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Effect of Different Organic Dyes and their Impregnation Periods on Photovoltaic Performance of ZnO Based Dye Sensitized Solar Cells

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Light absorption in dye sensitized solar cells (DSSCs) depends significantly on the type of sensitizer and its impregnation period. Since dye plays a vital role to broaden the light absorbance of semiconductor photoanode towards the visible region of spectra. The present study reports the effect of two types of organic dyes namely N719 and N749 (black dye) as well as their impregnation periods of 12 h and 24 h, respectively, on the photovoltaic performance of zinc oxide based DSSCs. Zinc oxide photoanode films were deposited on indium tin oxide substrates by doctor blade technique. The DSSC impregnated with N719 dye for the period of 24 h exhibited the highest value of photon conversion efficiency. This happened as the photoanode film impregnated with N719 dye for 24 h exhibited the highest optical absorption in the UV region as well as in visible region of spectra. The solar cell impregnated with N719 dye for the period of 24 h performed with the highest short-circuit density (J_{SC}) of 9.38 mA/cm^2, fill factor (FF) of 0.50, open circuit voltage (V_{OC}) of 0.71 V and conversion efficiency (η) of 3.32 %.

Keywords: ZnO, Sensitizer, Optical absorption, Impregnation period, Dye sensitized solar cells.

INTRODUCTION

The political, economical and environmental development of a society depends strongly on its sustainable energy resources [1]. The limited sources of fossil fuels and emission of green house gases upon their combustion has created terrible environmental crisis. Therefore, to fullfill world's growing energy demands the researchers have realized the urgent requirement to develop alternative energy resources that can decrease emission of carbon dioxide as well as air pollution [2]. In view of such concerns, solar energy is the most expectant for delivering sustainable power as it is a kind of safe, abundant, renewable and clean energy. Moreover, another important aspect of solar energy is power generation in remote areas [1,3]. The storage and conversion of solar energy can be attained by photoelectrochemical routes, and the most successful example of this approach is photosynthesis [4]. Currently, dye sensitized solar cells (DSSCs) invented in 1991 by Michael Gratzel and Brian O'Regan are the new variants in solar cell areas [5]. From the last two decades, DSSCs have achieved an enormous attention as a low cost and potential substitute to conventional Si solar cells [6,7]. A typical DSSC includes a photoanode (usually TiO_2) and a platinum counter electrode separated by an electrolyte having an iodide/triiodide (I^-/I_3^-) redox couple [8,9]. As zinc oxide (ZnO) and titanium dioxide (TiO_2) possess almost identical band gap energies as well as equal value of electron affinities hence ZnO can be considered as the closest and potential substitute to TiO_2 as photoanode material in DSSCs. In addition, ZnO has higher electron mobility, high electron diffusivity, more excitation binding energy, stability against photo-corrosion, availability at lower cost, and lower recombination rate as compared to TiO_2. Therefore, ZnO can be used as photoanode material in low-cost and highly efficient DSSCs [10-13].

A DSSC device generally uses ruthenium-based dyes such as N719, N3, Z907, N749, *etc*. for photoanode impregnation just because they have shown better DSSCs performances [14]. In DSSCs, the sensitizer dye plays an important role as it initiates the photovoltaic reaction by absorbing photons from sunlight. For enhancing performance of DSSCs, the sensitizer must be panchromatic *i.e.* it must absorb photons from the entire solar spectrum (from visible to near infrared region) as well as it must sustain enough driving force for regeneration and electron injection processes [15]. The photoconversion efficiency of a DSSC device depends strongly on the dye uptake by semiconductor photoanode film. To improve performance of DSSCs, uniform as well as monolayer of sensitizer dye is highly preferred so as to increase electron transfer kinetics [16]. Also the type of dye, impregnation period and dye concentration plays a significant role in enhancing the conversion efficiency of DSSC. A DSSC device can work efficiently if dye gets strongly adsorbed on photoanode surface [17,18].

The present work aims to investigate the effect of using two types of organic dyes namely N719 and N749 as photosensitizers for the different sensitization periods *viz.* 12 h and 24 h, respectively on the photovoltaic performance of ZnO based DSSCs. The photovoltaic performance of as prepared DSSCs is measured by XRD to reveal the structural properties of photoanode film, FESEM and EDX to measure morphology, porosity as well as purity of the photo-anode film, UV-visible absorption spectroscopy to study optical properties of photoanode sensitized with different dyes, and current density-voltage (J-V) curves to find out different photo-voltaic parameters of DSSCs under investigation.

EXPERIMENTAL

Zinc acetate dihydrate, N719 dye, N749 dye and ITO (15 Ω sq^{-1}) were acquired from Sigma-Aldrich (USA). Polyethylene glycol (PEG_{20000}) was purchased from Himedia (India). Deionized water was used throughout the experiments.

The ZnO nanopowder was synthesized using sol-gel process described elsewhere [10]. The coating procedure of ZnO photoanode film on indium tin oxide (ITO) was explained in the previous studies [19]. The ZnO film after drying at room temperature, was fired at 450 ºC in furnace for 30 min to improve their crystallinity and stability. This photoanode film was then impregnated in 0.5 mM ethanolic solution of N719 dye for 12 h and unadsorbed dye molecules were removed with excess of ethanol. Another ZnO film was also prepared with the same method as discussed above and sensitized with N719 dye for 24 h. The same procedure and impregnation time were repeated for another set of ZnO photoanode films sensitized with N749 dye. Thickness of all photoanode films was measured to be 9 µm.

Preparation of counter electrode: Platinum counter electrode is prepared by spin coating the acetonitrile solution of H_2PtCl_6 on ITO substrate.

Assembling of dye densitized solar cells: The DSSCs were assembled in a sandwich-type structure by placing the dye sensitized photo-anodes on the top of spin coated Pt counter electrodes. Finally, iodide-based liquid electrolyte was injected into the devices for completing the device structure. The schematics and operational principle of a DSSC device is shown in Fig. 1. Under simulated sunlight, the sensitizer dye after absorbing photon becomes oxidized and injects electron to the conduction band (CB) of the semiconducting oxide. The semiconductor oxide material collects only those photons that have energy more than the band gap energy. From the conduction band of semiconductor these photo-generated electrons

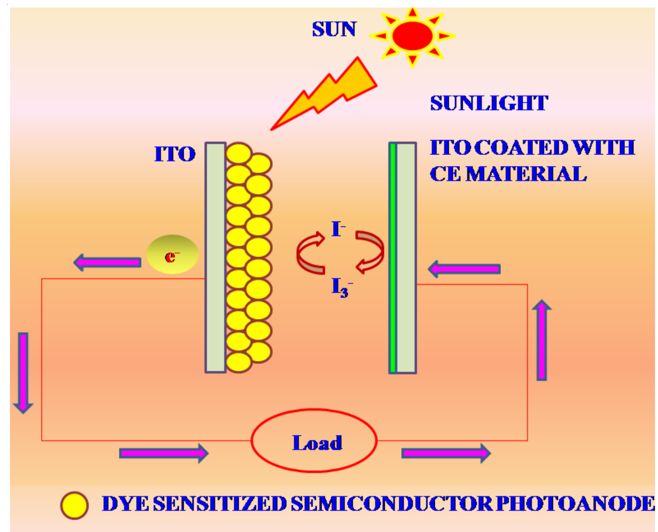

Fig. 1. Structure and operation of a DSSC device

are captured by the conducting glass substrate and then directed towards the external circuit. The oxidized dye is regenerated by capturing electron from the redox coupled electrolyte. The electrolyte gets reduced by collecting electron from the counter electrode material [4,10,20].

Characterization: The structure and phase of ZnO photoanode (without dye impregnation) films were determined by the X-ray diffraction from Rikagu Table-Top X-ray diffractometer. Morphological and compositional studies of these films were carried out with Field emission scanning electron microscope (FESEM) using TESCAN (model MIRA II LMH) and Energy dispersive X-ray (EDX) from INCA Penta FET×3 attached with FESEM set-up. Optical properties of ZnO photoanode films impregnated with N719 dye and N749 dye for different impregnation periods were examined by means of UV-visible absorbance spectroscopy using Varian UV-Vis spectrophotometer (Cary5000). The current density-voltage (J-V) characteristics of DSSCs were measured using a Keithley 2400 Source meter using a SS50AAA (Photo Emission Tech) solar simulator under AM 1.5G and 100 mW cm^{-2}. The active area for all DSSCs was kept to be 0.25 cm^2.

RESULTS AND DISCUSSION

Structural properties: To study the crystal structure and phases of ZnO photoanode film XRD measurements are carried out. The XRD patterns of ZnO film deposited on ITO substrate are shown in Fig. 2. The diffraction peaks attributed to hexagonal wurtzite structure of ZnO emerges at 2θ values of 31.9º, 34.6 º, 36.2º, 47.5º, 56.6º that are assigned to (100), (002), (101), (102), (110) planes, respectively [21]. No other peak related to impurity is observed in the spectrum.

Morphological and compositional analysis: Fig. 3a depicts the FESEM micrograph of ZnO photoanode film. It is observed that rice shaped structures of ZnO are formed as well as ZnO film possesses rough and porous morphology. The rough and porous nature of the photoanode films facilitates their use in DSSCs application due to huge specific area (1000 times more than bulk) available for dye adsorption and electrolyte diffusion [22].

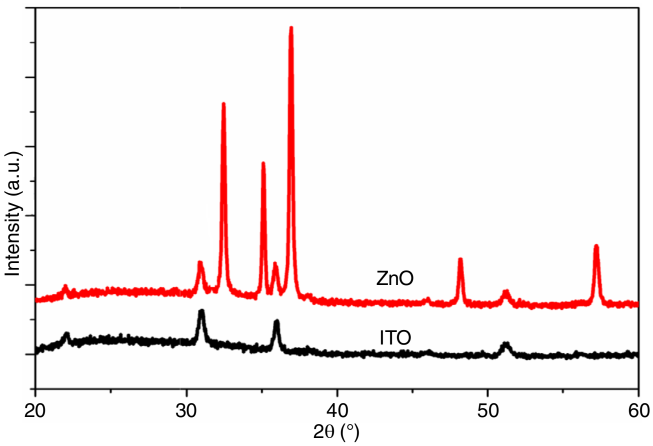

Fig. 2. XRD spectra of ZnO film deposited on ITO substrate

The EDX spectrum of ZnO film is shown in Fig. 3b. The spectrum contains peaks of zinc (Zn) and oxygen (O) along with the peaks of gold because gold coating is done prior to the EDX measurement. No impurity peak is detected in the EDX spectrum of ZnO film that confirms the purity of ZnO film.

Optical studies: As semiconductor ZnO (without sensitization) has a broad area of absorption in the wavelength region 300-800 nm (Fig. 4a) but in visible region its absorbance is small [14]. Figs. 4b and 4c display the UV-visible absorption spectra of ZnO semiconductor photoanode impregnated with N719 dye and N749 dye for 12 and 24 h, respectively. The characteristics absorption peaks for N719 dye are found at 375 nm and 525 nm (Fig. 4b) and that of N749 dye are 375 and 565 nm (Fig. 4c), respectively [23]. After dipping ZnO photoanode into dyes, the absorption in visible region increases significantly. It is also observed from Fig. 4b-c that the absorbance of the photoanode samples impregnated with N719 and N749 dyes for 24 h is higher than those impregnated for 12 h. Therefore, it is expected that the DSSC devices impregnated for 24 h with N719 and N749 dyes, respectively, would exhibit enhanced performance than the DSSCs impregnated for 12 h.

Photovoltaic performance of DSSCs: Fig. 5 demonstrates the photocurrent density-voltage (J-V) curves of ZnO based DSSCs impregnated with the dyes namely N719 and N749 with the impregnation periods 24 h and 12 h, respectively. Table-1 illustrates the performance parameters of ZnO based DSSCs impregnated with N719 and N749 dyes, respectively, for different

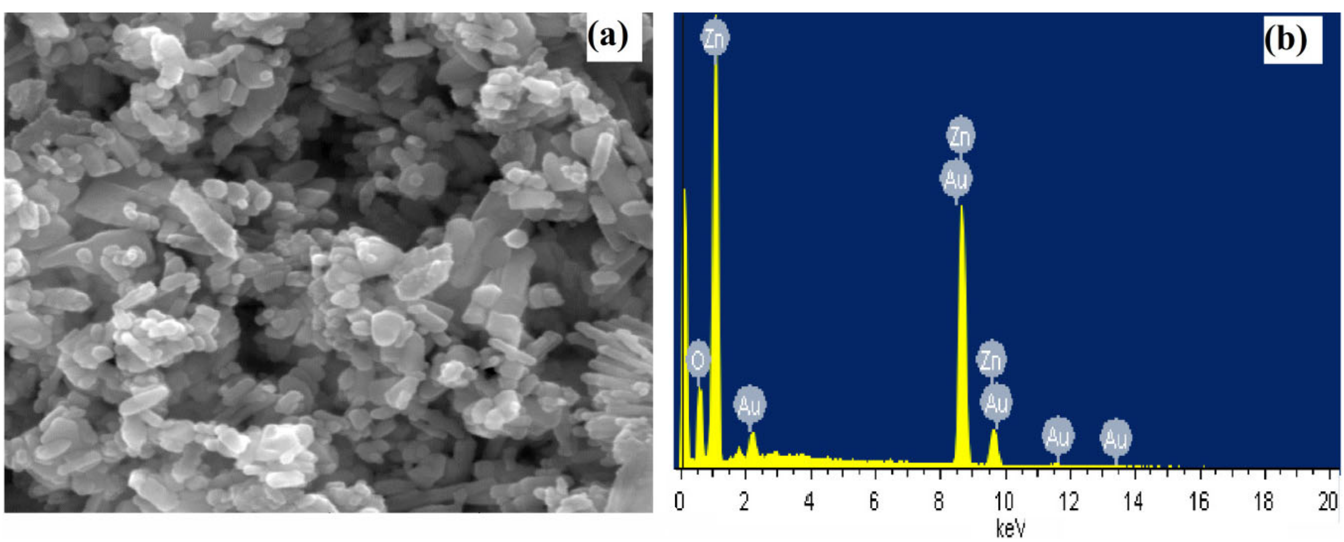

Fig. 3. (a) FESEM micrograph of ZnO film (b) EDX spectrum of ZnO film deposited on ITO substrate

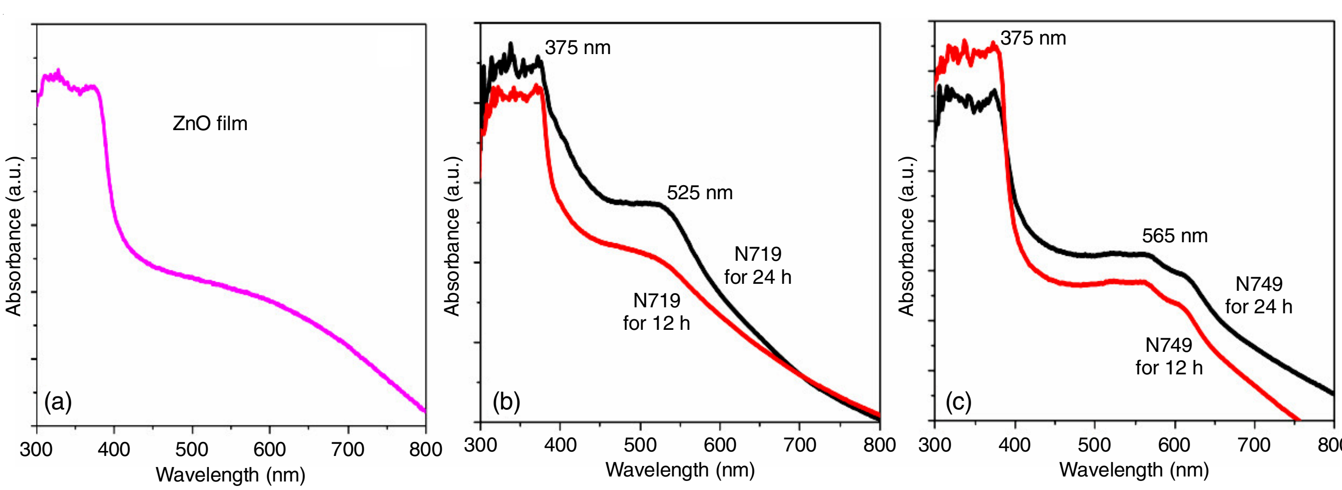

Fig. 4. UV-visible absorption spectra of (a) pure ZnO film (b) ZnO photoanode film impregnated with N719 dye for 24 h and 12 h (c) ZnO photoanode film impregnated with N749 dye for 24 h and 12 h

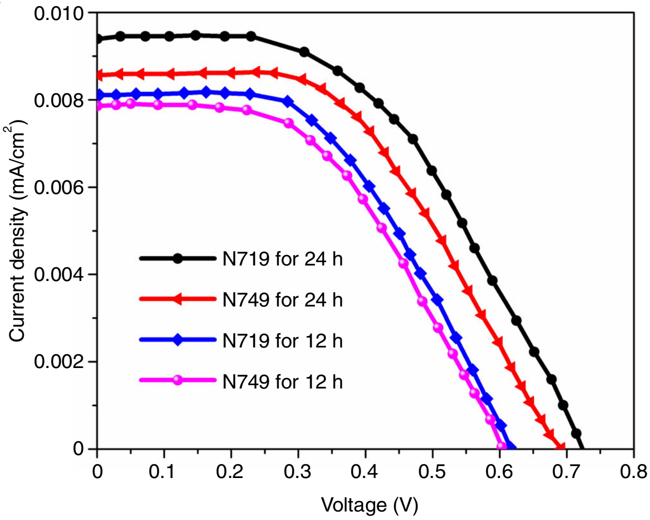

Fig. 5. J–V curves of ZnO based DSSCs impregnated with dyes N719 and N749 with different impregnation periods

TABLE-1
PHOTOVOLTAIC PARAMETERS OF ZnO BASED DSSCs SENSITIZED WITH N719 AND N749 DYES FOR DIFFERENT IMPREGNATION PERIODS

Sample	Impregnation period (h)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
N719	24	9.38	0.71	0.50	3.32
N749	24	8.56	0.69	0.49	2.89
N719	12	8.10	0.63	0.48	2.44
N749	12	7.86	0.60	0.46	2.16

time period (12 h and 24 h). It can be seen that the efficiency values of DSSCs impregnated with dyes N719 and N749 for 24 h are significantly higher than the DSSCs sensitized for 12 h. The maximum efficiency value (3.32 %) is obtained from the DSSC impregnated with N719 dye for 24 h. Hence, the type of organic dye and its impregnation period has an immense influence on the J_{SC} as well as conversion efficiency (η) of the solar cells. Meanwhile, the cell impregnated with N749 dye for 12 h shows the lowest efficiency. These results can be described on the basis of UV-visible absorption spectra (Fig. 4b), as the photoanode sensitized with N719 (24 h impregnation period) has the highest absorbance in the range of 300-400 nm as compared to the other competitors. As a result, upon illumination, more electrons are being inserted to the conduction band of semiconductor photoanode impregnated with N719 dye for 24 h that results in an improvement of photovoltaic parameters *viz.* short-circuit density (J_{SC}) and conversion efficiency (η) [23].

Conclusion

Zinc oxide based DSSCs impregnated with dyes such as N719 and N749 were successfully prepared and the influence of different impregnation period on the solar cell performance is reported. The DSSC impregnated with N719 dye having impregnation period 24 h demonstrated the highest photovoltaic conversion efficiency as compared to other cell sensitized with N749 dye with the same period of impregnation. Therefore, the type of organic dye adsorbed on the photoanode surface and period of impregnation has a great influence on light absorption by the DSSC device that results more and more charge carriers to transfer into conduction band of semiconductor photoanode consequently increasing performance of DSSC.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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