

2.1 Materials Synthesis

In this thesis work, I have developed one unique way to synthesis *in situ* grown nanoparticle inside TiO_2 thin film. By using that technique, I have synthesize both metal and metal sulphide nanoparticle inside TiO_2 thin film by using glass or FTO coated glass substrate. This synthesis requires a sequence of experimental steps that have been described in following sections.

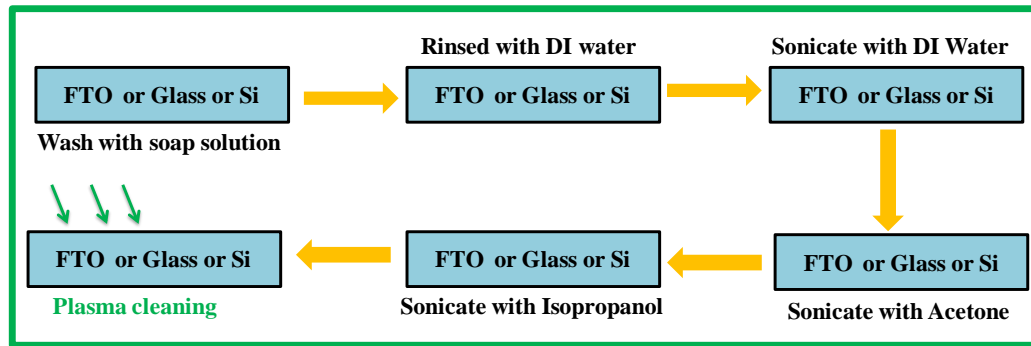


Figure 2.1: The schematic steps for the substrate cleaning process.

2.2 Substrate cleaning process

In the beginning, glass or FTO coated glass substrates were cleaned carefully in a multiple steps. The schematic presentation of this cleaning process is shown in **figure 2.1**. At first, FTO coated glass or glass substrates were cleaned by using soap solution followed by washing in deionized water (DI) water by keeping it in an ultrasonic bath. After that these substrates were cleaned with acetone and isopropanol sequentially for 15 minutes under ultra-sonication process. In final step of this cleaning process, substrates were kept inside plasma cleaner with oxygen atmosphere to make this substrate hydrophilic which is required for pin hole free sol-gel derived thin film fabrication.

2.3 Fabrication of metal oxide thin film

2.3.1 Synthesis and fabrication of TiO₂ thin film (sol-gel)

For sol-gel derive TiO₂ thin film fabrication, a precursor solution of titanium (IV) butoxide [Ti(OC₄H₉)₄] of concentration 300 mM has been prepared in ethanol solvent. Thin film was prepared on FTO coated glass by spin coating method with a spinning speed 5000 rpm. For TiO₂ NP thin film deposition, commercially available TiO₂ NP (GreatcellSolar's 18NR-T Transparent Titania Paste, average size ~ 20 nm) solution of concentration 20 mg/ml was spin-coated on FTO coated glass with a speed of 5000 rpm. Both types of TiO₂ coated substrates were then annealed at 500°C for 30 minutes to form a compact TiO₂ thin film.

2.3.2 Synthesis and fabrication ZnO thin film

For solution processed ZnO thin film fabrication, zinc acetate dihydrate, 2-methoxy ethanol, and monoethanolamine (MEA) were used as the precursor. To prepare this precursor, the mixed solution of zinc acetate dihydrate (300 mM) with 1% MEA (vol %) was continuously stirred for 30 minutes to obtain a clear solution. After that this solution was filtered using a syringe filter (PVDF membrane, 0.22 μm) to filter out the large particles. This solution was then spin-coated (5000 rpm) on glass substrate followed by an annealing process at 500°C for one hour [24] to obtain crystalline thin film of ZnO.

2.3.3 Fabrication of Ion conducting Li₄Ti₅O₁₂ thin film

The ion-conducting Li₄Ti₅O₁₂ ceramic thin film was prepared via a sol-gel technique and using titanium (IV) butoxide [Ti(OC₄H₉)₄] and lithium acetate as precursor materials (purchased from Sigma Aldrich). Two separate solutions of Ti(OC₄H₉)₄ and lithium acetate with the same concentration were prepared in ethanol solvent that has been

mixed with a 4:5 volume ratio to maintain the ratio of final $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) ceramic product. After that, citric acid was added to the solution as the chelating agent of the sol such a way that the final molar ratio of metal to citric acid was ~ 0.5 and the concentration of final precursor sol was 300mM. The mixture was then vigorously stirred for 5 hours to prepare a transparent solution, which is shown in **figure 2.2**. The resultant solution was deposited on a clean glass or FTO coated glass or Si substrate ($30 \times 20 \text{ mm}^2$) through a dip-coating process.

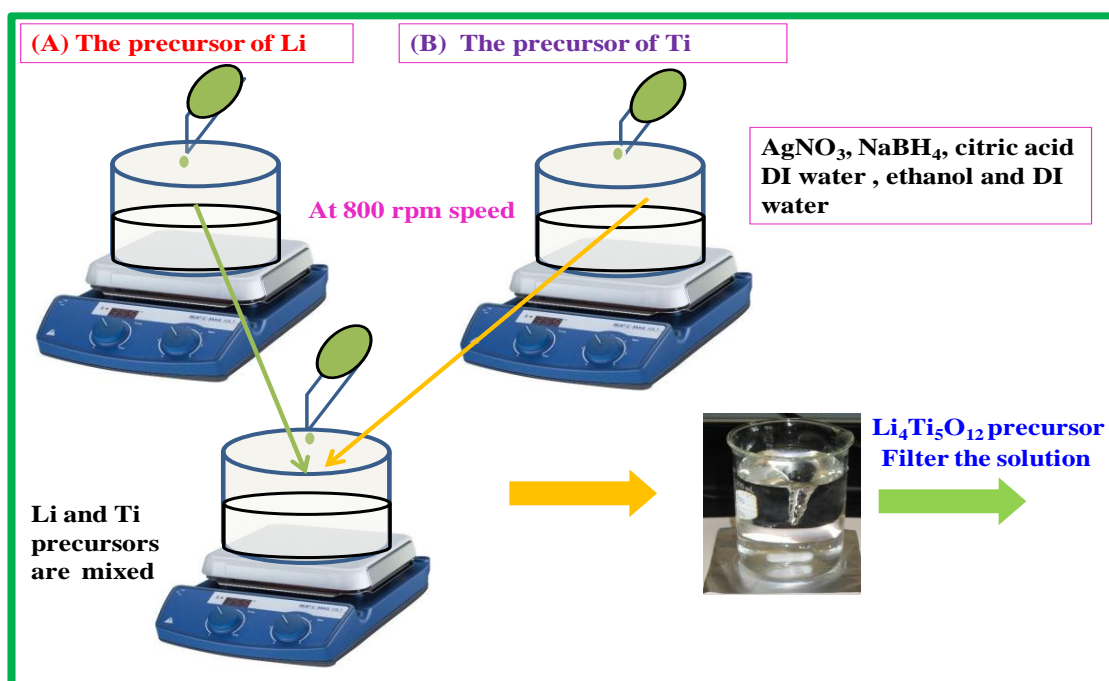


Figure 2.2: The schematic steps for the LTO solution preparation.

Dip coated samples were prepared with a drawing speed of 2 mm/sec. Immediately after dip coating, those substrates were annealed at 550°C for one hour to obtain a crystalline thin film of LTO. These processes were repeated for three times to obtain a desired thickness of LTO. For comparative study, a separate TiO_2 thin film sample was prepared by a one-time dip coating with 300 mM titanium (IV) butoxide $[\text{Ti}(\text{OC}_4\text{H}_9)_4]$ solution followed by annealing at 500°C for one hour.

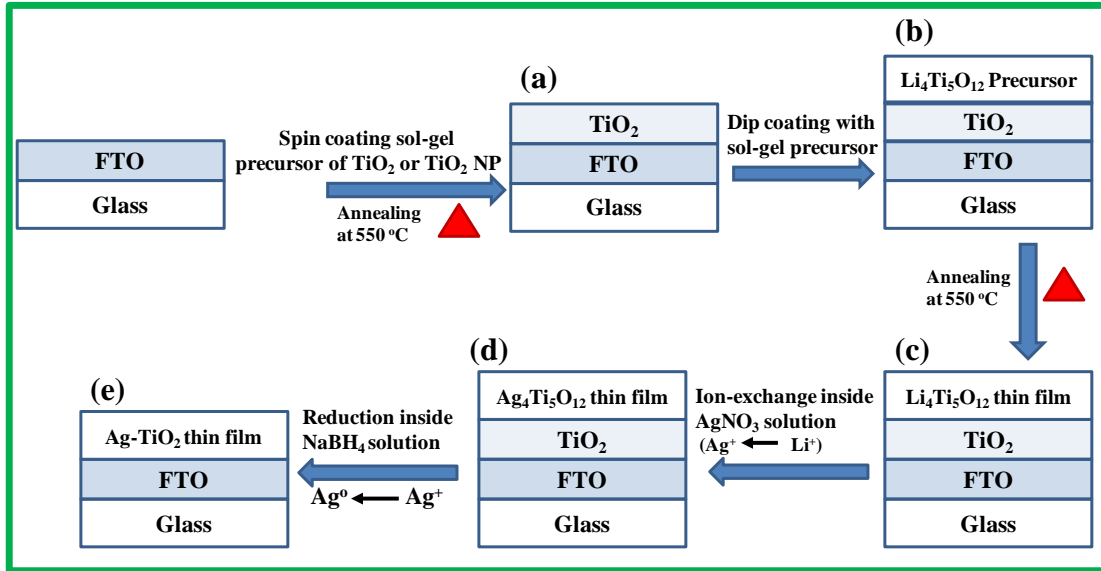
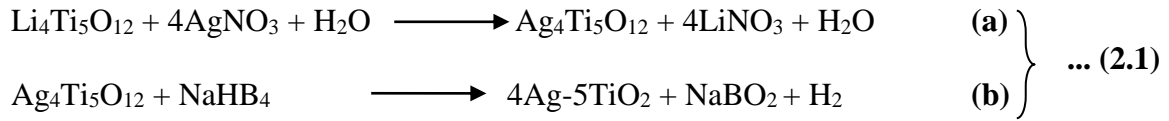


Figure 2.3: Schematic growth process of in-situ grown Ag-TiO₂ thin film in five successive steps (a) TiO₂ thin film on FTO coated glass by spin coating of sol-gel precursor or TiO₂ NP followed by annealing (b) dip coating of precursor of LTO thin film (c) annealing of precursor film at 550°C for 1 hour to obtain polycrystalline Li₄Ti₅O₁₂ thin film (d) ion exchange process to exchange Li⁺ ion of Li₄Ti₅O₁₂ by Ag⁺ of solution. (e) Reduction process that converts Ag⁺ to Ag⁰ to form Ag-TiO₂ thin film containing Ag NCs inside TiO₂ thin film.

2.3.4 Fabrication of Ag-TiO₂ thin film

In situ grown Ag nanocrystals (NCs) inside TiO₂ film was developed by two steps chemical reaction. At the beginning crystalline Li₄Ti₅O₁₂ thin films were coated on the three different substrates including FTO, TiO₂ (sol-gel)/FTO, TiO₂ NP/FTO, and glass. Then these samples were dipped inside a 100mM silver nitrate solution for 1 hr. During this process, silver ion (Ag⁺) of solution exchange with loosely bound lithium-ion (Li⁺) of Li₄Ti₅O₁₂ thin film through an ion-exchange process to form Ag₄Ti₅O₁₂, which turns the substrate's color from transparent to yellowish. After the ion-exchange process, substrates were cleaned with distilled (DI) water to remove extra AgNO₃ from the surface of the film. After washing, substrates were dipped inside a 300 mM NaBH₄ solution at room temperature for one hour. During this treatment, Ag⁺ reduce to silver metal (Ag⁰) to form

Ag-NCs and the initial $\text{Ag}_4\text{Ti}_5\text{O}_{12}$ crystal turns to Ag-TiO₂ nanocomposite thin film. This conversion of Ag⁺ to Ag nanoparticle formation is nearly 100%. Chemical reactions of this ion-exchange and reduction process are shown in equation (2.1(a)) and equation (2.2(b)) respectively. Finally, films were washed in DI water to remove excess NaBH₄ solution from the film. The schematic presentation of this growth process has been shown in **(Figure 2.3)**. However, this ion-exchange and reduction process is not specific for Ag metal. By this method, it is possible to grow heterojunction like Cu, Ni, and Au, etc.



2.3.5 Fabrication of Ag₂S-TiO₂ heterojunction thin film

To grow Ag₂S NPs inside TiO₂ thin film, polycrystalline Li₄Ti₅O₁₂ films were dipped inside a 100 mM silver nitrate solution for 1 hr. During this process, silver ion (Ag⁺) exchange with loosely bound lithium-ion (Li⁺) of Li₄Ti₅O₁₂ thin film through the ion-exchange process to form Ag₄Ti₅O₁₂, which turns the substrate's color from transparent to yellowish. After the ion-exchange process, substrates were cleaned with distilled (DI) water to remove extra AgNO₃. After washing, all substrates were dipped inside a 300 mM Na₂S solution at room temperature for one hour. During this chemical treatment, Ag⁺ ion of LTO converted to Ag₂S to form Ag₂S nanocrystals (NCs) that form Ag₂S-TiO₂ heterojunction thin film. Finally, films were washed in DI water to remove excess Na₂S solution. The schematic representation of the growth process of Ag₂S-TiO₂ thin film is shown in **(Figure 2.4)**, and related chemical reactions are shown in equation 2.2(a-c).

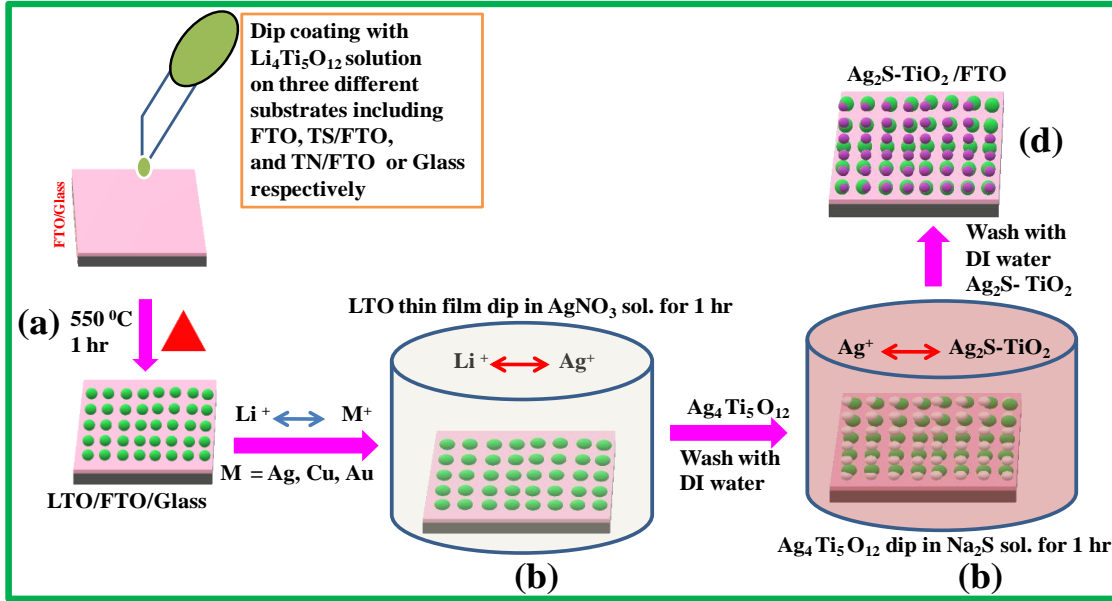
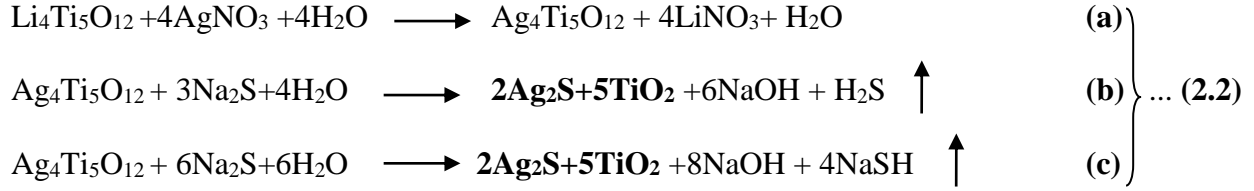
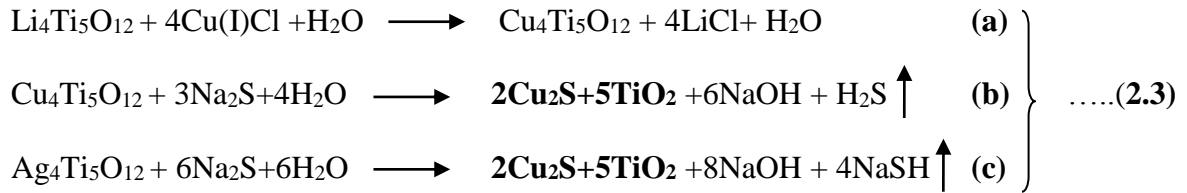


Figure 2.4: Schematic growth process of in-situ grown Ag₂S-TiO₂ thin film in four successive steps (a) Dip coating precursor of LTO on the FTO, TiO₂ (sol-gel)/FTO and TiO₂ (NPs)/FTO coated glass substrate followed by annealing respectively at 550°C for 1 hour to obtain polycrystalline Li₄Ti₅O₁₂ thin film (b) for ion exchange process to exchange Li⁺ ions by Ag⁺ (c) in this step sample dip for sulfurization process that convert Ag⁺ to Ag and to form Ag₂S inside TiO₂ thin film (d) this thin film wash with DI water to remove extra Na₂S solution from the samples.

2.3.6 Fabrication of Cu₂S-TiO₂ heterojunction thin film

The Cu₂S-TiO₂ heterojunction thin film has been fabricated similar way to Ag₂S-TiO₂ heterojunction thin film. Only difference of this fabrication is the ion-exchange process, which has been done by dipping Li₄Ti₅O₁₂ thin films inside 100 mM copper (I) chloride solution for 1 hr. During this process, metal ion (Cu⁺) exchange with loosely bound lithium-ion (Li⁺) of the Li₄Ti₅O₁₂ thin film through the ion-exchange process to form Cu₄Ti₅O₁₂ which turns the substrate's color from transparent to blackish. After the ion-exchange process, substrates were cleaned with distilled (DI) water to remove extra

Cu(I)Cl from the surface of the film. After washing, all substrates were dipped inside a 300 mM Na₂S solution at roomtemperature for one hour. During this treatment, Cu⁺converted to Cu₂S to form Cu₂S NCs crystal. Finally, films were washed in DI water to remove excess Na₂S solution from the film. The schematic presentation of this growth process of the Cu₂S-TiO₂ nanocomposite thin film is shown in (**Figure 2.5**). Related chemical reactions of this growth process are shown in equation 2.3(a-c). This Cu₂S-TiO₂ thin films were deposited on the different substrates including FTO, TiO₂ (sol-gel)/FTO, TiO₂ NP/FTO, ZnO coated glass and glass.



2.3.7 Fabrication of Cu₂S-TiO₂ heterojunction thin film

In situ grown Cu₂S-TiO₂ thin films have been fabricated on different substrates including on glass and ZnO coated glass substrate. This ZnO layer has been deposited by another sol-gel technique and fabrication process has been explained in section 2.1.2.2. For sol-gel derive ZnO thin film fabrication a precursor solution of zinc acetate of concentration 300 mM has been spin-coated (5000 rpm) on the glass substrate, followed by an annealing process at 500°C for one hour. Afterward, Cu₂S-TiO₂ nanocomposite thin film has been deposited by three steps growth process as it discussed earlier. Finally, aluminum (Al) electrodes were deposited by thermal evaporation to finish the device fabrication. The aluminum (Al) is deposition deposited under high vacuumed (1×10⁻⁶m.bar).

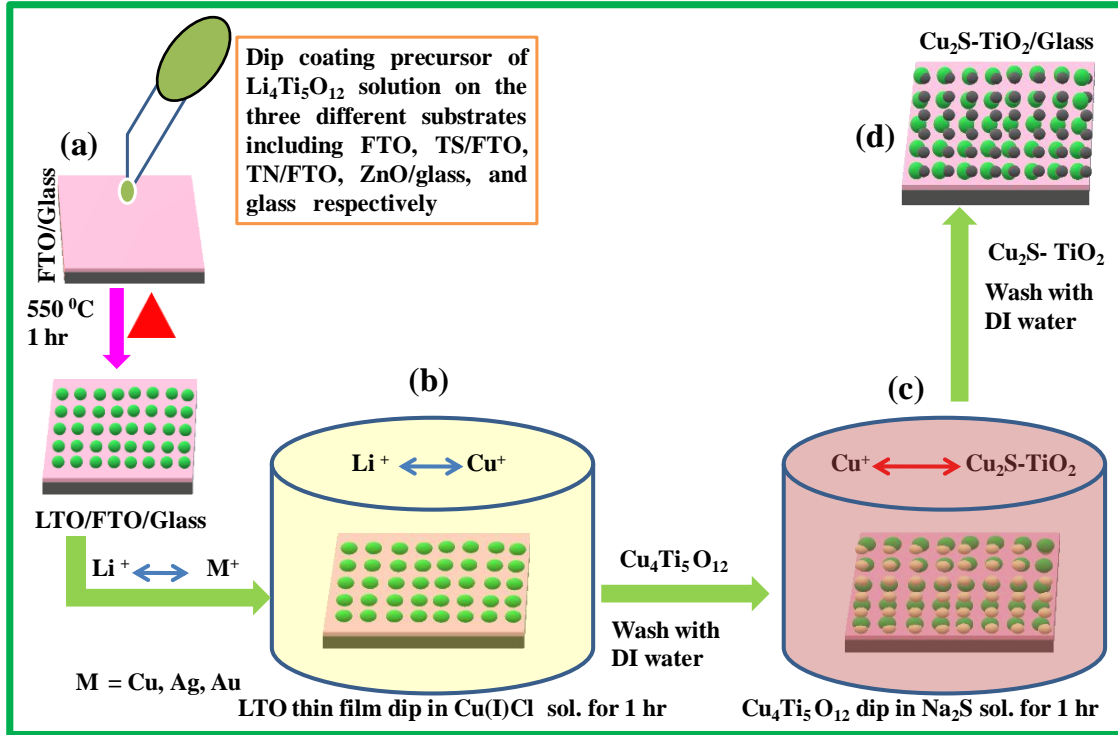


Figure 2.5: Schematic growth process of in-situ grown Cu₂S (NPs)-TiO₂ thin film in three successive steps (a) LTO precursor coated on the three different including FTO, TS/FTO, and TN/FTO, ZnO coated glass or glass substrate by dip coating followed by annealing respectively at 550°C for 1 hour to obtain polycrystalline Li₄Ti₅O₁₂ thin film (b) for ion exchange process to exchange Li⁺ ions by metal ion (Li⁺ ↔ Cu⁺), from metal solution) to form Cu₄Ti₅O₁₂ thin film. (c) For sulfurization process that converts Cu₄Ti₅O₁₂ to Cu₂S-TiO₂ thin films respectively and these thin films containing Cu₂S NPs inside TiO₂ thin film (d), these samples wash with DI water to remove extra Na₂S solution from the surface.

2.4 Characterization Techniques

2.4.1 X-ray diffraction (XRD)

The crystal structure and phase confirmation of different thin films were analyzed by using a Rigaku X-ray diffractometer with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) in the 2θ range of $10^\circ - 90^\circ$ with scan rate $2^\circ/\text{min}$. The particle size of different nanoparticles has been determined from the XRD pattern by using Scherrer's equation. ($t = \frac{K * \lambda}{B * \cos \theta_B}$), where $t =$

thickness of crystallite, $K =$ constant dependent on crystallite shape (0.89), $\lambda =$ x-ray

wavelength (1.54\AA for Cu target), B = (full width at half max) FWHM and θ_B = Bragg angle.

2.4.2 UV-visible spectrophotometer

The absorption properties of different nanoparticles have been studied by using UV-VIS absorption, spectroscopy within the range of 200-900 nm. These measurements have been done on thin films. The absorption spectra of different thin films have also used to determining the bandgap of the semiconductors.

2.4.3 High resolution scanning electron microscopy (SEM) and Transmission electron microscopy (TEM)

The microstructures and surface morphology of different samples were measured by high resolution-scanning electron microscopy (HR-SEM, Nova Nano SEM 450). The size of nanoparticle, particle distribution and crystallite nature of different nanoparticles have been analyzed by transmission electron microscopy (TEM, Tecnai G2 20 TWIN). For the elemental analysis and elemental mapping, energy dispersive spectroscopy (EDS) studies have been perform EDS analysis equipment which is attached in SEM and TEM instrument.

2.4.4 Incident photon to current efficiency (IPCE) measurements

Incident photon to current efficiency (IPCE) data was measured by illuminating photoanodes by monochromatic light from a monochromator under bias condition (Figure-2.6). Whereas, 300 W xenon lamp was used as source of light. Wavelength of illumination light was swept in the range from 350 nm to 800 nm. The IPCE in the photo-electrochemical system is defined by equation (2.4)[75].

$$\text{IPCE} = \frac{\text{Number of photogenerated electron}}{\text{Number of incident photon}}$$

$$\frac{1240 \times J_{ph}}{P \times \lambda} \times 100\% \quad (2.4)$$

Where J_{ph} , P, the λ is photocurrent density (mAcm^{-2}), input power (W/cm^2), and wavelength of light, respectively. Similar IPCE measurements have performed for photodetector device by illuminating the device with monochromatic light. Photocurrent was measured simultaneously for different wavelength of light and IPCE data were calculated from equation 2.4.

2.4.5 Electrochemical measurements

The photoelectrochemical performance of various photoanodes were studied in a conventional three-electrode system shown in **figure 2.7**. A platinum plate was used as the counter electrode and saturated Ag/AgCl as the reference electrode in the 1M KOH electrolyte solution. White xenon light source that has been used as simulated sunlight with a light intensity of 1000 W/m^2 . Light intensity was calibrated with standard silicon (Si) photodetector before this measurement. Photocurrents were recorded by using a Corr Test/Electrochemical and Corrosion Studio 5 [Model CS350 I COM4 SN:CS3501609178]. The electrochemical impedance spectra (EIS) were carried out with the same potentiostat. All potential is referenced to a reversible hydrogen electrode (RHE) by adding a value of $(0.197+0.059 \times \text{pH})$ volt [75, 76].

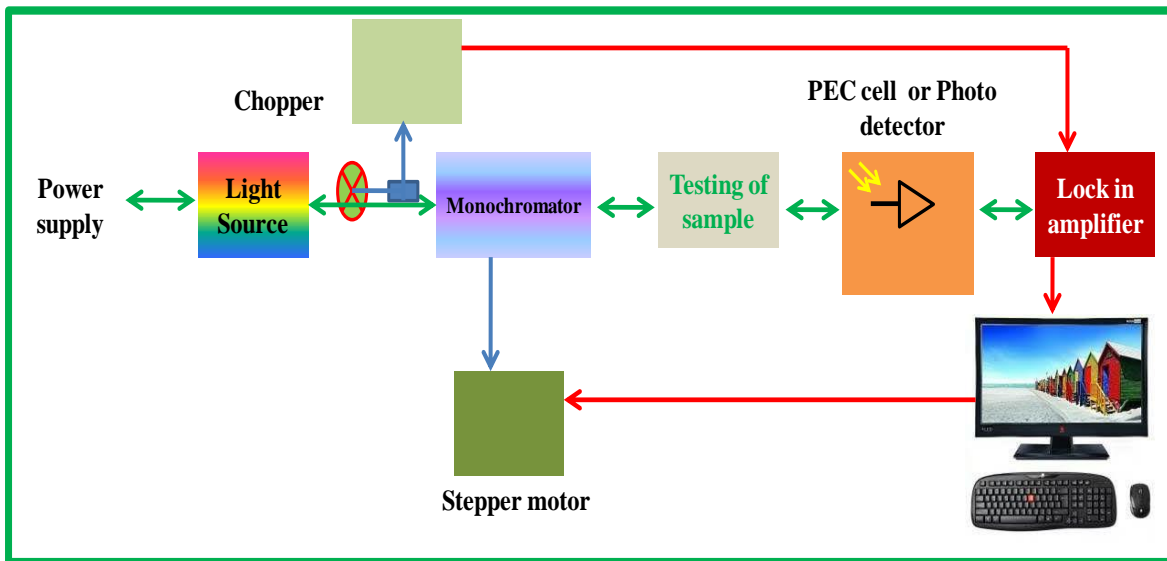


Figure 2.6: The schematic diagram of IPCE or EQE, Responsivity measurements for PEC cell or photodetector.

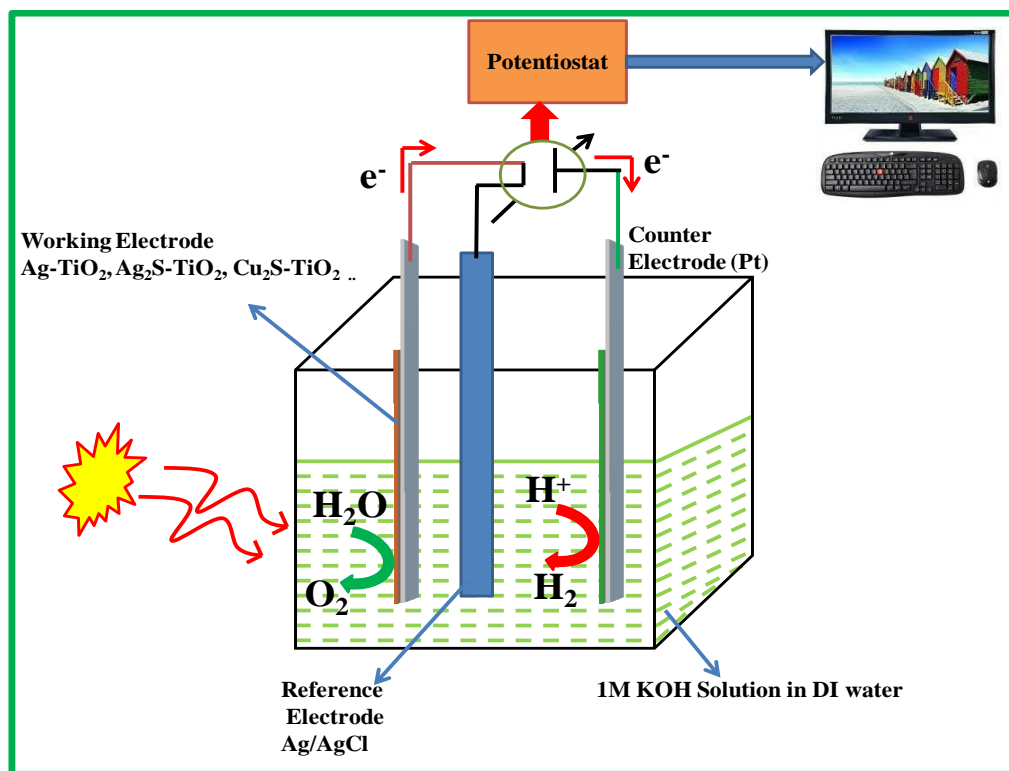


Figure 2.7: Schematic representation of three-electrode systems for linear sweep voltmeter, in this figure, Ag-TiO_2 , $\text{Ag}_2\text{S-TiO}_2$, and $\text{Cu}_2\text{S-TiO}_2$, we used as a working electrode, platinum as a counter electrode and Ag/AgCl as a reference electrode.

2.4.6 Impedance measurements

The internal resistance of electrolyte system with different photoanodes were measured in a frequency range from 1MHz to 0.1 Hz at an open-circuit voltage (OCV) of 0.3-0.5 V. This analysis has been used to obtain internal resistance free (iR-free) potential of the working electrode.