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Fabrication and Photovoltaic Characteristics of Alizarin Dye Based DSSCs

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ABSTRACT

Nano-TiO₂ layer was used as photoanode and redox electrolyte couple (I₃⁻/I⁻) of inorganic (KI) and organic R₄N⁺I⁻ (quaternary ammonium iodide salts) with iodine (I₂) were applied in acetonitrile solvent. Dye sensitized solar cells were fabricated with alizarin dye as sensitizer on FTO (fluorine-doped tin oxide) coated transparent fused silica substrate. The photovoltaic properties of DSSCs with alizarin dye investigated in expressions of short circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and efficiency (η) using J-V curve. The absorption spectrum of Alizarin dye showed peaks at 264 nm due to the π→π* transitions and 425 nm due to n→π* transition. The alizarin dye showed good thermal stability up to ~270°C temperature. The maximum efficiency was found excellent in DSSC with (CH₃CH₂CH₂)₄N⁺I₃⁻ redox couple electrolyte. The role of alizarin dye as sensitizer has been analyzed in fabricated DSSCs and obtained photovoltaic properties could be used as light harvesting material.

Keywords: DSSC, Alizarin dye, Alkyl quaternary ammonium iodide, Redox electrolyte.

INTRODUCTION

The energy consumption of the world increasing day by day due to enhanced in living standard of mankind's. The energy available from sun is 10000 times greater than the current demand of world's energy [1]. The energy available in form of solar radiation is nearly 3×10²⁴ J per year [2,3]. The massive needs of energy have enhanced the exhaustion of the fossil fuel and their combustion increases the atmospheric pollution by accumulative the concentration of greenhouse gases [3-5]. Due to these unpreventable worldwide challenges insist of growing more sustainable power sources, i.e. tidal power, solar thermal, hydropower and biomass and solar cell [6]. Solar cells or photovoltaic cells are one of the promising options of renewable energy source because these can produce energy near to end user, avoiding transmission losses and economical. The solar panels work without emissions of greenhouse gas, noise and toxicity which do not affect the environment. The major drawback of Si-based solar panel is high cost of fabrication and materials, which needs auxiliary of this technology [7]. An assortment of structures and materials were being sought after to supplant Si-based and other thin film innovations, in which the dye-sensitized solar cell (DSSC) created by Grätzel keeps on being one of the most effective "next generation" advances having good conversion efficiencies [8,9]. DSSC have the prospective to substitute the Si-based photovoltaic cells due to economical, easy construction and good proficiency [10,11]. The dye sensitizer solar cells consist of following components i.e., photoanode, sensitizer, counter-electrode and electrolyte solution with redox mediator. The photoanode is made-up of nano size metal oxides layer i.e., TiO₂, ZnO, NiO, SrTiO₃, SiO₂, SnO₂, Ga₂O₃, Nb₂O₅ and ZnO having thickness in few micrometers [12-15]. The sensitizer material is the main constituent of dye-sensitized solar cell due to its capability to harvests solar radiation and produce photo-excited electrons at the photoanode interface. The molar extinction coefficient of sensitizer should be high for radiation harvesting in near-infrared and visible region. Sensitizer should have excellent photo-stability, solubility and capability to adjoin with photoanode. With an intention for effective sensitizer many conventional materials, metal-complexes of transition and rare earth metals [16-18] and synthetics dyes [19-23] have been investigated for sensitization of extensive band gap of photoelectrodes. The redox electrolyte iodide-triiodide (I₃⁻/I⁻) has been accepted as most common redox couple due to its excellent rate of electron transfer i.e. rapid oxidation of I⁻ at interface of photoanode and electrolyte for the regeneration of dye molecule, slow reduction of I₃⁻ at interface of electrolyte and counter electrode for carrier collection. The redox electrolyte iodide-triiodide (I₃⁻/I⁻) also have easy preparation, economical, high stability and good solubility in various solvents [24]. Another important component of DSSC is counter electrode, it collecting electrons generally made up of platinum and graphite [25]. Platinum have higher electro-catalytic activity as compare to graphite but graphite is more common due to economic cost and excellent stability.

In this research article, the fabrication and investigation of DSSCs using alizarin dye as photosensitizer for the photoelectrochemical, electronic, optical and thermal characteristics. The proficiency of fabricated DSSCs is also studied with various redox electrolytic couples i.e. KI, alkyl quaternary ammonium iodides with I₂ in CH₃CN solvent.

EXPERIMENTAL

Material

The transparent conducting glass purchase from Sigma-Aldrich have layer of FTO with resistance 6-8 Ω/square. For the preparation of photoanode conventional available nano titania P25 powder (Sigma-Aldrich) have 20% rutile and 80% anatase form of TiO₂ with ~21 nm size was used. Alizarin was used as sensitizers in fabrication of DSSCs. The CH₃CN was used as solvent for redox electrolytic couple; analytic reagent grade potassium iodide (KI), iodine (I₂), tetramethylquaternaryammonium iodide [(CH₃)₄NI], tetraethylquaternaryammonium iodide [(CH₃CH₂)₄NI], tetrapropylquaternaryammonium iodide [(CH₃CH₂CH₂)₄NI] taken from Sigma-Aldrich and used as it is without purification.

Device fabrication

Cleaning and masking of the transparent conducting substrate

The cedepol i.e. neutral soap solution was used to clean the FTO coated transparent conducting substrates of adequate size. The substrates were sonicated for 15 min in neutral soap solution, and then rinsed several times with distilled water. Further reagent grade acetone was used for cleaning of substrate and sonicated for 15 min. The substrates were boiled in propan-2-ol solvent to remove the organic impurities and finally dried in oven at 80°C. Some portion of the substrates surface was cover to deposit the thin film of nano TiO₂ on desire place. Transparent adhesive elastic tape was utilized to shield the conducting glass in such a manner that a small strip of etched portion was concealed.

Preparation of TiO₂ layer

1 g powder of commercial nano-TiO₂ powder mixed with glacial acetic acid was place in pestle and mortar and further addition of glacial acetic acids in small increments. After grinding with pestle even and swelling free titanium dioxide paste was obtained. The TiO₂ paste was sonicated for 30 min in a small vial. The prepared titanium dioxide paste was spurted onto unmasked conducting glass substrate using doctor blade technique. After evaporation of acetic acid, adhesive tape was removed and then sintered at 300°C for 2 h.

Instrumentation and characterization

Shimadzu 2450 spectrophotometer with 180-1100 nm range was used for UV-Vis absorption spectra of the alizarin dyes. The STA-7300 thermal analyzer of Hitachi was used to record TGA and DTA. The substance heated with rate 10°C/min in inert atmosphere of N₂ gas. The material was heated in range 35°C to 500°C to obtain TGA and DTA. A digital Keithley 2450 Source meter with KICK START software was used to record the current density-voltage (*J-V*) curves. A 200 w tungsten (W) arc lamp was used for simulation light radiation in DSSCs.

RESULTS AND DISCUSSION

UV-Vis absorption spectrum of alizarin dye

0.1 M solution of Alizarin dye was prepared by dissolving in water. TiO₂ layer substrate was immersed in solution of dye solution for 24 h. The dye absorb on TiO₂ layer was good as represented in Figure 1.



Figure 1: Aqueous solution of Alizarin dye on watch glass and dye absorption on TiO₂ layer coated substrate

The absorption spectrum of Alizarin dye was taken in aqueous medium as represented in Figure 2. The absorption spectrum of Alizarin dye shows two main bands, one at 264 nm due to the $\pi \rightarrow \pi^*$ transitions of the phenyl moiety and another at 425 nm involves $n \rightarrow \pi^*$ transition which can be allotted to the non-bonding orbital of a lone pair on oxygen atoms in the anthraquinone groups in the dye molecule. The wavelength and intensity of absorption peaks usually reveal the transition energy and the transition dipole moment in transition from the ground state to the singlet-excited states of the molecules. A good sensitizer should have wide range to absorb the radiation from near infrared to visible region. The energy of sensitizer excited state should be relevant to the conduction band of the nano-titania layer. Tauc's relation can be used to determine the optical bandgap [26-28]. The calculated optical band gap value of Alizarin was 2.37 eV as represented in Figure 3.

The band gap of material can be calculated by using Tauc's equation as:

$$\mu h\nu = A(h\nu - E_g)^n \quad (1)$$

Where μ =Absorption coefficient,

h =Plank's constant

ν =Frequency

E_g =Band gap of substance,

A =Constant varies with transitions

n =An index may have values 1/2, 3/2, 2 and 3, dependent on electronic transition nature

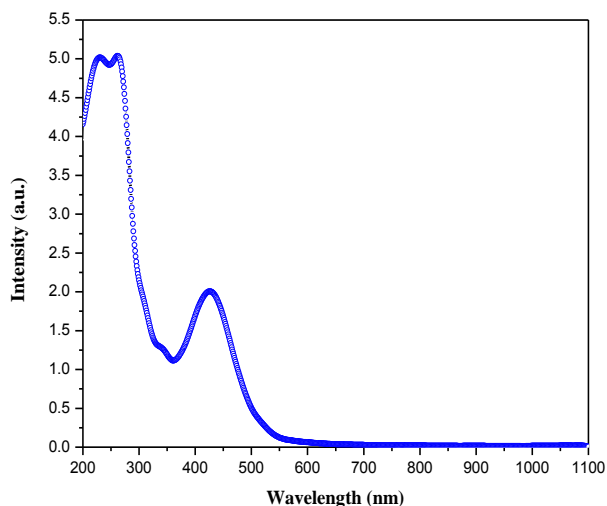
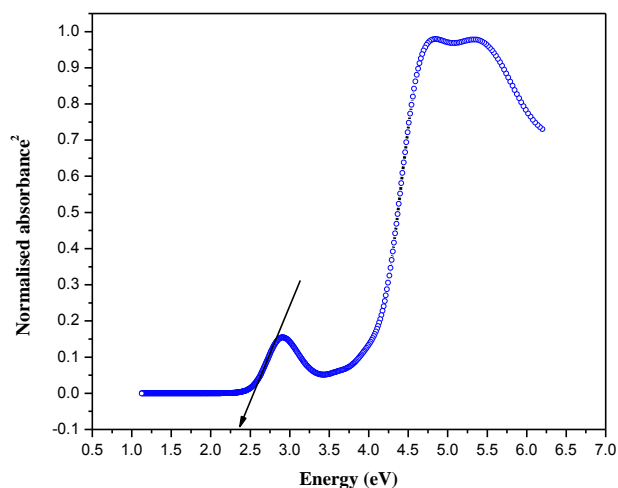


Figure 2: UV-Vis absorption spectrum of Alizarin dye

Figure 3: Normalized absorbance² vs energy (eV) curve of Alizarin dye

Thermal properties of alizarin dye

The thermo-gravimetric analysis and differential thermal analysis of Alizarin dye was carried out between 40 to 500°C with 10°C/min heating speed in the pure N₂ gas environment. The TGA-DTA recorded spectrum of is shown in Figure 4.

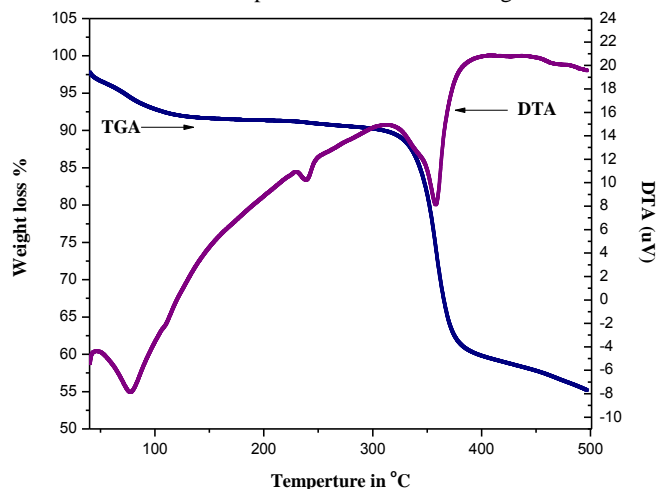


Figure 4: TGA and DTA curve of Alizarin dye

The initial mass of the dye was taken to be 9.392 mg and the final mass left out after the experiment was only 5.184 mg (loss 44.81%). In the earlier stage, weight loss due to evaporation of moisture or volatile substance. The remaining weight losses at different stages were due to decomposition of the dye molecule. At 1st step (40°C-160°C), the weight loss was 8.42% which most probably due to disappearance of volatile constituents of dye. A slightly change in mass of substance between 160°C to 300°C of temperature was obtained 9.84%. The molecular weight

of Alizarin dye is 240.21 gmol^{-1} , loss of mass percentage was 9.84% (23.616 g) which exhibit good thermal stability of dye upto 300°C of temperature. In the next step (300°C - 410°C), there was rapid decrease in mass of dye on heating. The weight loss in this stage was in 59.16 %. The results of differential thermal analysis (DTA) enumerate the absence of any endothermic or exothermic up to 78°C , which is supported by TGA results. All other endothermic appearing immediately above melting was assigned to degradation of the material. Differential thermal analysis (DTA) curve shows endothermic peaks at 78, 241 and 360°C . The huge peak at 360°C is assigned as melting point of dye with decomposition of the dye molecule.

Photovoltaic properties of alizarin dye as sensitizer

The fabrication DSSCs with following components: FTO (substrate)/ TiO_2 (Photoanode)/Alizarin dye (sensitizer)/KI or organic iodides with I_2 (electrolyte)/Graphite (catalyst)/FTO (substrate) as shown in Figure 5. The following combinations of the electrolytes were exploited-

- (i) Iodine (I_2) (0.01 M) with potassium iodide (KI) (0.1 M)
- (ii) Iodine (I_2) (0.01 M) with tetramethylquaternaryammonium iodide $[(\text{CH}_3)_4\text{NI}]$ (0.1 M)
- (iii) Iodine (I_2) (0.01 M) with tetraethylquaternaryammonium iodide $[(\text{CH}_3\text{CH}_2)_4\text{NI}]$ (0.1 M)
- (iv) Iodine (I_2) (0.01 M) with tetrapropylquaternaryammonium iodide $[(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NI}]$ (0.1 M)

The photovoltaic performances of fabricated DSSCs were assessed by open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF), and energy conversion efficiency (η). The V_{oc} and J_{sc} of each cell were assessed from their J - V curve. The power of DSSC was deliberate as $P=JV$ using the J - V data as represented in Figure 6. The corresponding parameters fill factor (FF) and efficiency (η) of every cell were calculated.

$$FF = \frac{V_{max} \cdot J_{max}}{V_{oc} \cdot J_{sc}} \quad (2)$$

$$\eta = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}} \times 100 \quad (3)$$



Figure 5: Sandwich type assembly of DSSC

The effect of various redox electrolytes using organic and inorganic iodides with I_2 on the proficiency of DSSCs was studied. J - V characterizations of DSSCs fabricated with alizarin dye as sensitizer with various electrolytes are presented in Figure 7.

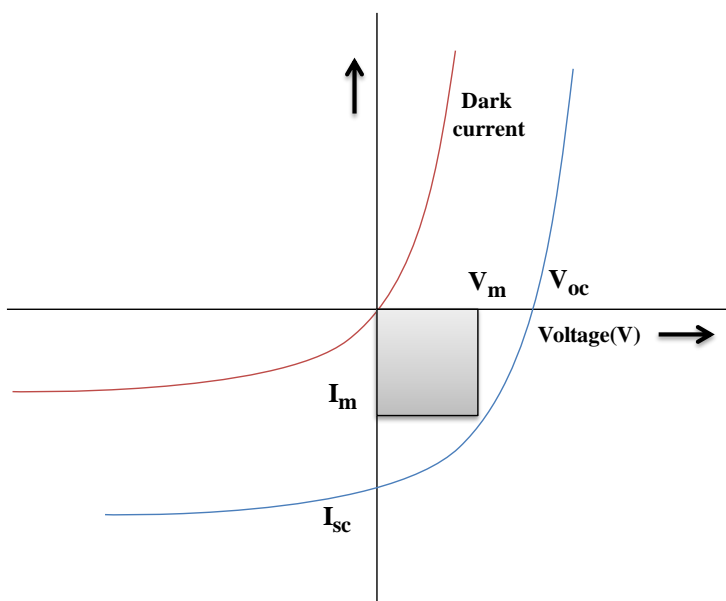


Figure 6: J-V curve of photovoltaic cell

The solar properties of the fabricated DSSCs are shown in Table 1. The configurations of fabricated DSSC were as:

FTO (substrate)/nanocrystalline TiO_2 (Photoanode)/ Alizarin dye (as sensitizer)/KI or $(\text{CH}_3)_4\text{NI}$ or $(\text{CH}_3\text{CH}_2)_4\text{NI}$ or $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NI}$ with I_2 (as electrolyte) /graphite (catalyst)/ FTO (substrate).

The DSSC fabricated with redox electrolyte KI- I_2 exhibit open circuit voltage (V_{oc}) 0.176 and maximum short circuit current (J_{sc}) was found 1.28 mA/cm^2 . In redox electrolyte $(\text{CH}_3)_4\text{NI}$ - I_2 the V_{oc} (0.233 V) get enhanced and J_{sc} (0.677 mA/cm^2) was found reduced. V_{oc} (0.275 V) value was

observed with $(\text{CH}_3\text{CH}_2)_4\text{NI-I}_2$ redox electrolyte having J_{sc} (0.972 mA/cm^2). J_{sc} (1.062 mA/cm^2) value was found with redox electrolyte $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NI-I}_2$ having the V_{oc} (0.289 V). The efficiency of fabricated DSSCs were obtained in order i.e. $(\text{CH}_3)_4\text{NI-I}_2 < \text{KI-I}_2 < (\text{CH}_3\text{CH}_2)_4\text{NI-I}_2 < (\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NI-I}_2$ with these electrolytic solution.

The photovoltaic performance of fabricated dye sensitized solar cells was found by the addition KI (inorganic iodide) and organic alkyl iodides i.e. tetra-alkylquaternary-ammonium iodides (R_4NI) where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ and C_3H_7 with I_2 as redox electrolytes. The efficiency of DSSCs enhanced as the size of cations increases from CH_3 to C_3H_7 . The ionic radius of the various cations may be responsible for this characteristic behavior [29]. The open circuit voltage of dye sensitized solar cells in $\text{R}_4\text{NI-I}_2$ redox electrolyte was consequence from the energy gap among the TiO_2 conduction band energy level and I^-/I_3^- redox potential of alkyl cations. Therefore, the conduction band of the TiO_2 layer moved adversely from CH_3 to C_3H_7 , leading to the rise of the V_{oc} and the vice-versa [30].

Table 1: Photovoltaic properties of DSSCs with Alizarin dye

S. No.	Electrolytes	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor (FF)	Efficiency
1	KI-I ₂	0.176	1.28	0.28	0.635
2	$(\text{CH}_3)_4\text{NI-I}_2$	0.233	0.677	0.242	0.383
3	$(\text{CH}_3\text{CH}_2)_4\text{NI-I}_2$	0.275	0.972	0.294	0.788
4	$(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NI-I}_2$	0.289	1.062	0.296	0.915

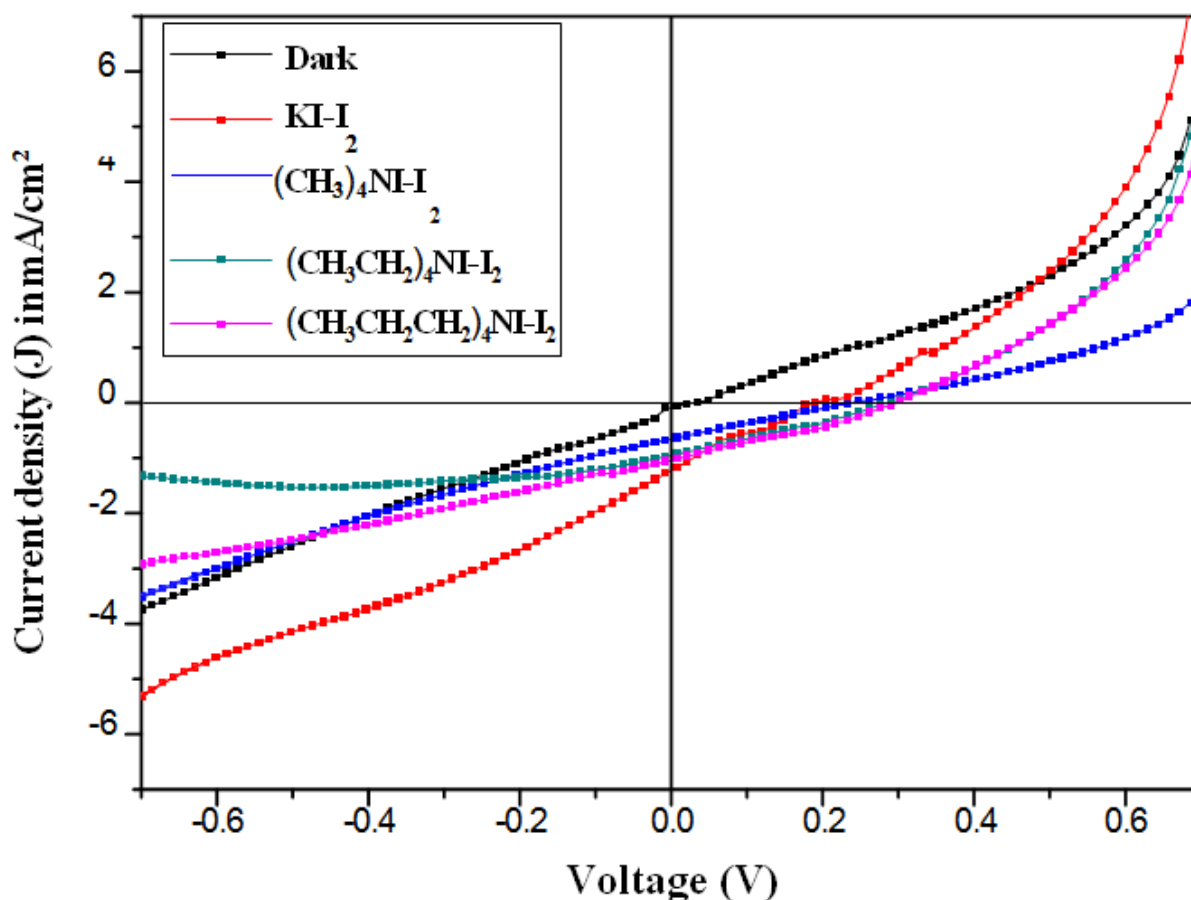


Figure 7: J- V curve of fabricated DSSCs with alizarin dye

CONCLUSION

DSSCs were assembled using Alizarin dye as sensitizer and employing four different redox couple electrolytes i.e. (KI), $[(\text{CH}_3)_4\text{NI}]$, $[(\text{CH}_3\text{CH}_2)_4\text{NI}]$ and $[(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NI}]$, with I_2 in CH_3CN solvent. The FTO coated conducting transparent glass substrate with nano-titania layer was used as photoanode in fabrication of DSSCs. The dye was used as effective photosensitizer in assemble of DSSCs as shown by absorption spectrum. It was also investigated that the proficiency of the DSSCs can be improved by using different redox couple electrolytes. The efficiency of fabricated DSSCs were obtained in order i.e. $(\text{CH}_3)_4\text{NI-I}_2 < \text{KI-I}_2 < (\text{CH}_3\text{CH}_2)_4\text{NI-I}_2 < (\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NI-I}_2$ with these electrolytic solution. The dyes could be effectively used as sensitizers because of transfer of electron from excited state to conduction band of nano-TiO₂ layer and therefore the consequent regeneration are viable in this dye as sensitizer.

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