence spectrum of roselle dye solution

Fluorescence spectrum of roselle dye solution was recorded using a luminescence spectrometer. The excitation wavelength was 380 nm. The dye solution of roselle was prepared from 14.7030 g/l of stock solution of dye. The concentration of roselle dye solution was 5 g/l.

1.2.2 Fluorescence spectrum of turmeric dye solution

Fluorescence spectrum of turmeric dye solution was recorded using a luminescence spectrometer. The excitation wavelength was 420 nm. The dye solution of turmeric was prepared from 12 g/l of stock solution of dye. The concentration of turmeric dye solution was 0.012 g/l.

1.2.3 Fluorescence spectrum of *Monascus* red dye solution

Fluorescence spectrum of *Monascus* red dye solution was recorded using a luminescence spectrometer. The excitation wavelength was 470 nm. The dye solution of *Monascus* red was prepared from 1.7021 g/l of

stock solution of dye. The concentration of *Monascus* red dye solution was 0.034 g/l.

1.2.4 Fluorescence spectrum of *Monascus* yellow rice culture dye solution

Fluorescence spectrum of *Monascus* yellow dye solution was recorded using a luminescence spectrometer. The excitation wavelength was 410 nm. The dye solution of *Monascus* yellow was prepared from 5.2997 g/l of stock solution of dye. The concentration of *Monascus* yellow dye solution was 0.21 g/l.

1.2.5 Fluorescence spectrum of N3 dye solution

Fluorescence spectrum of N3 dye solution was recorded using a luminescence spectrometer. The excitation wavelength was 460 nm. The concentration of N3 dye solution was 0.3 mM.

2. Electrochemical measurement

2.1 Voltammetric study of roselle dye solution

The cell used in cyclic voltammetry experiments was a three-electrode type. The electrochemical cell of roselle dye solution consisted of a platinum (Pt) electrode as a working electrode, a Ag/AgCl with saturated KCl as a reference electrode and a platinum wire as an auxiliary electrode. 1 M potassium nitrate and 0.1 M sodium sulphate in water as supporting electrolytes were used in cyclic voltammetry experiments. The procedure for obtaining the voltammogram was as follows: 10 mL of supporting electrolyte was placed in the voltammetric cell and 5 mL of 14.7030 g/l of roselle stock solution was added in the cell. The voltammogram of roselle dye solution was recorded with a scan rate of 100 mV/s, between -900 and 100 mV.

2.2 Voltammetric study of turmeric dye solution

The cell used in cyclic voltammetry experiments was a three-electrode type. The electrochemical cell of turmeric dye solution consisted of a platinum (Pt) electrode as a working electrode, a Ag/AgCl with saturated KCl as a reference electrode and a platinum wire as an auxiliary electrode. 1 M potassium nitrate, 0.1 M sodium sulphate as supporting electrolytes were used in cyclic voltammetry experiments. B-R buffer pH 4, acetate buffer pH 4 and phosphate buffer pH 3 in water and 0.1 M lithium perchlorate in ethanol as supporting electrolytes were used in cyclic voltammetry experiments when a glassy carbon was used as a working electrode. The procedure for obtaining the voltammogram was as follows: 10 mL of supporting electrolyte was placed

in the voltammetric cell and 5 mL of 12 g/l of turmeric stock solution was added in the cell. The voltammogram of turmeric dye solution was recorded with a scan rate of 100 mV/s, between -900 and 100 mV.

2.3 Voltammetric study of *Monascus* red dye solution

The cell used in cyclic voltammetry experiments was a three-electrode type. The electrochemical cell of *Monascus* red dye solution consisted of a platinum (Pt) electrode as a working electrode, a Ag/AgCl with saturated KCl as a reference electrode and a platinum wire as an auxiliary electrode. 1 M potassium nitrate, 0.1 M sodium sulphate as supporting electrolytes were used in cyclic voltammetry experiments. 1 M KCl, B-R buffer pH 4, acetate buffer pH 4 and phosphate buffer pH 3 in water and 0.1 M lithium perchlorate in ethanol as supporting electrolytes were used in cyclic voltammetry experiments when a glassy carbon was used as a working electrode. The procedure for obtaining the voltammogram was as follows: 10 mL of supporting electrolyte was placed in the voltammetric cell and 5 mL of 4.6312 g/l of *Monascus* red stock solution was added in the cell. The voltammogram of *Monascus* red dye solution was recorded with a scan rate of 100 mV/s, between -900 and 100 mV.

2.4 Voltammetric study of *Monascus* yellow dye solution

The cell used in cyclic voltammetry experiments was a three-electrode type. The electrochemical cell of *Monascus* yellow dye solution consisted of a platinum (Pt) electrode as a working electrode, a Ag/AgCl with saturated KCl as a reference electrode and a platinum wire as an auxiliary electrode. 1 M potassium nitrate, 0.1 M sodium sulphate as supporting electrolytes were used in cyclic voltammetry experiments. 1 M KCl, B-R buffer pH 4, acetate buffer pH 4 and phosphate buffer pH 3 in water and 0.1 M lithium perchlorate in ethanol as supporting electrolytes were used in cyclic voltammetry experiments when a glassy carbon was used as a working electrode. The procedure for obtaining the voltammogram was as follows: 10 mL of supporting electrolyte was placed in the voltammetric cell and 5 mL of 4.9600 g/l of *Monascus* yellow stock solution was added in the cell. The voltammogram of *Monascus* yellow dye solution was recorded with a scan rate of 100 mV/s, between -900 and 100 mV.

2.5 Voltammetric study of N3 dye solution

The cell used in cyclic voltammetry experiments was a three-electrode type. The electrochemical cell of N3 dye solution consisted of a glassy carbon as a working electrode, a Ag/AgCl with 0.1 M LiCl in methanol as a reference electrode and a platinum wire as an auxiliary electrode. 0.1 M

lithium chloride in methanol and 0.1 M lithium perchlorate in ethanol as supporting electrolytes were used in cyclic voltammetry experiments. The procedure for obtaining the voltammogram was as follows: 10 mL of supporting electrolyte was placed in the voltammetric cell and 5 ml of 0.3 mM N3 dye solution was added in the cell. The voltammogram of N3 dye solution was recorded with a scan rate of 10 mV/s, between 400 and 1000 mV.

3. Effect of dye concentration on adsorption amount of dye on TiO_2 film

TiO_2 film on a glass substrate was prepared by blending 3 g of TiO_2 powder with 5 mL of HNO_3 acid solution (pH 3) and 0.25 mL of acetylacetone solution in agate mortar, then the mixture was ground for 30 min. A clean glass sheet of 1.25 x 5 cm^2 was fixed with plastic adhesive tape on the four sides to restrict the thickness and area of TiO_2 film. TiO_2 paste was spread onto the glass sheet by using a glass rod. After that the tape was removed and the glass sheet was dried on a hot plate at 110 °C for 15 min. Finally, the glass sheet was sintered at 450 °C for 30 min in a furnace to form a nanocrystalline TiO_2 film on the glass substrate.

A series of roselle extract in ethanol solution of various concentrations of 0.5-8.5 g/l were prepared by using 15.694 g/l stock solution of dye and in each solution a plate of TiO_2 film was soaked for 20 hours to find optimum conditions for adsorption of dye on TiO_2 particles. The amount of dye adsorbed on TiO_2 particles was determined by spectroscopic measurement of the concentration change of the dye solution before and after adsorption.

A series of turmeric extract in ethanol solution of various concentrations of 0.5-9.0 g/l were prepared by using 12 g/l dye stock solution and in each solution a plate of TiO_2 film was soaked for 20 hours to find optimum conditions for adsorption of dye on TiO_2 particles. The amount of dye adsorbed on TiO_2 particles was determined by spectroscopic measurement of the concentration change of the dye solution before and after adsorption.

A series of *Monascus* red extract in ethanol solution of various concentrations of 0.02-2.8 g/l were prepared by using 4.0792 g/l stock solution of dye and in each solution a plate of TiO_2 film was soaked for 20 hours to find optimum conditions for adsorption of dye on TiO_2 particles. The amount of dye adsorbed on TiO_2 particles was determined by spectroscopic measurement of the concentration change of the dye solution before and after adsorption.

A series of *Monascus* yellow extract in ethanol solution of various concentrations of 0.02-2.8 g/l were prepared by using 5.2748 g/l stock solution of dye and in each solution a plate of TiO_2 film was soaked for 20 hours to find optimum conditions for adsorption of dye on TiO_2 particles. The amount of

dye adsorbed on TiO_2 particles was determined by spectroscopic measurement of the concentration change of the dye solution before and after adsorption.

4. The fabrication of dye-sensitized solar cell

4.1 Cleaning of indium tin oxide (ITO) conducting glass

An indium tin oxide (ITO) conducting glass was cleaned by being sonicated in 0.1 M sodium hydroxide, acetone and deionized water, respectrively and in an ultrasonic bath for 15 minute in each step.

4.2 Preparation of dye adsorbed on a nanocrystalline TiO_2 film electrode

A TiO_2 film electrode was prepared by blending 3 g of TiO_2 powder with 5 mL of HNO_3 acid solution (pH 3) and 0.25 mL of acetylacetone solution in agate mortar, then the mixture was ground for 30 min. A cleaned ITO conducting glass sheet of 1.5 x 1.25 cm^2 was fixed with plastic adhesive tape on the four sides to restrict the thickness and area of TiO_2 film to the area of 1 x 1 cm^2. TiO_2 paste was spread onto the conductive side of the conducting glass by using a glass rod. After that the tape was removed and the glass sheet was dried on a hot plate at 110 °C for 15 min. The glass sheet was sintered at 450 °C for 30 min in a furnace to form a nanocrystalline TiO_2 electrode. Finally, a nanocrystalline TiO_2 electrode was soaked in 2.5 mL of dye solution in refrigerator for 24 hours. After dipping, the electrode was washed with ethanol solution and was dried at room temperature. These are shown in Figure 17.

For the preparation of mixture of dye adsorbed on a nanocrystalline TiO_2 film, the dye impregnation was done by two methods. The first method: the TiO_2 film electrode was soaked in 2.5 mL of the first dye solution and kept in a refrigerator for 12 hours. After dipping, the electrode was washed with ethanol solution and soaked in 2.5 mL of another dye solution and kept in a refrigerator for 12 hours. After dipping, the electrode was washed with ethanol solution and was dried at room temperature. The second method: the TiO_2 film electrode was soaked in the mixture of dye solutions and kept in refrigerator for 24 hours. After dipping, the electrode was washed with ethanol solution and was dried at room temperature. The symbols “dye1/dye2” and “dye1 : dye2” seen in the results stand for the dye adsorbed on TiO_2 film electrode prepared by the first method and the second method, respectively.

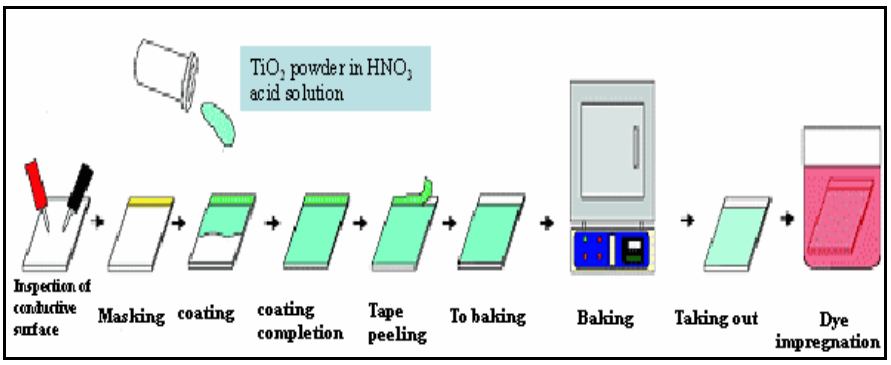

Figure 17 Preparation of dye adsorbed on a nanocrystalline TiO_2 film electrode

4.3 Preparation of counter electrode

A counter electrode was prepared by distributing 1-2 drops of 10 mM hydrogen hexachloroplatinate(IV) hydrate ($H_2PtCl_6 \cdot xH_2O$) in 2-propanol solution on the conductive side of conducting glass. After that the conducting glass was sintered at 400 °C for 30 min to obtain a thin film of platinum on the conductive surface of the conducting glass.

4.4 Preparation of liquid electrolyte

The liquid electrolyte solution consisting of 0.5 M potassium iodide (KI), 0.05 M iodine (I_2) and 0.5 M 4-tert-butylpyridine (TBP) in a mixture (9:1) of acetonitrile and 3-methyl-2-oxazolidineone (NMO) as solvent was prepared by dissolving 0.8295 g of potassium iodide, 0.1269 g of iodine and 0.6760 g of 4-tert-butylpyridine in mixture of 9 mL of acetonitrile and 1 mL of 3-methyl-2-oxazolidineone.

4.5 Preparation of solid polymer electrolyte

The solid polymer electrolyte consisting of polyethylene oxide (PEO), titanium dioxide (TiO_2), potassium iodide (KI) and iodine (I_2) in acetonitrile with a ratio of 61:9:25:5 was prepared by dissolving 0.0500 g of potassium iodide and 0.0100 g of iodine in 5 mL of acetonitrile and than adding 0.0180 g of titanium dioxide. The solution was stirred for 30 min, after that 0.1220 g of polyethylene oxide was added under continuous stirring and was stirred for 24 hours.

4.6 Assembling of dye-sensitized solar cell

4.6.1 Assembling of dye-sensitized solar cell using liquid electrolyte

A dye-sensitized solar cell of 1.0 cm^2 active area was assembled by filling a liquid electrolyte (as prepared in 4.4) between a TiO_2 porous film electrode (anode electrode) and a conductive glass sheet plated with Pt (cathode electrode). The two electrodes were clipped together.

4.6.2 Assembling of dye-sensitized solar cell using solid polymer electrolyte

A dye-sensitized solar cell using solid polymer electrolyte was assembled by dropping solid polymer electrolyte (as prepared in 4.5) on a TiO_2 porous film electrode (anode electrode) and then heating the plate to evaporate the solvent. After that a conductive glass sheet plated with Pt (cathode electrode) was attached with TiO_2 film electrode.

5. The current-voltage characteristics of dye-sensitized solar cell

The current-voltage characteristics of dye-sensitized solar cell were investigated by measuring the I–V character curves under irradiation with an illuminator (3,000 K) of light intensity 18,000 footcandle at 2 inches as a light source in ambient atmosphere. The distance between the illuminator and the test cell was 4.0 cm. The current-voltage (I-V) curves were measured as the set up shown in Figure 18.

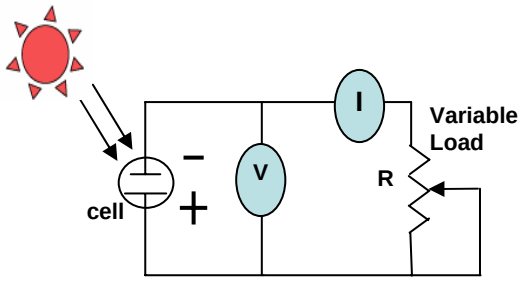

Figure 18 The experimental setup for measuring the current-voltage characteristics of dye-sensitized solar cell.

The short-circuit current (I_{sc}) and open-circuit current (V_{oc}) can be determined by attaching a multimeter directly to the two sides of the cell using wires with alligator clips attached to their ends. The negative electrode is the TiO_2 film electrode that attached to the black (-) wire of the meter, and the positive electrode is the counter electrode that attached to the red (+) wire of

the meter. The full current-voltage (I-V) curves are than measured using a variable load (0-1MΩ). Point by point current and voltage data can be gathered at each incremental resistance value and plotted on graph paper. Joining the points on the graph together produces a line called an I-V curve that shown in Figure 19.

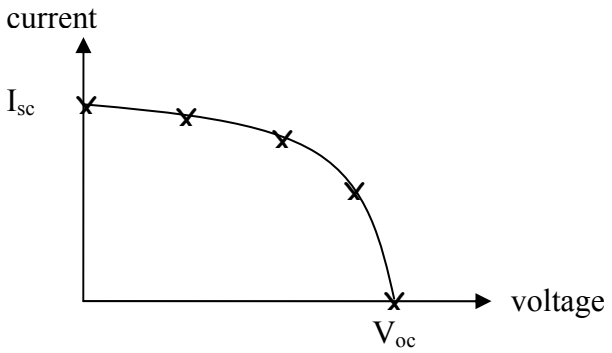

Figure 19 The current-voltage (I-V) curve

On using the Keithley 4200 semiconductor characterization system, the TiO_2 film electrode is attached to the negative electrode (-) of the power supply and the counter electrode is attached to the positive electrode (+) of the power supply. The potential of the power supply (as a variable load) resists the current of the cell.