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Research Paper

Pan Dye as an Organic Sensitizer of Tio2 Nanocrystalline Electrode in Dye Sensitized Solar Cell

Physics

KEYWORDS : Dye-sensitized solar cell, 1-(2-pyridylazo)-2-naphtol (PAN) dye, TiO2 nanocrystal, cyclic voltammetry

M. S. Yatnatti	Department of Studies in Physics, Karnatak University, Dharwad-580 003. Karnataka, India
J. S. Kadadevarmath	Department of Studies in Physics, Karnatak University, Dharwad-580 003. Karnataka, India
H. M. Mahesh	Electronic sciences department, Jnana Bharati Campus, Bangalore University, Bangalore
S. V. Lokesh	Electronic sciences department, Jnana Bharati Campus, Bangalore University, Bangalore
C. S. Naveen	Electronic sciences department, Jnana Bharati Campus, Bangalore University, Bangalore

ABSTRACT

This paper contains a preliminary report on 1-(2-pyridylazo)-2-naphthol (PAN) dye as an organic sensitizer in dye-sensitized solar cell. Initially, we have carried out absorption and cyclic voltammetric studies of (PAN) dye to investigate the absorption of light in the visible region and the conditions for the transition of electrons from photo-excited dye to TiO2 nanocrystal. Experimental results of these two studies indicate that PAN dye can be used as a TiO2 sensitizer. Thus, dye sensitized solar cell with PAN dye, sensitizing the TiO2 nanocrystal has been constructed. SEM and photovoltaic characterizations also were made. From SEM surface characteristics, better attachment of the dye particles with TiO2 nano crystalline particles has been observed. The fabricated DSSC provides requisite I-V characteristics but has poor efficiency.

2. Introduction

Dye-sensitized solar cells (DSSCs) are highly promising and an alternative to the photovoltaic devices as they are easy to fabricate, environmental friendly, economically feasible. They have been attracting researchers all over the world since the Gratzel and co-workers reported the high solar power conversion efficiency using Ruthenium metal complex photo sensitizers [1, 2]. Ru complexes are suitable photosensitizers for several reasons: they show a broad absorption band due to metal-to-ligand charge transfer (MLCT); the excited states of the complexes have long lifetimes; and an oxidized Ru (III) complex has long-term chemical stability. But Ru-complex dyes have low absorption coefficient necessitating the thickness of the TiO2 film layer to be thicker to adsorb large quantity of dye in order to harvest the incident light completely. This in turn increases internal resistance of the cell. Since Ruthenium is a rare earth material it is not abundantly available in nature. Therefore, producing DSSCs in large scale with Ruthenium metal complex dye may become a problem. Organic dyes such as series of 9-phenylxanthene, were used as photosensitizers for DSSCs in earlier studies [3-5]. Recently, construction of nanocrystalline DSSCs based on organic-dye photosensitizers has been reviewed thoroughly by P.Bauerle et.al [6]. Organic dyes have several advantages as photosensitizers for DSSCs: they have larger absorption coefficients (attributed to an intramolecular Π–Π* transition) than metal-complex photosensitizers thus they have efficient light-harvesting properties. Molecular designing of organic dye is possible by adding a variety of combinations of donor and acceptor moieties to their structures and they are abundantly available as they do not contain noble metals like Ruthenium. Requirements of organic dyes as sensitizer in DSSC are i) The dye should have broader absorption band width in the visible region of electromagnetic spectrum. ii) A HOMO level (i.e. Oxidation potential) of the dye must be at least 0.2V more positive than the red-ox potential (+0.4V) of I-/I3 electrolyte. iii) ELUMO value of the dye must be at least 0.2V more negative than the conduction band energy level (–0.5V) of TiO2.

In the present work, PAN dye is selected to verify its feasibility for the DSSC application. Molecular structure of PAN dye is shown in Fig. 1.

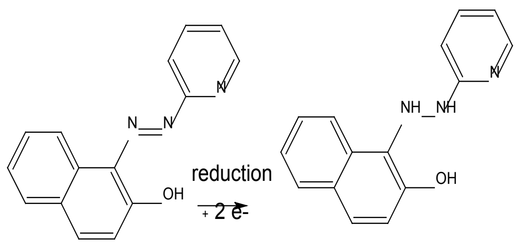

Fig.1. Chemical structure of PAN dye

PAN dye is an aromatic azo dye, used in several applications such as dye-stuff industry, medicine and dosimetry[7-14]. Puschel introduced the use of PAN dye for preconcentration purposes and Watanabe et.al, showed that PAN is an excellent dye for the determination of metal ions at the low ppm level [15, 16]. Energy disperse X-ray fluorescence determination of lanthanides after preconcentration on PAN was studied by Bhagavathi et al [17]. It is used as extractant in solid-liquid extraction of some trivalent rare earth elements [18]. Liquid-liquid extraction of RE (III) with PAN is reported in the literature [19]. Spectrophotometric method was studied by Rao et.al. [20], for the determination of micro-quantities of maneb after extraction of the manganese using PAN complex in isobutyl methyl ketone (MIBK). PAN modified carbon paste electrode (CPE) used to trace cobalt (II) determination by differential pulse cathodic voltammetry [21]. PAN has been used for the better selective and sensitive determination of Pb on PAN modified carbon electrode [22, 23]. The corrosion inhibition property of PAN dye on the corrosion of steel in hydrochloric acid, and its optical holographic recording properties have also been studied[24,25]. Considering all these diverse applications of PAN dye we thought of exploring the possibilities of PAN dye as sensitizer in DSSC and survey of literatures indicate that no report was available on PAN dye as sensitizer in DSSC. The optical properties, electrochemical properties, constructional details of solar cell, morphological properties and photovoltaic properties of PAN dye based solar cell are presented and discussed in this paper.

2. Experimental

2.1. Reagents, chemicals and materials used

Chemicals such as PAN (MERCK), Triton X-100, Lithium Iodide,

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Iodine and Polyethylene glycol (HiMedia laboratory) were purchased and used as obtained. The solvents viz. Ehanol, acetonitrile, acetone and acetyl acetone (A.R grade) etc. were used. P-25 TiO2 nano powder from sigma Aldrich and Pilkington NSG TEC15 FTO glass with 80% visible light transmission with 14Ω /sq sheet resistance were used to construct DSSC. Milli Q water was used for cyclic voltammetry studies and de-mineralized water was used for construction of DSSC.

2.2. Absorption spectrum

Absorption spectrum of PAN dye in Ethanol solvent was taken using Hitachi U-3010 spectrophotometer with 4mM dye concentration and is shown in Fig.2.

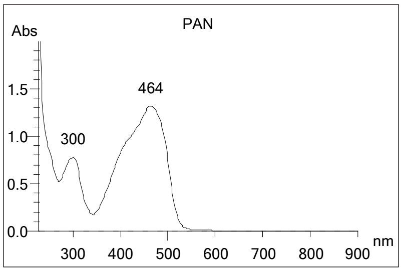

Fig.2. Absorption spectrum of PAN dye taken in ethanol solvent with 4mM concentration

This spectrum shows that absorption of the visible light is in between the range of 340nm to 560nm, peak of the absorption curve lies at 464 nm. Also, onset wavelength λ0 is found to be 560nm and using this value of λ0, corresponding ground state energy level (E00) of the PAN dye is estimated to be 2.217 eV [26].

2.3. Cyclic Voltammetric Studies

Cyclic voltammetric experiments were carried out employing a three-electrode configuration consisting of a glassy carbon disk (3 mm diameter) as a working electrode and saturated calomel electrode (SCE) as the reference electrode and a platinum rod served as counter electrode. All potential values were measured with respect to SCE. The electrochemical measurements were performed using Eco Chemie Potentiostat/Galvanostat, Autolab-100 and the analysis was carried out by GPES 4.9 electrochemical software. The glassy carbon electrode was successively polished with 5, 1, 0.3 and 0.05 lm alumina polish and then rinsed with 8 M nitric acid and distilled water before use. All the solutions were purged with high purity nitrogen for 15 minutes.

In cyclic voltammetry, keeping the sweep rate constant with known initial potential and switching potential, current versus applied potential curve (voltammogram) can be recorded. The curve provides information about oxidation and reduction potentials of the solute. In this experiment PAN dye solution with 4x10-3M concentration was prepared in an aqueous acetonitrile solvent with addition of sulpuric acid which acts as supporting electrolyte. Experiment was carried out keeping sweep rate, initial and switching potentials as 0.05 mVs-1, +1V and -1.1V respectively. The voltammogram obtained for PAN dye is shown in Fig.3.

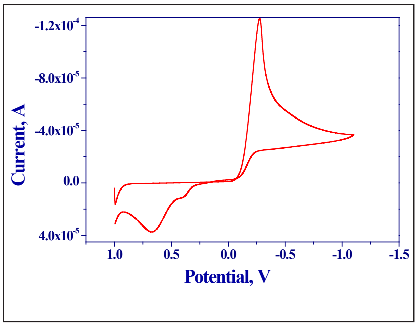

Fig. 3. Cyclic voltammogram of PAN dye.

From this figure, it is possible to measure, single cathodic peak, and two anodic peaks and these values are –0.272 V, 0.403 V and 0.672 V respectively. The voltage –0.272 V at cathodic peak is called cathodic potential or reduction potential (Epc) and the voltages 0.403 V and 0.672 V at two anodic peaks are called anodic potentials or oxidation potentials (Epa1 and Epa2) respectively. The current values corresponding to cathodic peak (ipc) and two anodic peaks are -125 µA (ipc), 11.27 µA(ipa1) and 37.32 µA (ipa2) respectively. The same values are also given in Table 1.

Table 1
Summary of cyclic voltammogram

Supporting electrolyte: 50 mM H2SO4
Electrode system: GCE/SCE/Pt
Scan rate: 0.05 V s-1
Concentration of PAN: 2×10-3 M
Solvent: Acetonitrile

Reduction peak		**1st oxidation peak**		**2nd oxidation peak**	
Epc (V)	ipc (µA)	Epa1(V)	ipa1(µA)	Epa2(V)	ipa2(µA)
-0.272	-125	0.403	11.27	0.672	37.32

In order to check whether the Energy level of LUMO (ELUMO) of PAN dye lies above the conduction band energy level of TiO2, it is required to calculate E LUMO. Where E LUMO = Eox – E00. Eox is the oxidation potential of the dye, here PAN dye has two oxidation potentials (HOMO levels) with 0.403 V and 0.672 V respectively. E00 is ground state energy level obtained from absorption studies and is 2.217 eV. Thus, ELUMO values for two oxidation potentials of the PAN dye are found to be -1.814V and -1.545 V respectively. As the conduction band energy level of TiO2 semiconductor is -0.5 V, the two oxidation potentials of PAN dye is found to be well above the conduction band energy of TiO2. Therefore, transition of electrons from photo excited dye [LUMO level] to the conduction band of nanocrystalline TiO2 semiconductor is energetically possible. Furthermore, the HOMO level of the dye should be at least +0.2 V more than the redox potential of I-/I3- electrolyte (i.e., +0.4V) to receive electron from the electrolyte in order to get regenerated. Thus out of the two oxidation peaks of the dye one oxidation peak that is +0.672 V is about +0.272V more than that of redox potential I-/I3- electrolyte. Therefore, these investigations suggest that that PAN dye satisfies most of the requirements as sensitizer in DSSC.

2.4. Construction of DSSC

2.4.1. Preparation of TiO2 layer on FTO glass plate

About 1.2g of TiO2 (P-25) nano powder was taken in a previously cleaned mortar and pestle. 0.4 ml of milli Q water and 0.1ml of acetyl acetone were added to it and grinded for 30 minutes in order to prepare TiO2 paste. Acetyl acetone prevents the aggregation of TiO2 nanoparticles. While grinding, 1.6 ml of water and 0.1 ml of Triton X-100 were added gradually to the colloidal solution. Triton X-100 helps in spreading the colloidal solution on the surface of the substrate and it also helps in creating the porosity in the TiO2 nanostructure layer.

Pilkington NSG TEC15 FTO glass, of dimension 2.3 mm thick, 2 cm length, 1.5 cm width and having 80% visible light transmission, 14Ω/sq sheet resistance was used as substrate for coating TiO2 layer. The conducting side of the FTO glass was covered by Scotch tape of 36 micron thickness. 1 cm2 area of the scotch tape attached to the glass was cut in a square shape and peeled off from the glass plate with a surgical blade by placing a cubical block of each surface area of 1 sq. cm. specially designed for this purpose. The cut area is now exposed and a few drops of TiO2 colloidal solution were put on the exposed area. The solution was spread uniformly by rolling a glass rod over the scotch tape and is left for drying in air. After one hour, the scotch tape attached to FTO glass was removed leaving behind wet film of TiO2 on the glass and same was placed on a specially designed holder with stand. The stand was then placed in crucible of the furnace whose temperature was gradually raised to 550 oC, at this temperature; the film was annealed for 30 minutes. While, the glass plate was cooled down to 100 0C, it was removed from the furnace and then kept on the hot plate maintained at 80 0C.

2.4.2. Sensitization of TiO2 with PAN dye

4mM solution of PAN dye in dry ethanol was prepared and taken in a large Petri dish. The sintered TiO2 coated glass plate is immersed in the dye solution while it is hot at 80 oC to prevent water condensation inside the TiO2 layer. Water droplets will reduce the cell performance by blocking electron transition between dye and TiO2 semiconductor. Petri dish was closed airtight using paraffin film to prevent the evaporation of ethanol. The film was then soaked in the dye solution for 48 hours.

2.4.3. Preparation of Electrolyte

Each 25ml solutions of 500mM Lithium Iodide (LiI), 50mM of Iodine (I2) and 0.4M of polyethylene glycol (PEG) respectively were prepared in acetonitrile (ACN) solvent. 10 ml from each of these three solutions were taken and mixed thoroughly in a separate flask and used as electrolyte containing I-/I3- ions. Role of PEG was to reduce the viscosity of electrolyte.

2.4.4. Fabrication of the Solar Cell

FTO glass coated with TiO2 film layer was taken out of the Petri dish after 24 hours of soaking in dye solution and placed on a hot plate and allowed to dry for 10 minutes at 500 C. The glass was cleaned with dry ethanol to remove dye stains attached on other part of the glass and then electrolyte was dropped on the TiO2 film layer. Surrounding the TiO2 film layer, a line bordering was made with a double solution adhesive gel commercially called araldite. Araldite does cementing of electrode and counter electrode and also acts as a spacer between them. A few more drops of electrolyte solution were dropped in a pool made by araldite. Another FTO glass of the same dimension was placed inverted on the TiO2 film layer with its conducting side facing the layer to form counter electrode, binder clips were used to hold the assembly firmly. A small area on one side of both the FTO glasses is left free for electrical connections. Before this cell is subjected for photovoltaic characterization, SEM characterization is performed.

2.5. SEM Characterization

Scanning Electron Microscopy (SEM) was done in order to study surface characteristics of each layer of DSSC. Layer by layer characterization of DSSC reveals the morphology of each layer. ESEM Quanta 200, FEI, with resolution of 3nm at 20 kV in high vacuum, was used for scanning. SEM photographs were taken at I.I.Sc., and Bangalore. These SEM photographs are shown in Figures.4a, 4b, 4c and 4d respectively.

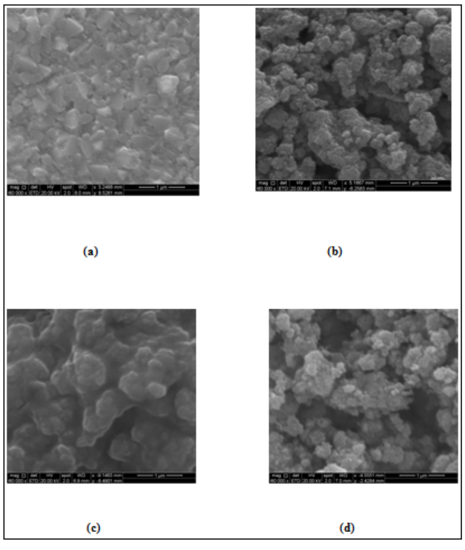

Fig. 4. (a) FTO glass plate (b) TiO2 before annealing (c) TiO2 after annealing (d) Dye soaked TiO2 after annealing

Uniform coating of tin oxide and the formation of TiO2 nano crystalline layer before annealing on FTO glass can be seen from Fig 4a and Fig 4b respectively. After annealing at 550 oc good interconnection between TiO2 nano crystalline particles can be seen in Fig.4c and the attachment of the dye particles with TiO2 nano crystalline particles can also be seen clearly in Fig.4d for dye soaked TiO2.

2.6. Photo voltaic Characterization

In order to study the photo voltaic characteristics, we have prepared about ten solar cells. Open circuit voltage (Voc) of these solar cells were measured with multi meter (RISHAB 14S) by keeping the DSSCs under actual sunlight at different times of the day. Eight of these cells showed fairly good values of Voc. We have measured the Voc value of each cell everyday for one month. About four of them have shown the same values consistently. Then we took the best cell out of four for final I-V characterization which was carried out in the department of Instrumentation, I.I.Sc, Bangalore. Measurements were performed using a Keithley model 6517A electrometer. The irradiance source of 100 W (Philips halogen lamp) with its power calibrated to 100mW/cm2 by single crystal silicon reference solar cell was used [27]. Measured voltage (V), current (I) and calculated power values are shown in Table 2.

Table 2
Summary of Photovoltaic characteristics.

S. No	Voltage in volt V	Current in nA I	Power P=VxI in n W
1	0	67.214	0
2	0.01	56.394	0.56
3	0.02	47.163	0.94
4	0.03	38.809	1.16
5	0.04	27.190	1.09
6	0.05	20.624	1.03
7	0.06	14.304	0.86
8	0.07	8.212	0.57
9	0.078	0	0

The graphs of current versus voltage and power versus current are shown in **Fig.5. (a) and Fig.5. (b) respectively.**

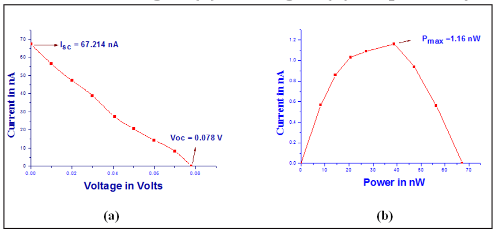

Fig. 5. (a) Current Vs Voltage (b) Power Vs Current

It is seen from the table 2 that the short circuit current (Isc), open circuit voltage (Voc) and the maximum power point (Pmax) values are found to be 67.214 nA, 0.078 V and 1.16 nW, respectively. Experimentally obtained maximum current (Imax) and voltage (Vmax) at Pmax, are 38.809 nA and 0.03V respectively. These experimental values are used to estimate fill factor (F.F) and efficiency (η) of DSSC. For estimation of efficiency of the cell the incident power (Pin) was kept 1000 w/m2 which is equal to the global intensity of 1.5 Air Mass solar radiation. Estimated parameters F.F and η are 0.213 and 1.1185x 10-8 respectively. These experimentally determined parameters were compared with some of the reported values and are shown in Table 3.

Table 3 Comparative results of fill factor and efficiency

Sl. No	Name of the dye used	Author's name	Fill Factor	Efficiency in percentage
1	N-719, Ruthenium complex dye	M.Gratzel. [29]	0.74	11.2
2	Mercurochrome organic dye	Kohjiro Hara et.al. [30]	0.73	1.44
3	Coumarin-derivative dye	Kohjiro Hara et.al. [31]	0.63	5.6
4	Merocyanine dye	Kazuhiro Sayama et.al. [32]	0.63	0.9
5	PAN dye	Present Work	0.21	1.12×10^{-8}

From this it is observed that efficiency of DSSC prepared using PAN dye is very much small compare to others. This may be due to the absence of proper anchoring group to PAN dye molecule resulting weak transition of electron from photoexcited dye molecule to TiO2 semiconductor [28]. Other reason could be increase of internal resistance of the cell as a result of absence of Pt coated counter electrode.

3. Results and Discussion

From the analysis of absorption spectrum it reveals that PAN dye has an absorption peak of 464 nm with absorption coefficient of 1.32 and ground state energy level of 2.217 eV. From cyclic voltammetric studies, the two oxidation potentials and reduction potential of PAN dye are 0.403V, 0.672 V and -0.272 V respectively. Using experimentally determined values of oxidation potentials and ground state energy level, energy level of LUMO for PAN dye has been calculated. For two oxidation potentials, energy levels of LUMO were found to be -1.814volt and -1.545 volt. It has also been noticed that, LUMO values of PAN dye are far more negative than conduction band energy level -0.5V of TiO2 nano crystal. This clearly suggests that transition of electrons from photoexceted dye to TiO2 may hence be possible. Further, it is found that one of the oxidation potentials is 0.272 V more positive than redox potential of I-/I3- electrolyte. Thus regeneration of PAN dye is possible from the transition of electrons from electrolyte. All these investigations indicate that, PAN dye may be suitable for sensitizing TiO2.

Based on the above investigations construction/fabrication of DSSC has been carried out to investigate SEM and photovoltaic characteristics. From SEM surface characteristics, better attachment of the dye particles with TiO2 nano crystalline particles has been observed. From photovoltaic characteristics fill factor F.F = 0.213 and efficiency η = 1.1185x 10-8 of fabricated dye sensitized solar cell has been estimated. Though the fabricated DSSC provides necessary I-V characteristics but has poor efficiency. This poor efficiency may be attributed to the absence of proper anchoring group to PAN dye molecule resulting weak transition of electron from photoexcited dye molecule to TiO2 semiconductor [28]. Other reason could be increase of internal resistance of the cell as a result of absence of Pt coated counter electrode.

Since our main aim was initially to check whether PAN dye could be used as sensitizer or not and to report experimental results as no report is available on PAN dye as a dye sensitizer. However, this study may help to the enrich literature and carry out further research on PAN dye in DSSC.

4. Conclusions

This paper describes the preliminary investigations carried out to check whether PAN dye can be used as sensitizer in DSSC. Though lot of diverse applications of PAN dye is available in the literature but no report is available as dye sensitizer in DSSC applications. Thus, initially we have carried out absorption and cyclic voltammetric studies of PAN dye to investigate absorption of light in the visible region and the conditions for the transition of electrons from photo-excited dye to TiO2 nanocrystal. These results indicate that PAN dye can be used as a TiO2 sensitizer. Based on the encouraging results of absorption and cyclic voltammeric studies, DSSC has been constructed. Later, SEM and photovoltaic characteristics has been performed. SEM surface characterization results better attachment of the dye particles with TiO2 nano crystalline particles. Photovoltaic characteristics provide necessary I-V characteristics but with poor efficiency. Poor efficiency may be due to the absence of proper anchoring group to PAN dye molecule resulting weak transition of electron from photoexcited dye molecule to TiO2 semiconductor [28]. Other reason could be increase of internal resistance of the cell as a result of absence of Pt coated counter electrode.

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