

Chapter 5

Application

The chapter is intended to explore the potential application of this work. As suggested earlier, there are several applications of up-conversion phosphors. One of the prominent applications is its use in Light Emitting Diodes by converting the emitted infrared energy into visible light. The use of up-conversion phosphors in bioimaging is also one of its major applications.

However, this work attempts to explore its utility in energy generation by using the material in a solar cell. Many types of solar cells are in use. Among them, the DSSC (Dye Sensitized Solar Cell) is a low cost alternative. It is based on a semiconductor which is formed between a photo-sensitized anode and an electrolyte [1].

The DSSC consists of two electrodes with electrolyte between them. The light falls on the top electrode or Anode, which is a transparent glass plate coated with Fluorine doped Tin Oxide.

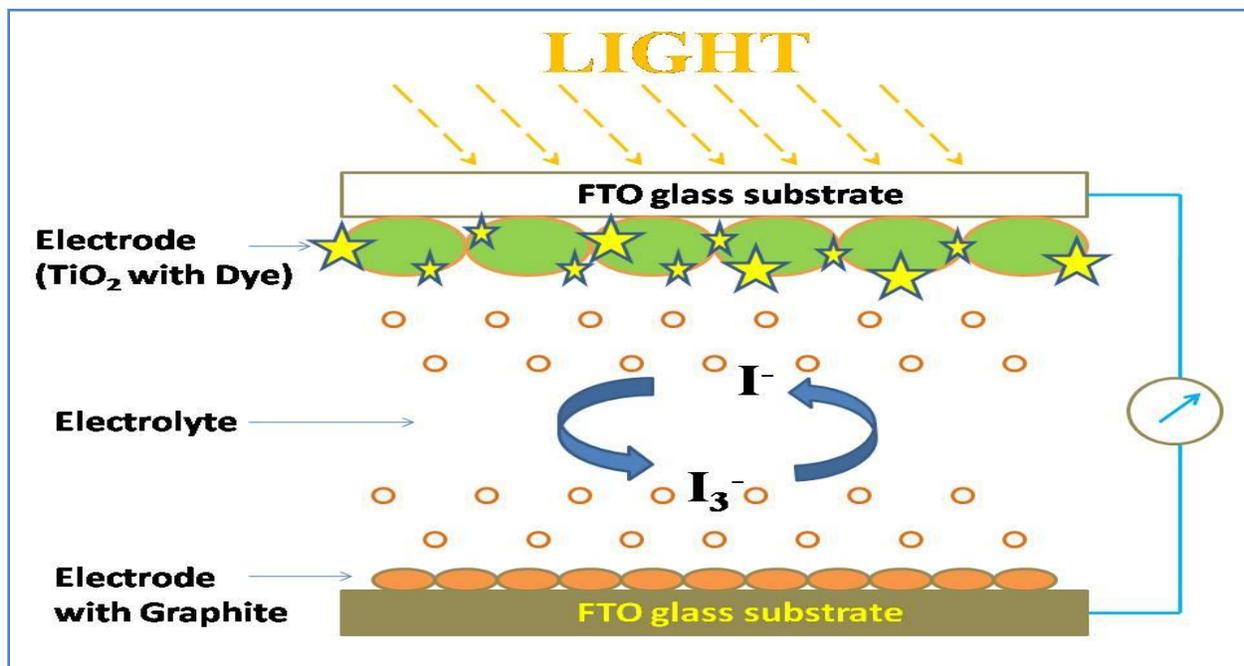


Figure 5.1: Mechanism of DSSC

5.1 Introduction

The light reaches the TiO₂ electrode layer but it can absorb only a fraction of the incoming radiation i.e. in the ultraviolet region. Most of the radiation in the solar spectrum is in visible and infrared. To increase the number of electrons generated by the incoming radiation, the electrode is immersed in a dye, which acts as a photosensitizer. The dye absorbs the photons and generates electrons. The TiO₂ layer on which the dye is adsorbed generally consists of TiO₂ nanoparticles, so that the larger surface to volume ratio enables more adsorption of the dye. This is followed by another layer of TiO₂ with higher particle size to scatter the photons back to the dye adsorbed TiO₂ layer. A counter electrode with a platinum/graphite layer is then used to cover the electrolyte layer from the other side.

The light passes through the anode into the dye layer, where electrons are generated and they flow into the TiO₂ layer. The electrons accumulated at the anode, move through the external circuit and get reintroduced in the cell through the electrolyte, which then transports them back to the dye molecules.

The amount of power generated would depend primarily on the photosensitizer, which generates the electrons. The spectral response of the dye which is the most widely used i.e. Ruthenium based dye [2] and that has been used in this study i.e. Anthocyanin [3] based dye is shown in the figures given below:

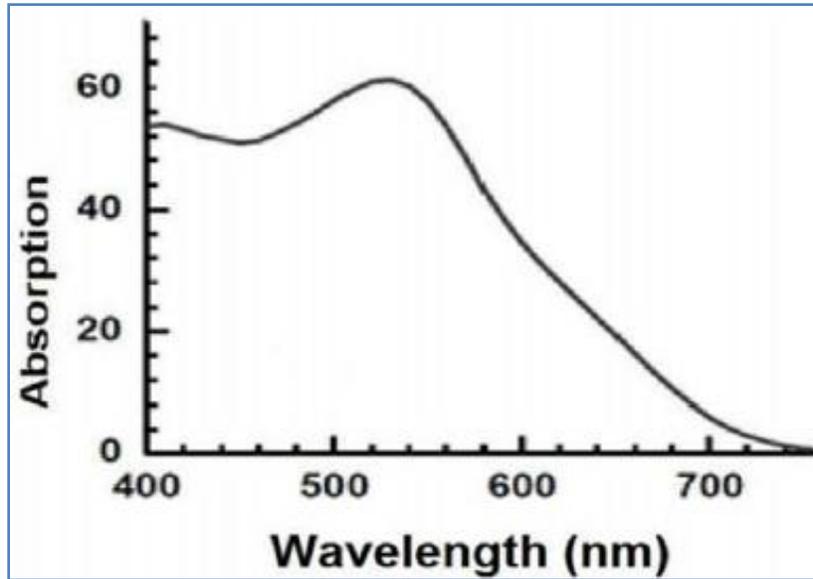


Figure 5.2: Spectral response of Ruthenium Dye

{Courtesy: Ref. 2}

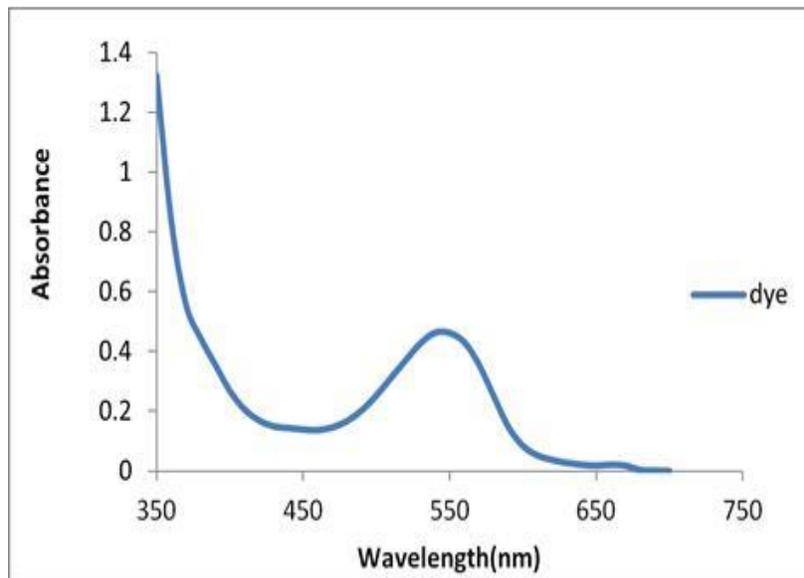


Figure 5.3: Spectral response of Anthocynin Dye

{Courtesy: Ref. 4}

It clearly shows that these dyes absorb only in the visible region. However, the solar spectrum is spread up to infrared. Hence, there is a scope for using up-conversion phosphors with TiO_2 so

that part of the solar spectrum can be converted into visible light, which the dye can absorb and generate more electrons.

Two components of DSSC make it relatively expensive. One is Ruthenium complex as a dye (photo sensitizer) and the other is platinum layer as a counter electrode. However, there are low cost alternatives. Carbon can be coated on a conducting plate to be used as a counter electrode instead of using platinum. Natural dye (organic dye) extracted from pomegranate juice can be used instead of using Ruthenium complex, which are obtained from renewable sources, are cheaper than metal oxides, have large absorption coefficients, have variety of structures for molecular design and cause no disposal problems.

5.2 Preparation of DSSC

The steps for fabrication of a DSSC can be described as under.

- (1) In the first step, a mixture of TiO_2 and up-conversion phosphor sample (in equal proportions) is grinded in an agate mortar paste with dilute acetic acid for 1 hour. Triton X – 100, which acts as a surfactant is added to prepare a smooth paste. {10 mg each of TiO_2 and up-conversion phosphor sample was taken for fabricating one sample}.
- (2) The ITO glass plate (conducting plate) is then cleaned using propanol.
- (3) The obtained paste of material is deposited on the ITO glass plate by Doctor's blade technique. Adhesive tapes are used as spacers. The film is dried in air at room temperature for 1 hour.
- (4) The coated conducting glass plate is sintered at 450°C for 30 min using hot plate and then cooled down to room temperature. This film acts as the photo electrode.

- (5) The plate is immersed in the dye so that the dye is adsorbed onto the material's surface. Anthocyanin dye present in pomegranate juice was used as a photo sensitizer [3]. The films are immersed into the pomegranate juice followed by storage at room temperature for 12 to 18 hours in dark place, so that it is properly adsorbed on the film. The film is washed with isopropanol to remove excess non adsorbed dye.
- (6) For the counter electrode, a graphite layer is used instead of expensive platinum layer. This thin layer of graphite is coated on another ITO glass plate by pencil, which works as a counter electrode.
- (7) Iodine solution, which acts as a electrolyte is added drop by drop between the plates. [5]
- (8) After preparation of photo electrode and counter electrode, a sandwich type Solar Cell (DSSC) is assembled. A film of polyethylene (double sided scotch tape) is placed on the sides of the photo electrode, which acts as spacer and provides insulation between two electrodes. The spacers are applied in a such a way that the active area remains 1 cm x 1 cm. One side is kept open for the next step.
- (9) The two electrodes are held together by binder clips. The electrolyte solution is then introduced into the gap between the counter electrode and the photo electrode drop by drop. To prepare the solution, 0.127 gm Iodine (I_2) was dissolved in 10 ml of ethylene glycol. 0.83 gm potassium iodide (KI) was mixed in this solution and stirred for half an hour. The solution is kept in a dark place.

DSSC being a form of photoelectric cell or device, the electrical characteristics like current, voltage and resistance vary when exposed to light. The power conversion efficiency of DSSC is impacted by many factors like the transmittance and the conductivity of the conducting substrate, type of dye, the electrode, properties of film and the electrolyte composition [6].

5.3 Measurement of parameters and calculations

The performance of dye-sensitized solar cell (DSSC) is assessed by measuring the parameters such as short circuit current (I_{sc}) and open circuit voltage (V_{oc}) under the source of illumination. The IV curve is used to find I_{max} and V_{max} , which gives maximum power (P_{max}). The conversion efficiency (η) of the solar cell can be obtained by measuring the open circuit photo voltage (V_{oc}) under normal conditions (not illuminated), the short circuit current (I_{sc}) drive from the I-V characteristics, the photocurrent density at short circuit (J_{sc}) which is calculated and the fill factor (FF) which is also calculated.

Open circuit voltage (V_{oc})

Open circuit voltage takes place when there is no current passing through the cell. V_{oc} is also the maximum voltage difference across the cell.

$$\mathbf{V = V_{oc} \quad for \ I = 0}$$

Short circuit current (I_{sc})

The short circuit current is the value of current, when the voltage across the solar cell is zero. For an ideal solar cell, I_{sc} is the maximum current or total current produced in the solar cell by photon excitation.

$$\mathbf{I = I_{sc} \quad for \ V = 0}$$

Maximum power (P_{max})

Maximum power produced by solar cell can be computed from I-V curve by finding I_{max} and V_{max} .

$$P_{max} = I_{max} \times V_{max}$$

Fill factor (FF)

The fill factor is the ratio of the maximum obtainable power to theoretical power. When the fill factor value is close to 1, it can be considered as an efficient cell. It is given by the following formula:

$$\text{Fill Factor (FF)} = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}}$$

Power conversion efficiency (η)

The power conversion efficiency of DSSC was calculated by the following formula:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

where P_{in} = Input power of light source i.e. Sunlight, which is taken as $1.367 \times 10^3 \text{ W/m}^2$ [7].

To measure the solar efficiency of the solar cell, the following set up was used as shown in the figure 5.4.



Figure 5.4: Actual view of measurement of Solar-Cell efficiency under Sunlight.

The electrical components used in this measurement are digital multimeter, digital DC voltmeter and ammeter, variable resistance, sample holder for solar cell and connecting wires. The circuit diagram for measuring I – V characteristics is illustrated in the figure 5.5.

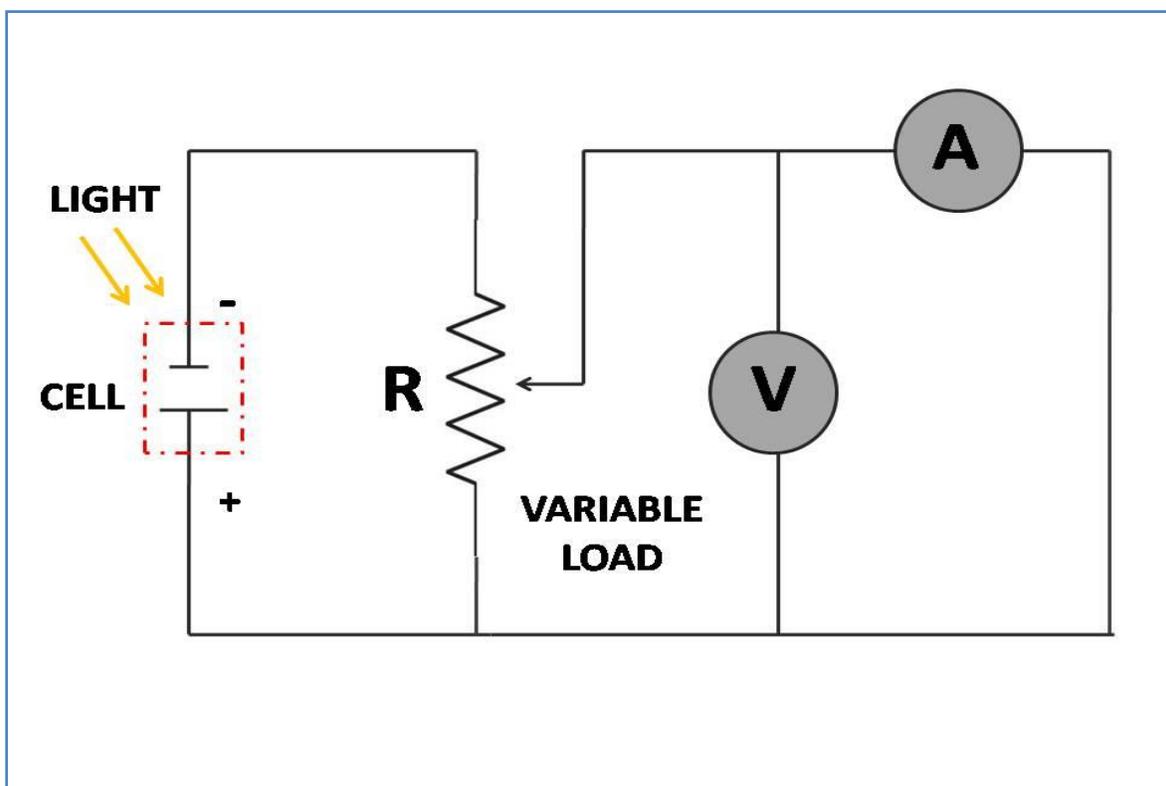


Figure 5.5: Circuit Diagram for measuring I – V Characteristics of Solar Cell.

5.4 I – V characteristics

5.4.1 I – V characteristics of Cell prepared with pure TiO_2

The I – V characteristics of DSSC fabricated with only TiO_2 powder was recorded initially. Thereafter, I – V characteristics of the cells fabricated using the mixed powder paste of TiO_2 and up-conversion phosphor samples in equal proportions were recorded. To check reproducibility of efficiency, several cells for the same material were prepared and I – V characteristics of all of them were measured. Among them the best characteristics have been reported.

Figure 5.6 show the I-V curves for the DSSC prepared with only TiO_2 powder under exposure to Sunlight.

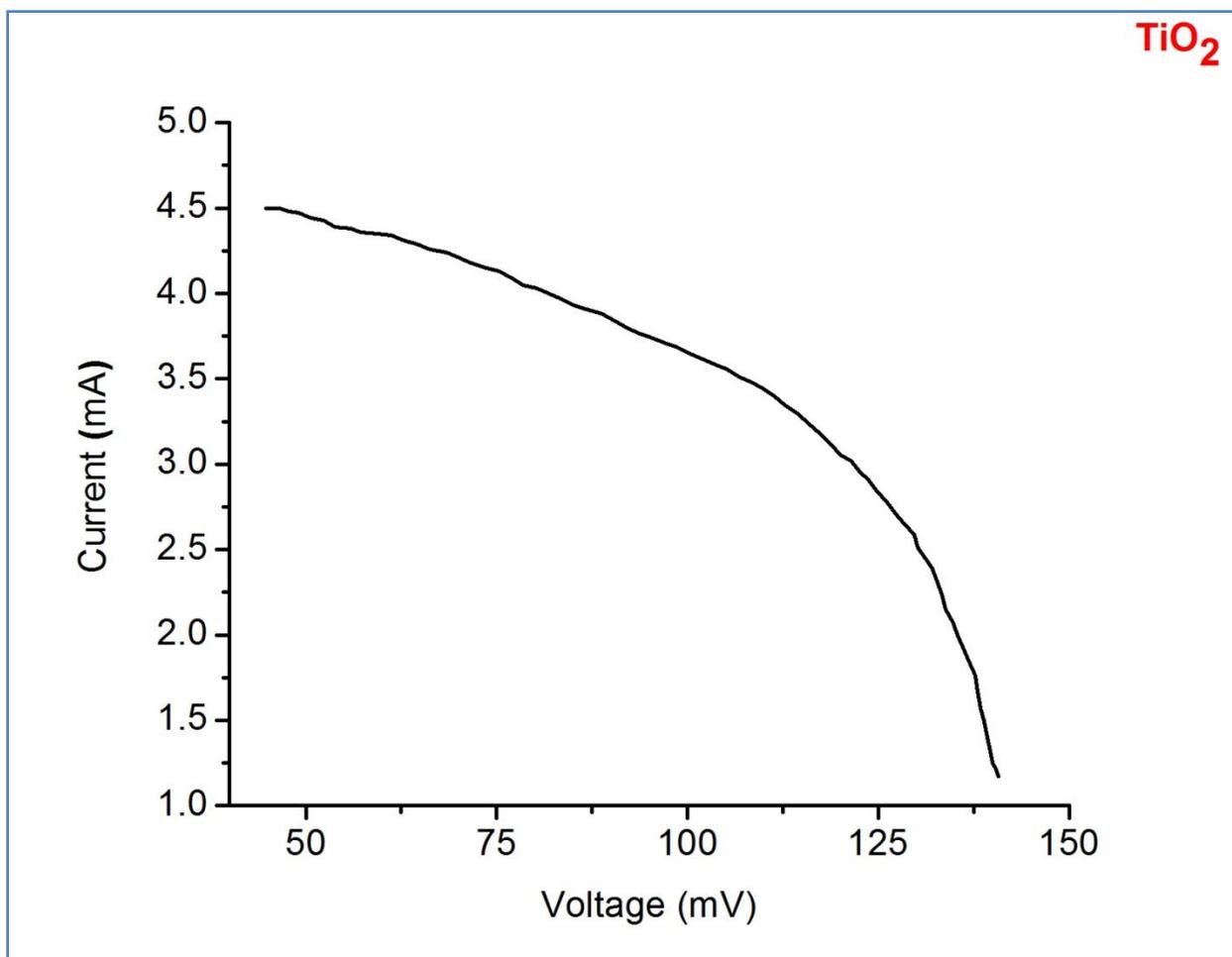


Figure 5.6: I – V curve of cell prepared with only TiO₂ powder

Cell	V _{oc} (mV)	I _{sc} (mA)	J _{sc} (mA/cm ²)	P _{max} x 10 ⁻⁶ W	FF (Fill Factor)	η (%)
(Area:1 cm ²) (measured)						
TiO ₂	201	4.5	4.5	378.465	0.4183	0.276

Table 5.1: DSSC parameters (TiO₂)

5.4.2 I – V characteristics of Cell prepared with TiO_2 + Up-conversion phosphor samples of $\text{La}_2(\text{MoO}_4)_3: \text{Yb}, \text{Er}$

Figure 5.7, 5.8 and 5.9 shows I – V curves of samples LMO 1, LMO 2 and LMO 3 respectively for sunlight.

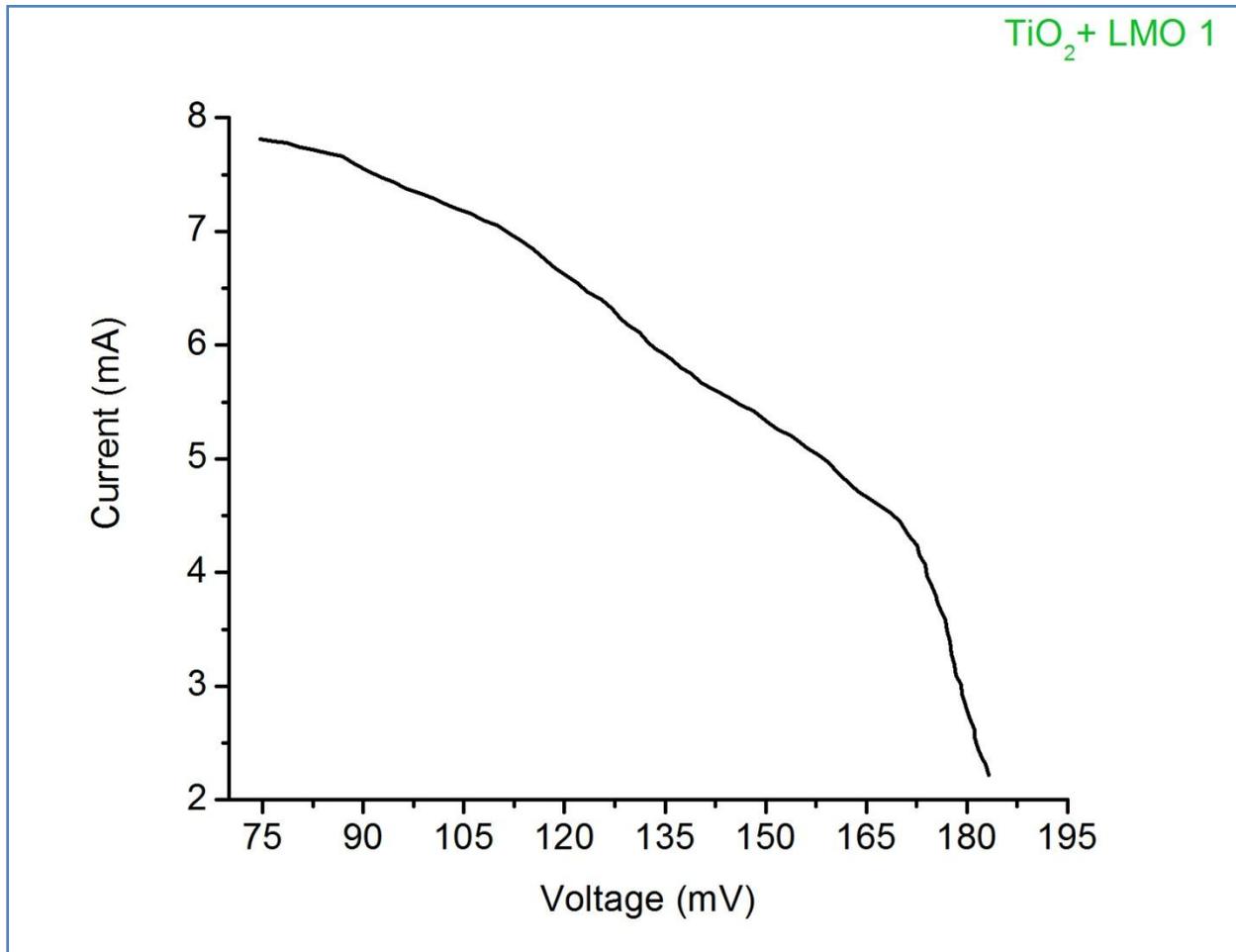


Figure 5.7: I – V curve of Solar cell prepared with TiO_2 + LMO 1

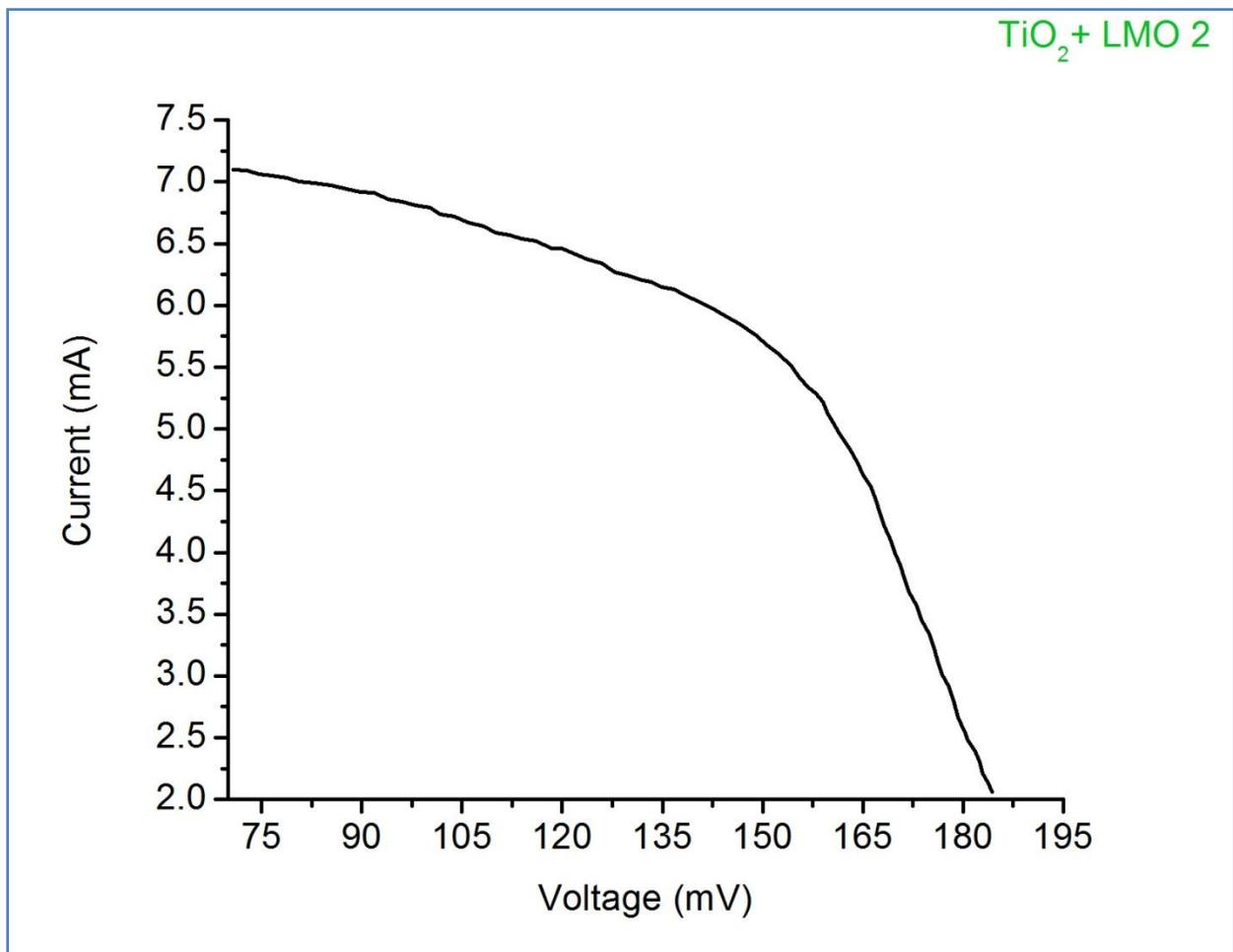


Figure 5.8: I – V curve of Solar cell prepared with TiO₂ + LMO 2

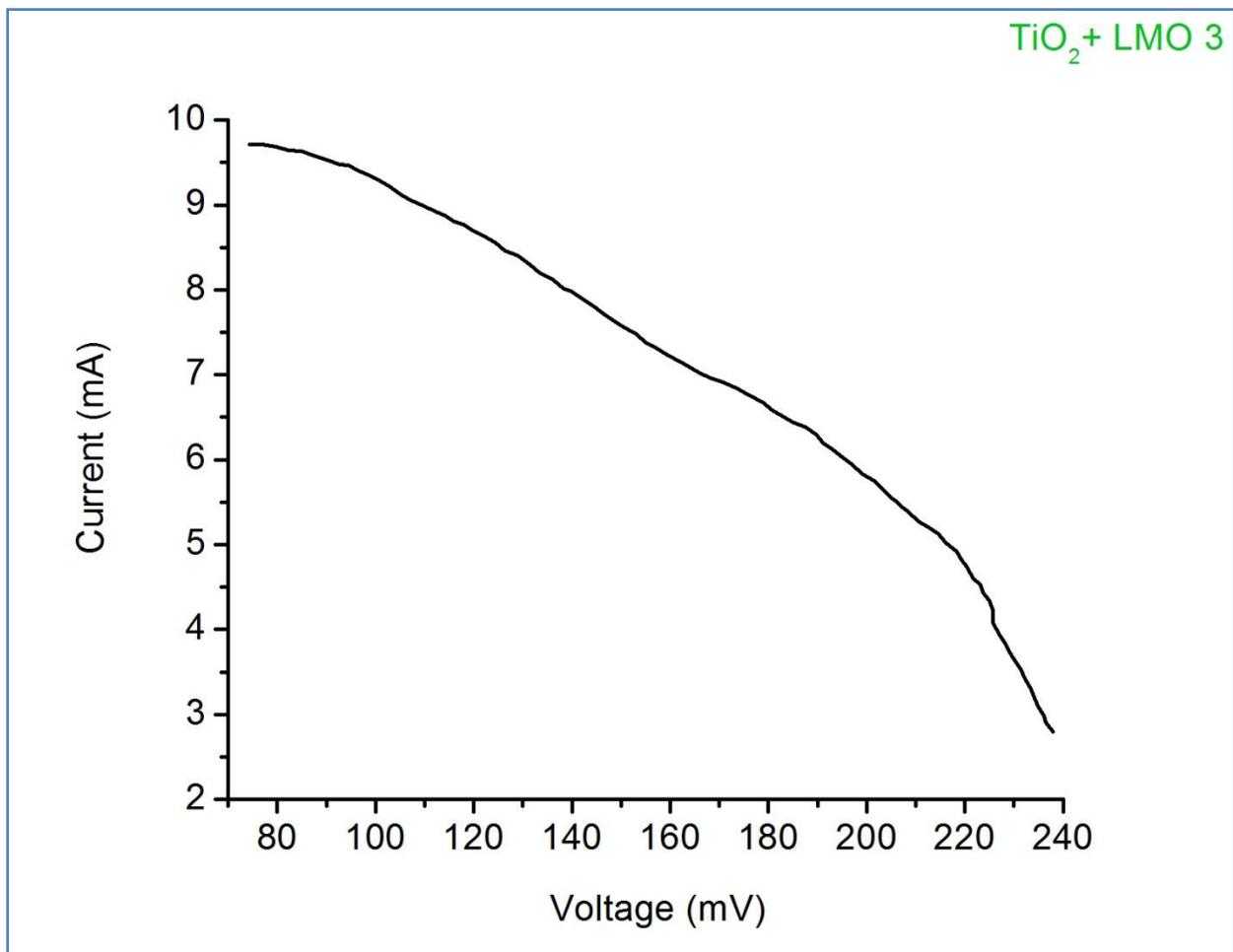


Figure 5.9: I – V curve of Solar cell prepared with TiO₂ + LMO 3 under

Cell	Voc	Isc	Jsc	P_{max}	FF	η
	(mV)	(mA)	(mA/cm²)	x 10⁻⁶ W	(Fill Factor)	(%)
(Area:1 cm²)	(measured)					
TiO₂ + LMO 1	219	7.8	7.8	803.515	0.4703	0.587
TiO₂ + LMO 2	216	7.11	7.11	857.844	0.5585	0.627
TiO₂ + LMO 3	241	9.71	9.71	1197.079	0.51156	0.875

Table 5.2: Cell parameters (La₂(MoO₄)₃:Yb,Er)

It has been observed from the table 5.2 that under the exposure of sunlight the efficiency of solar cell prepared using mixed (TiO₂ + LMO) samples is higher than pure TiO₂. It has been also observed that the efficiency increases with increasing amount of Erbium in the respective samples.

5.4.3 I – V characteristics of Cells prepared with TiO_2 + Up-conversion phosphor samples of Bi_2O_3 : Yb, Er

Figure 5.10, 5.11 and 5.12 shows the I – V curve of the samples BO 1, BO 2 and BO 3 respectively under the exposure of Sunlight.

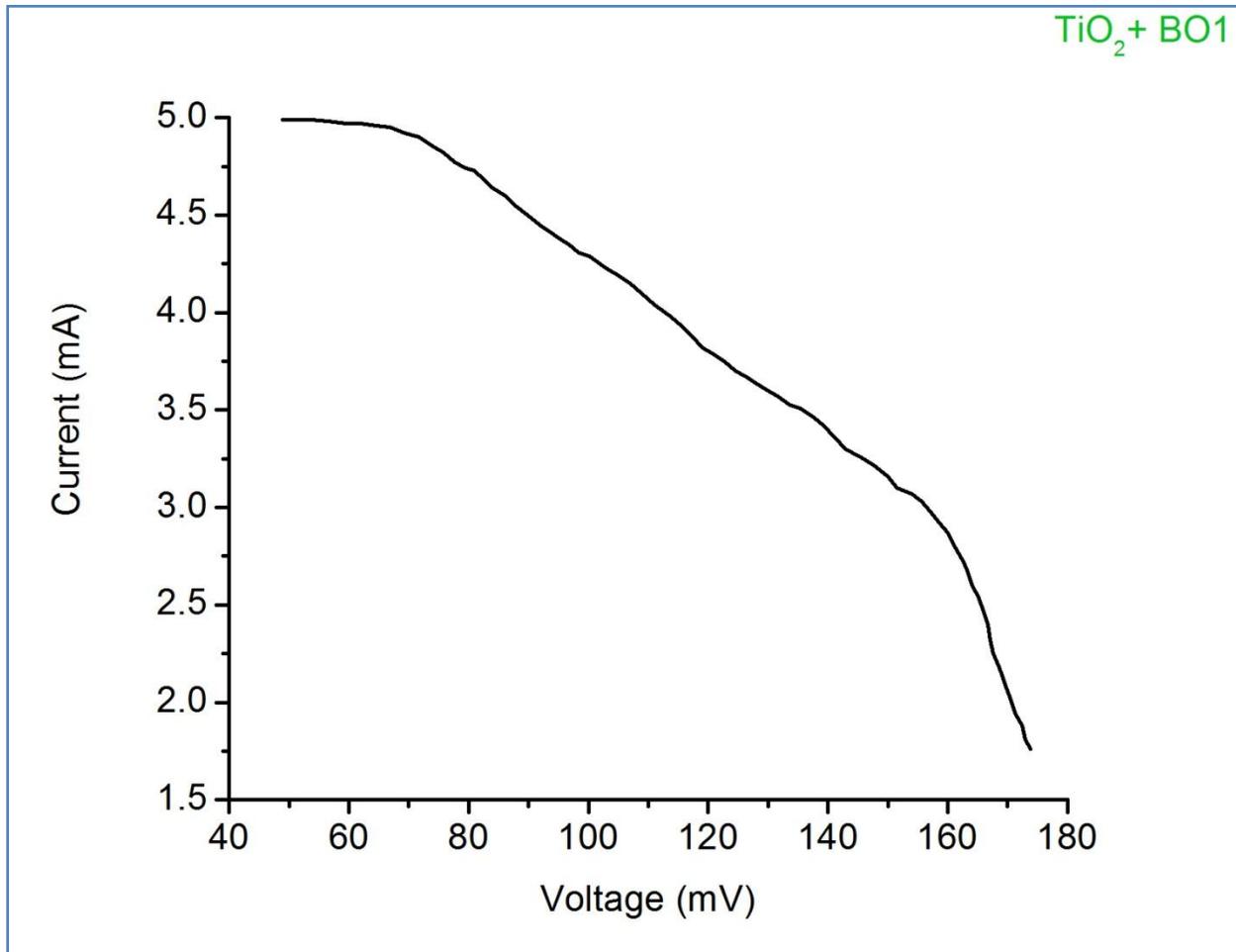


Figure 5.10: I – V curve of Solar cell prepared with TiO_2 + BO 1

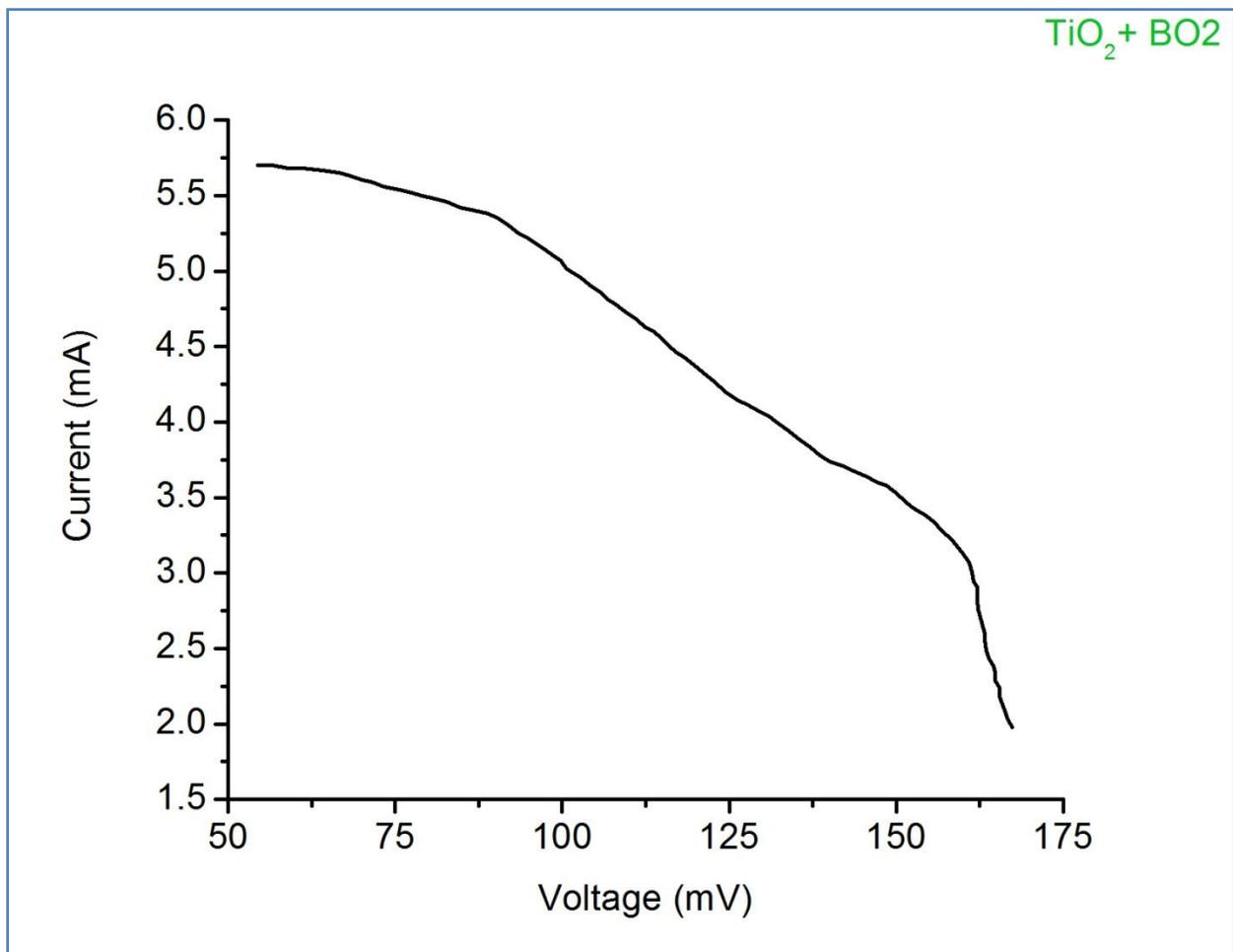


Figure 5.11: I – V curve of Solar cell prepared with TiO₂ + BO₂

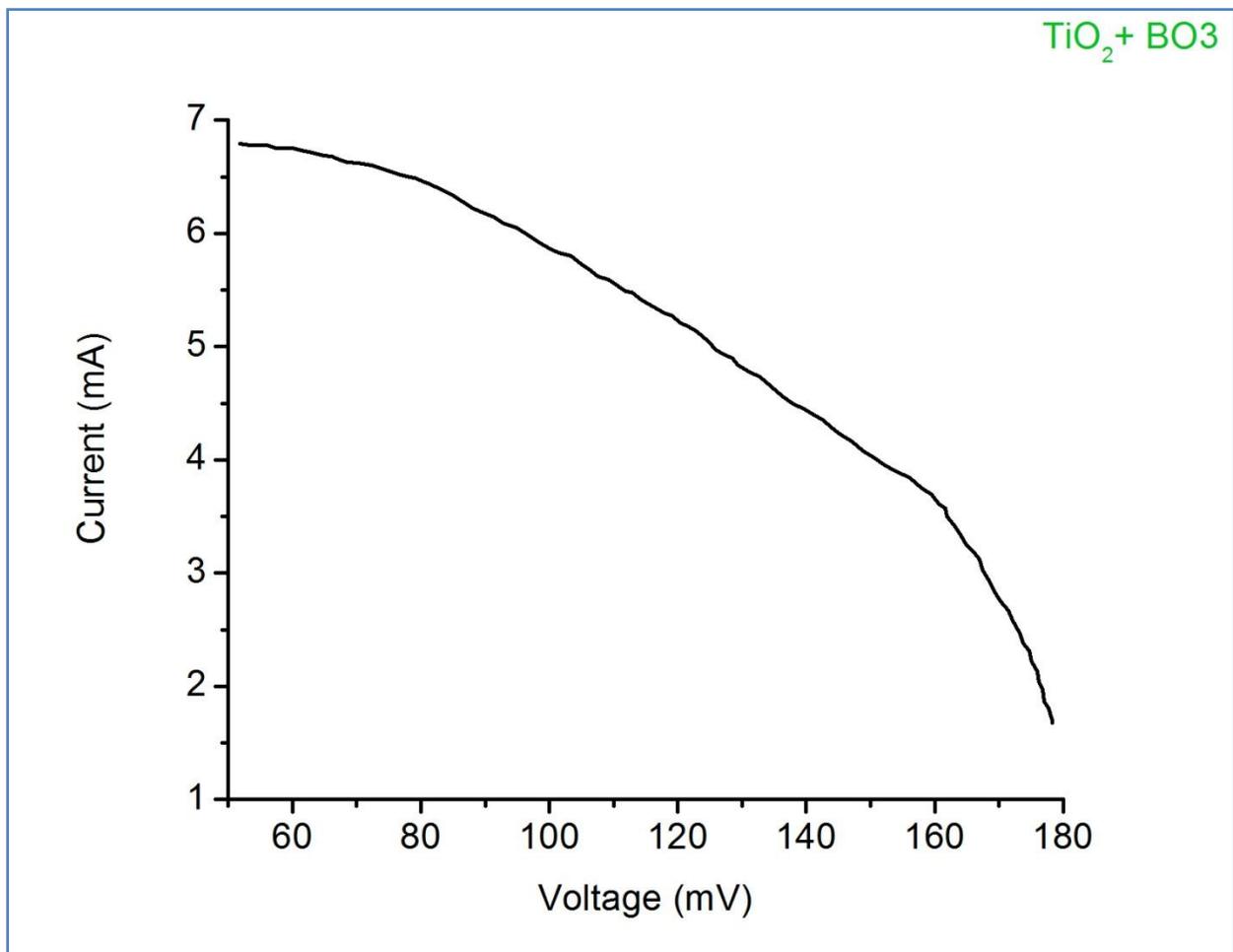


Figure 5.12: I – V curve of Solar cell prepared with TiO₂ + BO₃

Cell	Voc	Isc	Jsc	P_{max}	FF	η
	(mV)	(mA)	(mA/cm²)	x 10⁻⁶ W	(Fill Factor)	(%)
(Area:1 cm²)	(measured)					
TiO₂ + BO 1	217	4.99	4.99	476.476	0.4400	0.348
TiO₂ + BO 2	223	5.7	5.7	531.522	0.4181	0.388
TiO₂ + BO 3	247	6.78	6.78	631.092	0.3768	0.461

Table 5.3: Cell parameters (Bi₂O₃:Yb, Er)

It has been observed from the table 5.3 that under the exposure of sunlight the efficiency of solar cell prepared using mixed (TiO₂ + BO) samples is higher than pure TiO₂. It has been also observed that the efficiency increases with increasing amount of Erbium in the respective samples.

5.4.4 I – V characteristics of Cell prepared with TiO_2 + Up-conversion phosphor samples of $CdO: Yb, Er$

Figure 5.13, 5.14 and 5.15 shows the I – V curve of the samples CO 1, CO 2 and CO 3 respectively under the exposure of Sunlight.

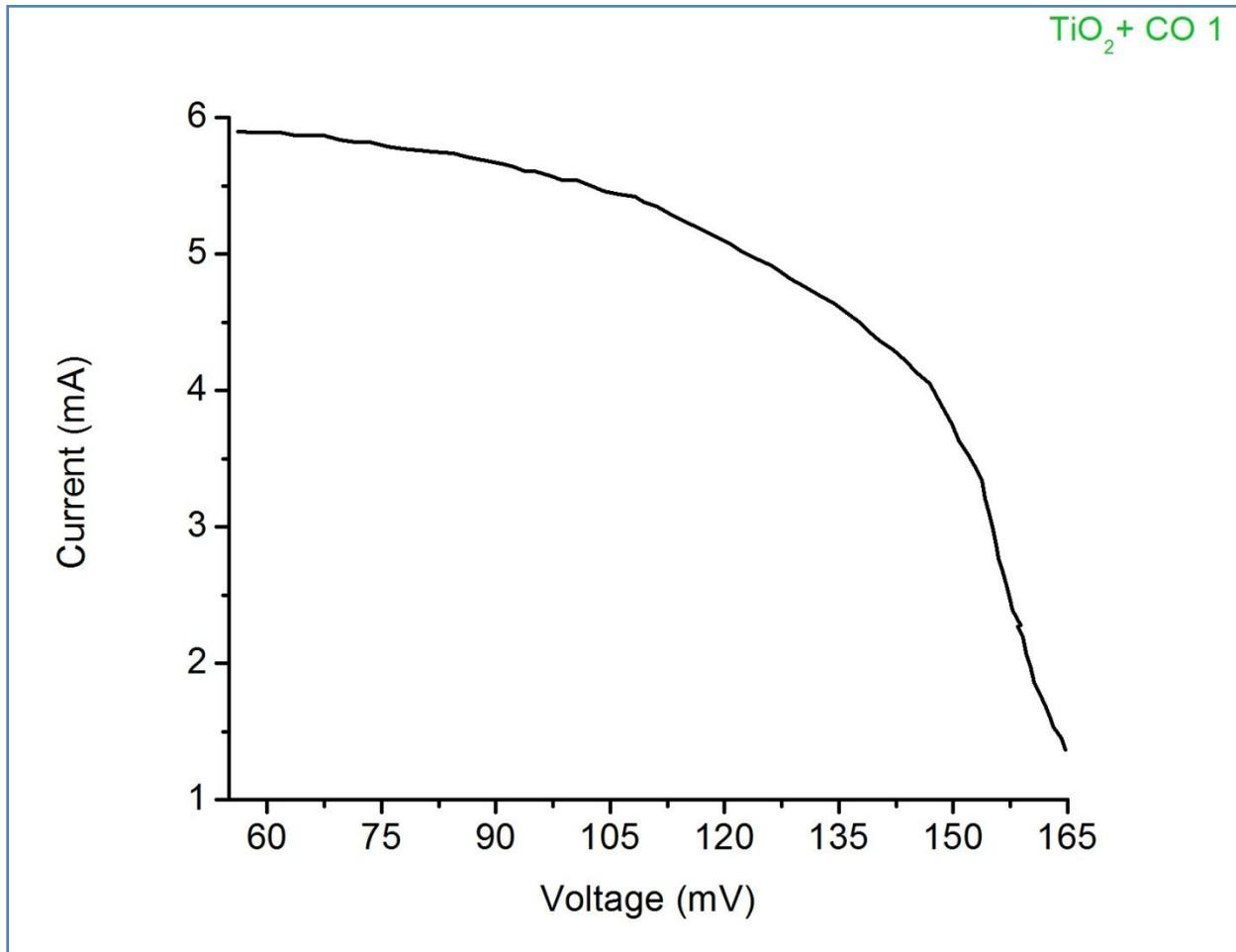


Figure 5.13: I – V curve of Solar cell prepared with TiO_2 + CO 1

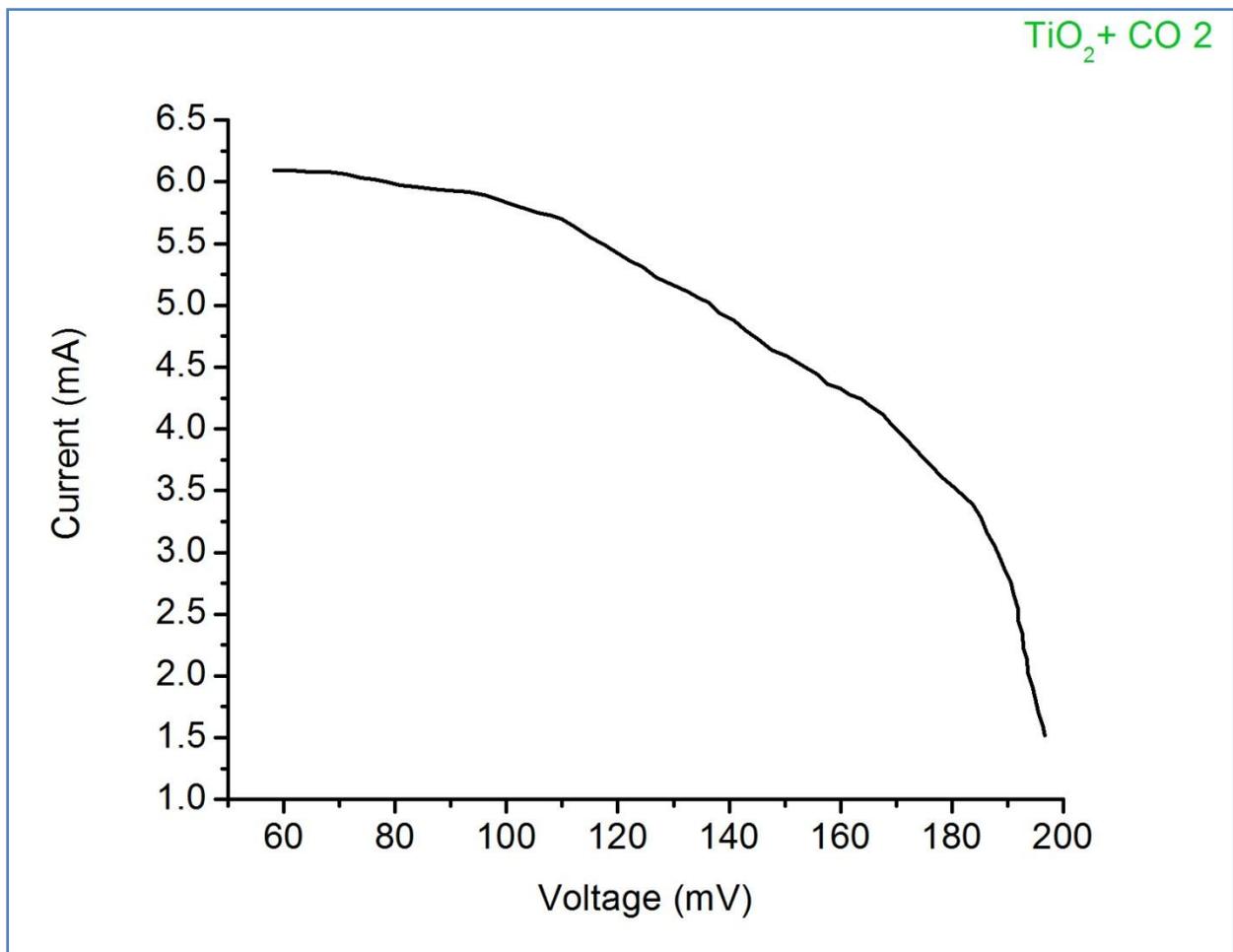


Figure 5.14: I – V curve of Solar cell prepared with TiO₂ + CO₂

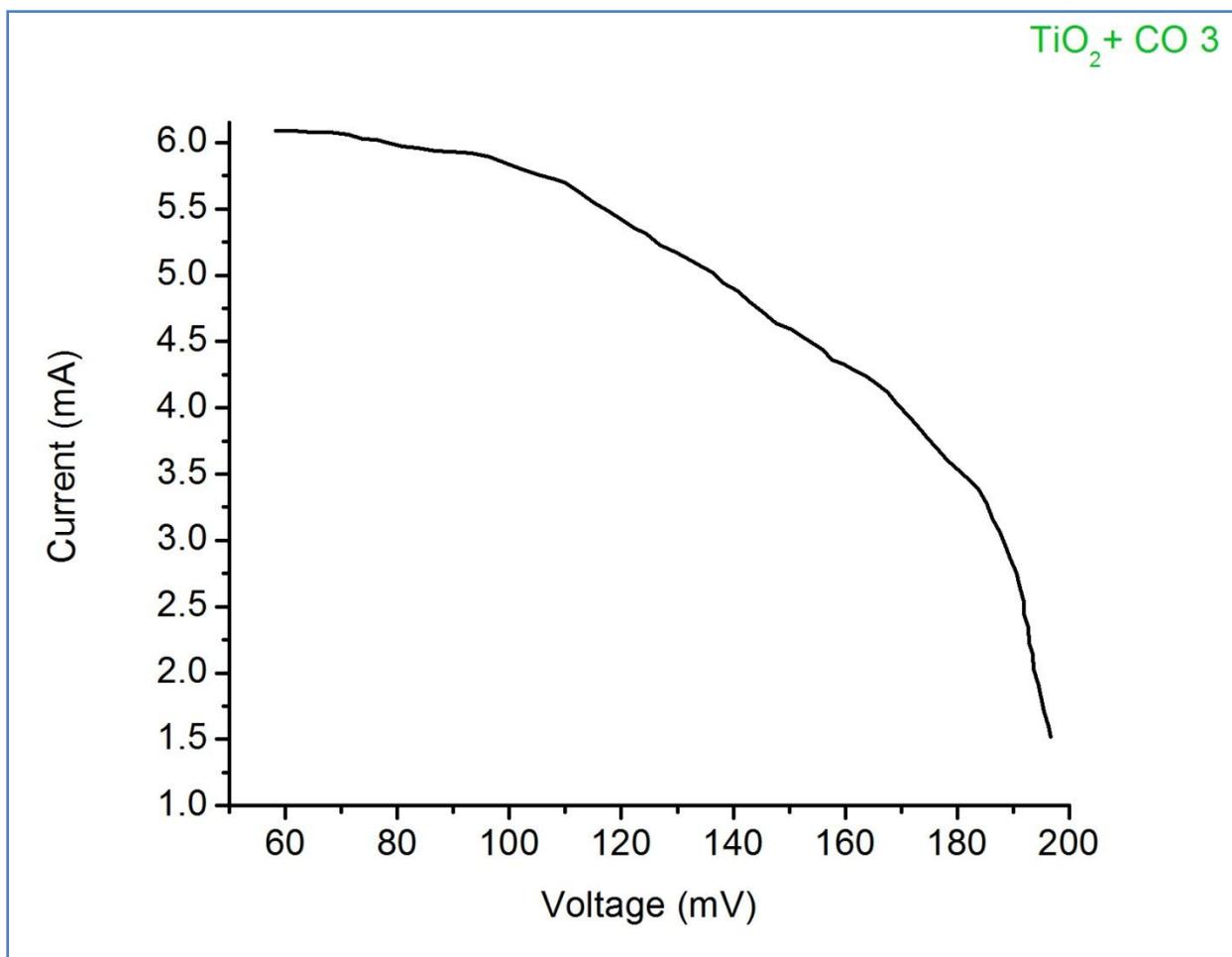


Figure 5.15: I – V curve of Solar cell prepared with $\text{TiO}_2 + \text{CO}_3$

Cell	Voc	Isc	Jsc	P_{max}	FF	η
	(mV)	(mA)	(mA/cm²)	x 10⁻⁶ W	(Fill Factor)	(%)
(Area:1 cm²)	(measured)					
TiO₂ + CO 1	219	5.9	5.9	623.1984	0.4823	0.455
TiO₂ + CO 2	223	6.09	6.09	694.300	0.4512	0.507
TiO₂ + CO 3	263	6.11	6.11	694.300	0.4320	0.507

Table 5.4: Cell parameters (CdO: Yb, Er)

It has been observed from the table 5.4 that the efficiency of cells prepared using mixed (TiO₂ + CO) samples is higher than pure TiO₂. It has been also observed that the efficiency increases with increasing amount of Erbium in the respective samples.

A comparative picture of the obtained efficiencies is presented below:

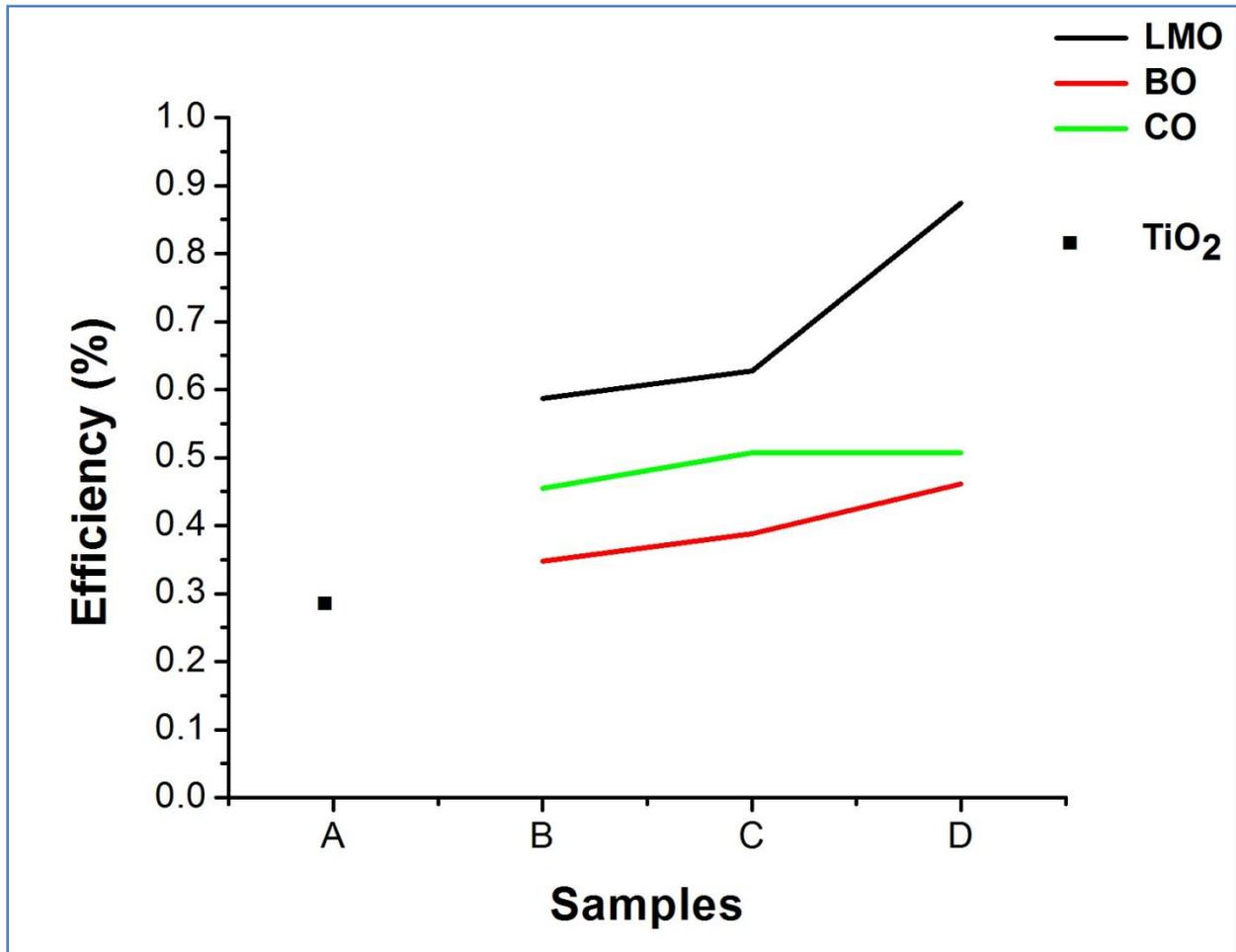


Figure 5.16: Comparison of efficiencies

As shown in the figure 5.16 the dot represents the efficiency of the cell prepared by taking only TiO₂ powder, while the lines represent the efficiencies of the cells prepared by taking the up-conversion phosphor samples i.e. La₂(MoO₄)₃: Yb, Er ; Bi₂O₃:Yb, Er ; CdO:Yb, Er along with TiO₂. It is clear from the figure 5.16 that the efficiencies of the cells prepared by mixing the up-conversion samples with TiO₂ are higher than the one prepared by only TiO₂. This vindicates the purpose of the study which proposes that the presence of up-conversion material would increase

the efficiency as part of the solar radiation which in infrared is converted into visible leading to increase in the number of charge carriers.

The figure 5.16 also indicates that the highest efficiencies are given by the cells with $\text{La}_2(\text{MoO}_4)_3:\text{Yb, Er}$ as the up-conversion phosphor. This is on expected lines as the emission of the LMO samples is in the green region (523 nm to 555 nm) where the efficiency of the Anthocyanin dye to absorbed sunlight is the maximum (see figure 5.3). Besides, the emissions spectra of the samples given in the last chapter 4 also indicate that the LMO samples give the maximum emission counts. The efficiencies are seen to be increasing with increase in the Erbium content of the respective samples. The same trend was observed in the emission characteristics as well.

5.5 *Summary*

One of the major applications of up-conversion materials is in dye sensitized solar cells, where it is expected that the use of up-conversion materials would increase the efficiency of the cells. To explore this aspect, DSSCs were fabricated in the laboratory using pure TiO_2 and mixture of TiO_2 with up-conversion materials synthesized for the study. The cell parameters were recorded using a conventional set up. The results show that the efficiencies of the cells fabricated by using the mixed samples give higher efficiencies. The best results are obtained for cells prepared by using $\text{La}_2(\text{MoO}_4)_3:\text{Yb, Er}$. Both the results are on expected lines.

5.6 *References:*

- [1] Na Li, Nengqain Pan, Danhong Li, Shwei Li, “International Journal of Photoenergy”, Vol. 2013, Article id- 598753, Hindawi Publication.
- [2] Anner Ur Rehman, Farooq Aslam and Haseeb Ahmad Khan, “Analyze the absorption properties and I-V characterization of DSSC using Ruthenium Dye”, American Journal of Engineering and Applied Sciences, 7 (4), 2014, pp. 387-390.
- [3] M. Hosseinnezhad, S. Moradian and K. Gharanjig, “Fruit extract dyes as photosensitizers in solar cells”, Current Science, Vol. 109, 5(2015), pp. 953-956.
- [4] Danladi Eli, J A Owolabi, G O Olowomofe and E Jonathan, “Plasmon-enhanced efficiency in DSSC decorated with size controlled silver nanoparticles based on Anthocyanins as light harvesting pigment”, J. Photonic Materials and Technology, 2 (1), 2016, pp. 6-13.
- [5] J. G. Rowley, B. H. Farnum, S. Ardo and G. J. Meyer, “Iodide chemistry in dye-sensitized solar cells: making and breaking I-I bonds for solar energy conversion”, J. Phys. Chem. Lett., 1 (2010), pp. 3132-3140.
- [6] Z. S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, “Coordination Chemistry Review”, Vol. 248, 2004, pp.- 1381.
- [7] Greg Kopp and Judith L. Lean, “A new, lower value of total solar irradiance: Evidence and climate significance”, Geophysical Research Letters, Vol. 38, 2011, pp. L01706 (1-7).