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Effect of Solvents on Mixture of Azur B and Sudan Black B Photosensitizer in Fabrication of DSSC

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Abstract: *The photoelectrodes of thin film of dye sensitized solar cells (DSSC) are generally fabricated from TiO₂ nanoparticles paste, above which dye is adsorbed. The aim of this paper is to study the influence of mixing different photosensitizer in different solvents on cell performance. To this end, identical method and materials except the photosensitizer will be used. Three sets of organic dyes (photosensitizer) with different solvent are prepared; Sudan Black B and Azur B are firstly examined and obtained results compared with the results of mixture of same dyes in distilled water, ethanol and dimethyl sulphoxide (DMSO) solvents. The effects of photosensitizer are studied because they play a major and foremost role in working of DSSC. Fully operating DSSC thus manufactured using mixture of organic dyes as sensitizer, an electrolyte and a counter electrode. Their photo-energy conversion efficiency has been measured in environmental conditions. High efficiencies for mixture of dyes are obtained when compared to results of their individual dyes, thus, showing the influence of mixture of dyes. Although the mixture of many other dyes not necessarily will increase the cell performance, sometimes other parameters of DSSC may affect the performance of cell.*

Keyword: *Dye sensitized solar cell, TiO₂ nanocrystal semiconductor, organic dyes.*

I. INTRODUCTION

Dye sensitized solar cell is an electrochemical cell belonging to thin layer film technology[1] and is simply based on principle of photosynthesis where dye acts as a photosensitizer, which harvests the sunlight and transfers solar energy into electrical energy[2]. The Dye sensitized solar cell has currently emerged as new dynamic research field for solar cells. It has opened up new dimensions for solar cell technology.

Research is going on to develop efficient DSSC to compete the conventional silicon based solar cells. From last few years great progress has been made on various aspects including efficiency, stability and commercialization. These developments can lead the basis for globalization of DSSCs. Also DSSC due to its attractive features like low cost, ease of production, transparency and good performance under typical conditions (temperature and illumination conditions) is proving itself better than Si- based cells, irrespective of its low efficiencies.

This technique was first developed by M. Grätzel and co-workers in 1991 thus also called as Grätzel cell[3]. Due to its good efficiency and easy manufacturing technique DSSC's have attracted considerable attention in research field. Since then work on synthesis of numerous organic dyes and using those as photosensitizer have been reported, from which metal contain organic dyes have shown far better results.

The highest conversion efficiency of 18.1 % has been achieved till now by two-terminal DSSC/silicon tandem solar cells [4]. Recently several groups have developed metal free organic sensitizers to overcome the prohibitive cost of ruthenium metal complexes[5-9]. Wang et al. reported 10.3% efficiency for a metal-free organic sensitizer [10]. Indoline[11-13], triphenylamine [14,15], and carbazole [16-18] derivatives have proved promising results with efficiency close to that of Ru-dyes[19]. Some organic dyes like hemicyanine dyes[20], thienothiophene and thiophene based dyes[21], oligothiophene dyes [22,23], and coumarine-based dyes [24,25] have shown impressive photovoltaic performance.

DSSC consists of photosensitized anode (a dye and a paste of nanocrystalline TiO₂ powder coated on Fluorine doped SnO₂ glass plate), an electrolyte solution and a counter electrode.

These components are arranged in sandwich like structure, as shown in Fig. 1. The transparent FTO glass plate is coated by paste of nanocrystalline TiO₂ particles (average size of 5-25nm) above which dye molecules are adsorbed. The counter electrode is coated by a catalyst (platinum) to speed up the redox reaction with electrolyte. Between TiO₂ electrode and counter electrode, a liquid electrolyte is encapsulated.

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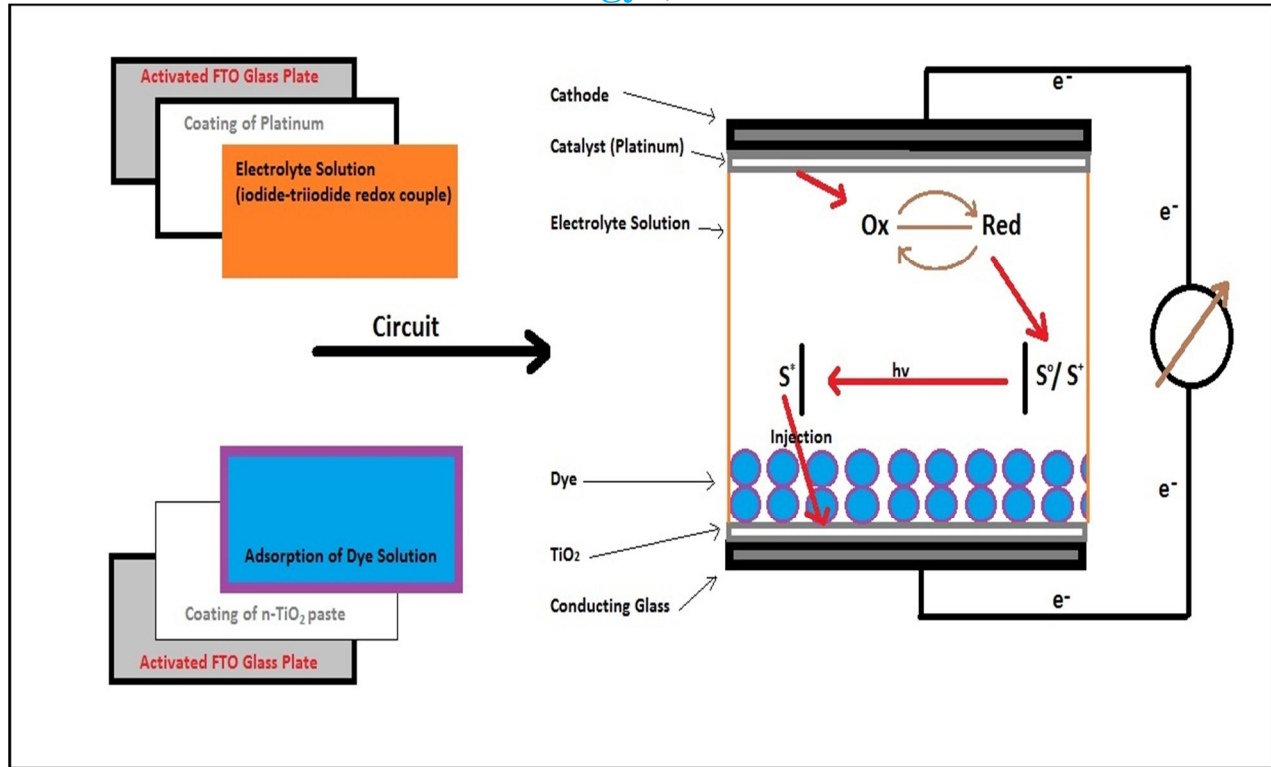


Fig.1. Working scheme of a typical dye sensitized solar-cell.

Although, metallic dyes provided higher conversion efficiency, there are many disadvantages like high cost, limited resources and long term unavailability. In contrast, organic dyes are cheaper and efficiency up to 9% has been reported [26]. In this paper mixture of two organic dyes are used and their cell performance are investigated in different solvents.

Working: When cell is placed under sunlight the molecules are then excited from ground state to excited state by absorption of photons, due to which electrons are transferred into conduction band of semiconductor layer. Then these excited electrons flow towards the transparent (FTO) electrode via TiO_2 , where they are collected for powering load. Afterwards these electrons arrive at the counter electrode and reintroduced in cell by flowing into electrolyte (recombined with tri-iodide and iodide agent again). The electrolyte transports the electrons back to the dye molecules. This process leads to the conversion of sunlight to electrical energy.

II. EXPERIMENTAL

A. Materials

All chemicals have been used as received unless stated for that. Nanocrystalline TiO_2 [P-25, Anatase (Aldrich)], H_2PtCl_6 (Aldrich), Nitric acid (55%), Ethanol (Absolute), Iodine (99.9%, Aldrich), KI (ASES Chemicals), Triton-X100 (Aldrich), Azur B and Sudan Black B (Loba Chemie) as photosensitizer, Conducting glass plate (FTO, Aldrich) (sheet resistance 11-13 Ω/sq) as substrate for fabricating TiO_2 mesoporous films, Distilled water, Dimethyl Sulphoxide and Glacial acetic acid (99%, Fischer Scientific), Ethylene Glycol (ASES Chemicals).

B. Preparation of materials

There are several kinds of materials needed to be prepared, i.e. TiO_2 suspension, electrolyte solution, counter electrode etc. **FTO electrical resistance:** The sheet Resistance of the FTO glass received $R_s = (11.05 + 0.24) \Omega/\text{sq}$, when washed with ethanol and sonicated for 30 minutes, it changed to $R_s = (13.57 + 0.04) \Omega/\text{sq}$, showing increase in sheet resistance. **Preparation of TiO_2 suspension:** 3gm of TiO_2 measured and dissolved in 4.5ml of glacial acetic acid, where glacial acetic acid acts as a binder. This solution then stirred for 30 minutes. For maintaining pH 3-4, dil. HNO_3 was added and stirred for next 12 hours at room temperature. Then 2-3 drops of surfactant (Triton-X100) was added in paste to break the nanoparticles clot, and is kept for overnight on magnetic stirrer. **Preparation of electrolyte solution:** 0.127 gm of 0.05M of iodine (I_2) and 0.823 gm of 0.5M Potassium iodide

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(KI) dissolved in ethylene Glycol, and mixture was stirred and stored in dark bottle. *Preparation Of counter electrode:* The counter electrode was platinized by H_2PtCl_6 solution prepared in 0.01M ethanol on FTO glass. This glass plate then calcined in hot air oven at $380^\circ - 400^\circ C$ for 30 minutes. *Preparation of dye solution:* 0.1M solution of Azur B and Sudan Black B were mixed and prepared in 50ml of distilled water, ethanol and DMSO. Afterwards the individual 0.1M dye solution of Azur B in DMSO, and 0.1M of Sudan Black B in DMSO was prepared.

C. DSSC assembly

The edges of transparent activated FTO glass plate were covered with 50 μm thick adhesive tape, leaving $1 \times 1 cm^2$ areas. A drop of TiO_2 paste was poured on one edge and film prepared by sliding it with glass rod as in Doctor- Blade technique. The spreaded layer was dried first at room temperature for 30 minutes then calcined at $500^\circ C$ for 1 hour. The morphology and thickness of the mesoporous TiO_2 layer was characterized by scanning electron microscopy (SEM). Later, these plates were made adsorbed by dye solution by placing the TiO_2 film upwards in a petridish and pouring dye solution in it ensuring the full coverage of TiO_2 layer. This was kept overnight (24 hours) and washed with water to remove non-adsorbed dye. 2-3 drops iodide/tri-iodide (redox couple) electrolyte was introduced over photosensitized mesoporous TiO_2 film. This liquid electrolyte of I_2/KI is widely been used as a charge mediator. Finally the Pt-counter electrode was placed on the top of TiO_2 film. Fabricated cells were characterized by using digital multimeter. This method was repeated four more times with dye solution prepared in different solvent.

III. RESULTS AND DISCUSSIONS

A. SEM and XRD analysis

The surface morphology of $SnO_2:F$ photoelectrodes coated with TiO_2 nanocrystal film coated illustrated in figure (2), taken by SEM. It showed that the obtained photoelectrodes have typical porous structure for DSSC. The morphological study of the TiO_2 layer is important as it affects the efficiency of the solar cell. The optimum thickness and porosity enhances open circuit voltage. The electron transport rate, which highly depends on the crystallinity, morphology, and the surface area of semiconductors, affects the efficiency of DSSCs. The mesoporous structure of the TiO_2 layer was examined by scanning electron microscopy (SEM). Porosity is main feature of TiO_2 thin layer, which makes the adsorption of dye more effective, help in increasing efficiency of cell. Mesoporous structure of TiO_2 layer shows porous nature of the TiO_2 layer, which can be clearly seen from the SEM image. The mesoporous has high surface area which helps in greater dye loading thus increasing photo excited electron. Also porosity helps in scattering of the light within the layer. The x-ray diffraction instrument is used to collect the intensities of the scattered signals to get the diffraction pattern of the measured sample. This pattern is normally as the signal intensity versus the phase angle. When such a pattern is used in the crystal surface calibration process for the sample, the material's crystalline structure, such as the orientation and phase angles, can be obtained. From figure (3) data was taken for the 2θ range. XRD spectra of TiO_2 powder is shown in Figure 4.10. XRD patterns exhibited strong diffraction peaks at 25° and 48° indicating TiO_2 in the anatase phase.

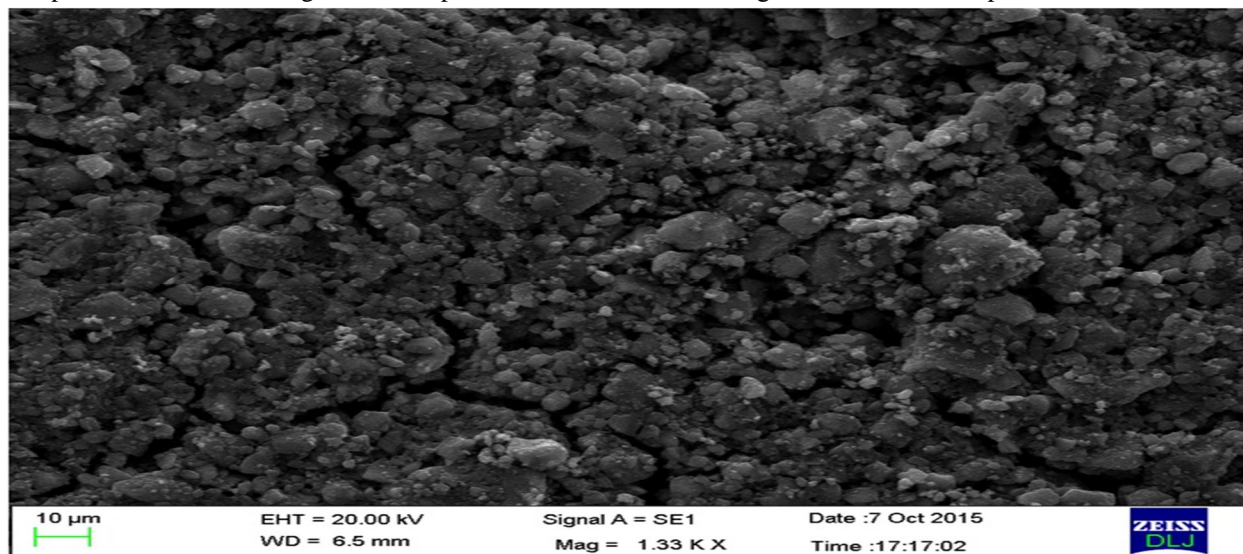


Fig.2. SEM image of TiO_2 layer coated on FTO glass slide

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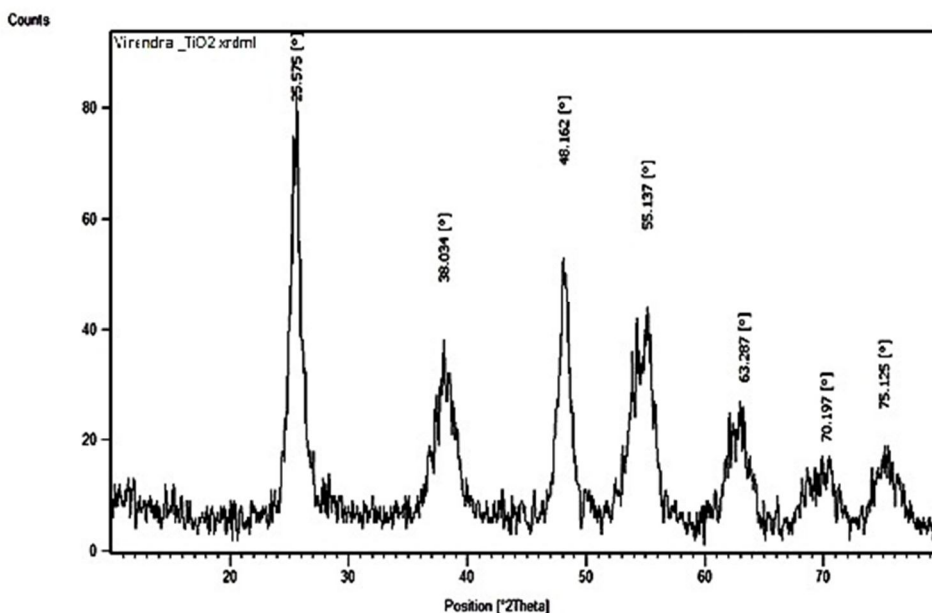


Fig.3. XRD analysis of the TiO₂ powder

B. UV visible absorption spectroscopy

The individual organic dyes (Azur B and Sudan Black B fig.4a and 4b) in DMSO and mixture of dyes in different solvents exhibited typical UV-visible absorption spectra as shown in figure 5. The absorption maxima of Azur B in DMSO locates at 640 nm and has absorption wavelength range from 190nm to 717nm, whereas Sudan Black B showed absorption maxima at 640 nm, wavelength range from 270nm to 800nm in DMSO as solvent. The mixture of both dyes in solvents; distilled water, ethanol, DMSO showed absorbance peak at 662nm, 653nm, and 640nm, with wavelength range of 500nm to 700nm, 200nm to 690nm and 256nm to 790nm respectively.

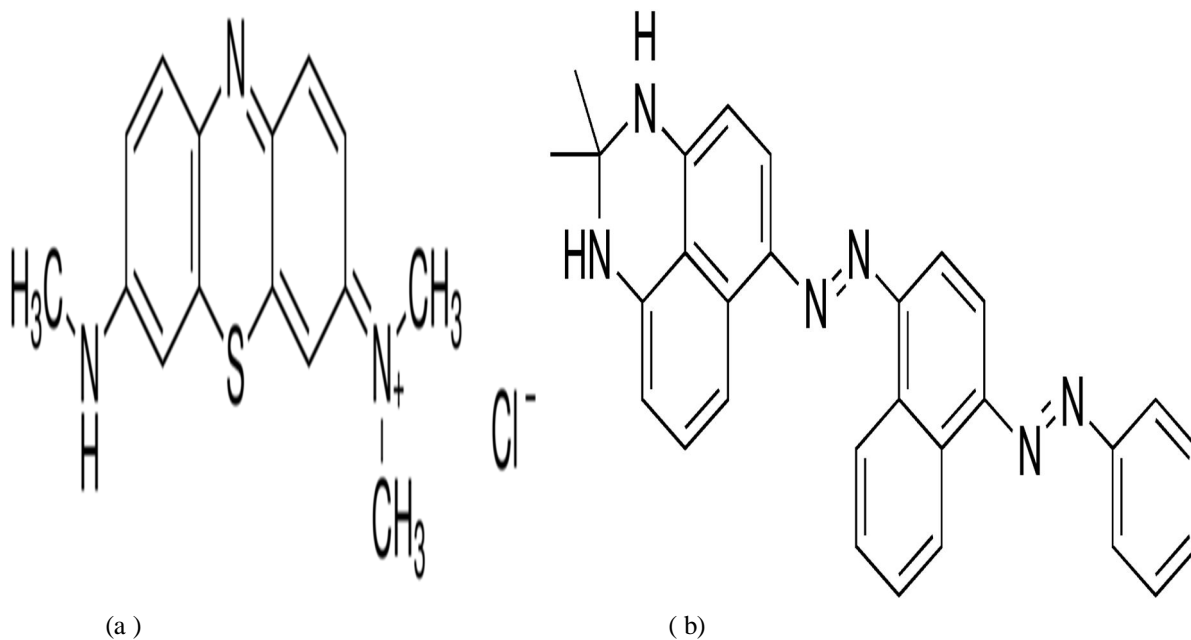
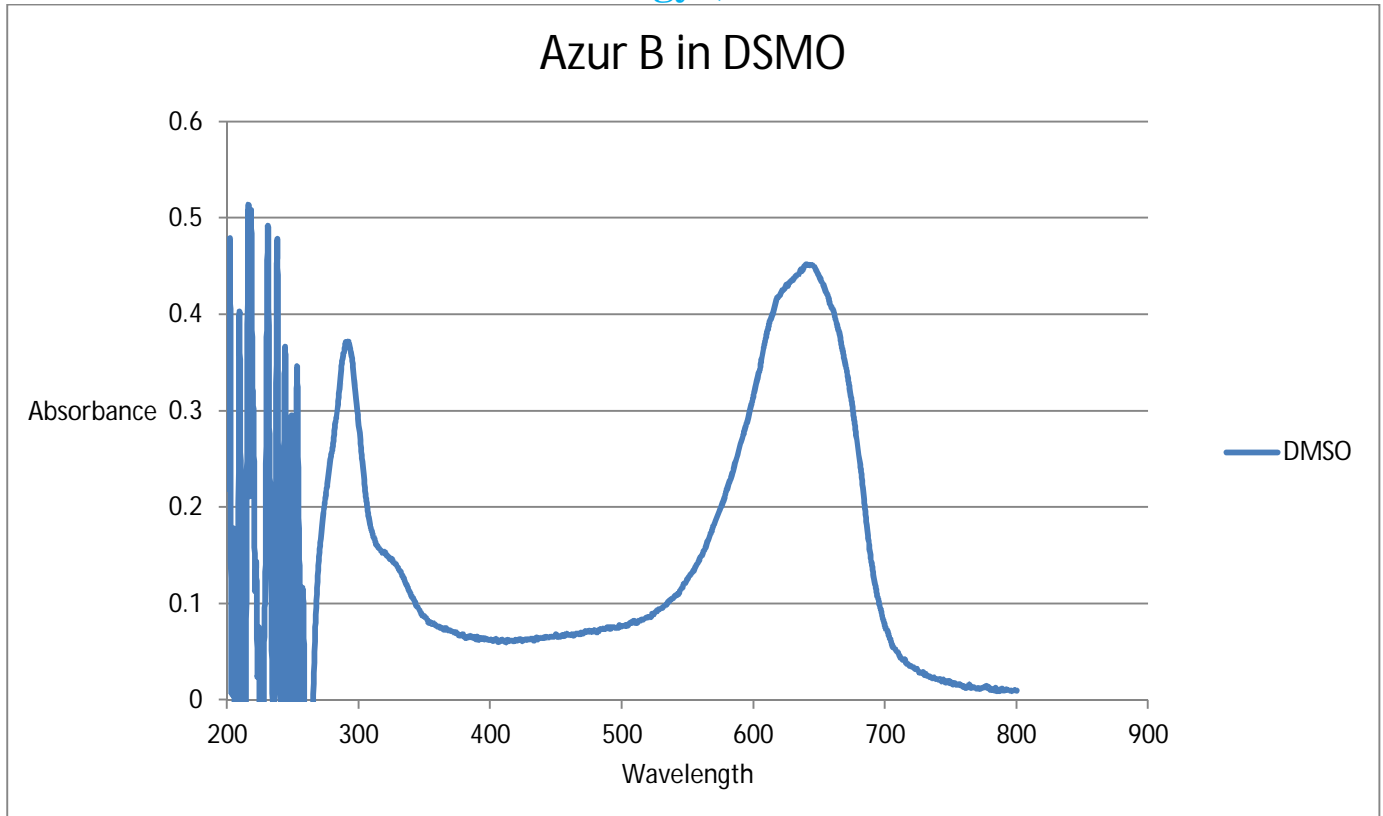
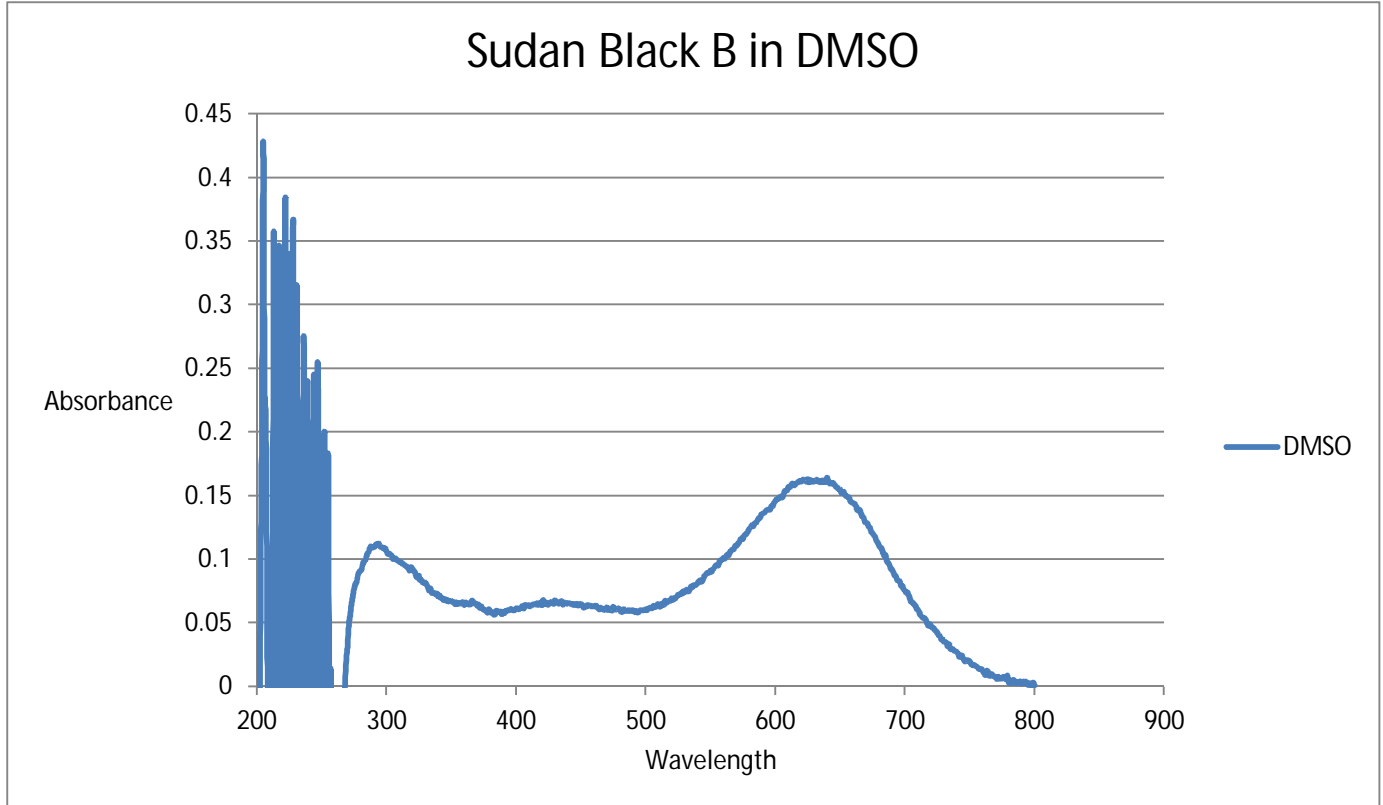


Fig.4. Structure of (a) Azur II and (b) Sudan Black B

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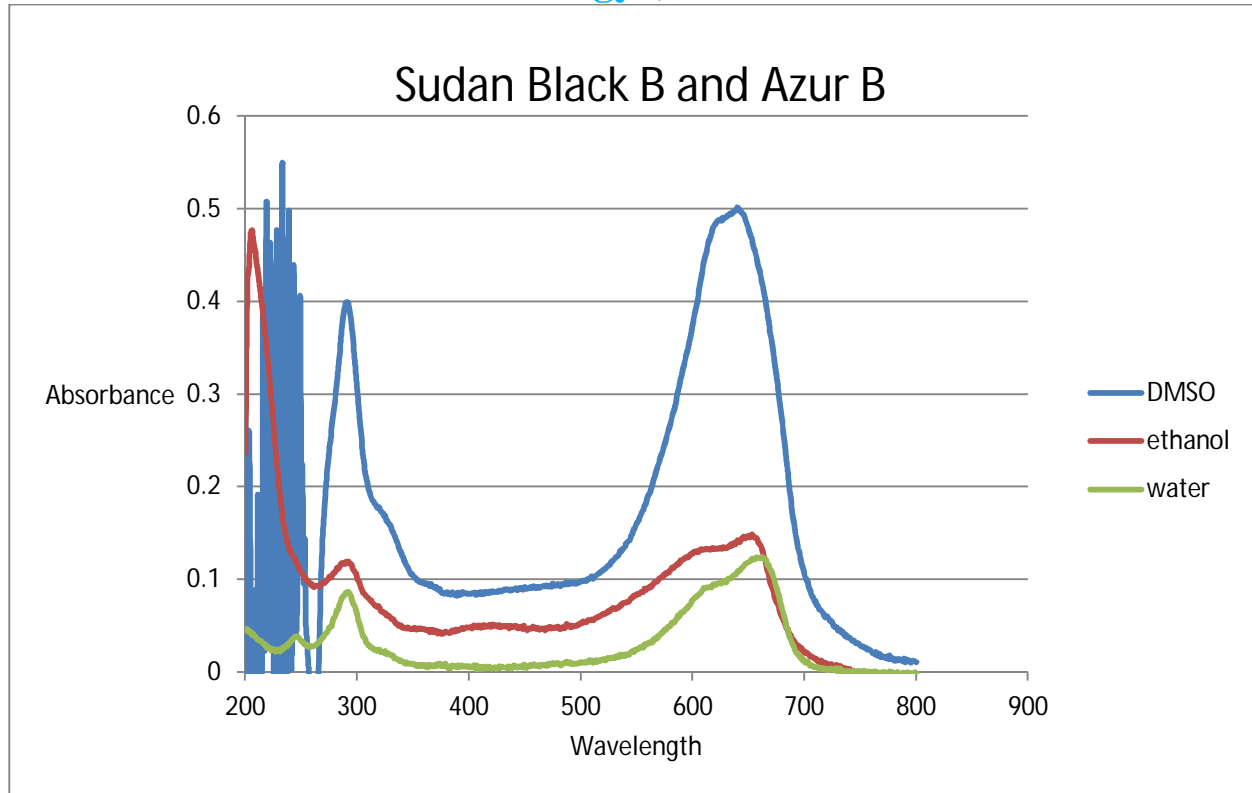


(a)



(b)

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(c)

Fig.5. (a) Absorption spectra of Azur B in DMSO. (b) Absorption spectra of Sudan Black B in DMSO. (c) Absorption spectra of mixture of Azur B and Sudan Black B in different solvents (viz. distilled water, ethanol, dimethyl sulphoxide)

C. Cell performance

Photocurrent and voltage measurements of DSSC's were carried out under direct solar radiation (at noon), working with similar light irradiation in all tests: 1000 W/m^2 ($\pm 5\%$ error tolerance). Figure 6 shows the I-V curves of solar cells fabricated with each one of the dye solutions in different solvents. The characteristics electrical parameters such as open-circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and efficiency (η) obtained are shown in Table 1. The values of short circuit current (J_{sc}) obtained by I-V curve for Sudan Black B in DMSO (fig. a), Azur B in DMSO (fig. b), Mixture of Azur B and Sudan Black B in DMSO (fig. c), Mixture of Azur B and Sudan Black B in Ethanol (fig. d), Mixture of Azur B and Sudan Black B in distilled water (fig. e), which are 0.467mA, 0.523 mA, 0.510 mA, 0.498 mA, 0.397 mA respectively and the values of open-circuit voltage (V_{oc}) are 0.550 V, 0.680 V, 0.780 V, 0.750 V, 0.450V respectively for different DSSC system as shown below in Table 1.

The cell performance was observed for all the cells in different solvents. The comparative performance and photoelectrochemical parameters are summarized in Table -1. Conversion efficiency of the device was determined by the following equation:

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \times 100\%$$

Where, η = conversion efficiency of the cell

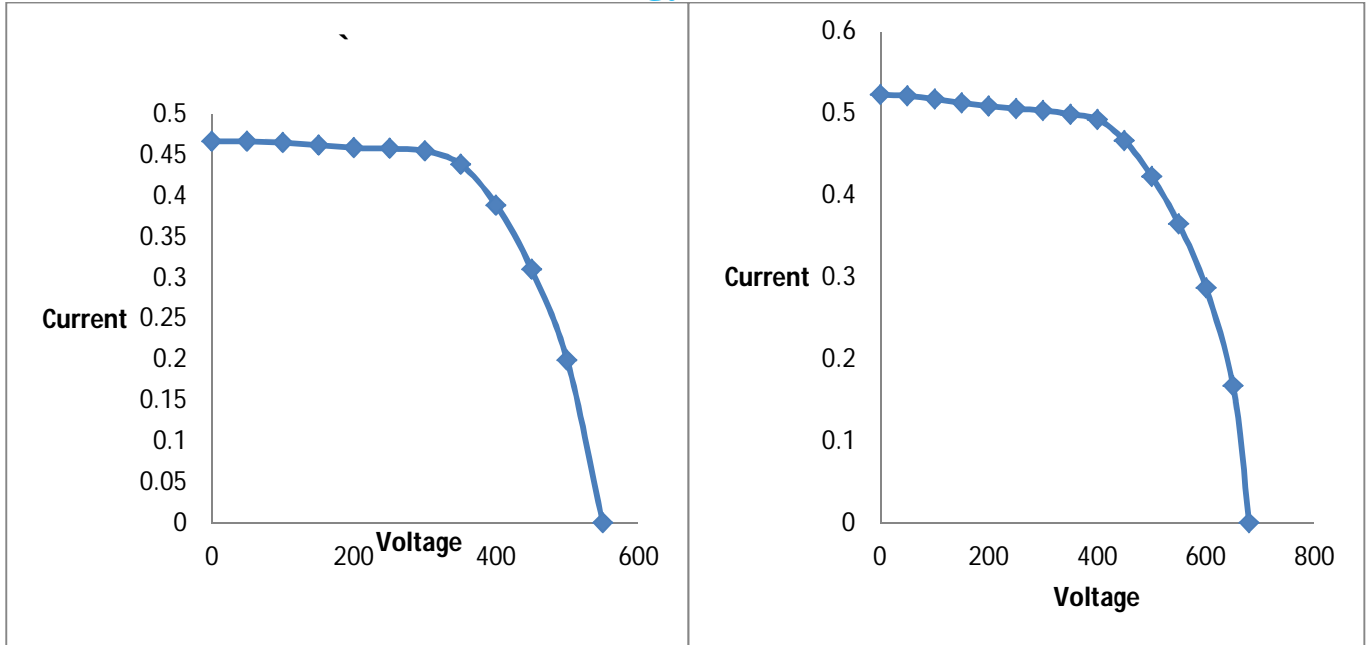
V_{oc} = open circuit voltage (highest voltage when current is zero)

I_{sc} = short circuit current (highest current when voltage is zero)

FF = Fill Factor

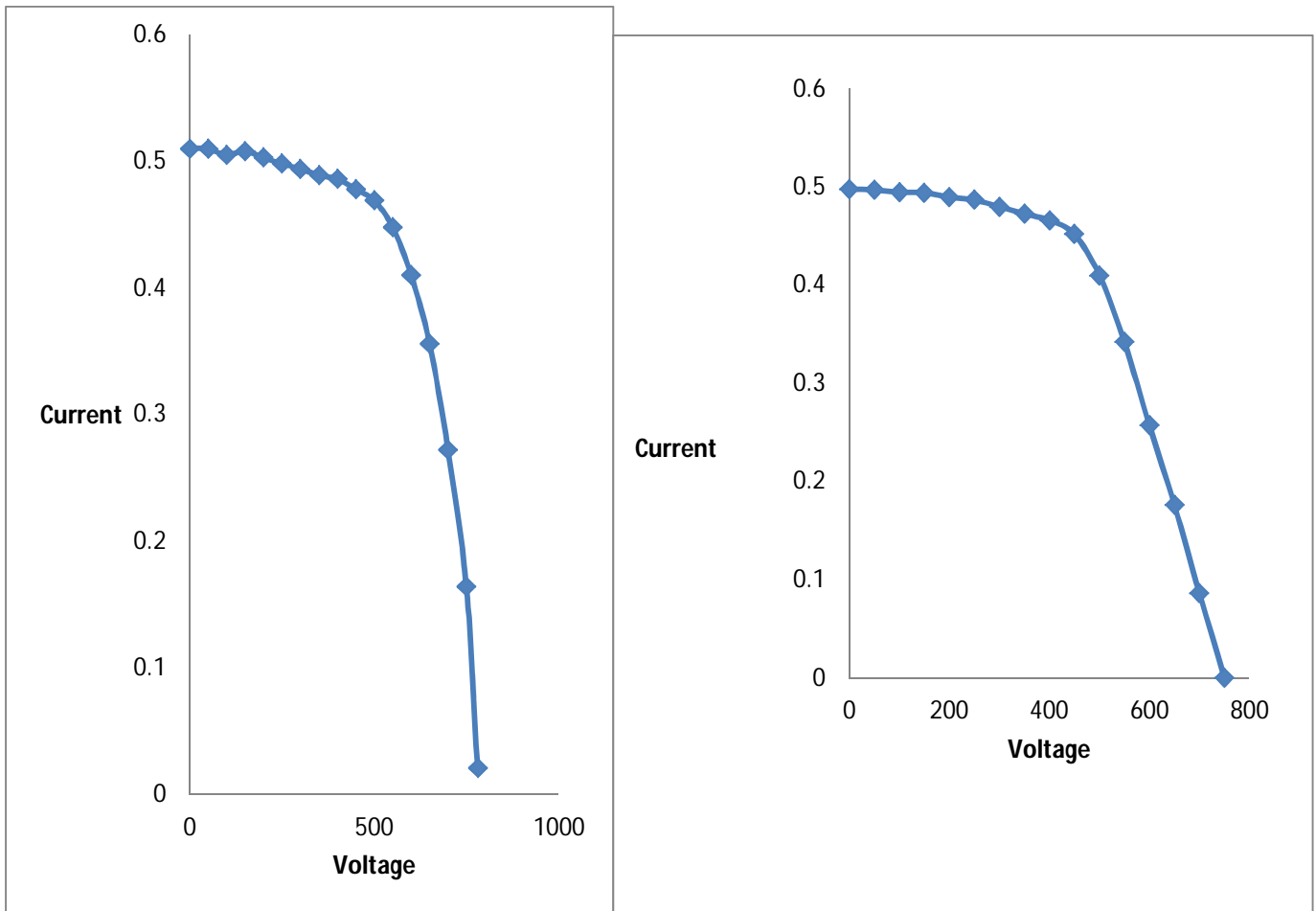
P_{in} = power input

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(a)

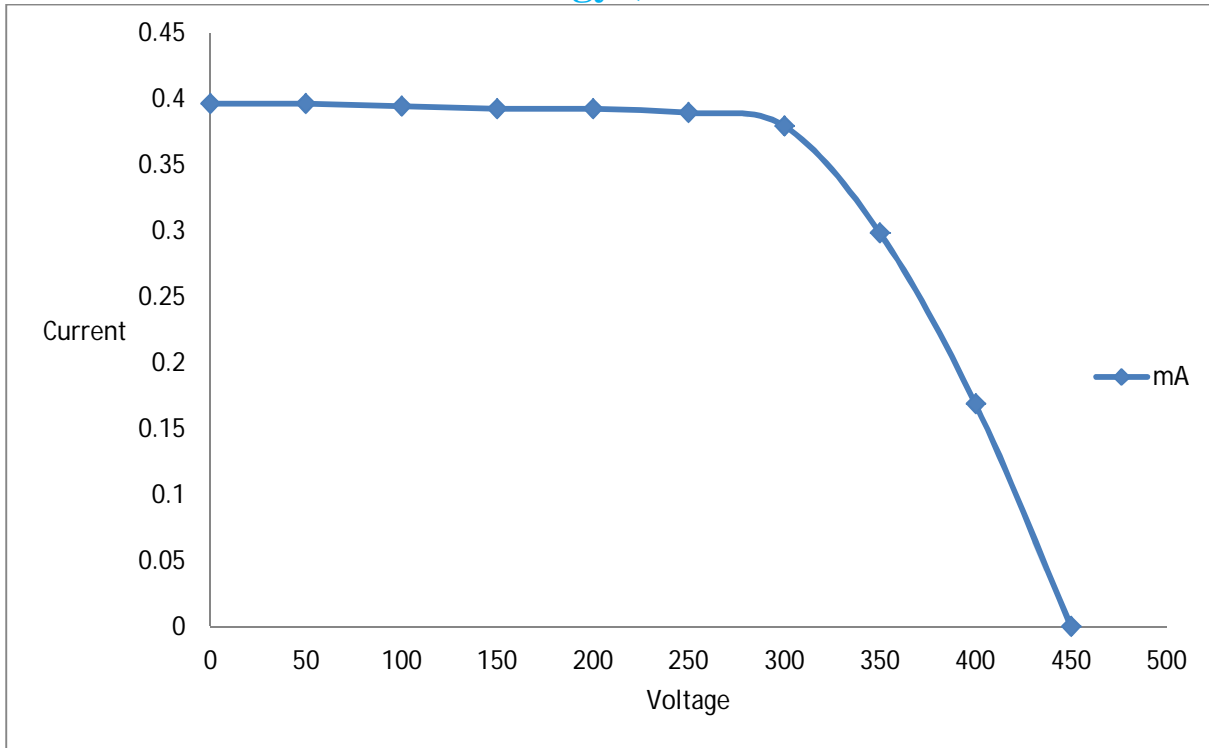
(b)



(c)

(d)

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(e)

Fig.6. Curve obtained between current (mA) and Voltage (mV) I-V curve for (a) Sudan Black B in DMSO. (b) Azur B in DMSO. (c) Mixture of Azur B and Sudan Black B in DMSO. (d) Mixture of Azur B and Sudan Black B in Ethanol. (e) Mixture of Azur B and Sudan Black B in distilled water.

S. No.	Name Of Dye	Solvent	V_{oc} (mV)	J_{sc} (mA)	FF	η (%)
1.	Sudan Black B	DMSO	550	0.467	0.59	0.15
2.	Azur B	DMSO	680	0.523	0.59	0.21
3.	Azur B + Sudan Black B	DMSO	780	0.510	0.61	0.24
4.	Azur B + Sudan Black B	Ethanol	750	0.498	0.54	0.20
5.	Azur B + Sudan Black B	Distilled water	450	0.397	0.63	0.11

Table 1. Observed values of open-circuit voltage (V_{oc}), short circuit current (J_{sc}), and calculated fill factor (FF) and efficiency (η) are shown in table given below.

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It can be clearly seen from Table 1, that an increased conversion efficiency of cell has been obtained when dyes were dissolved in a solvent which solubilizes them better. Since, Sudan Black B ($\eta = 0.15\%$) and Azur B is soluble in DMSO ($\eta = 0.21\%$), these results when compared with results of their mixture in different solvents (distilled water, ethanol and DMSO) of same concentration (0.1M) showed better and improved efficiency of 0.24% in DMSO, 20% in Ethanol, and 0.11% in distilled water.

IV. CONCLUSION

In conclusion when two different photosensitizer (organic dyes) with different solubility is mixed and dissolved in particular solvent owing to great absorbance, results in increased FF, J_{sc} , V_{oc} , of corresponding DSSC's which strengthen the conversion efficiency (η). Organic dye, Sudan Black B and Azur B show lower sensitization activity than that of mixture of both dyes because mixture of dyes show more adsorption of photon by sunlight or more intake of photon and hence efficiency reached at higher value. The higher conversion efficiency (η) was obtained for the system; 0.1M Azur B + 0.1M Sudan Black B (DMSO as solvent, $\eta = 0.24\%$), compared to those of system in distilled water ($\eta = 0.11\%$), and Ethanol ($\eta = 0.20\%$). The value η of mixture dissolved in distilled water is mainly dependent on Azur B while Sudan Black B (insoluble in water) suppresses the results, resulting in low conversion efficiency.

V. ACKNOWLEDGEMENTS

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