

Research Article

Study of Light Harvesting Properties of Different Classes of Metal-Free Organic Dyes in TiO₂ Based Dye-Sensitized Solar Cells

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In dye-sensitized solar cells, the photosensitization of TiO₂ thin film semiconductor was accomplished by using different classes of metal-free (fluorone, triarylmethane, azo and thiazine based) organic dyes as photosensitizer. The broad electronic absorption spectra of these dyes have been obtained in the visible region due to the presence of chromophoric groups in these dyes. The contribution of these dyes as light harvesting species is seen from the photocurrent action spectrum of the cell. Here, we report the sensitization activity of these dyes in terms of current-potential curve, open-circuit potential, fill factor, IPCE, and overall solar energy conversion efficiency which have been evaluated under 100 mW/cm² light intensity. The results suggest that dyes based on fluorone and azo groups are promising candidates for high performance, dye-sensitized solar cells because of better anchoring groups (–COOH, –OH, and –SO₃[–]) present in these dyes. Better anchorage of dyes to the surface of TiO₂ semiconductor helps in charge transfer phenomenon.

1. Introduction

Direct conversion of sunlight into electricity using solar cells is a steadily growing energy technology which is gaining tremendous popularity because they can produce electricity near the end user, avoiding transmission losses and costs. The solar panels operate without noise, toxicity, or greenhouse gas emissions. However, due to the high material and fabrication cost of Si solar cells, the PV electricity generated is less than 0.1% of the total energy demand of the world. Dye-sensitized solar cells (DSSCs) have the potential to be a low-cost alternative to silicon solar cells due to their low cost and high power conversion efficiency [1–15].

A typical dye-sensitized solar cell is depicted in Figure 1. The device is constituted of two transparent conducting oxide substrates (TCO) such as fluorine doped tin oxide (FTO) on glass or polymeric substrates [16]. One TCO is a photoanode, composed of a sensitizer adsorbed onto the surface of the nanocrystalline semiconductor electrode (typically nanostructured TiO₂) and the other is a photoinert

counterelectrode with a thin layer of a catalyst (for instance, platinum) sandwiching an electrolyte/relay medium (usually a solution containing the I₃[–]/I[–] pair). *n*-TiO₂ is the most employed semiconductor material in dye-sensitized photoelectrochemical solar cells due to its favorable energetics, good stability, low cost and facile processing [17–19].

In a regenerative DSSC, visible light is efficiently converted into electricity without any permanent chemical change (Figure 2). All the processes involved in the functioning of such cells in general are summarized below.

First Step. Photoexcitation of sensitizer (dye) molecules anchored onto the surface of the S.C. electrode:



Second Step. Electron injection from excited dye molecules into the conduction band of the S.C. is as follows:



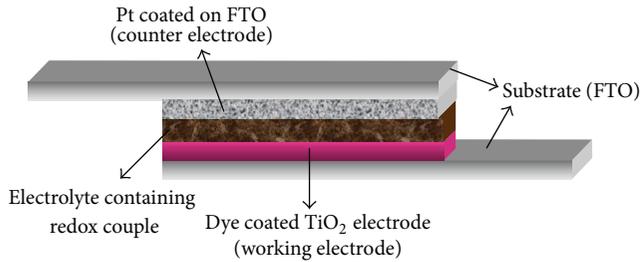
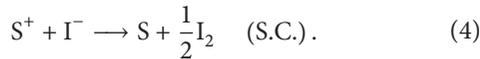


FIGURE 1: Sandwich type assembly of DSSCs.

Third Step. Flow of injected electrons to C.E. through external circuit and accomplishing reduction reaction is as follows:



Forth Step. Reduction of oxidized dye molecules resulting after electron injection (regeneration process) is as follows:



Net Result (Sum of All the 4 Steps). The net results of the four steps involved are:

- (i) No net chemical change ($\Delta G = 0$).
- (ii) Only light is converted to electricity.

Till date, a variety of frameworks and materials are being pursued to replace Si based and other thin film technologies in which the dye-sensitized solar cell (DSSC) developed by Grätzel continues to be one of the most efficient “next generation” technologies having power conversion efficiencies (η) in excess of 10% [4, 8]. But owing to the limited resources, environmentally unfriendly nature, and high cost of ruthenium metal, the efforts have been continued to search for more and more efficient sensitizers. With an objective to search for efficient sensitizers, many new commercial [20–25] and synthetic dyes (organic compounds and inorganic metal complexes) [26–29] have been studied for spectral sensitization of wide band gap semiconductor electrodes.

Many efforts have been made to change the different parts of organic dyes to optimize DSSC performance. To date, hundreds of *n*-type organic dyes including coumarin dyes, indoline dyes, tetrahydroquinoline dyes, triarylamine dyes, heteroanthracene dyes, carbazole dyes, *N,N*-dialkylaniline dyes, hemicyanine dyes, merocyanine dyes, squaraine dyes, perylene dyes, anthraquinone dyes, boradiazaindacene (BOD-IPY) dyes, oligothiophene dyes, and polymeric dyes have been adopted to act as sensitizers for DSSCs and impressive efficiencies have been obtained. The structures and their photovoltaic parameter have been reviewed by Hagfeldt and coworkers [30].

Meanwhile, fluorone, triarylmethane, azo, and thiazine based organic dyes as sensitizers have been applied successfully to sensitization of nanocrystalline TiO_2 -based solar cells and the corresponding photovoltaic properties are presented

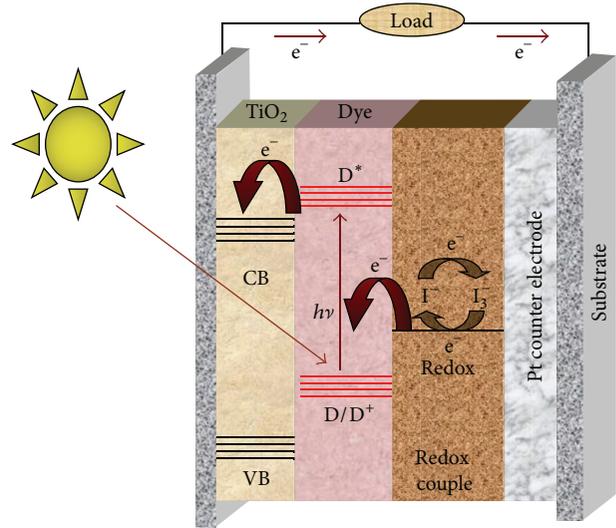


FIGURE 2: Working principles of dye-sensitized solar cells.

in this paper by using iodine/iodide redox couple in propylene carbonate as a cell electrolyte.

2. Experimental Study

2.1. Materials. The propylene carbonate (Merck) was employed as a medium of electrolyte solution; LiI (Aldrich) and I_2 (BDH) were used as redox couple in PEC experiments. Titanium paste (HT) was used for preparing TiO_2 electrode; platinum catalyst (T/SP) used as the counter electrode and sealing agent (SX1170-60, 50 μm) were obtained from Solaronix. Conductive glass plate was obtained from Pilkington, USA. The fluorone, triarylmethane, azo, and thiazine based organic dyes were purchased from CDH, India.

2.2. Preparation of TiO_2 Electrode (Photo Anode) and Counterelectrode. TiO_2 film electrode (photoanode) was prepared by spreading a highly transparent paste of TiO_2 (Titanium-HT) on a conductive glass plate (15 Ω/cm^2 , Pilkington, USA) by the doctor's blade method and annealing at 450 $^\circ\text{C}$ for half an hour in air. The dye was attached to the TiO_2 surface by immersing the TiO_2 coated electrodes in the solution of dye according to their solubility for 8 h. The nonadsorbed dye was washed with anhydrous ethanol. Platinum counterelectrode was prepared by deposition of Pt catalyst T/SP paste on another conductive glass and annealed at 400 $^\circ\text{C}$ for half an hour in air.

2.3. DSSC Assembly. Before assembling the components of the cell, the dye was anchored onto the surface of the TiO_2 thin film electrode by immersing it for 6 h in the dye solution prepared in a suitable solvent (methanol or DCM). The nonadsorbed dye was washed off with anhydrous ethanol. To assemble the cell, the platinum catalyst-coated counterelectrode was placed over dye-coated TiO_2 electrode

in such a way that the conductive side of the counter electrode faced the dye-coated TiO₂ film, and the cell was sealed on three sides by using the spacer SX1170-60, 50 μm (Solaronix, heating it at ~80°C); one side was left open for the injection of electrolyte solution. The cell electrolyte (0.2 M lithium iodide mixed with 0.02 M iodine in propylene carbonate) was injected through opening and was drawn into the space between the electrodes by capillary action. Thereafter, the open side was also sealed carefully with araldite. On uncovered portion of the electrodes, the tips of the copper wires were attached using silver paste which was subsequently covered with araldite and dried before use.

2.4. Apparatus and Instruments. A bipotentiostat (model number AFRDE 4E, Pine Instrument Company, USA) and recorder (e-Corder 201, Australia) were used for all current-potential measurements. For PEC measurements, a 150 W xenon arc lamp (Oriel Corporation, USA) was used as the light source and the semiconductor electrode was illuminated after passing the light beam through a water column 6 inches in length (to filter IR) and condensing it with the help of fused-silica lenses (Oriel Corporation, USA). The light was monochromatised, when required, by using a grating monochromator (Oriel model 77250 equipped with model 7798 grating). The width of the exit slit of the monochromator was kept at 0.5 mm. To obtain the action spectrum ($I_{\text{photo}}-\lambda$) of the dye-sensitized TiO₂ electrode, the monochromatic light-induced photocurrent was measured with a digital multimeter (Philips Model No. 2525) in combination with the potentiostat. The intensities of light were measured with a digital photometer (Tektronix model J16 with model J 6502 sensor) in combination with neutral density filters (model number 50490-50570, Oriel, USA).

3. Result and Discussion

The electronic absorption spectra of these dyes display bands in the visible region (400–700 nm) of electromagnetic spectrum. The absorption peak values (λ_{max}), molecular formula, molecular weight, and structure of the dyes are presented in Table 1.

The power output parameters of the dye-sensitized photoelectrochemical (PEC) cell (TiO₂ electrode/dye-containing electrolyte/platinum counter electrode) were determined from current-potential curves (J - V) obtained under illumination with 100 mW/cm² light intensity. Keeping the cell (DSSC) illuminated with desired light, the potential at the working electrode is swept in a selected range and generated current is recorded. From such current-potential curve, all cell output parameters (open-circuit photovoltage (V_{OC}), fill factor (FF), and overall power conversion efficiency (η)) were obtained.

The maximum output power (P_{max}) is obtained by choosing a point “x” on experimentally determined (J - V) curve (black line in Figure 3) corresponding to which the product of current (J_{max}) and voltage (V_{max}) gives maximum value.

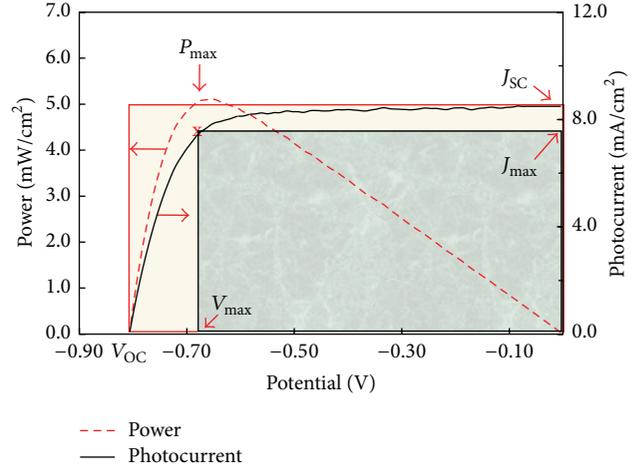


FIGURE 3: Representative (J - V) curve, corresponding power curve, and various terms required to calculate fill factor (FF) and power conversion efficiency of the cell.

The fill factor (FF) and power conversion efficiency (η) are evaluated using the following relations:

$$\text{FF} = \frac{P_{\text{max}}}{P_{\text{ideal}}} = \frac{J_{\text{max}} (\text{A/cm}^2) \times V_{\text{max}} (\text{V})}{J_{\text{SC}} (\text{A/cm}^2) \times V_{\text{OC}} (\text{V})}$$

$$\eta (\%) = \frac{P_{\text{max}}}{\text{Input Power (light intensity)}} \times 100 \quad (5)$$

$$= \frac{J_{\text{max}} (\text{A/cm}^2) \times V_{\text{max}} (\text{V})}{I_{\text{inc}} (\text{W/cm}^2)} \times 100.$$

Here, J_{SC} , V_{OC} , and I_{inc} are short-circuit photocurrent, open-circuit potential, and intensity of incident light, respectively. The fill factor is obviously always less than unity for any cell and it is the measure of the fraction of the ideal power ($J_{\text{SC}} \times V_{\text{OC}}$) which is obtainable at the best for external use.

To ascertain unambiguously the sensitization of photocurrent by the dye under investigation, the action spectrum of dye-modified TiO₂ electrode was determined. The close resemblance of the nature of such spectrum with the absorption spectrum of the respective dye-coated electrode indicates the sensitization of photocurrent by dye. Initially, the short-circuit photocurrent (J_{photo}) induced by monochromatic light was determined in the range of visible light (400–700 nm wavelength). From the values of J_{sc} and the intensity of the corresponding monochromatic light (I_{inc}), the incident photon-to-current conversion efficiency (IPCE) was calculated at each excitation wavelength (λ) by using following equation:

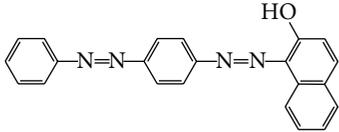
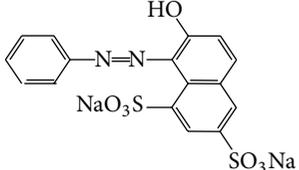
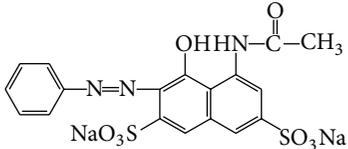
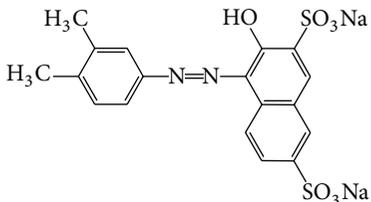
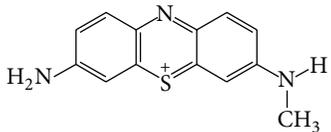
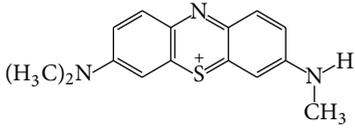
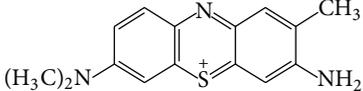
$$\text{IPCE} (\%) = \frac{\text{number of electrons generated}}{\text{number of incident photons}} \times 100$$

$$= \frac{1240 J_{\text{photo}} (\text{A/cm}^2)}{\lambda (\text{nm}) \cdot I_{\text{inc}} (\text{W/cm}^2)} \times 100. \quad (6)$$

TABLE 1: Molecular formula, colour, solubility, λ_{\max} value, and structure of fluorone, triarylmethane, azo, and thiazine based metal-free organic dyes.

| Dyes | Colour | Formula (M. Wt.) | Solubility | λ_{\max} (nm) | Structure |
|---------------------------|--------------|--|---|-----------------------|-----------|
| Fluorone based dyes | | | | | |
| Phloxine B | Red | $C_{20}H_2Br_4Cl_4Na_2$ (829.7) | Slightly in water and ethanol | 548 nm | |
| Ethyl eosin | Red | $C_{22}H_{11}O_5Br_4Na$ (714) | Slightly in ethanol and water | 532 nm | |
| Eosinol | Red | $C_{20}H_8Br_4O_5$ (647.9) | Slightly in water and moderately in ethanol | 524 nm | |
| Erythrosin B | Maroon | $C_{20}H_6O_5I_4Na_2$ (879.9) | Slightly in water and ethanol | 524 nm | |
| Triarylmethane based dyes | | | | | |
| Victoria blue 4R | Blue | $C_{34}H_{34}N_3Cl$ (520.1) | Ethanol and slightly in water | 591 nm | |
| Methyl green | Green | $C_{26}H_{33}N_3Cl_2$ (458.5) | Soluble in ethanol | 630 nm, 420 nm | |
| Acid fuchsin | Red | $C_{20}H_{17}N_3Na_2O_9S_3$ (585.6) | Water, slightly in ethanol | 540–546 nm | |
| Chromoxane cyanin R | Yellow brown | $C_{23}H_{15}O_9SN_3$ (536.4) | Readily soluble in water and ethanol | 518 nm | |

TABLE I: Continued.

| Dyes | Colour | Formula (M. Wt.) | Solubility | λ_{\max} (nm) | Structure |
|---------------------|--------|--|--|-----------------------|---|
| Azo based dyes | | | | | |
| Sudan III | Red | $C_{22}H_{16}N_4O$ (352.4) | Slightly in ethanol | 507 nm |  |
| Orange G | Orange | $C_{16}H_{10}N_2O_7S_2Na_2$ (452.386) | Slightly in water and ethanol | 475 nm |  |
| Azophloxine | Red | $C_{18}H_{13}N_3O_8S_2Na_2$ (509.44) | Soluble in water and slightly soluble in ethanol | 532, 506 nm |  |
| Xylidine Ponceau | Red | $C_{18}H_{14}N_2O_7S_2Na_2$ (480.44) | Soluble in water and slightly soluble in ethanol | 503 nm |  |
| Thiazine based dyes | | | | | |
| Azure C | Blue | $C_{13}H_{12}N_3SCl$ (277.8) | Readily soluble in ethanol | 616 nm |  |
| Azure B | Blue | $C_{15}H_{16}N_3SCl$ (305.8) | Readily soluble in ethanol | 648 nm |  |
| Toluidine blue O | Blue | $C_{15}H_{16}N_3SCl$ (305.8) | Slightly in water and ethanol | 626 nm |  |

The (IPCE versus λ) plots (action spectra) thus obtained for TiO_2 electrodes coated with different dyes were compared with the electronic absorption spectra of the dyes. The close resemblance of action spectrum and electronic absorption spectra reveals the contribution of these dyes as a light harvesting material/component in the dye-sensitized solar cells.

3.1. Fluorone Based Dyes. The current-potential curves, obtained by using fluorone based (Phloxine B, ethyl eosin, Eosinol, and Erythrosine B) dyes as sensitizers, adsorbing on nanocrystalline TiO_2 thin film electrode are shown in Figure 4. Ethyl eosin shows the highest photocurrent ($J_{sc} = 3.35 \text{ mA/cm}^2$) and the highest efficiency ($\eta = 1.25\%$) among the fluorone based dyes. The decreasing trend of cell

efficiencies of the fluorone based dyes is as follows: ethyl eosin (1.25%) > Erythrosine B (1.10%) > Eosinol (1.03%) > Phloxine B (0.92%). The remarkable efficiencies have been obtained in fluorone based dyes due to better anchoring group ($-\text{COOH}$, $-\text{OH}$) present in the system for better interaction to the surface of TiO_2 semiconductor for efficient electron injection.

The close resemblance of the absorption spectrum of these dyes with the respective action spectrum confirms the sensitization of the photocurrent by dye (Figure 5). The onset wavelength of the IPCE spectrum of DSSC on the fluorone based dyes is 650 nm. The highest value of the IPCE, obtained among these dyes was 33% at 535 nm in the case of ethyl eosin. The output parameters such as J_{sc} , V_{oc} , FF, η , and IPCE, obtained by using these dyes, are summarized

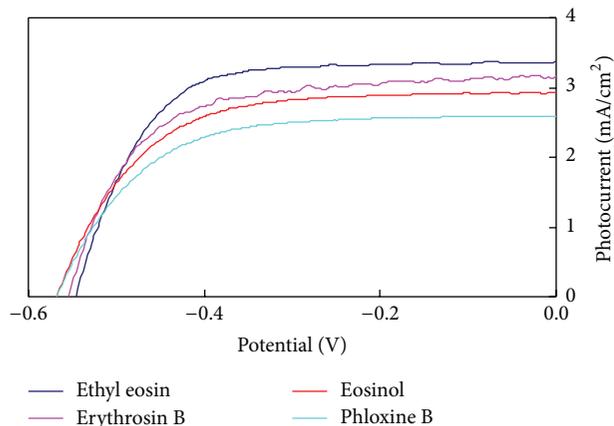


FIGURE 4: Photocurrent-voltage characteristics of TiO_2 electrodes sensitized with fluorone based dyes under illumination with 100 mW/cm^2 light intensity.

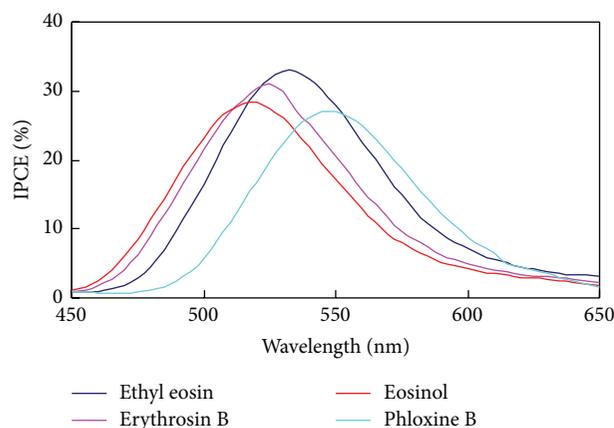


FIGURE 5: Action spectrum of incident photon-to-current conversion efficiencies (IPCE) obtained for nanocrystalline TiO_2 solar cells sensitized by fluorone based dyes.

in Table 2. These IPCE values obtained under short-circuit conditions can be increased if the semiconductor photoanode is externally biased with positive potential.

3.2. Triarylmethane Based Dyes. The triarylmethane based dyes (Victoria blue 4R, acid fuchsin, chromoxane cyanin R, and methyl green) display short-circuit current and open-circuit voltage in the ranges of 2.16 to 2.63 mA/cm^2 and -0.614 to -0.626 V , respectively (Figure 6). The highest photocurrent and efficiency were obtained by using chromoxane cyanin R ($J_{sc} = 2.63 \text{ mA/cm}^2$, $V_{oc} = -0.614 \text{ V}$, $\text{FF} = 0.68$, and $\eta = 1.09\%$).

Figure 7 displays incident photon-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength of the triarylmethane based dyes. The IPCE spectra for these dyes showed good agreement with the absorption behavior of the dyes on TiO_2 film, indicating the photosensitization of TiO_2 thin film semiconductor by these dyes. The IPCE spectrum exhibits a maximum of 30% for chromoxane

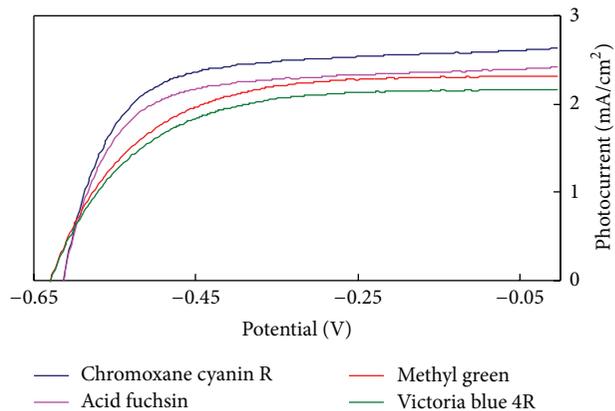


FIGURE 6: Photocurrent-voltage characteristics of TiO_2 electrodes sensitized with triarylmethane based dyes under illumination with 100 mW/cm^2 light intensity.

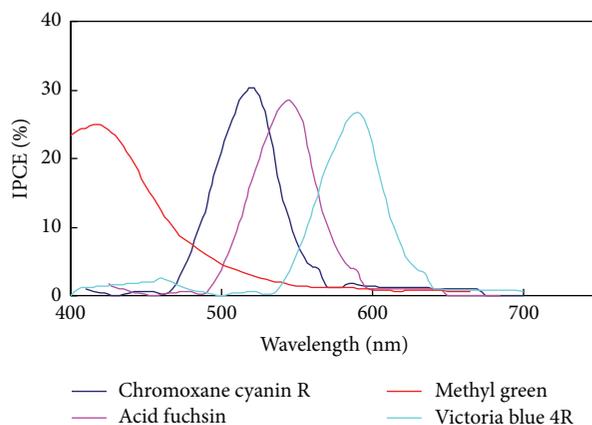


FIGURE 7: Photocurrent action spectra obtained with the use of triarylmethane based dyes as photosensitizers.

cyanin R at 520 nm. The short-circuit current, efficiency, and IPCE maximum value for methyl green and Victoria blue 4R are lower than those obtained in other triarylmethane based dyes, possibly due to poor anchorage of dye with TiO_2 surface. On the other hand, chromoxane cyanin R and acid fuchsin with anchoring groups, $-\text{COOH}$ and $-\text{SO}_3^-$, showing better efficiency and IPCE value. The photovoltaic parameters obtained by using these triarylmethane based dyes are shown in Table 3.

3.3. Azo Based Dye. Photovoltaic performances of the azo based dye (Orange G, Sudan III, Azophloxine, and Xylidine ponceau), sensitizing TiO_2 film electrodes, are listed in Table 4, and the corresponding photocurrent-voltage curves are shown in Figure 8. Azophloxine also shows better efficiency among this class of dyes. The decreasing trend of efficiency for these dyes is as follows: Azophloxine > Xylidine ponceau > Orange G > Sudan III. The short-circuit current and open-circuit voltage of Sudan III are lower than the others, which can be attributed to the poor injection efficiency

TABLE 2: DSSC performance parameters of fluorone based dyes.

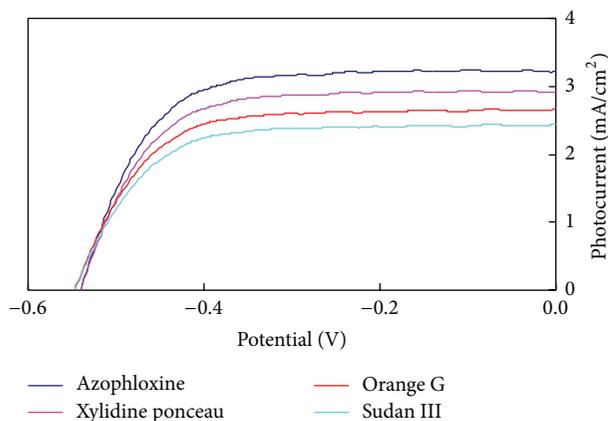
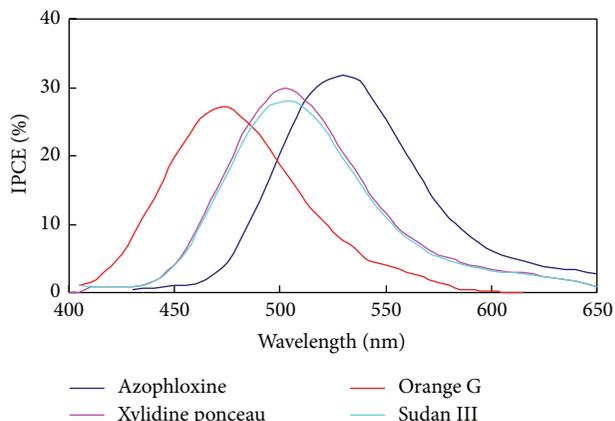
| Dyes | Fluorone based dyes | | | | |
|--------------|--------------------------------|--------------|------|------------|----------|
| | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | η (%) | IPCE (%) |
| Ethyl eosin | 3.35 | -0.546 | 0.68 | 1.25 | 33 |
| Erythrosin B | 3.23 | -0.554 | 0.63 | 1.10 | 31 |
| Eosinol | 2.92 | -0.566 | 0.63 | 1.03 | 28 |
| Phloxine B | 2.58 | -0.566 | 0.63 | 0.92 | 26 |

TABLE 3: DSSC performance parameters of triarylmethane based dyes.

| Dyes | Triarylmethane based dyes | | | | |
|---------------------|--------------------------------|--------------|------|------------|----------|
| | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | η (%) | IPCE (%) |
| Chromoxane cyanin R | 2.63 | -0.614 | 0.68 | 1.09 | 30 |
| Acid fuchsin | 2.42 | -0.614 | 0.67 | 1.00 | 28 |
| Methyl green | 2.31 | -0.626 | 0.62 | 0.88 | 25 |
| Victoria blue 4R | 2.16 | -0.626 | 0.61 | 0.82 | 27 |

TABLE 4: DSSC performance parameters of azo based dyes.

| Dyes | Azo based dyes | | | | |
|------------------|--------------------------------|--------------|------|------------|----------|
| | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | η (%) | IPCE (%) |
| Azophloxine | 3.23 | -0.546 | 0.68 | 1.19 | 32 |
| Xylidine ponceau | 2.92 | -0.546 | 0.67 | 1.07 | 30 |
| Orange G | 2.65 | -0.544 | 0.69 | 0.98 | 27 |
| Sudan III | 2.42 | -0.544 | 0.68 | 0.90 | 28 |

FIGURE 8: Photocurrent-voltage characteristics of TiO₂ electrodes sensitized with azo based dyes under illumination with 100 mW/cm² light intensity.FIGURE 9: The action spectra (IPCE- λ) of nanocrystalline TiO₂ thin film electrodes sensitized by azo based dyes.

of the dyes. This may be the result of the small energy gap between electrolyte and dyes.

The action spectra obtained by using azo based dyes (Figure 9) show resemblance with the absorption spectra for these dyes, thereby confirming the sensitization of photocurrent by these dyes. The maximum IPCE obtained with Azophloxine (32%) and the lowest IPCE value obtained among these azo based dyes is for Orange G with 27%. The

onset wavelength of the IPCE for the Azo based dyes are 600 nm.

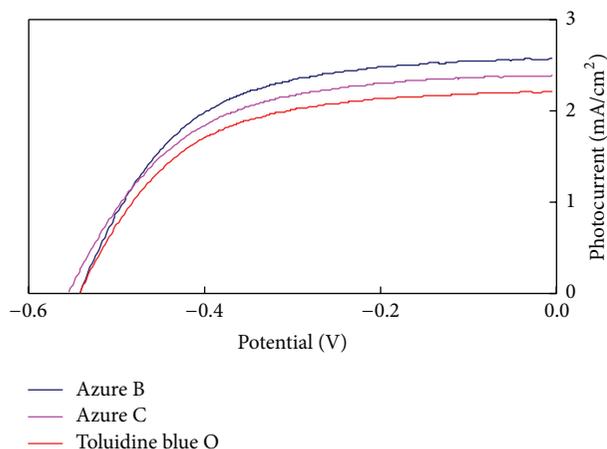
3.4. Thiazine Based Dyes. The thiazine based dyes (Azure C, Azure B, and Toluidine blue O) show their photosensitization activity by current-potential curve in Figure 10. The photocurrent obtained by using these dyes was in the range of 2.21 to 2.57 mA/cm² and the open-circuit potential was in the range of -0.538 V to -0.552. In thiazine based dye series,

TABLE 5: DSSC performance parameters of thiazine based dyes.

| Dyes | Thiazine based dyes | | | | |
|------------------|--------------------------------|--------------|------|------------|----------|
| | J_{sc} (mA/cm ²) | V_{oc} (V) | FF | η (%) | IPCE (%) |
| Azure B | 2.57 | -0.538 | 0.58 | 0.79 | 28 |
| Azure C | 2.39 | -0.552 | 0.56 | 0.73 | 25 |
| Toluidine blue O | 2.21 | -0.538 | 0.57 | 0.68 | 22 |

TABLE 6: Electrochemical parameters of fluorone and thiazine based dyes.

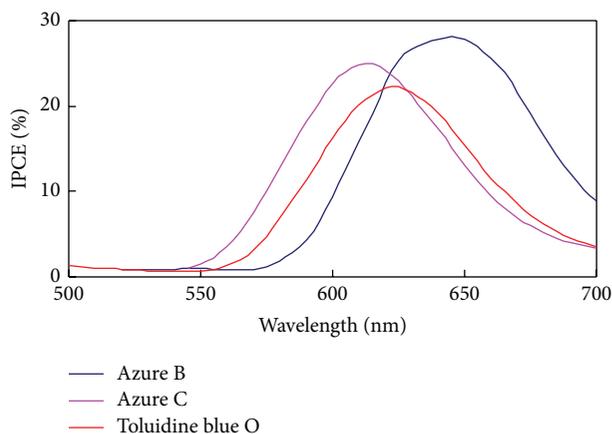
| | $E_{p,a}$ (V) | $E_{p,c}$ (V) | $\Delta E = E_{p,a} - E_{p,c}$ (V) | $E^{\circ} = (E_{p,a} + E_{p,c})/2$ (V) | $E \cdot S = E^{\circ} + h\nu$ (V) |
|------------------|---------------|---------------|------------------------------------|---|------------------------------------|
| Phloxine B | 0.190 | 0.090 | 0.100 | +0.140 | -2.12 |
| Ethyl eosin | 0.354 | 0.248 | 0.106 | +0.301 | -2.02 |
| Eosinol | 0.356 | 0.240 | 0.116 | +0.298 | -2.06 |
| Erythrosin B | 0.348 | 0.148 | 0.200 | +0.248 | -2.11 |
| Azure C | 0.596 | 0.322 | 0.274 | +0.459 | -1.55 |
| Azure B | 0.760 | 0.536 | 0.224 | +0.648 | -1.26 |
| Toluidine blue O | 0.802 | 0.526 | 0.276 | +0.664 | -1.31 |

FIGURE 10: Photocurrent-voltage characteristics of solar cells based on a TiO₂ thin film electrode sensitized by thiazine based dyes under illumination of 100 mW/cm² light intensity.

Azure B shows the maximum photocurrent (2.70 mA/cm²) and the maximum power conversion efficiency (0.79%). Toluidine blue O shows the lowest photocurrent and cell efficiency, having the values of 2.21 mA/cm² and 0.68%, respectively, in thiazine series.

The IPCE values exceed 28% for Azure B, 25% for Azure C, and 22% for Toluidine blue O at their characteristic absorption wavelengths (Figure 11). The corresponding open-circuit voltage (V_{oc}), short-circuits current density (J_{sc}), fill factor (FF), and power conversion efficiency (η) for thiazine based dyes are listed in Table 5. The lowest efficiency of this class of dye compared to other classes of dyes is due to the poor interaction of thiazine based dyes to the surface of TiO₂ because of the poor anchoring group present in thiazine based dyes.

The decreasing order of efficiencies of these classes of dyes is as follows: fluorone based > azo based > triarylmethane

FIGURE 11: Action spectra of TiO₂ electrode sensitized by different thiazine based dyes.

based > thiazine based dyes. Among these, the fluorone and azo based dyes show better photovoltaic performances due to better anchorage property to the surface of TiO₂, chemical stability, and wide visible spectrum.

There are some general principles for dyes to be efficient sensitizers.

- (1) The dye should be absorbed into the whole visible region (400–700 nm).
- (2) The dye used as photosensitizers should be fulfilling the reversibility criteria for long term application.
- (3) The LUMO level of the dye should be more negative and above the conduction band edge whereas the HOMO level of the dye should lie below the energy level of the redox mediator to allow efficient regeneration of the oxidized dye.
- (4) The dye should possess better anchoring group which favors strong adsorption onto the semiconductor surface.

- (5) It should not desorb into the electrolytic solution.
- (6) The dye should not aggregate onto the semiconductor electrode.

The electrochemical studies of some fluorone and thiazine based dye are summarized in Table 6 for the comparison of better performance of fluorone based sensitizers and poor performance of thiazine based sensitizers. These dye are well absorbed in visible region but they are not following the reversibility criteria ($\Delta E = 60$ mV). In fluorone based dyes, this value is not more than 200 mV whereas, in thiazine based dyes, these values are more than 200 mV. Both groups show quasireversible process which is one of the main factors for the poor performance of these dyes compared to the ruthenium based dyes. In fluorone based dyes, the LUMO level is sufficiently more negative than in the thiazine based dyes leading to better electron injection properties from excited state of dyes to the conduction band of the TiO₂ [31]. Another important factor for poor performances of thiazine and triarylmethane based dyes is lack of proper anchoring group for adsorption onto the surface of semiconductor electrode whereas, in fluorone and azo based dyes, $-\text{COOH}$ and $-\text{SO}_3\text{H}$ are the main anchoring group which facilitates the greater adsorption on the semiconductor electrode.

4. Conclusion

Comparative behavior of these fluorone, triarylmethane, azo, and thiazine based commercial dyes has been shown in this paper, which is essential for the further studies of chromophoric group behavior as photosensitizers. With the use of these commercial dyes, the spectral response of wide band gap TiO₂ electrode can be extended well into the visible region (up to 700 nm wavelength).

Action spectra with these dyes adsorbed on TiO₂ electrode provide clear evidence for its sensitization effect as photosensitizers. Amongst all the series of the organic dyes used, the best performance was shown by fluorone based dye (ethyl eosin), having photocurrent of 3.35 mA/cm² and power conversion efficiency of about 1.25%. The Azo based dyes also show better performance with cell efficiency of about 1.19% (Azophloxine). This is probably due to better interaction between the sulfonic (SO_3^-) groups of Azophloxine and carboxylate group (COO^-) of the ethyl eosin to the TiO₂ surface. These dyes have properties such as better anchorage to the TiO₂ surface, short adsorption time, chemical stability, and wide visible spectrum which makes them promising candidates for use as sensitizer in dye-sensitized solar cell. Although, they show low photovoltaic performance in comparison to inorganic dye based DSSCs, still owing to their easy fabrication technique and low cost, these organic dyes provide a potential method for the development of efficiently low-cost DSSCs.

Conflict of Interests

The authors declare no competing financial interests.

Acknowledgments

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References

- [1] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films," *Nature*, vol. 353, no. 6346, pp. 737–740, 1991.
- [2] Z. Wang, F. Li, and C. Huang, "Highly efficient sensitization of nanocrystalline TiO₂ films with styryl benzothiazolium propylsulfonate," *Chemical Communications*, no. 20, pp. 2063–2064, 2000.
- [3] K. Sayama, K. Hara, N. Mori et al., "Photosensitization of a porous TiO₂ electrode with merocyanine dyes containing a carboxyl group and a long alkyl chain," *Chemical Communications*, no. 13, pp. 1173–1174, 2000.
- [4] M. K. Nazeeruddin, P. Péchy, T. Renouard et al., "Engineering of efficient panchromatic sensitizers for nanocrystalline TiO₂-based solar cells," *Journal of the American Chemical Society*, vol. 123, no. 8, pp. 1613–1624, 2001.
- [5] A. Ehret, L. Stuhl, and M. T. Spitler, "Spectral sensitization of TiO₂ nanocrystalline electrodes with aggregated cyanine dyes," *Journal of Physical Chemistry B*, vol. 105, no. 41, pp. 9960–9965, 2001.
- [6] K. Hara, T. Sato, R. Katoh et al., "Molecular design of coumarin dyes for efficient dye-sensitized solar cells," *Journal of Physical Chemistry B*, vol. 107, no. 2, pp. 597–606, 2003.
- [7] T. Horiuchi, H. Miura, K. Sumioka, and S. Uchida, "High efficiency of dye-sensitized solar cells based on metal-free indoline dyes," *Journal of the American Chemical Society*, vol. 126, no. 39, pp. 12218–12219, 2004.
- [8] M. K. Nazeeruddin, F. De Angelis, S. Fantacci et al., "Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers," *Journal of the American Chemical Society*, vol. 127, no. 48, pp. 16835–16847, 2005.
- [9] M. Velusamy, K. R. J. Thomas, J. T. Lin, Y. Hsu, and K. Ho, "Organic dyes incorporating low-band-gap chromophores for dye-sensitized solar cells," *Organic Letters*, vol. 7, no. 10, pp. 1899–1902, 2005.
- [10] K. Hara, T. Sato, R. Katoh et al., "Novel conjugated organic dyes for efficient dye-sensitized solar cells," *Advanced Functional Materials*, vol. 15, no. 2, pp. 246–252, 2005.
- [11] S. Kim, J. K. Lee, S. O. Kang et al., "Molecular engineering of organic sensitizers for solar cell applications," *Journal of the American Chemical Society*, vol. 128, no. 51, pp. 16701–16707, 2006.
- [12] X. Liu, Y. Luo, H. Li et al., "Room temperature fabrication of porous ZnO photoelectrodes for flexible dye-sensitized solar cells," *Chemical Communications*, no. 27, pp. 2847–2849, 2007.
- [13] M. Tsai, Y. Hsu, J. T. Lin, H. Chen, and C. Hsu, "Organic dyes containing 1*H*-phenanthro[9,10-*d*]imidazole conjugation for solar cells," *Journal of Physical Chemistry C*, vol. 111, no. 50, pp. 18785–18793, 2007.
- [14] M. Liang, W. Xu, F. Cai et al., "New triphenylamine-based organic dyes for efficient dye-sensitized solar cells," *The Journal of Physical Chemistry C*, vol. 111, no. 11, pp. 4465–4472, 2007.

- [15] K. R. J. Thomas, Y. Hsu, J. T. Lin et al., "2,3-disubstituted thiophene-based organic dyes for solar cells," *Chemistry of Materials*, vol. 20, no. 5, pp. 1830–1840, 2008.
- [16] A. Hagfeldt and M. Grätzel, "Light-induced redox reactions in nanocrystalline systems," *Chemical Reviews*, vol. 95, pp. 49–68, 1995.
- [17] H. O. Finklea, *Semiconductor Electrodes*, Elsevier, Amsterdam, The Netherlands, 1988.
- [18] P. V. Kamat, "Photochemistry on nonreactive and reactive (semiconductor) surfaces," *Chemical Reviews*, vol. 93, no. 1, pp. 267–300, 1993.
- [19] A. Mills and S. Le Hunte, "An overview of semiconductor photocatalysis," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 108, no. 1, pp. 1–35, 1997.
- [20] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara, and H. Arakawa, "Highly efficient photon-to-electron conversion with mercurochrome-sensitized nanoporous oxide semiconductor solar cells," *Solar Energy Materials and Solar Cells*, vol. 64, no. 2, pp. 115–134, 2000.
- [21] K. Hauffe and U. Bode, "Photosensitization of the charge transfer across ZnO interfaces by binary dye mixtures," *Faraday Discussions of the Chemical Society*, vol. 58, pp. 281–291, 1974.
- [22] M. Nakao, K. Itoh, and K. Honda, "Optimization of the donor density of a semiconductor electrode for enhancement of the quantum yield of the dye-sensitized photocurrent," *The Journal of Physical Chemistry*, vol. 88, no. 21, pp. 4906–4907, 1984.
- [23] R. Kay, R. Humphry-Baker, and M. Grätzel, "Artificial photosynthesis. 2. Investigations on the mechanism of photosensitization of nanocrystalline TiO₂ solar cells by chlorophyll derivatives," *The Journal of Physical Chemistry A*, vol. 98, pp. 952–959, 1994.
- [24] L. Bahadur and J. P. Pandey, "Photoelectrochemical studies of sprayed thin film n-ZnO/acetonitrile based photocell sensitized by rhodamine B," *Indian Journal of Chemical Technology*, vol. 1, pp. 53–59, 1994.
- [25] J. Ohlsson, H. Wolpher, A. Hagfeldt, and H. Grennberg, "New dyes for solar cells based on nanostructured semiconducting metal oxides. Synthesis and characterisation of ruthenium(II) complexes with thiol-substituted ligands," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 148, no. 1–3, pp. 41–48, 2002.
- [26] M. Grätzel, "Highly efficient nanocrystalline photovoltaic devices—charge transfer sensitizers based on ruthenium and osmium achieve outstanding performance," *Platinum Metals Review*, vol. 38, no. 4, pp. 151–159, 1994.
- [27] L. Bahadur and L. Roy, "Characterization of [Fe(o-phen)₃][Ni(CS₃)₂] as a photosensitizer for wide-band gap semiconductor (ZnO) electrodes in acetonitrile media," *Journal of Photochemistry and Photobiology, A: Chemistry*, vol. 92, no. 3, pp. 207–212, 1995.
- [28] M. K. Nazeeruddin and M. Grätzel, "Separation of linkage isomers of trithiocyanato (4,4',4''-tricarboxy-2,2',6,2''-terpyridine)ruthenium(II) by pH-titration method and their application in nanocrystalline TiO₂-based solar cells," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 145, no. 1–2, pp. 79–86, 2001.
- [29] C. G. Garcia, A. K. Nakano, C. J. Kleverlaan, and N. Y. Murakami Iha, "Electron injection versus charge recombination in photoelectrochemical solar cells using *cis*-[(dcbH₂)₂Ru(CNpy)(H₂O)Cl₂] as a nanocrystalline TiO₂ sensitizer," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 151, no. 1–3, pp. 165–170, 2002.
- [30] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson, "Dye-sensitized solar cells," *Chemical Reviews*, vol. 110, no. 11, pp. 6595–6663, 2010.
- [31] A. Kumar, R. Chauhan, K. C. Molloy, G. Kociok-Köhn, L. Bahadur, and N. Singh, "Synthesis, structure and light-harvesting properties of some new transition-metal dithiocarbamates involving ferrocene," *Chemistry: A European Journal*, vol. 16, no. 14, pp. 4307–4314, 2010.



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