

Effect of Ligand Attached to Fluorescein on the Photocurrent of dye sensitized Solar Cells

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Abstract

In today's society, it is becoming ever important to find alternative sources of energy that are both cheap and efficient. Converting solar energy into electricity provides a much-needed solution to the energy crisis the world is facing today. With continuous research studies conducted in this field, we have come across the third generation of solar cells; the dye sensitized solar cells. Several types of dyes have been individually employed to study sensitization process of TiO₂/sensitizer/p-semiconductor type solar cells and to produce low-cost dyes; much work is being directed toward synthesizing all-organic, ruthenium-free dyes with high extinction coefficients and broad absorption bands with large solar spectrum overlap. An enhancement of efficiency of this type of solar cells was observed by appropriate coupling of dyes with a same chromophore and different ligand attachments. A comparable study of multi-dye systems was carried out by means of understanding the charge transfer mechanism of multi-dye coated electrodes. The dyes used in this study are organic dyes without any metal influences. They have given photocurrent of 172 μAcm^{-2} , 252 μAcm^{-2} and 127 μAcm^{-2} and a lower efficiency of performance compared to any metal centered dyes.

Keywords: Fluorescein; Ligand effect; Photocurrent; Dye sensitized solar cell; Anthrance A; 5(6) Carboxy fluorescein; Erythrosin B.

1. Introduction

Energy crisis has become a threatening issue to the current world. Many alternative sources have been found to overcome this concern. Solar energy is one of those choices. With continuous researches conducted in this field, we have come across the third generation of solar cells; the dye sensitized solar cells. In the field of dye-sensitized solar cells, the number of different sensitizing dyes is increasing rapidly. In this study, 5(6) Carboxyfluorescein dye, Anthrance A dye and Erythrosin B dye are used as sensitizers to fabricate solar cells. These dyes have the same chromophore with different attachments of ligands and also they have different surface chelating groups and making bonds easily with metal oxides this was confirmed by FTIR measurements. These dyes were coated on titanium coated conducting glass substrates and were attached to counter electrode and the space was filled by I⁻|I₃⁻ electrolyte by capillary action. I-V characteristics were measured under light illumination. DSSCs with these dyes has given photocurrent of 172 μAcm^{-2} , 252 μAcm^{-2} and 127 μAcm^{-2} were obtained for cells with 5(6) Carboxyfluorescein dye, Anthrance A dye and Erythrosin B dye respectively. This shows the efficiency of these three dyes for DSSC is very low.

2. Materials and Methods

2.1 Preparation of screen printing TiO₂ pastes on glass substrates

2.1.1 Nano-crystalline TiO₂ paste

An amount of 12 g of acetic acid was added to 58.6 g of titanium iso-propoxide stirring for 15 min at room temperature. The mixture was poured into 290 mL water, as quickly as possible, with vigorous stirring (700 rpm). The hydrolysis reaction was stirred for one hour. 5.4 mL of 65% nitric acid was added to the mixture and heated from room temperature to 78°C, within 40 min, and peptized for 75 min. Water was added as the mixture was cooling until 370mL. The suspension was kept in a 570mL titanium autoclave and heated to 250°C for 12 h. 2.4 ml of 65% nitric acid was added and the particles dispersed with a 200W ultrasonic titanium probe at a frequency of 15 pulses per second. The resultant colloidal solution was concentrated with a rotary-evaporator to contain 18% TiO₂. The solution was centrifuged to remove the nitric acid and washed with ethanol three times to produce a precipitate containing 40% TiO₂ in ethanol. An amount of 16 g of TiO₂ precipitate was mixed with 64.9 g of terpineol and a solution of ethyl cellulose in ethanol. The precipitate was well mixed and rotary-evaporated.

2.1.2 Micro-crystalline TiO₂ paste

400 nm particles (in aqueous solution) are transferred into ethanol by repeatedly centrifuging and removing supernatant then topping up with pure ethanol and mixing. 5 parts of 400 nm titania paste and 1 part of 18 nm titania paste were mixed with 3.5 parts of ethyl cellulose and 30.5 mL of terpineol. The mixture was rotary-evaporated until ethanol is removed.

2.2. Preparation of TiO₂ films on glass substrates

Conducting glass plates (FTO) were cut into 1 x 2.5 cm² pieces, cleaned by detergent, thoroughly washed with distilled water and dried in an oven. One of the edges of FTO (1 x 1cm²) was covered with 3M tape and placed horizontally on a

hotplate facing the conducting side to air. Temperature of the hotplate was gradually increased to 450°C. A solution of titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich) in isopropanol(1:9) was sprayed over the FTO quickly at the thermal equilibrium at 450°C and allowed to reach to room temperature by disconnecting power of the hotplate.

The microcrystalline TiO₂ paste was coated followed by coating nano-crystalline TiO₂ paste on the compact TiO₂/FTO substrates by screen-printing. The TiO₂ coated films (0.5 cm x 0.5 cm) were backed at 450°C for 30 min. Finally TiO₂ substrates were wetted from a 0.05 M TiCl₄ (aq) in 20% HCl is diluted from a 2.0 M stock solution and again backed at 450°C for another 30 min.

2.3 Preparation of dye solutions

5(6) Carboxyfluorescein, Anthrance A and Erythrosin B dye solutions were prepared by dissolving the dyes in methanol, Water and Acetonitrile.

2.4 Dye coating process for TiO₂ thin films on glass cells

TiO₂ thin films were immersed in 5(6)-Carboxyfluorescein, Anthrance A and Erythrosin B dye solutions prepared with methanol. Thin films were kept overnight to adsorbed dye on to TiO₂ layer.

2.5 Assembling of the cell

2.5.1 Preparation of Pt coated electrodes on FTO substrate

10 mM H₂PtCl₆ in isopropanol solution was prepared. One drop of this solution was put onto the conductive side of FTO electrode and allows drying. FTO counter electrode (active side up) was inserted into ceramic tube, gradually heated up to 400°C leave for 15 min., allowed to cool electrode. A hole with a diameter of 1 mm was made on the Pt coated FTO electrode.

2.5.2 Preparation of solar cell with glass substrates

A rectangular hole with the dimension of 0.5 cm x 0.5 cm was made the center of 1cm x 1cm Surlyn film (thickness is 25µm). This film was placed on the dye coated TiO₂ film as the rectangular hole superimpose with the dyed TiO₂ film (0.5cm x 0.5cm). A Pt coated FTO electrode hole with a diameter of 1mm was placed on this TiO₂ electrode with the Surlyn film and heated by applying pressure on glass electrodes as Surlyn film melts and adhesive with two electrodes. The electrolyte that was composed of 0.04M I₂, 0.4M 4tert-butylpyridine, 0.4M lithium iodide, 0.3M N-methylbenzimidazole in acetonitrile and 3-methoxypropionitrile by volume 1:1 was filled in to the device from the back hall and hall was sealed.

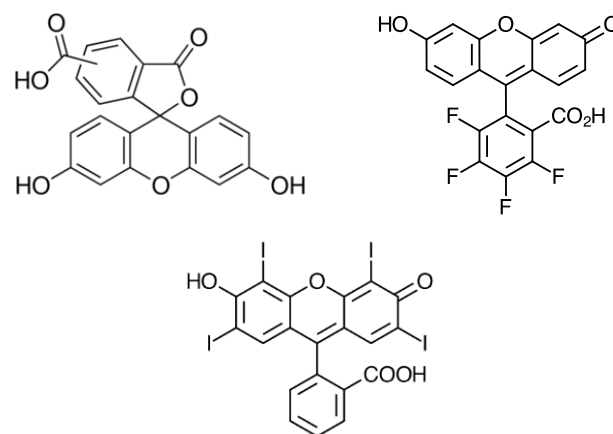
2.6. Measurements

Absorption spectra of dye 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 Pt-coated FTO glass plate on the TiO₂/dye/CuIelectrodes. 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 analyser (Hewlett Packard HP 4145B), under 1.5 AM condition. Scan speed was maintained as 0.01 Vmin⁻¹.

3. Results and discussion

Molecular structures of (a) 5(6)-Carboxyfluorescein, (b) Erythrosin B and (c) Anthrance A dyes are shown in Scheme 1



Scheme 1. Molecular structures 5(6)-Carboxyfluorescein, (b) Anthrance A and (c) Erythrosin B dyes.

Flouresceine ligand exists in all three dye molecules. It is Known that the differences in absorption of these three dyes are due to other ligands attached on the main body.

Absorption spectra of (a) 5(6)-Carboxyfluorescein, (b) Erythrosin B and (c) Anthrance A dye solutions in methanol are shown, in Fig. 3.1 Three major electron transitions were observed at 440,462 and 490 nm for 5(6)-Carboxyfluorescein in methanol. A significant red shift in the absorption spectrum with two different electron transitions correlated at 442 and 490 nm were observed for Anthrance A in methanol. Two predominant electron transitions were observed at 500 and 538 nm for Erythrosin B in methanol. It is known that dye molecules have different absorption characteristics in same solvent due to their chemical structure and substituent groups.

They behave in different manner in similar environments, probably due to enforcement of Van der Waals interaction strength between substituent groups of dye molecules and solvents depending on their polarity. Polarity of dye molecules can be differing due to the chemical structure of the molecules.

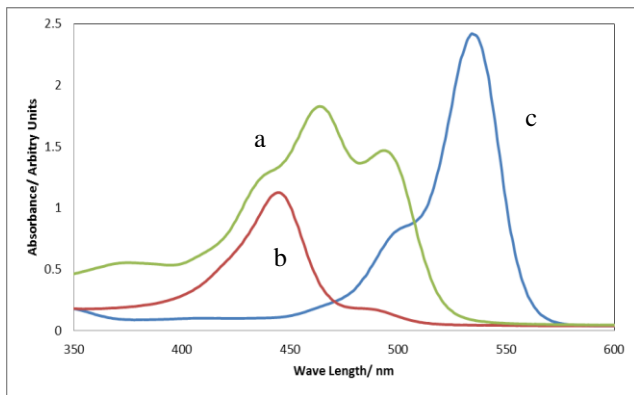


Figure 3.1: Absorption spectra of (a) 5(6)-Carboxyfluorescein dye (b) Erythrosin B dye and (c) Anthrance A dye

The strong solvatochromic behavior can be observed for dye molecules with large dipole moment changes during transitions between two electronic states. The solvatochromic behavior of a dye is the shift of absorption wavelength due to the presence of solvent with different polarity, which is due to the interaction between the solute and solvent molecules. In this study Methanol, Water and acetonitrile are used as the solvents to check the absorption efficiency. Methanol, Water and acetonitrile have polarities of 0.762, 1, 0.46 respectively. The visible absorption spectra of 5(6)-Carboxyfluorescein, Erythrosin B and Anthrance A dyes were obtained at room temperature in three different solvents with different polarity (Figure 3.2 (a) (b) (c)). According to this results Methanol was selected as the suitable solvent for the study.

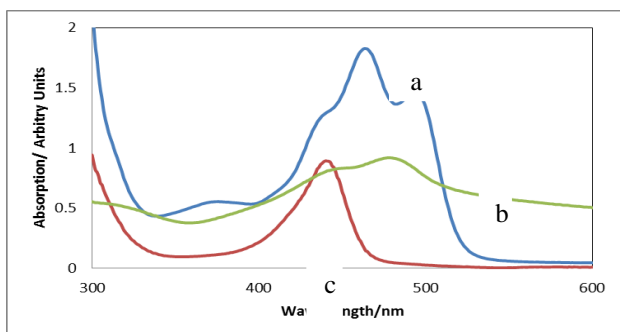


Figure 3.2(a): Absorption spectra of 5(6) Carboxyfluorescein dye (a) in methanol (b) in water and (c) in acetonitrile

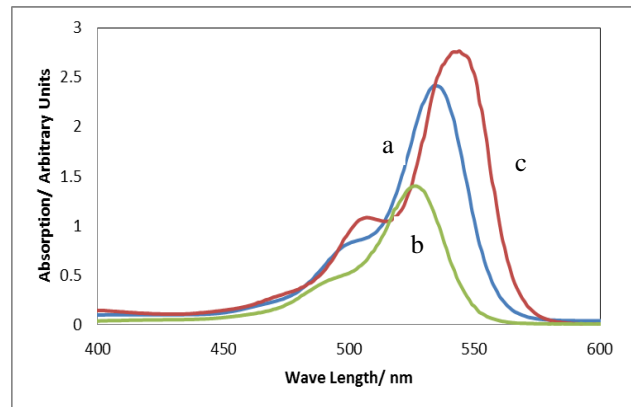


Figure 3.2(b): Absorption spectra of Erythrosin B dye (a) in methanol (b) in water and (c) in acetonitrile

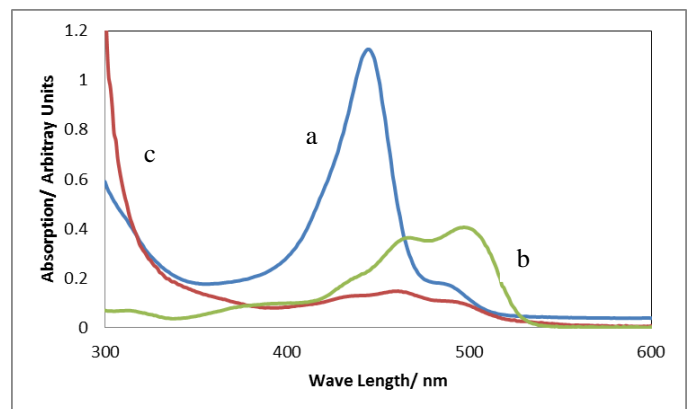


Figure 3.2(c): Absorption spectra of Anthrance A dye (a) in methanol (b) in water and (c) in acetonitrile

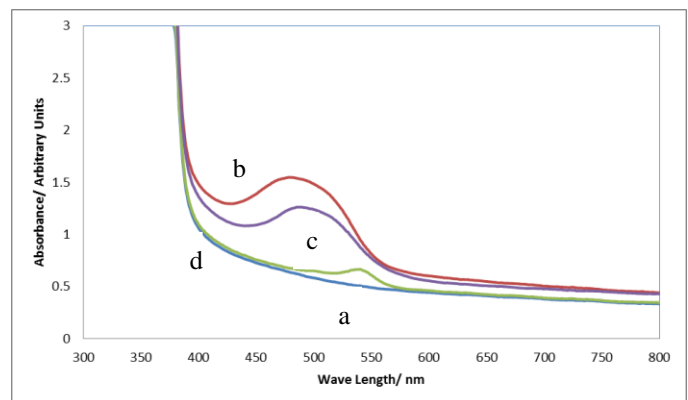


Figure 3.3: Absorption spectra of (a) bare and (b) 5(6)Carboxyfluorescein dye (c) Anthrance A dye and (d) Erythrosin B dye coated TiO₂ films.

TiO₂ electrodes were kept immersed in 5(6)Carboxyfluorescein, Anthrance A and Erythrosin B dye solutions and absorption of dyed TiO₂ films were separately measured. Absorption spectra of bare and dyes coated TiO₂ films are shown in Fig. 3.3. As is shown in this figure, the dyes coated TiO₂ films have a higher electron transition than the bare TiO₂ film. Because when dye molecules attached to TiO₂ film they can catch the electrons and emit them due to energy. Here the absorbance of 5(6) Carboxyfluorescein dye is greater than the other two dyes.

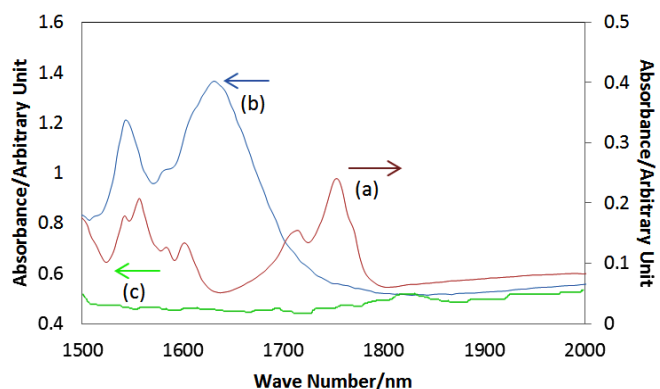


Figure 3.3: FTIR spectra for (a) Erythrosin B dye (b) Erythrosin B dye coated TiO₂ powder (c) Bare TiO₂ powder

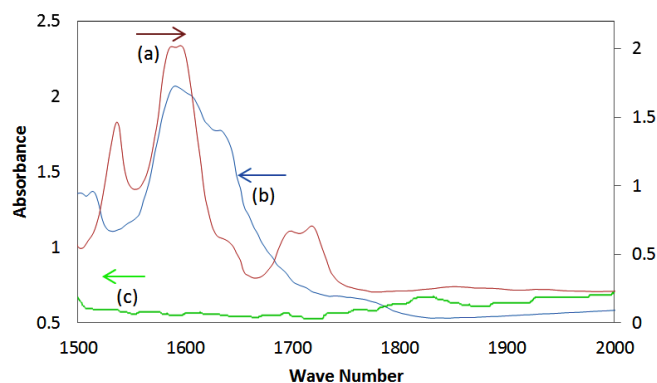


Figure 3.4: FTIR spectra for (a) 5(6)Carboxyfluorescein dye (b) 5(6)Carboxyfluorescein dye coated TiO₂ powder (c) Bare TiO₂ powder

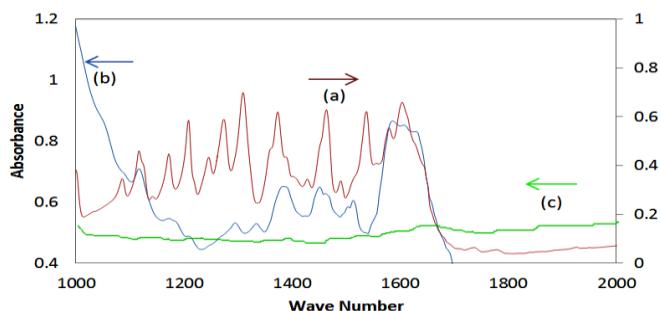


Figure 3.5: FTIR spectra for (a) Anthrance A dye (b) Anthrance A dye coated TiO₂ powder (c) Bare TiO₂ powder

FTIR spectroscopy for dye powders and dye coated TiO₂ powders were performed. FTIR spectra for (a) Erythrosin B dye and (b) Erythrosin B dye coated TiO₂ powder within the wavenumber region from 1500 to 2000 cm⁻¹ are shown in Fig. 4.6. Significantly enhanced peaks were observed for Erythrosin B dye coated TiO₂ powder dye powder samples while peaks with moderate intensities were observed for pure Erythrosin B dye most probably due to high concentration of dye on TiO₂ powder. The peak at $\nu = 1666\text{cm}^{-1}$ in curve a is correlated with COOH group. This peak has completely disappeared after chelation of dye with TiO₂. This indicates enrolment of bonding of COOH group with TiO₂ film. Peaks at $\nu = 1540\text{cm}^{-1}$, $\nu = 1710\text{cm}^{-1}$ and $\nu = 1750\text{cm}^{-1}$ also completely disappeared after chelation of dye with TiO₂. This shows the enrolment of bonding of corresponding functional groups with TiO₂.

FTIR spectra for (a) 5(6)Carboxyfluorescein dye (b) 5(6)Carboxyfluorescein dye coated TiO₂ powder within the wavenumber region from 1500 to 2000 cm⁻¹ are shown in Fig. 4.7. Here significantly enhanced peaks were observed for pure 5(6)Carboxyfluorescein dye powder samples. However, peaks with moderate intensities were observed for 5(6)Carboxyfluorescein dye coated TiO₂ powder most probably due to low concentration of dye on TiO₂ powder. Peaks at $\nu = 1540\text{cm}^{-1}$, $\nu = 1700\text{cm}^{-1}$ and $\nu = 1720\text{cm}^{-1}$ curve a completely disappeared after chelation of dye with TiO₂. This indicates the enrolment of bonding of corresponding functional groups with TiO₂.

FTIR spectra for (a) Anthrance A dye (b) Anthrance A dye coated TiO₂ powder within the wavenumber region from 1000 to 2000 cm⁻¹ are shown in Fig. 4.8. Here both spectrums are nearly in the same intensity range. Many are completely disappeared after chelation of dye with TiO₂. This indicates the enrolment of bonding in many places (functional groups) of the dye molecule with TiO₂.

Cells fabricated by using these three dyes are evaluated by means of I-V characteristics of the cell under light illumination. The results are shown in Fig 3.6, Fig 3.7 and Fig 3.8.

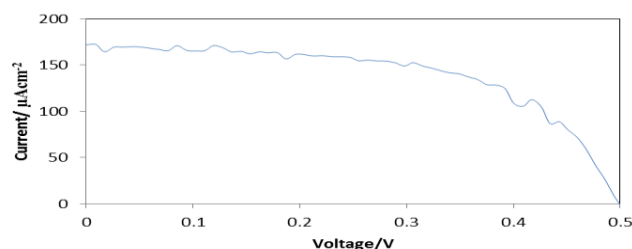


Figure 3.6: I-V characteristics of the cell with 5(6)Carboxyfluorescein dye under light illumination

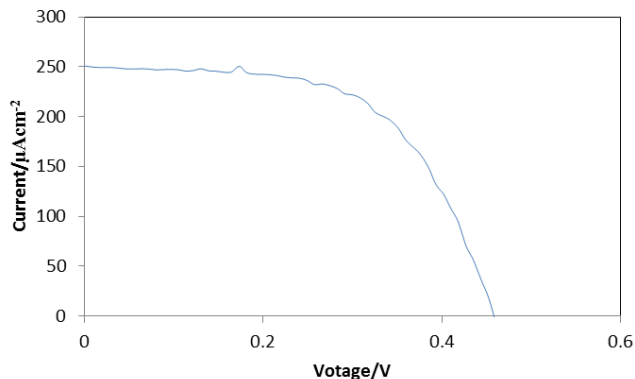


Figure 3.7: I–V characteristics of the cell with Anthrance A dye under light illumination

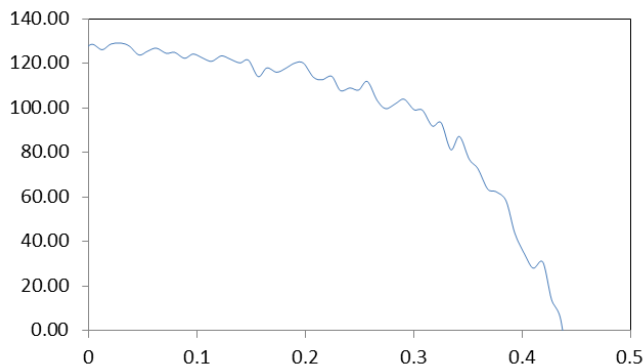


Figure 3.8: I–V characteristics of the cell with Erythrosin B dye under light illumination.

Table 1

The performances of cells, where J_{sc} , V_{oc} , η denote photocurrent, open circuit voltage, and efficiency of the cell.

Dye	J_{sc} , $\mu A\ cm^{-2}$	V_{oc} , mV	η (%)
5(6)Carboxyfluorescein	172	502	0.3%
Anthrance A	252	461	0.28%

Erythrosin B	127	435	0.22%
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4. CONCLUSION

Photocurrent of $172\ \mu Acm^{-2}$, $252\ \mu Acm^{-2}$ and $127\ \mu Acm^{-2}$ were obtained for cells with 5(6)Carboxyfluorescein dye, Anthrance A dye and Erythrosin B dye respectively. These values are very low when compared with any other metal centered dyes. This shows the efficiency of these three dyes for DSSC is very low. So when fabricating DSSCs 5(6)Carboxyfluorescein dye, Anthrance A dye and Erythrosin B dye should be avoided. It is better to use any metal centered dye for better performance.

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