



INSTITUTE OF PHYSICS - SRI LANKA

**Research Article**

**Preparation of ZnO films with different morphologies and their applications in dye sensitized photo-voltaic cells**

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**Abstract**

ZnO films with different morphologies were synthesized electrochemically. The characteristics of ZnO films were studied. Addition of selected precursors into the electrolyte changes the morphology of ZnO films and yields hybrid organic-ZnO films. Highly porous ZnO films were obtained by extracting eosin Y from hybrid ZnO|eosin Y films. Different organic dyes were used to sensitize ZnO films by means of utilization as light harvesting electrodes in dye sensitized photovoltaic cells. Photo-effects of sensitized ZnO electrodes were studied in  $I^-|I_3^-$  redox-electrolyte. Among tested dyes an indoline dye D149 produced better performance.

**Keywords:** Eosin Y; Hybrid ZnO films; D149 dye

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**1. INTRODUCTION**

The history of photo-voltaic began with the investigation of photo-effects on silver halides in 19<sup>th</sup> century. The first photovoltaic cell was demonstrated by Becquerel in 1873 which was composed of silver chloride coated metal electrode immersed in an electrolyte. Fabrication of cost effective solar cell is a scientific hurdle. Dye sensitized solar cells are the best example for cheap solar cells. The major break through out in this direction is usage of nano-porous titanium dioxide films with a large photoactive area and capability of usage in wide range of dyes to sensitize titanium dioxide by a Swiss research group<sup>1</sup>. The sensitization process occurs via participation of only conduction band in this type of

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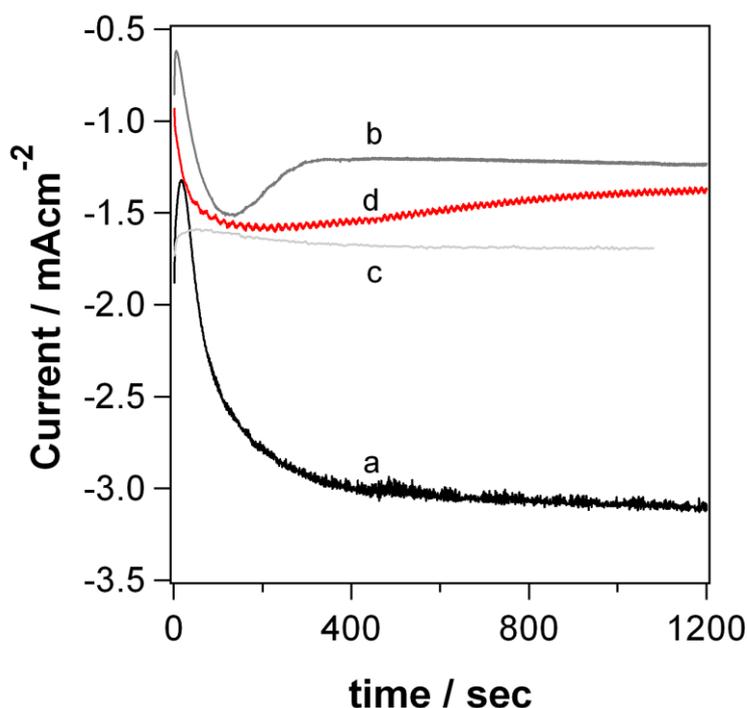
solar cells, as is proposed by Mott and Gurney. Recently, tremendous growth has been built for utilization of other materials than titanium dioxide. ZnO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> are other promising oxides in this view point<sup>2</sup>. We have made an attempt to use sensitized ZnO films as light harvesting electrodes in photo-electrochemical cells. Photo-electrochemical properties of sensitized electrochemically prepared ZnO films are reported herein.

## 2. EXPERIMENTAL

Fluorine doped tin indium oxide coated glass substrates (FTO) are not fully active for deposition of ZnO by electrochemically. Activation of these substrates was carried out by applying a constant potential of -1.0 V vs SCE, at oxygen saturated atmosphere (bubbling rate 100 ml/min) in 0.1 M KCl for 20 min. ZnO was deposited on activated FTO as follows; ZnCl<sub>2</sub> was added to the electrolytic bath (until concentration reaches 5 mM) and electrolysis was carried out for 20 min by replacing Pt counter electrode used for pre-electrolysis from a pure Zn wire, under similar potentiostatic conditions. Resulted ZnO film was used as a template for deposition of hybrid films. Hybrid films were prepared by adding eosin Y or 4, 4'-dicarboxylic acid-2, 2'-bipyridine (dcbpy) into the electrolyte. The concentration of eosin Y was maintained as 45 μM in the electrolytic bath and concentration of dcbpy was maintained as 20 μM. Electrolysis was carried out by applying similar conditions for another 20 min, in both cases. Electrochemical deposition processes were carried out in a single compartment cylindrical cell, at a constant temperature of 70°C, in an aqueous medium by using three electrode configurations. The working electrode was kept at electrolyte|air interface and was rotated at a constant speed of 500 rpm throughout the experiment. We have firmly maintained physical parameters such as temperature of electrolytic bath, applied potential, concentration of oxygen in the bath and rotating speed, since these parameters strongly influence on the current across the electrodes. Characteristics of hybrid ZnO films were studied. De-sorption of eosin Y was carried out by immersing them in KOH (at pH =10.5). Removal of eosin Y from hybrid eosin Y|ZnO film has resulted highly porous ZnO film. Different organic dyes were coated on hybrid ZnO-dcbpy and porous ZnO films, in the view point of fabrication of dye sensitized photovoltaic cells. A Pt coated FTO electrode was attached to sensitized ZnO electrode as the counter electrode. The electrolyte was spread in between two electrodes by capillary action. Electrolyte used was I<sup>-</sup>|I<sub>3</sub><sup>-</sup> redox-couple (tetrapropylammoniumiodide/iodine, 0.5M/0.05M) in acetonitrile and ethylenecarbonate by volume 4:6. Cells were characterized under illumination of monochromatic and polychromatic light (100 mWcm<sup>-2</sup>).

## 3. RESULTS AND DISCUSSION

Figure 1 (curve a) illustrates chronoamperogram for pre-electrolysis of FTO electrode. It is observed that current generated due to reduction of molecular oxygen initially increases with time and reaches a saturation level. Saturation of current indicates activation of FTO for oxygen and seems to be due to limitation of diffused oxygen in the electrolyte.

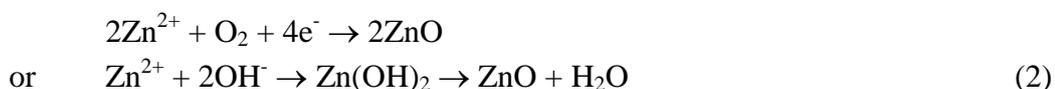


**Figure 1:** Chronoamperograms for (a) pre-electrolysis of FTO (b) deposition of ZnO, (c) deposition of hybrid eosin Y|ZnO and (d) deposition of hybrid dcbpy|ZnO films

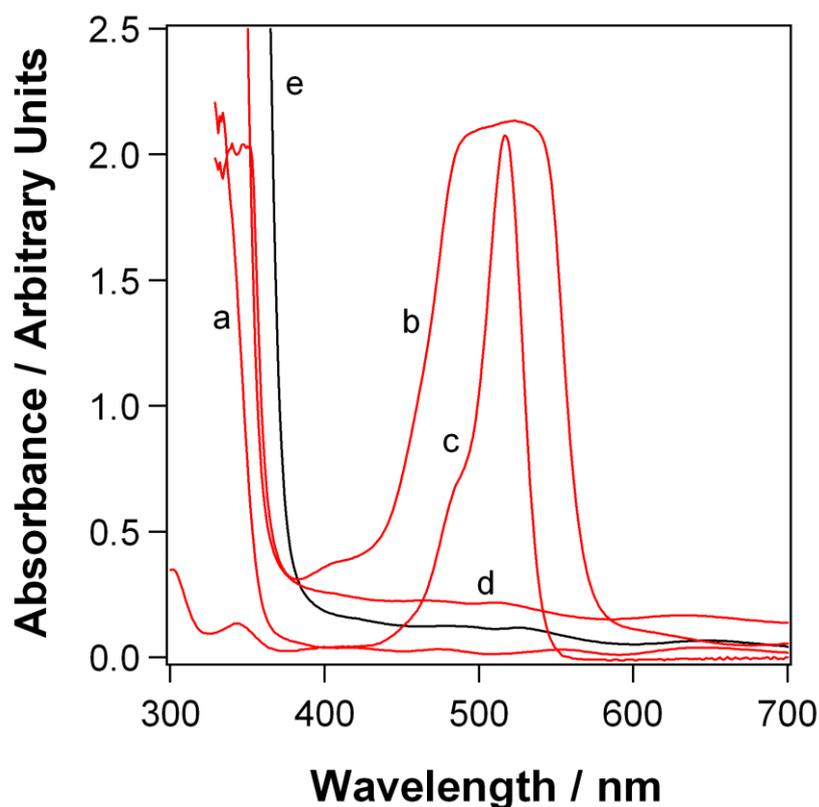
Reduction of molecular oxygen takes place via four electron reduction process in aqueous media and can be summarized as follows<sup>3,4</sup>,



Addition of  $\text{Zn}^{2+}$  into the electrochemical bath changes kinetics in the system and forms ZnO on FTO. Formation of ZnO nucleus exhibits peculiar variation of current as soon as  $\text{ZnCl}_2$  is added to the electrolyte (curve b, Figure 1). Formation of ZnO seems to be kinetically controlled process and takes place via following process<sup>4</sup>,

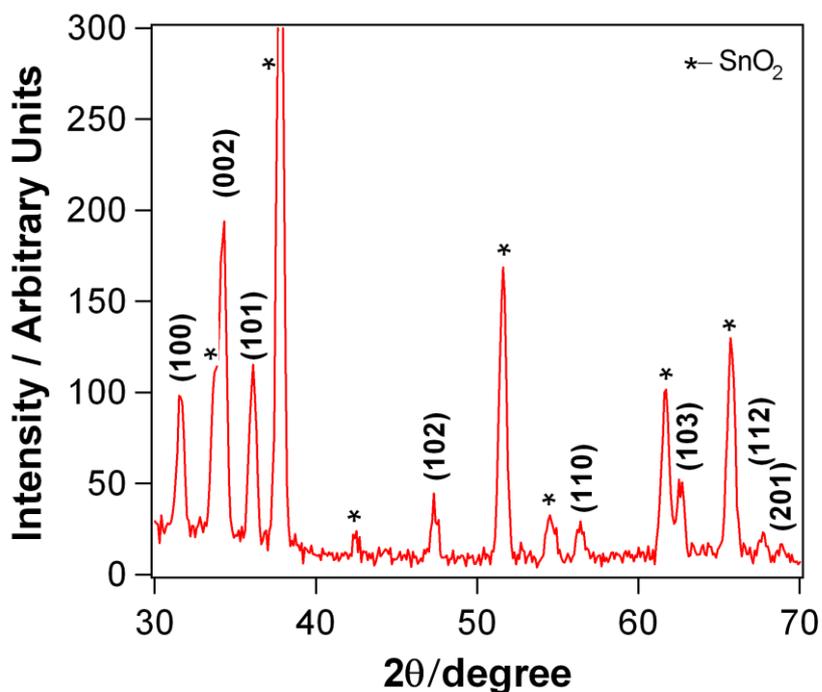


Electrolysis results fairly uniform ZnO layer on FTO. Thickness of the film can be easily controlled by changing the deposition time. These films exhibit over 90% transmittance for visible light (not shown in the text) and high degree of crystallinity with the nature of highly compact structure (shown in Figures 3 and 4(a), respectively). Several organic molecules have been identified as competent for fabrication of hybrid films with ZnO by electrochemically<sup>5,6</sup>. We have made an attempt to prepare hybrid ZnO films by using eosin Y and dcbpy. Chronoamperogram for deposition of hybrid (c) ZnO|eosin Y and (d) ZnO|dcbpy films are also shown in Figure 1. These hybrid films exhibit almost colorless nature as soon as the electrolysis processes are completed. However, hybrid ZnO|eosin Y films become dark reddish color due to aerial oxidation by aging. No color change is observed on hybrid dcbpy|ZnO electrode being aged.



**Figure 2:** Absorption spectrum of (a) compact ZnO film, (b) hybrid eosin Y|ZnO film, (c) aqueous solution of eosin Y in water (50  $\mu$ M), (d) after de-sorption of hybrid eosin Y|ZnO film and (e) dc bpy|ZnO film

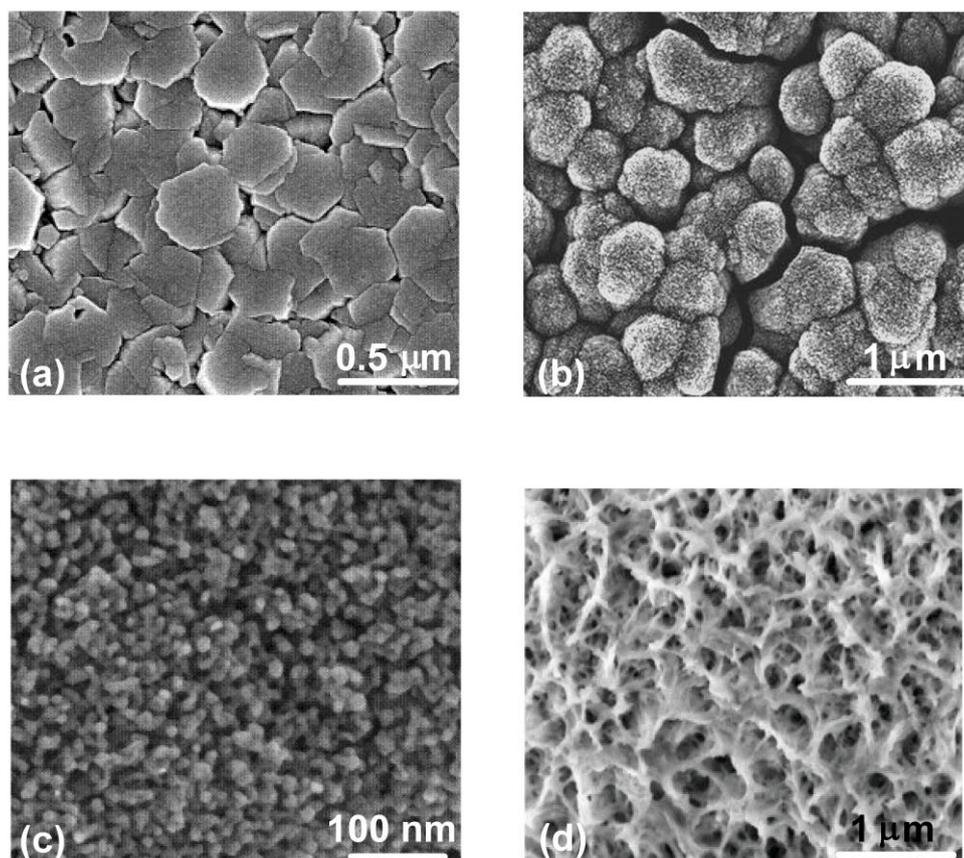
Absorption spectrum for compact ZnO films is shown in Figure 2 (curve a). The onset of optical absorption reflects band gap energy of thin ZnO films is about 3.4 eV. It is observed that hybrid ZnO|eosin Y films absorb light in two different regions of wavelengths where ZnO and eosin Y absorb light (curve b). These hybrid ZnO|eosin Y films exhibit a saturation of absorbance in 475-550 nm wavelength range. This situation is contrast with that of without ZnO. Absorption spectrum of Eosin Y is shown as curve c in Figure 2. Eosin Y exhibits two predominant electronic transitions at 520 (maximal) and 480 (shoulder) nm. This shoulder and maximum are correlated with the monomers of eosin Y and common characteristic for xanthene dyes<sup>2</sup>. Enhancement of absorption in shorter wavelengths and broadening of the spectrum are due to chelation of eosin Y with ZnO and a peculiar property for H-type aggregation<sup>7</sup>. Absorption maximum and a shoulder with almost equal intensities suggest equilibrium of eosin Y aggregates and monomers on ZnO. Absorption spectrum of ZnO film after de-sorption of dye from hybrid eosin Y|ZnO film is also shown in the same figure (curve d). Absorption spectrum of a ZnO|dc bpy film is shown as curve e in Figure 2. These films exhibit slightly red shift in absorption onset compare to that of without dc bpy. This may be due to enhancement of size of ZnO grains with association of dc bpy.



**Figure 3:** X-ray diffractogram of ZnO film

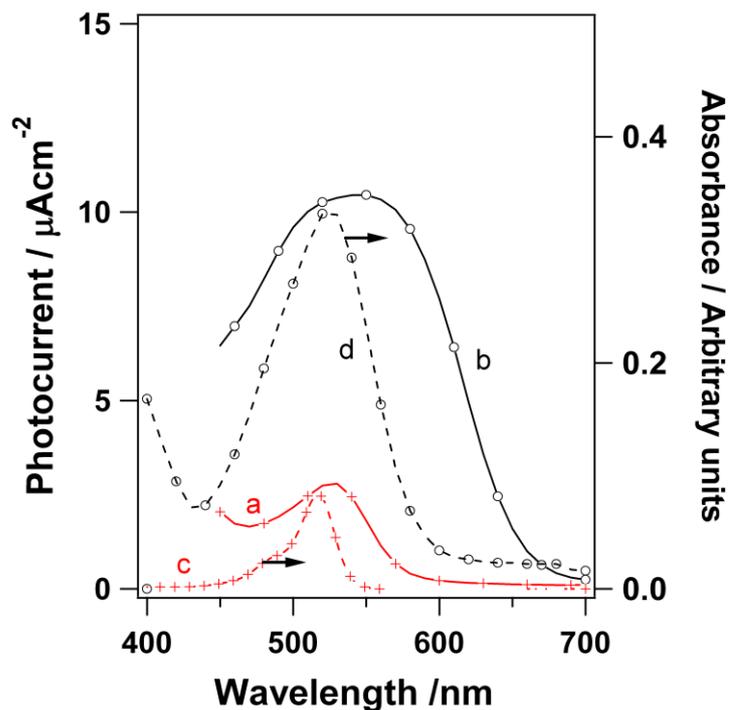
We have also studied crystallography of electrochemically deposited ZnO films. X-ray diffractogram of a ZnO film is shown in Figure 3. It is observed that ZnO films exhibit predominant orientation parallel to (0,0,2) axis. Growth of thin films with a preferred orientation is a specific feature of thin films<sup>8</sup>. However peaks belonging to other lattice planes are also observed at higher angles. Characteristic peaks of ZnO belonging to (0,0,2) and (1,0,3) lattice planes overlap with that of (1,0,1) and (3,1,0) lattice planes correspond to SnO<sub>2</sub>. Characteristic peaks observed for hybrid ZnO films overlap that of without eosin Y or dcbpy, probably due to low molecular ratio between ZnO and precursors.

Morphologies of ZnO film and hybrid ZnO films exhibit different in nature (Figure 4). Electro-chemically deposited ZnO films exhibit highly compact hexagonal structure, as shown in image a. Hybrid eosinY|ZnO films exhibit grains with a round headed top and well separation between grains (image b). De-sorption of eosin Y from hybrid films results highly porous ZnO films. Morphology of such a film is also shown in the same figure (image c). These porous ZnO films occupy higher degree of surface area than compact ZnO films prepared by 1<sup>st</sup> step of electrolysis. The porosity of these films can be changed by choosing organic molecules with slightly different structure than eosin Y (such as 5(6) carboxy eosin, 2,4,5,7-tetrabromo-sulfo-fluoresein)<sup>9</sup>. However, extraction of these organic dyes is not possible when more positive potential than  $E^{1/2}$  is opposed on the electrode, during electro-deposition. The morphology of hybrid dcbpy|ZnO film is shown in image d. A completely different morphology, like a sponge was observed for electrochemically deposited hybrid dcbpy|ZnO films.



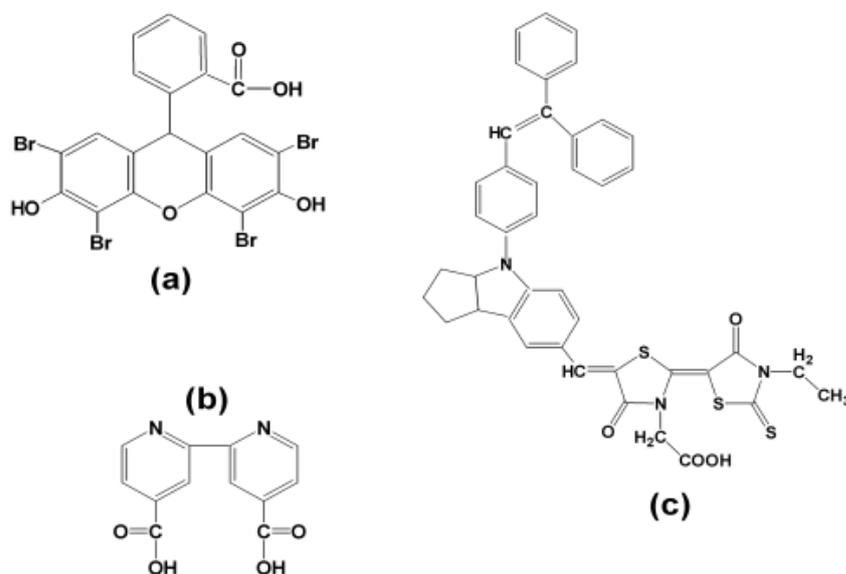
**Figure 4:** Morphology of (a) compact ZnO film, (b) hybrid eosin Y|ZnO film, (c) nano-porous ZnO film (after dye extraction from hybrid ZnO|Eosin Y film), and (d) hybrid dcbpy|ZnO film

When an attempt is made to utilize ZnO films in photo-voltaic cells, it is necessary to have a sensitizer on ZnO films, due to poor absorption of ZnO in visible region. However, hybrid eosin Y|ZnO films absorb visible light by itself due to red color in nature. Action spectrum of cell composed of hybrid eosin Y|ZnO electrode as shown in curve a in Figure 5. Rather low current generation is observed on this electrode, probably due to recombination of photo-generated carriers at the ZnO|dye interface. The maximum power conversion efficiency is observed at 530 nm. The wavelength the maximum power conversion efficiency observed is slightly red shifted compare to that of absorption spectrum of eosin Y, indicating strong bonding of eosin Y with ZnO. We have fabricated similar type of cells using eosin Y reloaded on nano-porous ZnO films obtained by extracting eosin Y from hybrid eosin Y|ZnO films. Action spectrum of such electrodes exhibit similar pattern of current generation, compare to that of hybrid eosin Y|ZnO electrodes, with a higher magnitude of photocurrent at each wavelength.



**Figure 5:** Action spectrum of cell composed of (a) hybrid eosin Y|ZnO film (b) D149 sensitized nano-porous ZnO film in poly-iodide electrolyte (area of the cell  $0.25\text{cm}^2$ ) and absorption spectra of (c) eosin Y and (d) D149

As shown in SEM, these ZnO films exhibits different morphology than compact and hybrid ZnO films. This may be one of the reasons for enhance photo-current on sensitized nano-porous ZnO electrodes. It is known that ZnO films prepared by extracting eosin Y from ZnO|eosin Y hybrid films exhibited high degree of efficiency of collection of photo-generated electrons from FTO layer under the ZnO layer when associated in photovoltaic cells, before they recombine with  $\text{I}_3^-$  ions in the electrolyte, due to less grain boundaries existing in the direction of electron diffusion<sup>10</sup>. It is expected, that organic dye D149 exhibited much better charge separation in photovoltaic cells based on ZnO electrodes than eosin Y. Thus, we have used D149 as a sensitizer for ZnO films. Action spectrum of D149 sensitized nano porous ZnO electrode (obtained by extracting eosin Y from hybrid eosin Y|ZnO films) is shown as curve b in Figure 5. D149 sensitized compact ZnO and hybrid dcbpy|ZnO films also exhibited similar pattern of current generation. However, photocurrent did not exceed that of for sensitized nano-porous electrodes. These results indicate that, magnitude of photocurrent of sensitized ZnO films changes with the morphology of the film. Molecular structures of used precursors and dyes are shown in scheme 1.



Scheme 1: Molecular structure of (a) eosin Y , (b) dcbpy and (c) D149

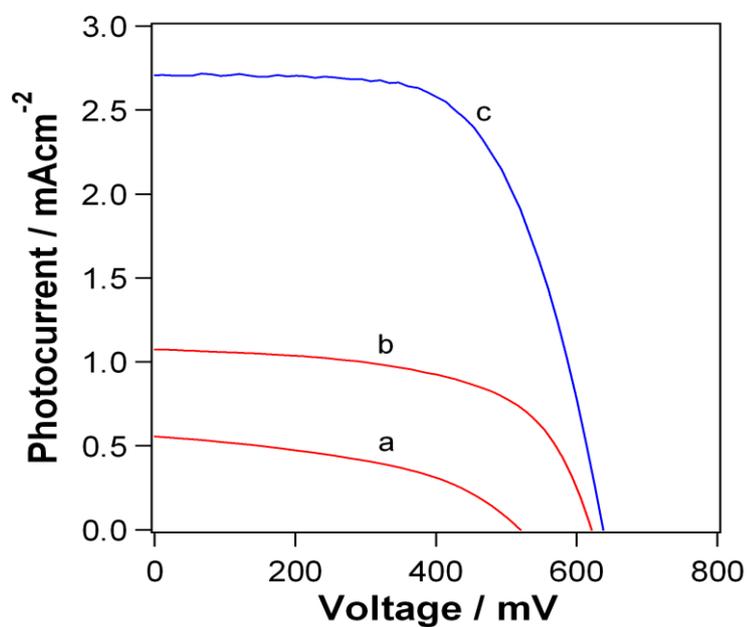
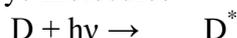


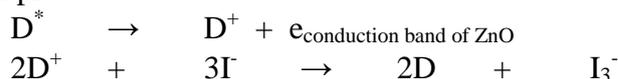
Figure 6: Current-voltage characteristics of cell composed of D149 sensitized (a) compact ZnO, (b) hybrid dcbpy/ZnO and (c) nano-porous ZnO films, Area of the cell is 1cm<sup>2</sup>

Figure 6 illustrates current-voltage characteristics of D149 sensitized (a) compact ZnO, (b) hybrid dc bpy/ZnO and (c) nano-porous ZnO films. Maximum photocurrent of 2.7 mAcm<sup>-2</sup> and photo-voltage of 620 mV are obtained for ZnO|D149|electrolyte cell made from nano-porous ZnO films. Charge generation of ZnO|Dye|electrolyte cell can be summarized as follows,

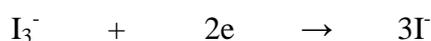
excitation of dye molecules



charge transfer process



Reduction of tri-iodide ion at counter electrode



Here D denotes dye molecules. The above mentioned intermediate steps are governing the performance of the cell. However, several reverse reactions are also identified as blocking factors of the cell<sup>11</sup>, thus limiting optimum photocurrent of the system.

#### 4. CONCLUSIONS

An attempt is made to utilize sensitized ZnO films with different morphologies in dye sensitized photovoltaic cells. Among tested dyes, organic Indolin dye D149 exhibits better performance for ZnO based photovoltaic cells.

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