



Synopsis of the Thesis entitled

**Investigation Of Properties of Recombination Inhibiting Barrier  
Layer For Dye Sensitized Solar Cell**

to be submitted to

**The Maharaja Sayajirao University of Baroda**

for the degree of

**Doctor of Philosophy**

**In**

**Applied Physics**

**By**

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**April 2024**

## **Introduction**

The demand of energy is increasing day by day. At present, most of the energy consumed comes from fossil fuel. The world energy consumption is made up of about 88% fossil fuel, 6% hydroelectricity, 6% nuclear power and a small fraction from biomass as well as non-conventional energy including solar energy sources [1]. Fossil fuels cause environmental pollution and are limited in nature. There is a need to find alternative sources of energy such as solar or wind energy. The solar energy is the largest carbon free energy source [2].

Silicon based solar cells are environmentally clean and have comparatively high-power conversion efficiency, the best being about 20% [3, 4]. Silicon solar cells are quite expensive due to the processing cost and amount of material required for production. Harnessing solar energy with inexpensive materials and manufacturing methods has become an important challenge. Alternate forms of solar cells are thus being investigated.

Dye Sensitized Solar Cells are considered to be a promising alternative to conventional silicon based photovoltaic devices because of their simple assembly and low cost fabrication. The dye sensitized solar cell comprises of anode, redox electrolyte and counter electrode [5]. Anode is a semiconducting film deposited on transparent conducting glass plate generally covered with the monolayer of Ruthenium based synthetic dye or any other dye to absorb light and produce electron hole pairs. Counter electrode is a Platinum coated transparent conducting glass plate. Michael Gratzel created a low-cost Dye Sensitized Solar Cell (DSSC) with  $\text{TiO}_2$  and obtained a solar cell efficiency of 10.4% in 1991 [6].

## **Objective of the work**

- ✚ The main focus of this work is to explore the performance of photo anode material and to increase the power conversion efficiency of dye sensitized solar cells by minimizing the recombination rate using barrier layer between photoelectrode and dye. There are several parameters which affect the efficiency of DSSC. The photo anode is the key component for enhancing the efficiency.
- ✚ Interfacial charge recombination is a problem that exists in DSSC and causes a loss of photogenerated electrons [7]. In figure 1, a dashed arrow represents two possible recombination mechanisms: (i) recombination between the injected electron and the

oxidized dye molecule, (ii) recombination between the injected electron and triiodide in the electrolyte.

✚ TiO<sub>2</sub> is the most widely used semiconducting material for photo anode. A thin film of TiO<sub>2</sub> is coated on transparent conducting glass plate. For enhanced performance, it must possess suitable structural, electrical and optical properties. The material should be of small particle size and high surface area so that more dye molecules can be adsorbed on the surface and more current can be produced. Porosity is also important as it provides higher surface area and can lead to accommodation of large number of dye molecules [8, 9]. The electrical conductivity of material should be high enough to transfer electrons generated by the dye through the film and reach the conducting plate easily. The material with high refractive index is desired, as the incident light can stay longer inside the material and get trapped for the dye to absorb it. To generate large number of electrons, large number of photons should be absorbed by the material and for that the optical absorption coefficient of the material should be high. On the basis of described properties ZnO, TiO<sub>2</sub>, CeO<sub>2</sub>, CdS, ZrO<sub>2</sub> and CuO were sort listed for photoanode preparation.

✚ The main focus is to prepare photo anode with optimized properties for application in DSSC. For this purpose, different layers of material with different combination were deposited on conducting glass substrate. The deposition of material was based on their HOMO and LUMO band level values. The proposed mechanism has been shown in figure 2.

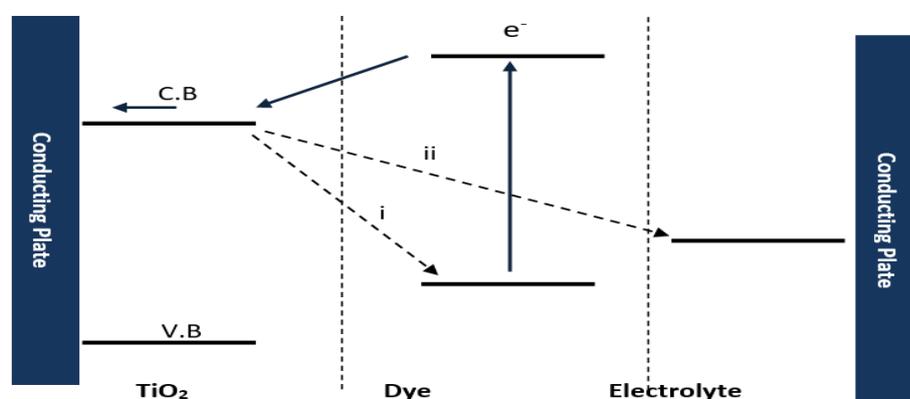


Figure 1: Recombination process in DSSC

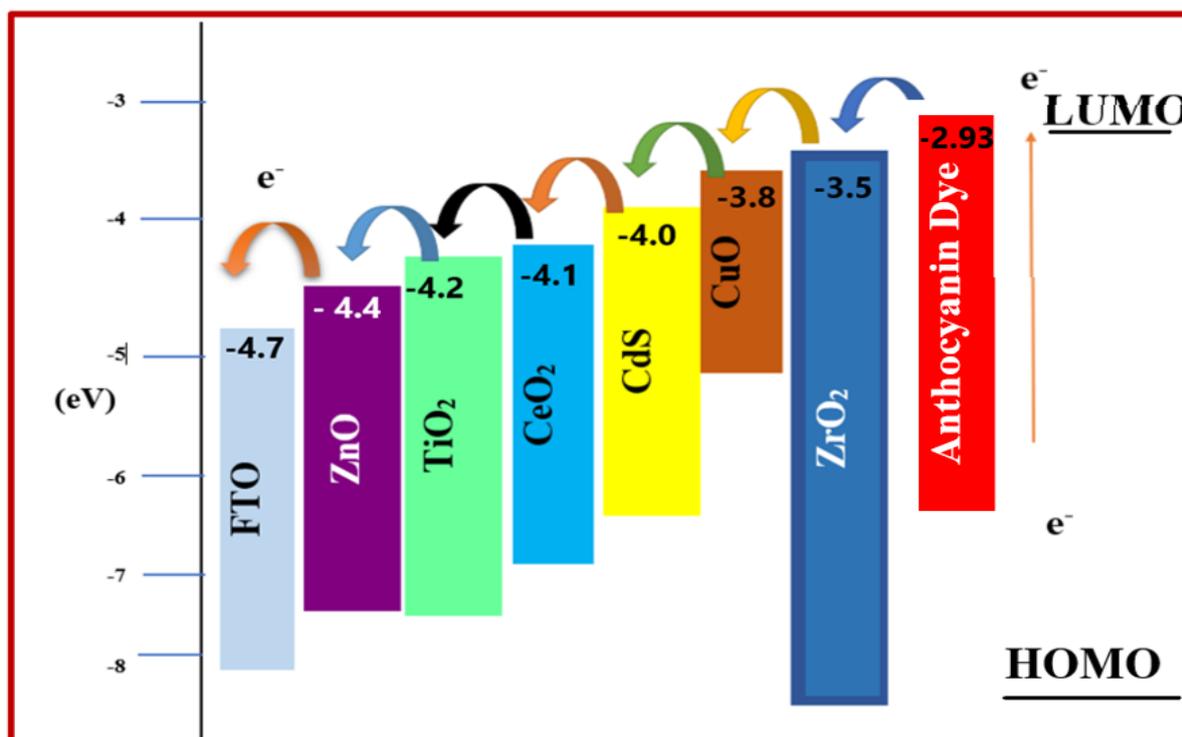


Figure 2: proposed electron transport mechanism in DSSC

## Summary of the work

### Synthesis of different material and its characterization

- + Pure (TiO<sub>2</sub>, ZnO, CdS, CeO<sub>2</sub>, CuO and ZrO<sub>2</sub>) nanoparticles have been prepared by precipitation as well as hydrothermal method. The XRD results confirmed the formation of material in pure crystalline form. The TiO<sub>2</sub> has been formed in Anatase form which is most favorable phase for DSSC application. The crystallite size was found to be in nano meters. The average crystallite size of all the samples was between 10 to 23 nm. The band gap of prepared materials was calculated from UV-Vis spectra and varies from 1.34 eV to 4.8 eV.

### Fabrication of DSSC and efficiency calculation

- + A simple and inexpensive dye sensitized solar cells using prepared materials were fabricated and its efficiency parameters were determined.

**Table 1: Efficiency parameters of DSSCs prepared using different materials.**

Sample	Thickness ( $\mu\text{m}$ )	Area $\text{Cm}^2$	Jsc $\text{mA}/\text{cm}^2$	Voc V	FF	$\eta$ %
<b>ZnO</b>	10.45	1.44	7.10	0.445	0.39	<b>2.46</b>
<b>TiO<sub>2</sub></b>	11.34	1.44	7.12	0.478	0.41	<b>2.77</b>
<b>CeO<sub>2</sub></b>	11.56	1.44	5.10	0.367	0.24	<b>0.89</b>
<b>CdS</b>	10.78	1.44	4.71	0.362	0.23	<b>0.76</b>
<b>ZrO<sub>2</sub></b>	11.34	1.44	3.92	0.345	0.24	<b>0.63</b>
<b>CuO</b>	10.98	1.44	3.62	0.356	0.14	<b>0.35</b>

**Table 2: Efficiency parameters of DSSCs prepared using ZnO/TiO<sub>2</sub> electrode**

Sample	Thickness of ZnO	Thickness of TiO <sub>2</sub> ( $\mu\text{m}$ )	Area $\text{Cm}^2$	Jsc $\text{mA}/\text{cm}^2$	Voc V	FF	$\eta$ %
<b>ZnO + TiO<sub>2</sub></b>	~2.4 $\mu\text{m}$	4.86	1.44	4.49	0.513	0.21	<b>0.94</b>
		11.01	1.44	5.17	0.682	0.27	<b>1.89</b>
		12.96	1.44	8.64	0.667	0.34	<b>3.90</b>
		19.80	1.44	6.64	0.678	0.30	<b>2.64</b>

**Table 3: Efficiency parameters of DSSCs prepared using ZnO/CeO<sub>2</sub> electrode**

Sample	Thickness of ZnO	Thickness of CeO <sub>2</sub>	Area $\text{Cm}^2$	Jsc $\text{mA}/\text{cm}^2$	Voc V	FF	$\eta$ %
<b>ZnO + CeO<sub>2</sub></b>	~2.4 $\mu\text{m}$	3.24	1.44	7.09	0.421	0.39	<b>2.32</b>
		7.56	1.44	7.27	0.671	0.36	<b>3.41</b>
		11.34	1.44	8.34	0.689	0.37	<b>4.25</b>
		13.45	1.44	6.41	0.454	0.36	<b>2.07</b>

**Table 4: Efficiency parameters of DSSCs prepared using ZnO/CdS electrode**

Sample	Thickness of ZnO	Thickness of CdS	Area Cm <sup>2</sup>	J <sub>sc</sub> mA/cm <sup>2</sup>	V <sub>oc</sub> V	FF	η %
<b>ZnO + CdS</b>	~2.4 μm	4.23	1.44	6.65	0.73	0.41	<b>3.90</b>
		8.23	1.44	8.18	0.768	0.36	<b>4.54</b>
		12.56	1.44	12.40	0.630	0.37	<b>5.68</b>
		15.89	1.44	12.04	0.634	0.30	<b>4.55</b>

**Table 5: Efficiency parameters of DSSCs prepared using ZnO/ZrO<sub>2</sub> electrode**

Sample	Thickness of ZnO	Thickness of ZrO <sub>2</sub>	Area Cm <sup>2</sup>	J <sub>sc</sub> mA/cm <sup>2</sup>	V <sub>oc</sub> V	FF	η %
<b>ZnO + ZrO<sub>2</sub></b>	~2.4 μm	3.78	1.44	4.71	0.665	0.27	<b>1.70</b>
		7.91	1.44	4.56	0.687	0.28	<b>1.78</b>
		12.81	1.44	5.33	0.678	0.29	<b>2.07</b>
		18.23	1.44	5.26	0.676	0.26	<b>1.82</b>

**Table 6: Efficiency parameters of DSSCs prepared using ZnO/CuO electrode**

Sample	Thickness of ZnO	Thickness of CuO	Area Cm <sup>2</sup>	J <sub>sc</sub> mA/cm <sup>2</sup>	V <sub>oc</sub> V	FF	η %
<b>ZnO + CuO</b>	~2.4 μm	5.67	1.44	6.94	0.550	0.13	<b>0.94</b>
		8.12	1.44	6.48	0.546	0.17	<b>1.21</b>
		12.89	1.44	7.10	0.584	0.28	<b>2.29</b>
		17.45	1.44	4.47	0.435	0.39	<b>1.49</b>

Table 7: Efficiency parameters of DSSCs prepared using three different layers

Sample	Thickness	Area Cm <sup>2</sup>	J <sub>sc</sub> mA/cm <sup>2</sup>	V <sub>oc</sub> V	FF	η %
ZnO / TiO <sub>2</sub> / CeO <sub>2</sub>	11.89	1.44	10.03472	0.634	0.42817	<b>5.34</b>
ZnO / TiO <sub>2</sub> / CdS	12.13	1.44	9.95833	0.657	0.34977	<b>4.49</b>
ZnO / TiO <sub>2</sub> / ZrO <sub>2</sub>	12.78	1.44	12.27778	0.649	0.47547	<b>7.43</b>
ZnO / TiO <sub>2</sub> / CuO	11.98	1.44	10.26389	0.678	0.47052	<b>6.42</b>
ZnO / CeO <sub>2</sub> / CdS	12.89	1.44	10.1875	0.645	0.42213	<b>5.44</b>
ZnO / CeO <sub>2</sub> / ZrO <sub>2</sub>	11.67	1.44	13.43056	0.657	0.49357	<b>8.54</b>
ZnO / CeO <sub>2</sub> / CuO	12.45	1.44	11.42361	0.639	0.45005	<b>6.44</b>
ZnO / CdS / ZrO <sub>2</sub>	12.01	1.44	14.89	0.634	0.48564	<b>8.99</b>
ZnO / CdS / CuO	<b>12.24</b>	1.44	<b>18.05</b>	<b>0.657</b>	<b>0.51</b>	<b>9.93</b>
ZnO / ZrO <sub>2</sub> / CuO	13.45	1.44	9.26	0.623	0.39	<b>4.39</b>

Table 8: Efficiency parameters of DSSCs prepared using multilayered electrode

Sample	Thickness (μm)	Area Cm <sup>2</sup>	J <sub>sc</sub> mA/cm <sup>2</sup>	V <sub>oc</sub> V	FF	η %
ZnO / TiO <sub>2</sub> / CeO <sub>2</sub> / CdS	18.23	1.44	5.33	0.365	0.225	<b>0.86</b>
ZnO / TiO <sub>2</sub> / CeO <sub>2</sub> / ZrO <sub>2</sub>	19.45	1.44	4.85	0.387	0.19	<b>0.71</b>
ZnO / TiO <sub>2</sub> / CeO <sub>2</sub> / CuO	19.67	1.44	5.11	0.368	0.20	<b>0.76</b>
ZnO / TiO <sub>2</sub> / CeO <sub>2</sub> / CdS / ZrO <sub>2</sub>	22.13	1.44	4.71	0.478	0.14	<b>0.64</b>
ZnO / TiO <sub>2</sub> / CeO <sub>2</sub> / CdS / CuO	22.56	1.44	4.77	0.567	0.13	<b>0.69</b>
ZnO / TiO <sub>2</sub> / CeO <sub>2</sub> / CdS / ZrO <sub>2</sub> /CuO	23.45	1.44	4.73	0.456	0.11	<b>0.47</b>

### Chapter wise details:

#### *Chapter 1: Introduction*

In Chapter 1, the importance of solar energy is discussed. The introduction of different materials, their structures, physical properties and applications are also discussed.

#### *Chapter 2: Solar cells*

In Chapter 2, The discovery and development of solar cells are explained. Three generation of solar cells along with their construction, working, efficiency comparison,

advantages and disadvantages has been discussed. The recombination process in DSSC has been discussed in detail. Different causes for recombination and possible solution is explained in detail. The energy level structure of materials used for DSSC and electron transport properties has been discussed briefly.

### ***Chapter 3: Characterization Techniques***

In this chapter, the explanation of principle of instrumentation which is used for characterization of prepared materials is given. The structural properties of the material are investigated using XRD. UV-Vis spectroscopy was used to study the optical properties of the material. Operating principle, construction and working of all these instruments has been discussed briefly.

### ***Chapter 4: Material Synthesis and Characterization***

In Chapter 4, synthesis of ZnO, TiO<sub>2</sub>, CeO<sub>2</sub>, CdS, ZrO<sub>2</sub> and CuO nano particles using different synthesis methods has been discussed. Structural and optical properties of prepared samples have been explained from XRD and UV-Vis analysis respectively.

### ***Chapter 5: Fabrication of dye sensitized solar cell and its characterization***

In this chapter, fabrication process of dye sensitized solar cell has been explained. The efficiency parameters and their calculations are given. The mechanism of electron transport process in DSSC, recombination process and charge separation process has been described. Preparation of set up for the efficiency measurements is also described. Measurements of efficiency parameters of DSSCs prepared using different materials and combinations, results and discussion is presented.

### ***Chapter 6: Summary and Future work***

This chapter summarizes of the work carried out in this thesis. The scope for further work in materials for solar cells and reduction in production cost by replacement of expensive components with cheaper one is also presented.

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## Publications

### Papers in referred journals

1. Effect of Preparation method on Optical and Structural properties of TiO<sub>2</sub>/ZrO<sub>2</sub> Nanocomposite, Laxmi J. Tomar, **Piyush J. Bhatt**, Rahul K. Desai, Bishwajit S. Chakrabarty (J. Nano. Adv. Mat. 2, No. 1, 27-33 (2014))
2. Investigation of Optical Properties of TiO<sub>2</sub>/CdS/PbS Multilayered Thin Film, Laxmi J. Tomar, Rahul K. Desai, Piyush J. Bhatt and B. S. Chakrabarty (Indian Streams Research Journal, Volume-3, Issue-12, Jan-2014)
3. Synthesis and Characterization of Nanostructured PbS Thin film, Laxmi J. Tomar, **Piyush J. Bhatt**, Rahul K. Desai, Bishwajit S. Chakrabarty (Int.J. ChemTech Res.2014, 6(3), pp 1923-1925)
4. Enhancement of Optical Properties of Hydrothermally Synthesized TiO<sub>2</sub>/ZrO<sub>2</sub> Nanoparticles by Al, Ce Co-doping, Laxmi J. Tomar, **Piyush J. Bhatt**, Rahul K. Desai, Bishwajit S. Chakrabarty (Solid State Physics, AIP Conf. Proc. 1665, 050124-1–050124-3, (2015))
5. Pure Single Crystallographic Form of TiO<sub>2</sub> Nanoparticles: Preparation and Characterization, **Piyush J. Bhatt**, Laxmi J. Tomar, Rahul K. Desai, Bishwajit S. Chakrabarty (Solid State Physics AIP Conf. Proc. 1665, 050125-1–050125-3, (2015))
6. Al and Mg Doped TiO<sub>2</sub>-ZrO<sub>2</sub> Nanocomposites for Dye Sensitized Solar Cell Application, Laxmi J. Tomar, **Piyush J. Bhatt**, Rahul K. Desai, Bishwajit S. Chakrabarty (Invertis Journal of Renewable Energy, Vol. 5, No. 4, 2015; pp. 220-224)
7. Improved Conversion Efficiency of Dye Sensitized Solar Cell Using Zn Doped TiO<sub>2</sub>-ZrO<sub>2</sub> Nanocomposite, Laxmi J. Tomar, **Piyush J. Bhatt**, Rahul K. Desai, B. S.

Chakrabarty, C. J. Panchal (Solid State Physics AIP Conf. Proc. 1731, 050132-1–050132-3 (2015))

8. Enhanced Efficiency of Dye Sensitized Solar Cell Using Eu Doped TiO<sub>2</sub>-ZrO<sub>2</sub> Nanocomposite, Laxmi J Tomar, **Piyush J. Bhatt**, Rahul K. Desai, Bishwajit S. Chakrabarty, (Recent Patents on Nanotechnology, Vol. 16, Issue. 4, pp 333-338, January 2022)
  
9. Construction of hybrid solar cell exploiting the interaction of TiO<sub>2</sub>/Photosystem I complexes, Rahul K Desai, Alex S khristy, **Piyush J Bhatt**, Laxmi J Tomar, Preet D vyas, C Ratna Prabha, Kireetkumar D Patel, Bishwajit S Chakrabaty, (Indian Journal of Biochemistry & Biophysics. Vol.60, pp 567-571, July 2023)

### **Papers under Review Process**

1. Investigation of Power conversion Efficiency of TiO<sub>2</sub>/ZnO multi-layered Anode for Dye Sensitized Solar Cell, **Piyush J. Bhatt**, Laxmi J. Tomar, Rahul K. Desai, Bishwajit S. Chakrabarty, (presented at National Conference on Advances In Solar Energy Materials (ASEM-23), Banaras Hindu University, March 16-18, 2023)
  
2. Enhancement of Power Conversion efficiency of DSSC using Fe Doped TiO<sub>2</sub> -ZrO<sub>2</sub> nanocomposite, Laxmi J Tomar, **Piyush J. Bhatt**, Rahul K. Desai, Bishwajit S. Chakrabarty, (presented at National Conference on Advances In Solar Energy Materials (ASEM-23), Banaras Hindu University, March 16-18, 2023)
  
3. Formulation of Polypyrrole and Polyaniline inks for flexible solar cells of low thermally stable substrates, Rahul K Desai, Mohit Ahir, Manali Tandel, **Piyush Bhatt**, Laxmi Tomar, Bishwajit Chakrabarty, (presented at National Conference on Advances In Solar Energy Materials (ASEM-23), Banaras Hindu University, March 16-18, 2023)

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