

Charge Generation in Multi-Dye Coated Solid-State Solar Cells

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Abstract: Several types of dyes have been employed to study sensitization process on high band-gap semiconductors. An enhancement of efficiency of this type of solar cells was observed by appropriate coupling of dyes. A comparable study of multi-dye systems was carried out by means of understanding the charge transfer mechanism of multi-dye coated electrodes. The enhancement of power conversion efficiency of multi-dye coated electrodes is due to either enhance of charge injection process or decrease quenching processes under illumination.

Keywords: organic dyes, natural pigments, metal complexes, sensitization process, power conversion efficiency, dye-sensitized solar cells.

I. INTRODUCTION

The entire earth receives solar irradiation of 1000 Watts/meter² over a 24-hour day. If this free, clean green energy converts into viable form of electricity, there would be no energy crises in the world. Dye-sensitized solar cells are 3rd generation of solar cells and meeting both high efficiency and low-cost. Usage of highly porous oxide films with a large photoactive area is a peculiar property of dye-sensitized solar cells. Photoactivity of these electrodes extends toward the visible region by sensitizer. In this context, sensitizer must be firmly affixed to the semiconductor. Chelation of dye molecules with metal oxide semiconductors takes place via different anchoring groups. Hydroxyl, carboxylic, sulphonic groups are the best examples for anchoring groups. The other major requirement that has to be satisfied for efficient charge transfer process is proper matching of the HOMO and the LUMO levels of the dye with the band structure of the semiconductor. In the case of anodic sensitization, the conduction band of semiconductor must lie in between HOMO and LUMO levels of the dye molecules. Likewise, cathodic sensitization takes place when valence band of the semiconductor lies in between the HOMO and the LUMO levels of the dye molecules. A dye-sensitized solar cells fabricated by a Swiss research group is the major breakthrough out of this field. Firstly, a dye sensitized solid-state cell was developed by a Sri Lankan research group in 1985. Even though the power conversion efficiency of this cell is moderate, it opened the mind for different type of solar cell. An enhancement of the performance of the cell was achieved by adding crystal growth inhibitors for the p-type semiconductor. Crystal growth inhibitors control growth of CuI and thereby firm penetration of CuI into titania electrodes was observed. Thus, makes better contact between CuI and TiO₂ yields an enhancement in the efficiency of the cell. An enhancement of efficiency of those types of solar cells could be expected by appropriate coupling of several dyes as a result of fully coverage of visible spectrum. An overview of sensitization process of multi-dye sensitized solid state solar cells are discussed.

II. EXPERIMENTAL SECTION

2.1 DEPOSITION OF COMPACT TiO₂ LAYER ON CONDUCTING GLASS PLATES

Fluorine doped tin oxide coated conducting (FTO) glass plates (Sigma-Aldrich) were cut into 1x2.5 cm² pieces, cleaned by detergent, thoroughly washed with distilled water and dried in an oven. One of the edges of FTO (1x1cm²) was covered with 3M tape and placed horizontally on a hot-plate facing the conducting side to air. Temperature of the hotplate was gradually increased to 450°C. A solution of titanium diisopropoxide bis(acetylacetonate) 75wt% (Sigma-Aldrich) in isopropanol (1:9) was sprayed over the FTO quickly at the thermal equilibrium at 450°C and allowed to each to room temperature by disconnecting power of the hotplate.

2.2 DEPOSITION OF MESOPOROUS TiO₂ LAYER ON COMPACT FILMS

A 16.5 ml of glacial acetic acid and 15 ml of tetraisopropyl titanate (Sigma-Aldrich) were mixed with 30 ml of 2-propanol. 10 ml of distilled water was added to the above mixture followed by adding TiO₂ powder (2g, Nihon Aerisol) and kept under vigorous stirring for 2-3 h. Resulted TiO₂ semi-colloidal suspension was used as the stock solution. A small amount of this stock solution was spread on compact TiO₂ layer coated FTO preheated at ~150°C by a plastic dropper and allowed to dry for few minutes. TiO₂ coated glass plate was fired at 450°C for 30 min and taken out after reaching them to room temperature by shutting down the power supply of the furnace. Loosely, bounded crust was removed by wiping TiO₂ film smoothly by piece of cotton wool. The thickness of TiO₂ film was achieved as 10 µm by repeating the coating procedure, successively. Finally, TiO₂ coated conducting glass plates were cleaned by washing with acetonitrile.

2.3 DYE (PIGMENT) COATING PROCEDURE ON TiO₂ FILM

Dyes used in the present experiment were purchased from well-reputed manufactures and used as purchased. Dyes were dissolved in dry ethanol (especially if not mentioned in the text) until concentration reaches ~10⁻⁴ M. Dye was coated on TiO₂ electrodes as follows: TiO₂ coated glass plates were kept immersed in the dye solution and temperature of the dye solution was maintained as 40 °C. Dye-coating process was carried out in an oil bath. Natural pigments were extracted just squeezing flowers or fruits in ethanol. Natural pigments were coated on TiO₂ electrodes by boiling them in extracted solution. Dye (pigment) amount on TiO₂ electrodes was controlled by varying the immersion time in the dye (pigment) solution. Multiple coating of dyes or pigments was carried out by coating dyes (or pigments) layer-by-layer technique or co-absorption of dyes same time, as appropriate.

2.4 COATING PROCEDURE OF HOLE-CONDUCTOR ON DYED TiO₂ FILM

CuI was mixed with 15 ml of moisture-free acetonitrile and excess CuI was allowed to precipitate. The filtrate was separated. A drops of crystal growth inhibitor was added to the CuI solution. A small amount of above solution was carefully spread on the surface of the dye(pigment) coated TiO₂ plate heated at 150°C. This procedure was repeated until the conductivity of the CuI film reaches 50 Ωcm⁻¹.

2.5 MEASUREMENTS

Absorption spectra of CuI, dye (or pigment) solutions and dye coated TiO₂ films were measured by using UV-VIS-NIR spectrometer (Jasco V-570). Morphology of the cell was studied using optical microscope and scanning electron microscope. The cell was constructed by pressing a Ni-coated FTO glass plate on the hole conductor coated electrodes. Photo-effects of the cell were studied by illuminating the cell through TiO₂ layer. The variation of photocurrent current of the cell with the wavelength was measured using monochromator (Jasco) coupled with single-phased lock-in amplifier (NF Instrument-5600 A), under constant photon energy illumination mode. Current-voltage characteristics were recorded with a solar simulator (Wacom) coupled with semiconductor parameter analyzer (Hewlett Packard HP 4145B), under 1.5 AM condition. Scan speed was maintained as 0.01 Vmin⁻¹.

III. RESULTS AND DISCUSSION

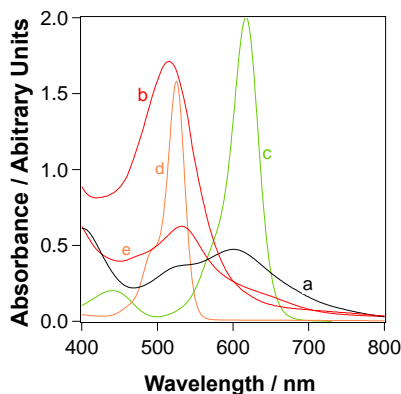


Fig. 1. Absorption spectra of used dyes and natural pigment are shown in Fig 1(a) black dye [BD], (b) cyanidin 3-glucoside [CG] (c) fast green [FG], (d) mercurochrome [MC] and (e) N719

Absorption spectra of selected different dyes and natural pigment are shown in Fig 1 (a) black dye, (b) cyanidin 3-glucoside (c) fast green, (d) mercurochrome and (e) N719. Dyes and pigments absorb unique portion of visible light. The onset of light absorption increases in the order of mercurochrome, cyanidin 3-glucoside, fast green, N719 and black dye. The optical properties of these dyes have been thoroughly discussed previous studies.

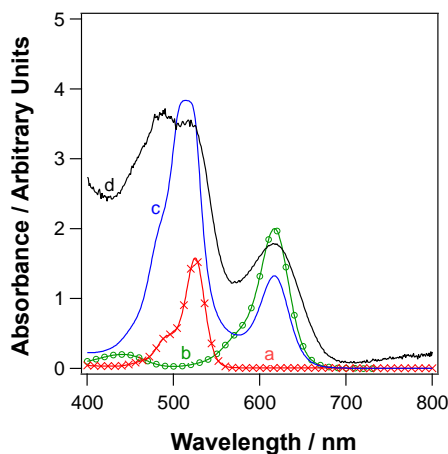


Fig. 2. Absorption spectrum of (a) mercurochrome, (b) fast green, (c) a mixture of mercurochrome and fast green and (d) both mercurochrome and fast green coated electrode

Used Ru-dyes, organic dyes and pigment have different anchoring groups and firmly bound with metal oxide semiconductors. It is well known that, dye coated electrodes absorb only a part of the solar spectrum. In this viewpoint, multi-dye systems have received much attention. Properties of multi-dye coated electrode have been studied. For example, absorption spectrum of (a) mercurochrome, (b) fast green, (c) a mixture of mercurochrome and fast green, (d) both mercurochrome and fast green coated electrodes are shown in Fig. 2. As is shown, more coverage of solar spectrum was observed on multi-dye coated electrodes.

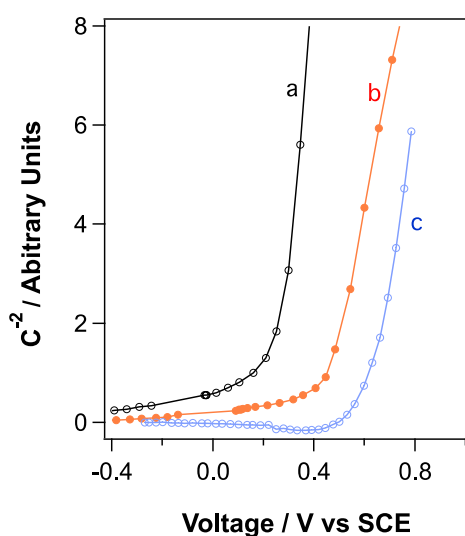


Fig. 3. Mott-Schottky plot of (a) TiO₂, (b) mercurochrome and (c) mercurochrome, fast-green coated electrode

We have also studied the variation of capacitance with voltage of dye coated electrodes. Mott-Schottky plot of (a) bare, (b) mercurochrome and (c) mercurochrome|fastgreen coated electrode is shown in Fig. 3. The more positive shift in the flat band potential is noted in TiO₂|multi dye coated electrodes, possibly better surface coverage or coupling of several dyes makes an apparent shift of the flat band potential.

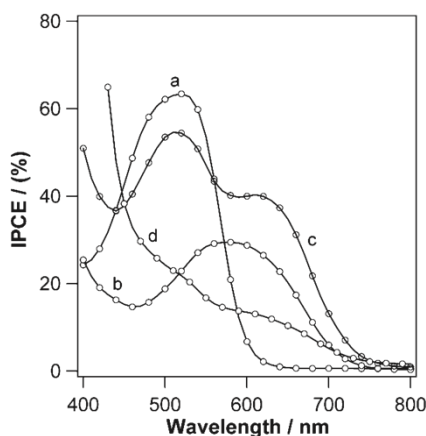


Fig 4. The action spectrum of (a) mercurochrome [MC], (b) cyanidin 3-glucoside [CG], (c) mercurochrome-cyanidin 3-glucoside, (d) cyanidin 3-glucoside-mercurochrome dye systems

The action spectrum of a multi-dye system studied in this study is shown in the Fig 4. As is observed multi-dye systems produced much higher performance of the cell as light absorption coverage is increased. The photo performance of dye sensitized solar cells are listed in table 1.

Table 1. Photo performance of multi-dye sensitized solar cells. I_{sc} , V_{oc} , ff, η indicate short circuit photocurrent, open circuit voltage, fill factor, efficiency of the cell

Cell Configuration	$I_{sc}/mAc m^{-2}$	V_{oc}/mV	ff(%)	η (%)
TiO ₂ MC FG CuI	8	380	37	1.1
TiO ₂ MC FG CuCNS	1.5	590	36	0.3
TiO ₂ MC CG CuI	6.5	370	36	0.8
TiO ₂ MC CG CuCNS	1.6	612	38	0.4
TiO ₂ (BD+N719) CuI	14	500	55	2.1
TiO ₂ (BD+N719) CuCNS	1.8	530	38	0.4

An appropriate coupling in multi-dye coated systems produced much higher photocurrent than dye individually. High photocurrent resulted in TiO₂|dye|CuI cells than TiO₂|dye|CuCNS cells and vice versa in voltage are due to higher energy level of the conduction band of CuCNS than CuI. An appropriate coupling of several dyes improved the power conversion efficiency of the cell than that was dyes in individually due to broadening of the absorption of the electrode, enhance of charge injection process or decrees quenching processes. However, selection of couple of dyes that increases photo-performance is a difficult task.

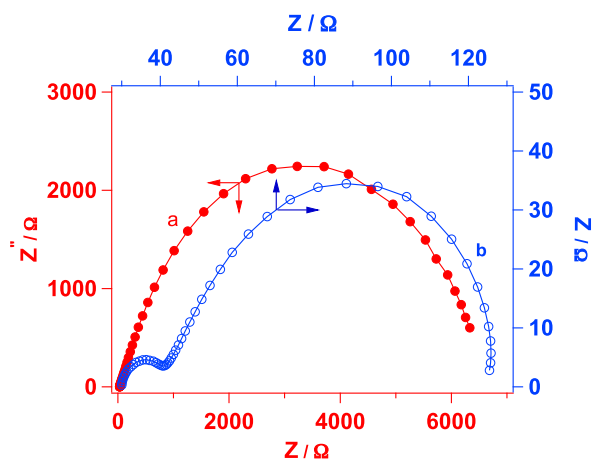


Figure 5 represent the impedance spectroscopy of a TiO₂(Black dye + N719)|CuI type solar cell.

Figure 5 represent the impedance spectroscopy of a TiO_2 (Black dye + N719)|CuI solar cell. A typical characteristics semi-circle was observed in Nyquist plot for the cell at natural biased in dark, which corresponds to electron transportation in the TiO_2 network and resistivity at the interfaces (curve a). Two typical characteristics semi-circles were observed in Nyquist plots for the cell at natural biased under illumination (curve b). However, the Nyquist plot significantly shifted toward the lower impedance direction and resistivity of the device become very small. This effect may be due to reduction of band bending, under illumination. The semicircle belonging to high frequencies and moderate frequencies are due to CuI|counter electrode interface and to electron transportation in the TiO_2 as well as holes diffusion in the CuI network.

The morphology of films also plays a major role in charge generation of this type of solar cells. The microscopic image of a TiO_2 |dye|CuI cell from CuI side is shown as image a in Fig. 6. A non-uniform distribution of CuI was observed on TiO_2 electrodes. Image b illustrates the cross section of the cell. Four different components were observed in this image by difference of morphologies. They are glass substrate, F:SnO₂, TiO_2 and CuI from the order of top to bottom of the image. Non-uniform distribution of both TiO_2 and CuI phases was observed. The photocurrent image of the same cell is also shown as image c, in the same figure.

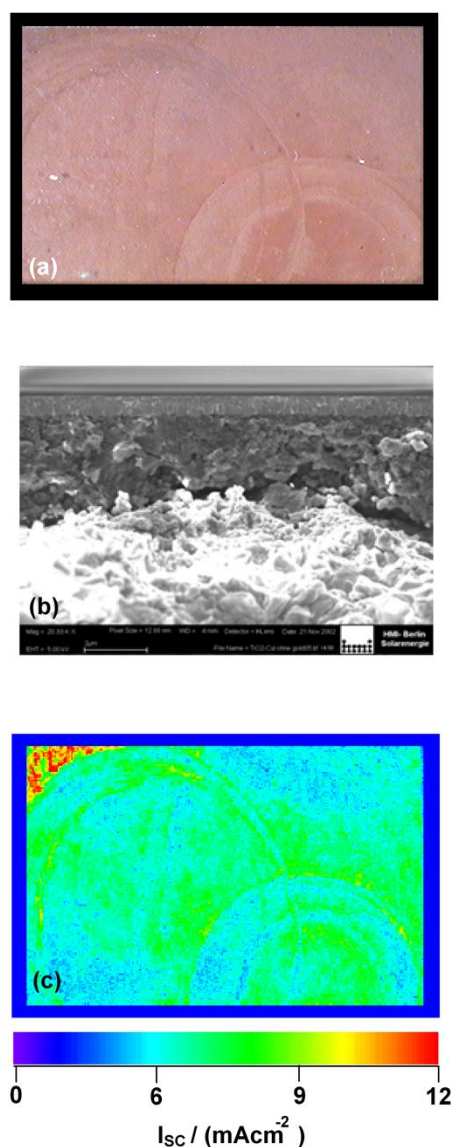


Fig. 6. (a) The microscopic image of a TiO_2 |dye|CuI cell from CuI side (b) cross section of the cell and (c) photocurrent image of the same cell.

IV. CONCLUSION

An appropriate coupling of several dyes enhanced the photo performances of solid-state dye sensitized solar cells due to either enhance of charge injection process or decreases quenching processes under illumination.

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