

## CHAPTER III

### METHODOLOGY

#### 3.1 Fabrication of TiO<sub>2</sub> nanotube arrays by anodization

##### *3.1.1 Chemicals and Materials*

The following chemicals were used without further purification in the preparation of TiO<sub>2</sub> nanotubes process: sodium fluoride (Alfa Aesar, 98.0%), ammonium fluoride (Alfa Aesar, 98.0%), glycerol (Mallinckrodt Chemicals), ethylene glycol (Spectrum Chemical), poly (ethylene glycol) 400 (PEG 400) (Aldrich), D-mannitol (Alfa Aesar, 98.0%), sodium sulfate (Aldrich, 99%), ammonium sulfate, ammonium phosphate, ammonium acetate (Fisher) acetic acid, and phosphoric acid (Alfa Aesar).

##### *3.1.2 Instrumentation*

Anodization was employed by a multioutput power supply (Switching System International, CA) and a 420X Power Supply (The Electrosynthesis Company, Inc., NY). The electrochemical cell was connected in series to a variable resistor (100 kΩ) that was decreased to zero to simulate a voltage ramp of ~0.2 V/s, a multi-output power supply (Switching System International, CA) connected to a digital multimeter.

##### *3.1.3 Preparation of TiO<sub>2</sub> Nanotubes*

Titanium foil (Alfa Aesar, 0.25 mm thick, 99.95%) was used as the substrate for growth of the oxide nanotubes arrays. Strips (1.4 cm x 1.4 cm) were cut and mechanically polished to mirror finish using SiC paper of successively finer roughness (220, 320, 600, 1200, 1500 and 2000 grit) following by alumina micropolish suspension down to 0.05 μm. Mirror finish surfaces showed an homogenous distribution of nanotubes and contrasted with preferential growth along grooves occurring when the Ti surfaces are left with microscopic grooves resulting from rough sand paper polish. Once the Ti surfaces were polished, they were then

cleaned in three 5 min steps in ultrasonicated acetone, 2-propanol, and finally ultrapure water before drying in flowing  $N_2$  stream; the cleaned strips were used immediately. Anodization was performed in a two-electrode cell configuration using a large Pt coil as a cathode/counterelectrode. The titanium foil was contacted and then pressed against an O-ring in an electrochemical cell, leaving  $0.63 \text{ cm}^2$  exposed to the electrolyte. A two-electrode configuration was used for anodization. Titanium foil ( $14 \times 14 \times 0.25 \text{ mm}$ ) was used as anode while a large platinum coil was used as cathode. Anodization experiments were carried out using a multi-output power supply (Switching System International, CA) connected to a digital multimeter.

For the pulse anodization treatment, a square waveform shown in Figure 3.1(b) was employed. Voltages were pulsed between 20 V and 0 V or between 20 V and -4 V. The pulse duration ( $t_1 \sim 3 \text{ min}$ ) at the anodic limit was set longer than the pulse duration ( $t_0$ ) at the lower potential of the waveform, with  $t_0$  adjusted between 2 and 30 s. Films were grown for 3 h and compared to those obtained at constant voltage (20 V), a square waveform shown in Figure 3.1(a) for the same period of time. All films were grown at room temperature ( $25 \pm 2 \text{ }^\circ\text{C}$ ) and from 0.36 M  $NH_4F$  electrolyte without and with medium modifiers. Solutions were prepared from reagent grade chemicals and deionized water ( $18 \text{ M}\Omega \text{ cm}$ ). After formation of the oxide, the anodized Ti foil was removed from the O-ring assembly and carefully washed by immersion in deionized water and then dried in a flowing  $N_2$  stream. The as-grown porous layers were annealed at  $450 \text{ }^\circ\text{C}$  for 30 min in a furnace and were allowed to cool gradually back to the ambient condition. All thin film catalysts prepared by anodization of Ti foils as substrate in fluoride containing media electrolyte (0.36 M  $NH_4F$ ) with addition of various media modifiers. (see Table 3.1)

Table 3.1 Anodization condition of nanoporous films grown by anodization.

Entry No.	Condition
1	0.36 M $\text{NH}_4\text{F}$
2	0.36 M $\text{NH}_4\text{F}$ + EG:H <sub>2</sub> O (90:10)
3	0.36 M $\text{NH}_4\text{F}$ + Glycerol:H <sub>2</sub> O (90:10)
4	0.36 M $\text{NH}_4\text{F}$ + 1 M D-mannitol
5	0.36 M $\text{NH}_4\text{F}$ + PEG:H <sub>2</sub> O (90:20)
6	0.36 M $\text{NH}_4\text{F}$ +1 M $\text{Na}_2\text{SO}_4$
7	0.36 M $\text{NH}_4\text{F}$ +1 M $(\text{NH}_4)_2\text{SO}_4$
8	0.36 M $\text{NH}_4\text{F}$ +1 M $\text{H}_3\text{PO}_4$
9	0.15 M $\text{NH}_4\text{F}$ + 1 M $(\text{NH}_4)_2\text{HPO}_4$
10	0.36 M $\text{NH}_4\text{F}$ +1 M $\text{CH}_3\text{COOH}$
11	0.36 M $\text{NH}_4\text{F}$ +1 M $\text{CH}_3\text{COONH}_4$

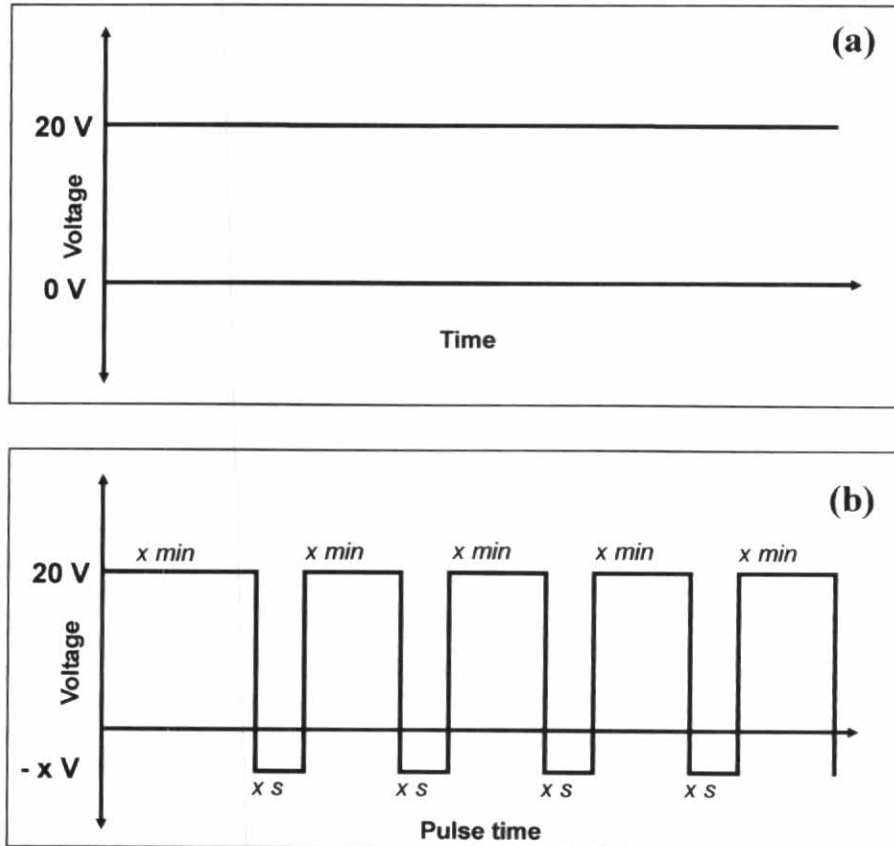


Figure 3.1 (a) Constant potential used for anodic growth of  $\text{TiO}_2$  nanotube (b) Potential pulse waveform used for the anodic growth of  $\text{TiO}_2$  nanotube arrays.

## **3.2 Metal-modified TiO<sub>2</sub> nanotubes**

### ***3.2.1 Chemicals and Materials***

The following chemicals were used without further purification in the preparation of TiO<sub>2</sub> nanotubes process: Sodium fluoride (Alfa Aesar, 98.0%), ammonium fluoride(Alfa Aesar, 98.0%), glycerol (Mallinckrodt Chemicals), ethylene glycol(Spectrum Chemical), poly (ethylene glycol) 400 (PEG 400) (Aldrich), lithium fluoride (99%) nickel fluoride(98%), manganese fluoride(99.8%), vanadium fluoride(99.5%), niobium fluoride(99%) were used as source of metal for TiO<sub>2</sub> nanotube doped from Alfa Aesar.

### ***3.2.2 Metal-modified TiO<sub>2</sub> nanotubes preparation***

From pulse anodization strategy affords an expeditious route to doping of the nanotube host by judicious choice of the negative voltage limit (-4 V) and the electrolyte composition. The investigate metal and use TiO<sub>2</sub> as the host. A variety of metals such as Nb, Li, Ni, Mn, and V can be used for this purpose. Using pulse anodization adjusting the pulse time at negative (-4 V) from 2-15 seconds in different metal loading between 10-40%. The experiments were separated in to 3 parts as following, (1) Find optimum metal loading, (2) Find optimum pulse time, and (3) Effect of media modifier during the formation of the semiconductor nanotubes. Glycerol, ethylene glycol, and PEG were used as media modifier. For optimum condition judgment was done by photocurrent. A summary of metal-modified TiO<sub>2</sub> nanotubes conditions are shown in Figure 3.2

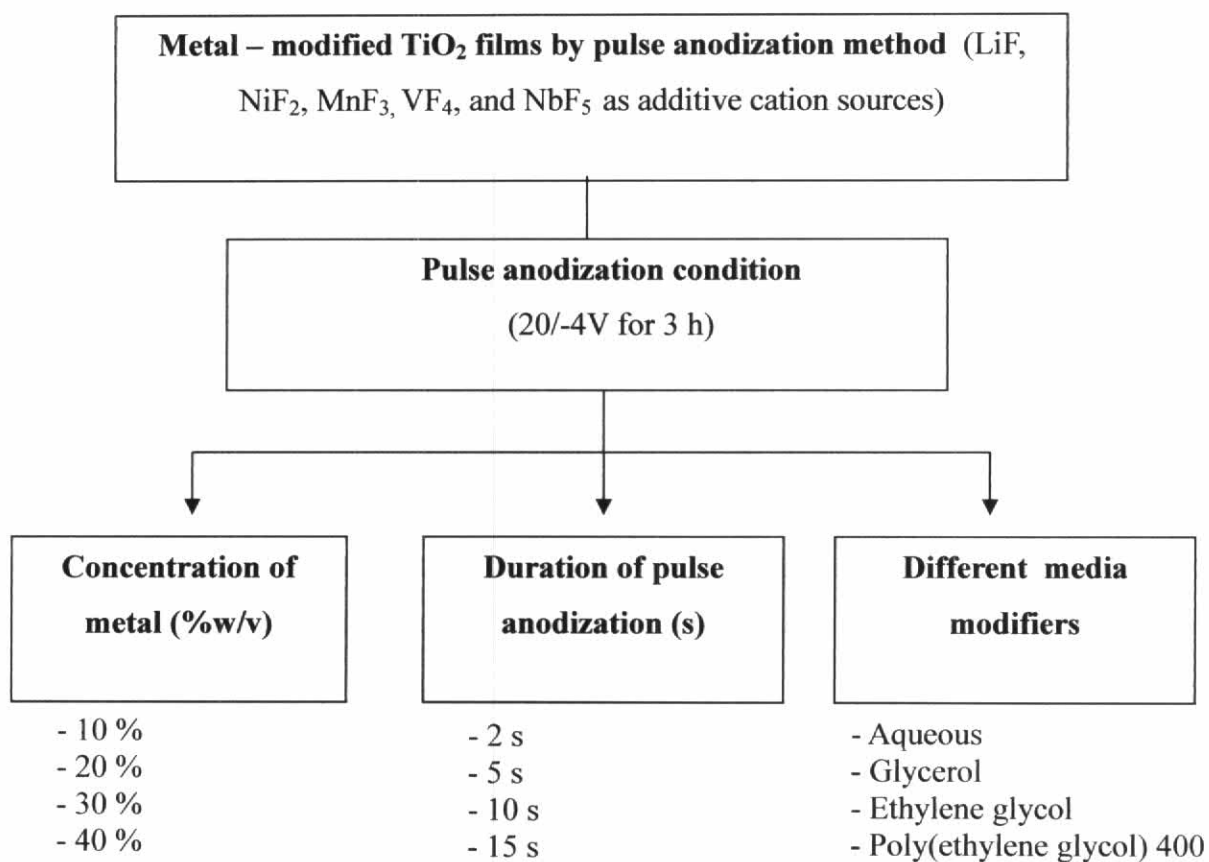


Figure 3.2 Diagram for experimental setup of synthesis metal doped TiO<sub>2</sub> nanotube measured parameters.

### 3.3. Photoelectrochemical Measurement

#### 3.3.1 Instrumentation

Photovoltammetry and photoaction spectroscopy were performed on a Model CV-27 BAS Voltammogram equipped with a Soltec X-Y recorder Model VP-6414S. Electrochemical Analyzer [Bioanalytical Systems (BAS), W. Lafayette, IN]. A 400 W medium pressure Hg arc lamp (Philips) served as the UV light sources and a 150 W was a 150 W xenon arc lamp (Oriental, Stratford, CT served as the light source for measurement photocurrent. The incident photon flux of these light sources was measured with an Oriel Model 70260 radiant power/energy meter. The monochromator used (Thermo Jarrel Ash Corporation Model 82-415) had a grating blazed at 300 nm.

#### 3.3.2. Photocurrent measurement

A standard single-compartment, three-electrode electrochemical cell was used for the photoelectrochemical measurements. A 100 mL quartz beaker, TiO<sub>2</sub> nanotube working electrode, and a Ag|AgCl|saturated KCl were used as working electrode and reference electrode respectively. A Pt spiral was additionally employed as the counterelectrode for the photovoltammetry experiments. The supporting electrolytes in all cases were pre-purged with ultrapure N<sub>2</sub> prior to the experiments. The UV light source (150W xenon arc lamp) was the light source in the photovoltammetry experiments. For the linear sweep photovoltammetry experiments was chopped irradiation (chopping frequency = 0.1 Hz). The light source was 8 cm away from the TiO<sub>2</sub> nanotube working electrode surface, and the incident photon flux (as measured with an Oriel Model 70260 radiant power/energy meter) was in the 0.59 mW/cm<sup>2</sup> at 340 nm with a bandwidth of 4 nm. The photon flux was monochromatically measured on an Oriel model 70260 Radiant Power/Energy meter. Photovoltammetry profiles were recorded on a model CV-27 Voltammogram (Bioanalytical Systems, West Lafayette, IN) equipped with a model VP-6414S Soltec X-Y recorder in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. The photovoltammogram scans were obtained using a slow potential sweep (2 mV/s) in conjunction with interrupted irradiation (0.1 Hz) of the semiconductor film. All electrolyte solutions were spurge with ultrapure N<sub>2</sub> for at

least 20 min prior to use. All measurements described below were performed at the laboratory ambient temperature ( $25\pm 2^\circ\text{C}$ ). The basic electrochemical cell setup used for electrodeposition is shown in Figure 3.3

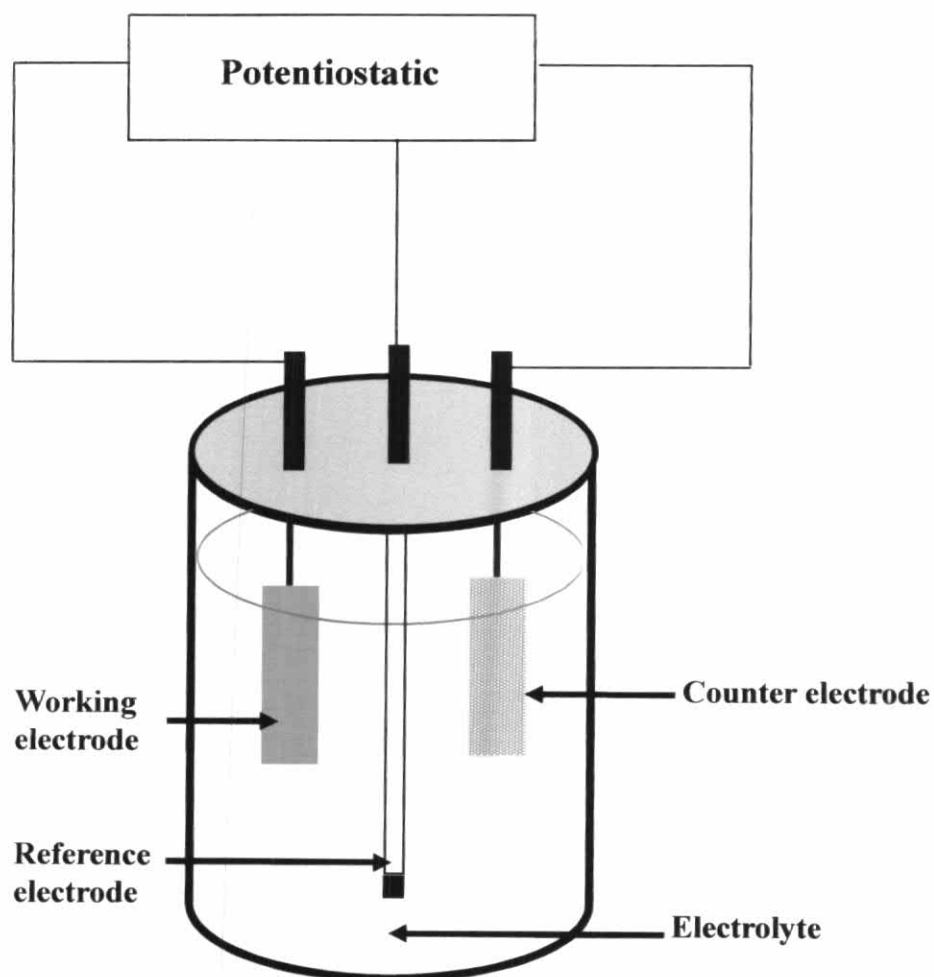


Figure 3.3 Schematic diagram of a standard single-compartment, three-electrode electrochemical cell used for electrodeposition in this study.

### 3.4 Dye sensitized TiO<sub>2</sub> nanotube

#### 3.4.1 Chemicals and Materials

In dye sensitized process, Zn(II)-5,10,15,20-Tetra(4-carboxyphenyl)porphyrin (Acid 1), Zn(II)-5-(3,5-bicarboxyphenyl)-10,15,20-trimesitylporphyrin (Acid 3), and Zn(II)-5,10,15,20-Tetra(3-carboxyphenyl)porphyrin (Acid 4), prepared by Prof. Galoppini at Rutgers University (Rochford *et al.*, 2007), methanol (99.9%, Alfa Aesar), lithium iodide (Aldrich), iodine and, 4-*tert*-butyl pyridine were from Sigma, ACS reagent, and acetonitrile (Alfa Aesar).

#### 3.4.2 Preparation of a nanotube TiO<sub>2</sub> films

Titanium dioxide films were prepared by constant potential anodization of titanium foil at 20 V for 3 h in three different media modifier such as glycerol, ethyl glycol, and poly(ethyl glycol) 400 in ammonium fluoride electrolyte (prepared with different nanotube diameter and wall thickness). The TiO<sub>2</sub> nanotube preparation as described in the topic 3.1.3. The nanotube were packed in approximately hexagonal symmetry with an average inner diameter and wall thickness ranged from 55-120 nm and 13-16 nm, respectively. The average nanotube lengths of 600-850 nm (see detail in Table 4.2)

#### 3.4.3 Sensitization of TiO<sub>2</sub> nanotube film electrodes

All porphyrin chromophores prepared by Prof. Galoppini at Rutgers University (Rochford *et al.*, 2007). Before dye adsorption, the TiO<sub>2</sub> film was calcined at 150 °C for 30 min in air to remove water adsorbed on the TiO<sub>2</sub> surface, and then it was cooled to 80 °C and immediately soaked in a dye solution. Adsorption of the dye on the TiO<sub>2</sub> surface was carried out by soaking the TiO<sub>2</sub> electrode in a dry methanol solution of the dye (standard concentration:  $3 \times 10^{-4}$  mol/L) at room temperature for 30 min, and then the electrode was washed with pure methanol to remove physisorbed dye. Short binding times were chosen to prevent aggregation of the porphyrins at the metal oxide surfaces. The TiCl<sub>4</sub> solution pretreatment the metal oxide films were tested, All films were kept in dark and dry condition.



### 3.4.4 Photoelectrochemical Measurement and Characterization of Dye-Sensitized Film.

The amount of adsorbed dye was determined by diffuse reflectance spectroscopy model Perkin-Elmer Lambda 35 UV-vis spectrophotometer equipment. For measuring the IPCE value, the dye-sensitized semiconductor electrode was incorporated into a thin-layer sandwiched solar cell. The area of the semiconductor electrode was roughly  $0.7 \text{ cm}^2$ , a TCO glass with  $15 \text{ \AA}$  of e-beam evaporated transparent Pt as counter electrode, and a sealing separator ( $60 \text{ }\mu\text{m}$ ) for providing the electrolyte chamber and short-circuiting when the counter and working electrodes were clamped together. The electrolyte solution consisted of a mixture of LiI (0.3 M), iodine (15 mM), 4-tert-butyl pyridine (0.2 M), ethanol (15%v/v), and acetonitrile as a solvent. The cell is illuminated from the top through the counter electrode and the light intensity is measured monochromatically to normalize the photocurrent response, the one schematized in Figure 3.4. The incident photon flux (as measured with an Oriel Model 70260 radiant power/energy meter) was  $0.59 \text{ mW/cm}^2$  at 340 nm with a bandwidth of 4 nm. The photon flux was monochromatically measured on an Oriel model 70260 Radiant Power/Energy meter.

The performance of the porphyrin sensitizers has been studied in a regenerative photo-electrochemical cell using  $\text{I}_3^-/\text{I}^-$  as electron mediators in acetonitrile. The cell performance is usually evaluated by the incident photon-to-current conversion efficiency (IPCE) sometimes referred to also as “external quantum efficiency” corresponds to the external circuit divided by the monochromatic photon flux that strikes the cell. This key parameter can be expressed by the product

$$\text{IPCE}(\lambda) = 1240 (I_{\text{sc}} / \lambda \Phi) \quad (\text{Eq. 3.1})$$

Where  $\lambda$  is the light wavelength,  $I_{\text{sc}}$  is the current at short circuit ( $\text{mA/cm}^2$ ), and  $\Phi$  is the incident radiative flux ( $\text{W/cm}^2$ ).

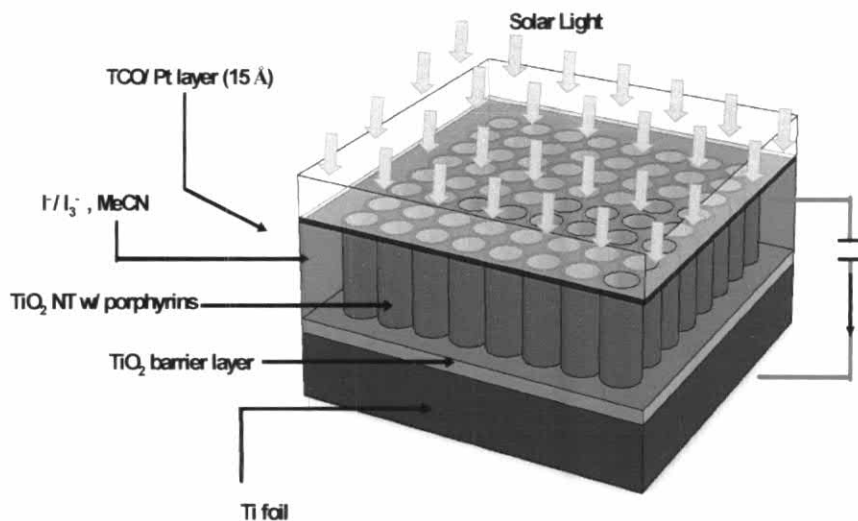


Figure 3.4 Schematic representation of porphyrin sensitized TiO<sub>2</sub> nanotube arrays containing DSSC device. Illumination is done through the TCO glass coated with a transparent Pt layer (15 Å).

### 3.5 Photocatalytic reaction of TiO<sub>2</sub> nanotube

#### 3.5.1 Chemicals and Materials

For photocatalysis process, potassium dichromate (Alfa Aesar) for prepared Cr(VI) solution, sulfuric acid (Aldrich), and pure nitrogen gas were used. All other chemicals used were also from commercial sources and were the highest purity available. They were used without further purification.

#### 3.5.2 Instrumentation

The concentrations of the Cr(VI) was spectrophotometrically monitored at analytical wavelengths of 350 nm on an Agilent Model 8453 instrument. For ultraviolet (UV) light photocatalysis, the 400 W xenon arc lamp was used as light source.

#### 3.5.3 Ultraviolet (UV) light photocatalysis

In this part, the TiO<sub>2</sub> nanotubes films from constant potential anodization, pulse anodization and metal doped TiO<sub>2</sub> nanotube were used as catalyst in photocatalysis experiments for hazardous waste removal by photocatalytic process. Hexavalent

chromium (Cr (VI)) was used as models of hazardous wastes for photocatalytic studies. Cr (IV) solution was prepared by dissolving potassium dichromate ( $K_2Cr_2O_7$ ) in distilled water. The concentration of the Cr (VI) solution is 200  $\mu$ M/L. The pH of the resultant solution was adjusted to 3 by 0.1 M  $H_2SO_4$  and pure  $N_2$  gas was spurge in solution in between dark adsorption and photocatalytic experiment. For ultra-violet (UV) light photocatalysis, the 400 W xenon arc lamp was used as light source.

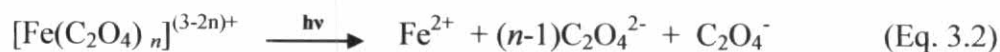
### 3.6 Determination of the quantum yield

#### 3.6.1 Chemicals and Materials

All chemicals used were of reagent grade quality. Potassium tris(oxalato) ferrate (III) trihydrate, 1,10-phenanthroline (Aldrich, ACS grade), and buffer were freshly prepared as described below. The 1,10-phenanthroline solutions were kept in the dark and used within 3 days of preparation to avoid degradation problem. The specific molar absorbance at 510 nm for the  $[Fe(phen)_3]^{2+}$  ion was determined by using Agilent Model 8453 spectrophotometer.

#### 3.6.2 Photon flux measurement

The method of photon flux measurement is potassium ferrioxalate actinometry (Braun *et al.*, 1991). For the ferrioxalate actinometer the production of the reduction of ferric ions to ferrous ions proceeds by the following reactions:



Normally, the moles of  $Fe^{2+}$  formed are determined spectrophotometrically by development with 1,10-phenanthroline (phen) to form the red  $[Fe(phen)_3]^{2+}$  moiety ( $\lambda_{max} = 510.0$  nm) (Demas *et al.*, 1981).

A 8 mL solution of 0.006 M potassium tris(oxalato) ferrate (III) trihydrate (0.020 g) in 0.05 M  $H_2SO_4$  (0.02 mL) was prepared along with 0.1% solution of phenanthroline (0.1g phenanthroline to 100 mL of DI water), and buffer solution consisting of 8.2 g sodium propionate in 99 mL of DI water and 1 mL  $H_2SO_4$ . An initial UV spectrum of the ferrioxalate solution was take, and was then added to the

photoreactor according to the set volume for each photoreactor. The ferrioxalate was then irradiated for 60 s with the UV light. A 1 mL aliquot of this irradiated solution was then added to a vial containing 4 mL 0.1% phenanthroline, 0.5 mL buffer, and 4.5 mL DI water. A 1 mL aliquot of ferrioxalate that had not been irradiated was also taken and added to a vial of the same contents for use as a reference. Both solutions were placed in the dark for 1 hour to allow for full color development. A UV spectrum of both solutions was then taken. The photon flux (P) was then calculated by (Braun *et al.*, 1991):

$$P = \left[ \frac{(A_s - A_b) \times V_d \times V_p \times N_A}{\epsilon_{Fe^{2+}} \times l \times \Phi_{Fe^{2+} \text{ at } 0.006M} \times V_a \times t} \right] \quad (\text{Eq. 3.4})$$

where P is the photon flux in photon s<sup>-1</sup>; A<sub>s</sub> and A<sub>b</sub> are the developed absorbance of sample and blank, respectively, at 510.0 nm; V<sub>d</sub>, V<sub>p</sub> and V<sub>a</sub> are the final developed, photolyzed, and aliquot volumes, respectively (all in liters); N<sub>A</sub> is Avogadro number (6.023 × 10<sup>23</sup>); ε<sub>Fe<sup>2+</sup></sub> is the specific molar absorbance for [Fe(phen)<sub>3</sub>]<sup>2+</sup> at 510.0 nm (11,110 L cm<sup>-1</sup> mol<sup>-1</sup>); *l* is the light path length of the spectrophotoreactor (1.95 cm); Φ<sub>Fe<sup>2+</sup></sub> is quantum yield for the photoreduction of the ferrioxalate ions (Φ<sub>Fe<sup>2+</sup></sub> = 1.20, Demas *et al.*, 1981); and *t* is the irradiation time in seconds.

The photon flux was found to be 1.53 × 10<sup>17</sup> photon/s for this photoreactor.

### 3.7 Other Instrumentation

For annealing and calcination of the samples were carried out using a Model 650-14 Isotemp Programmable Muffle Furnace (Fisher Scientific) in air before characterization and photoelectrochemical measurements. A linear heat ramp (at 25 °C/min) from room temperature to a preselected final temperature of 450 °C was followed by a 30 min equilibration at the final temperature. The samples were then allowed to cool via natural convection in the furnace back to the ambient condition. Scanning electron microscopy used is a Zeiss Supra 55 instrument with a nominal electron beam voltage of 5 kV.

Raman spectra were recorded with a Horiba Jovin Yvon ARAMIS instrument was used to identify specific vibration mode that might indicate the surface

interactions between porphyrin chromophores on  $\text{TiO}_2$ . The samples that were studied included solution of zinc porphyrin and zinc porphyrin / $\text{TiO}_2$  electrodes prepared by adsorption from methanol solution using excitation wavelength at 473 nm, and a grating of 600 line/mm. In all the cases the slit was 10  $\mu\text{m}$ , the time exposition was 10 s, and 10 scans were accumulated for each spectrum. Spectra were obtained for  $\text{TiO}_2$  nanotube arrays after annealing and after being subjected to adsorption from the preparative electrolytic bath.