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# Enhanced Photoelectrochemical Solar Cells Based On Natural Dye-Sensitized Al-Doped Zinc Oxide Electrodes

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# ABSTRACT

A study has been successfully carried out on the photosensitizing action of a natural dye obtained from Indigofera arrecta plant (a herbicious plant) on nanocrystalline Al-doped zinc oxide (AZO) thin film electrodes synthesized by chemical bath deposition (CBD) technique. The porous nanostructures of the AZO enhanced dye-sensitized solar cell performance. This dye with strong absorption in the visible range with almost constant absorption peak, was found to convert visible light in the range of 300–750 nm into electrical energy. The electron injection by photo-excited dye molecules into the conduction band of AZO was evidenced by electrochemical impedance lowering of the dye-capped AZO electrode at optimum Al impurity level of 2 at % which facilitate fast charge carrier transport in the conduction band of the semiconductor. On irradiation of the dye-capped AZO thin film electrodes with white light of intensity 80 mW/cm<sup>2</sup>, power conversion efficiency ( $\eta$ ) of the (AZO electrode/Indigofera arrecta plant dye-containing electrolyte/platinum electrode) cell was found to be 0.51 % with fill factor of 0.47. The values of short circuit photocurrent I<sub>sc</sub> and open-circuit photovoltage V<sub>oc</sub>, measured as 1.35 mA/cm<sup>2</sup> and 0.643 V confirmed the applicability of the natural dye in solar cells.

Key words: Photoelectrochemical, Al-doped ZnO, *Indigofera arrecta* plant dye, Natural dye, Dye-sensitized solar cell, Electrochemical impedance

## **INTRODUCTION**

Dye-sensitized photoelectrochemical (PEC) cells based on nanocrystalline semiconductor thin film electrodes have become an attractive subject of research in the recent times due to their high promise to be cost effective and efficient types of photovoltaic solar cells (Wolcott et al. 2009). The attractive result reported by Grätzel and co-workers for PEC solar cell based on nanocrystalline TiO<sub>2</sub> thin film electrode sensitized by RuII(2,20-bipyridle-4,40-dicorboxylate)2(NCS)<sub>2</sub>, have yielded the most efficient dye-sensitized photovoltaic cell with light-to-electrical energy conversion efficiency  $\approx$ 10% (Dhas et al. 2008)This result stimulates earnest curiosity in this area of research. Nanocrystalline semiconductor thin film electrodes are the key components of the dye-sensitized solar cells (DSSCs) due to their large effective surface area available for adsorption of dye molecules, which enhances absorption of incident light for improved power conversion efficiency(Wolcott et al. 2009; Dhas et al. 2008; Shet et al. 2013).

Transition-metal oxides are promising candidates for PEC solar cell applications. However, to date, only TiO<sub>2</sub> has received extensive attention (Lu et al. 2011; Srivastava and Bahadur, 2012). ZnO has similar bandgap and bandedge positions compared to TiO<sub>2</sub>(Shet et al. 2013; Lu et al. 2011). Furthermore, ZnO has a direct bandgap and higher electron mobility than TiO<sub>2</sub> (Hardin et al. 2012); as such, ZnO is expected to be an even better candidate for PEC cell applications (Kuang et al. 2006). The bandgap of ZnO (about 3.37 eV) is too large to effectively absorb visible light, since the solar spectrum has maximum intensity at about 2.7 eV (Grätzel, 2001; Sekar and Gehlot,

2010; Argazzi et al. 2004; Nazeeruddin et al. 2006). It is therefore imperative to reduce the bandgap of ZnO for better PEC performance. Doping has been one of the most efficient methods to reduce the bandgap of ZnO. It has been reported that Al-doping can successfully narrow the bandgap of ZnO and push the photoresponse in the long-wavelength region (Shet et al. 2013; Mayo et al. 2006).

Ruthenium based dyes are the most widely studied and the best performing sensitizers for DSSC application due to the presence of one or more anchoring groups (carboxylic or phosphonic acid) as a peripheral substituent or prominent polypyridyl derivatives. However, one of the important factors in the choice of dyes is the cost. Because Ru is a rare metal with very low annual yield, metal-free-organic dyes have been preferred and a wide variety of pure organic dyes have been investigated (Mayo et al. 2006; Grätzel, 2004; Chen et al. 2009; Jiang et al. 2006), which include novel compounds such as phthalocyanines, hemicyanine, polyenes, mercurochrome (Ito et al. 2004), coumarins, Rose Bengal, rhodamine 6G and indoline(Shet et al. 2013; Kuang et al. 2006;Jiang et al. 2006; Souad et al. 2013; Raidou et al. 2010; Taya et al. 2013; Chu et al. 2011). With further efforts to search for newer dyes, natural dyes from plants, are recently been discovered as organic dyes whose performance are attractive (Zhang et al. 2009). Many organic sensitizers including plant dye has been investigated; Souad et al reported a  $I_{sc}$  of 0.93 mAcm<sup>-2</sup>,  $V_{oc}$  of 394 mV and a conversion efficiency,  $\eta$  of 1.5 % for Sumac(a flowering plant)(Souad et al. 2013). Roy et al. also reported DSSC performance of Rose Bengal dye as sensitizer with  $I_{sc}$  and  $V_{oc}$  of 3.22 mAcm<sup>-2</sup> and 0.89 V, respectively resulting to  $\eta$  of 2.09 % (Roy et al. 2008). Hara et al. reported a  $I_{sc}$  of 14.0mAcm<sup>-2</sup>,  $V_{oc}$  of 0.60 V, a  $\eta$  of 6.0 % and fill factor of 0.71 for coumarin dye on nanocrystalline TiO<sub>2</sub>, the highest performance among DSSCs based on organic-dye as photosensitizers (Hara et al. 2003).

Organic dyes, especially natural dyes (from plants) can replace synthetic dyes since they can be easily extracted from fruits, vegetable and flowers with simple and direct chemical procedures, whereas the former normally requires many steps procedures, organic solvents and purification procedures (Chu et al. 2011; Zhang et al. 2009; Roy et al. 2008; Hara et al. 2003). The pigments are present in the different part of the plant including flowers petals, fruits, leaves, stems and roots.

A natural dye extracted from *Indigofera arrecta* (Beba, a herbicious plant from the Guinea savannah region of Benue State, Nigeria) is extensively used for dying locally woven textile materials. This dye has never been investigated for its chemical structure and DSSC applications however; it shows high potential as an efficient photosensitizer in DSSCs. The current work investigates the DSSC performance of a natural dye extracted from *Indigofera arrecta* plant as sensitizers of nanocrystalline AZO thin film electrodes in acetonitrile. Most semiconductor thin film electrodes are found to be fairly stable in acetonitrile as medium of electrolyte under cell operating conditions(Sarto et al. 2004).

#### MATERIALS AND METHODS

#### 2.1. Materials

 $Zn(NO_3)_2.6H_2O$  (sd fine chemicals) was used as the source of  $Zn^+$ ,  $Al(NO_3)_3.9H_2O$  (Lobo Chemie-India) as the source of  $Al^{3+}$ . NH<sub>3</sub> solution (28 %) (Thomas Baker) was the complexing agent, acetonitrile (SDFCL-India) was used as the medium of electrolyte. KI (Romaali-India) and I (Lobachemie) dissolved in acetonitrile (SDFCL-India) were used as electrolyte and redox agent, respectively. Fresh leaves of *Indigofera arrecta* plant were obtained from its growth environment, dried and crushed into fine powder. All chemicals were used as received, without any further purification.

#### 2.2. Methods

AZO thin films were synthesized by chemical bath deposition technique. An aqueous solution of 0.1 M  $Zn(NO_3)_2.6H_2O$  was prepared, to this solution, aluminium nitrate  $Al(NO_3)_3.9H_2O$  was added. The Al in the solution was varied from 1 to 5 at. %. Aqueous NH<sub>3</sub> solution (28 %)was then added under constant stirring at room temperature. A white precipitate of Al-Zn(OH)<sub>2</sub> was initially observed, which subsequently dissolved back into the solution upon further addition of NH<sub>3</sub>solution. The solution was maintained at pH $\approx$ 11.5. Ultrasonically cleaned microscope glass slide and stainless steel substrates were immersed vertically in the solution using a bakelite holder and the bath temperature was maintained at 353 K. The substrates coated with AZO thin film were removed after5 h, washed with double distilled water dried in air and preserved in the vacuum desiccator. Further, as-deposited films were air annealed at 673 K for 2 h.

Fresh leaves of *Indigofera arrecta* plant were dried in an airy room shielded from direct sun rays until they were completely dried. The dried leaves were crushed into fine powder and an appropriate quantity was heated in a beaker containing acetonitrile at a temperature of 313 K for 5 h and then filtered using WHATMAN filter paper to obtain a fine greenish dye solution. The AZO thin film electrodes were immersed in the dye solution for about 12 h to fix the

dye onto their surfaces. After dye adsorption, the colour of the films was changed to dark green. The electrodes were rinsed in double distilled water to remove the loosely adsorbed dye molecules and finally dried in air for use. The dye was characterized for optical absorption.

#### 2.3. Apparatus and instruments

Unless otherwise stated, all DSSC measurements were carried out in a two-electrode, single compartment cell. A platinum wire was used as counter electrode and the *Indigofera arrecta* dye-sensitized AZO electrode was used as the photoelectrode.

A potentiostat was used for all current-potential measurements. For DSSC measurements, 80W xenon arc lamp was used as the source of white light to illuminate the semiconductor photoelectrode area of 1 cm<sup>2</sup>. Optical properties of the synthesized AZO thin films and the absorption spectrum of the dye in acetonitrile solution were recorded with a Shimadzu, UV-1800spectrophotometer. Structural properties of AZO thin films were studied using Philips PW 1830 X-ray diffractometer with CuKaradiation ( $\lambda = 1.5406$  Å) in the range between 20 – 80° in 20. Surface morphology was studied with scanning electron microscope (SEM) (using JOEL JSM-6360).

#### **RESULTS AND DISCUSSION**

## 3.1. Structural characterizations of ZnO thin films

Fig. 1depicts the XRD micrographs of the AZO thin films annealed at 673 K. It was observed that all the film samples were polycrystalline with hexagonal wurtzite structure with lattice constants a=3.24982 Å and c=5.20661Å corresponding to those of the ZnO patterns from the JCPDS data card (Powder Diffraction File, Card no: 00-036-1451).From XRD patterns, a strong preferential growth of high intensity in the (002) crystal plane was observed for the undoped ZnO and AZO film with2 at. % Al concentration, which is the most dense plane in wurtzite ZnO, however, for 1 and 5 at. % Al concentrations the intensity was reduced (Fernando and Sendeera, 2008; Hao et al. 2000; Mishra et al. 2009; Tyona et al. 2013). After annealing at 673 K, the Zn(OH)<sub>2</sub>was converted into ZnO through the following reactions (Bahadur and Srivastava, 2003; Chow et al. 2013; Shinde et al. 2005).

$$Zn(OH)_{2} \rightarrow [Zn^{2+} + 2(O^{2-} + H^{+})]^{Solid} \xrightarrow{\Delta} [Zn^{2+} + O^{2-}] + [O^{2-} + 2H^{+}] \rightarrow$$

$$[ZnO]^{Solid} + H_{2}O^{Gas} \qquad (1)$$



Fig. 1. XRD micrographs of AZO with different Al dopings: (a) undoped ZnO (b) 1 at. % (c) 2 at. %. and (d) 5 at. %

The  $H_2O$  vapours and other impurities in vapour form are released during annealing. For AZO films, the intensities of the (002) plane however, remained the same after heat treatment except for 2 at. % Al concentration where a slight increase was observed (as-deposited not shown here).

The intensity of the peak corresponding to ZnO (002) was observed to decrease upon incorporation of Al into ZnO (ie Al/Zn of 1 at. %) and after Al concentration was increased beyond 2 at. %. However, it increased sharply when the Al content was increased from 1 at. % to 2 at. % as revealed in Fig. 1. This indicated that the incorporation of Al impurities into the ZnO lattice induces crystallographic defects and hence reduced the crystallinity of the film. Increasing the Al concentration to 2 at. % (optimum concentration) also increases carrier concentration and mobility in the conduction band of the semiconductor thereby reducing the amount of crystallographic defects in the film. This result suggests that the crystallinity of the film in the ZnO (002) plane at this concentration of Al would improve significantly as depicted in Fig. 1c(Drici et al. 2004; Yao et al. 2010; Lee et al. 2010). Further as the Al concentration that there is more compressive strain resides in the films at higher doping level(Yao et al. 2010;Lee et al. 2010). Additionally, according to Barna and Adamik structure zone model for polycrystalline metallic films(Yao et al. 2010), as the impurities content increased, more impurities segregation occurred at the grain boundaries of the film which result in shrinkage in grains size(Yao et al. 2010) which is similar to the case observed here.

Another interesting observation here is the shift in angular peak position (2 $\theta$ ) corresponding to the (002) upon incorporation of Al impurities in the ZnO. It was clearly noticed that diffraction peak shift of 0.656° in 2 $\theta$  towards the higher angle occurred for all Al-doped films. This would be assigned to the difference in ionic radii of Zn<sup>2+</sup> and Al<sup>3+</sup> (which is higher for Zn<sup>2+</sup> as compared to Al<sup>3+</sup>)such that the length of the c-axis is expected to be shorter when Al atoms are substituted into Zn sites in the crystal lattice (Drici et al. 2004; Yao et al. 2010).

The mean crystallite size of the AZO thin films along the plane of most preferred growth (002) was calculated on the basis of full width at half maxima (FWHM) using Scherrer's formula(Bahadur and Srivastava, 2003;Chow et al. 2013):

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

where  $\lambda$ ,  $\beta$ , and  $\theta$  are the X-ray wavelength ( $\lambda = 1.54056$  Å), full width at half maximum (FWHM) and diffraction peak angle, respectively. The estimated crystallite sizes showed that the mean crystallite size of undoped ZnO film increased from 28 to 29 nm for AZO as depicted in Table 1.

% Doping of Al	Mean crystallite size (nm)
0	28
1	12
2	29
5	14

#### 3.2. Surface characterizations of ZnO thin films

The surface morphology of AZO thin films was studied using scanning electron microscope (SEM) images (using JOEL JSM-6360).Fig. 2depicts SEM micrographs of AZO thin films (as-deposited and annealed)with different Al concentration (1, 2 and 5 at. %) at constant substrate temperature. These SEM micrographs confirmed that the surface morphology of the films was affected by concentration of the dopant. The porosity of the films decreases upon introduction of Al impurities as was suggested by XRD study. This behaviour could be assigned to the difference between the ionic radius of Zn and the doping elements, Al (Musat et al. 2004;Shrestha et a. 2010).Further, with increasing Al concentration (up to an optimum concentration of 2 at. %), the microstructures of the film became denser as in Fig. 2d.

The SEM micrograph of the as-deposited AZO (1 at. %) film as depicted in Fig. 2 (a) showed fibrous surface morphology with interconnected and well-defined nanoflakes grown randomly on the substrate, constitutes thin solid films of Al-Zn(OH)<sub>2</sub>. Each nanoflake is crystalline and indexed to hexagonal crystal structure. The average thickness of the flakes was of the order of  $\approx$  60 nm. After annealing at 673 K, the hydroxide phases in the nanoflakes were converted to pure AZO with fibrous nanodendrites morphology of average rod diameter of  $\approx$  40 nm, leading to large surface area as depicted in (b).The compression in size as earlier mentioned, may be due to release of H<sub>2</sub>O vapour by the reaction explained in Eqn. 1. Such novel morphology may find applications in dye sensitized solar cells (DSSC), gas sensors and super capacitors(Hsu and Chen, 2012).



Fig. 2. SEM micrographs of AZO thin films with different Al dopings (a, b) 1 at. %, as-deposited and annealed (c, d) 2 at. %, as-deposited and annealed (e, f) 5 at. %, as-deposited and annealed

Fig. 2 (c and d) shows the SEM micrographs of as-deposited and annealed AZO with Al: ZnO of 2 at. %. The asdeposited film samples are identified with dense nanodendrite morphology of varying rod sizes with average rod diameter of 70 nm and high porosity as well as high surface roughness. On post annealing treatment at 673 K, the fibrous, nanodendrites morphology of varying rod sizes were transformed to fibrous nanodendrites of well-defined and uniform rod sizes (rod diameter of  $\approx$  50 nm) as depicted in (d), this kind of morphology is very suitable for DSSC application.

Fig. 2 (e) depicts SEM micrographs of as-deposited AZO with Al concentration of 5 at. %. Dense and randomly oriented nanorods of average diameter 65 nm were observed. After post annealing treatment at 673 K, dense, uniform and randomly oriented nanorods of diameter 42 nm, with fine structures were obtained as in (f). These observations agree with that observed by Shrestha et al. using sol-gel synthesis of AZO thin films (Jayaprakashan and Hodes, 2003; Mondal et al. 2013).

## 3.3. Optical characterization of AZO thin films

Actual information about optical properties of semiconductors is essential for the design and analysis of various optical and optoelectronic devices including many other applications. The absorption and transmittance spectraof AZO thin films were studied at room temperature in the wave length range from 300 to 800 nm. Air annealing of the AZO thin films converts any hydroxide to oxide and this explains the effect of annealing on optical absorption (Lee et al. 2010; Musat et al. 2004; Shrestha et al. 2010; Hsu and Chen, 2012; Burstein, 19540).

Fig. 3, illustrates the absorption spectra of Al-doped ZnO thin films for various Al concentrations. The absorption spectra (Fig. 3) revealed that all AZO films exhibited low absorbance in the visible region (from 400 nm) as compared to undoped ZnO especially for the sample with Al: ZnO, 1 at. %. However, the absorption edge for AZO films with 2 and 5 at. % Al concentration were red-shifted (430 and 450 nm, respectively). This could be attributed to the enhancement in optical properties induced by Al doping(Burstein, 19540; Moss, 1954; Cebulla et al. 1998).



Fig. 3. Absorption spectra of AZO thin film for different Al concentrations: (a) 0 at. % (b) 1 at. % (c) 2 at. % and (d) 5 at. %

Fig. 4, depicts the plot of  $(\alpha hv)^2$  as a function of hv from which optical energy band gaps (E<sub>g</sub>) of the films were estimated using Tuac's relationship between the absorption coefficient,  $\alpha$ , and the photon energy, hv (Lee et al. 2010):

$$\alpha = \frac{\alpha_o (h\upsilon - E_g)^n}{h\upsilon}$$
(3)

where,  $\alpha_o$  is a constant,  $E_g$  is the optical energy band gap and n is a constant which depends on the probability of transition (it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition, respectively). The estimated  $E_g$  values of AZO thin film are presented in Table 2. The optical band gap shows a marginal increase for 2 and 5 at. % AZO films though more pronounced for 2 at. % as compared to undoped ZnO. For undoped ZnO, the band gap is 3.12 eV and for 2 and 5 at. % AZO, it increases to 3.15 and 3.10 eV, respectively. Such widening of optical energy band gap with Al



Fig. 4. Optical band gap of AZO thin film for different Al concentrations (a) 0 at. % (b) 1 at. % (c) 2 at. % (d) 5 at. %

doping have been described by Burstein–Moss effect(Shrestha et al. 2010; Hsu and Chen, 2012; Jayaprakashan and Hodes, 2003; Mondal et al. 2013; Burstein, 1954). Burstein-moss pointed out that an increase in the Fermi level in the conduction band ofdegenerate semiconductors leads to widening of theenergy band (blue shift)(Shrestha et al. 2010; Hsu and Chen, 2012;Burstein, 19540; Moss, 1954; Cebulla et al. 1998; Lin et al. 2005; El Manouni et al. 2006).Enhancement of band gap also ensures the successful doping of aluminium in the ZnO thin films(Mondal et al. 2013; Burstein, 1954; Moss, 1954; Cebulla et al. 1998).

On the other hand, it was observed that a decrease in band gap occurs for 1 at. % AZO film. Such unusual red-shift of fundamental absorption edge has been reported by Mohanty et al (Mohanty et al. 2009) and was explained in terms of stress relaxation mechanism. The reduction in slope of the linear portion of the plot observed in the present work suggests introduction of defect states within the band gap. Thus we interpret this shift due to merging of impurity band into the conduction band, thereby shrinking the band gap(Bhattacharya and Datta, 2005; Nogami et al. 2004; Kim and Honma, 2004). Formation of such impurity band giving rise to new donor electronic states just below the conduction band is possible and this arises due to hybridization between states of the ZnO matrix and of the Al dopant (Musat et al. 2004; Moss, 1954; Cebulla et al. 1998). It seems that such formation of donor levels compensates the Burstein-Moss effect and results in the narrowing of the effective band gap of AZO. The reduction of stress is due to enhanced thickness (Moss, 1954; Cebulla et al. 1998; Lin et al. 2005; El Manouni et al. 2006) of AZO films as compared to undoped ZnO may also have some contribution to the observed red-shift(Musat et al. 2004). Therefore the optical band gap of the AZO makes a peak increase at Al:ZnO of 2 at. % which may obvious be the optimum doping concentration for AZO.

Table 2. Estimated values of energy band gap and optical transmittance for AZO thin films for different Al concentrations

% Al doping	Energy band gap (eV)	Transmittance (%)
0	3.12	90
1	2.80	72
2	3.15	88
5	3.10	42

The transmittance spectra, Fig. 5 depict the variation of optical transmittance of undoped (as reference) and Aldoped ZnO films on microscope glass slide substrate in the visible range. The doping effect of Al on the transparency and homogeneity of the AZO prepared samples was evaluated and depicted in Fig. 5. Regardless of the Al concentration, all films are highly transparent in the visible region(400-800 nm) (Lee et al. 2010). The transmittance of Al-doped films showed moderately high values in the range from42 to 90 % in the visible range as shown in Table 2 and Fig. 5. The optical transmittance is found to decrease significantly at higher doping concentration (undoped ZnO film  $\approx$  90 %) owing to the segregated Al<sub>2</sub>O<sub>3</sub> and also due to decrease in the crystalline quality of the Al-doped films. The effect of Al concentration in AZO thin films on transmittance is shown by the inset of Fig. 5.



Fig. 5. Transmittance of AZO thin films for different Al concentrations (a) 0 at. % (b) 1 at. % (c) 2 at. % (d) 5 at. %

3.4. Optical property of Indigofera arrecta plant dye

The absorption spectra of *Indigofera arrecta* plant dye extracted in acetonitrile is shown in Fig. 6 along with that of unsensitized AZO thin film for comparison (only 2 at %). It is clear that the dye shows very good light absorption across the spectrum from UV to visible light in the range of 300-750nm wavelength with almost constant absorption peak across the range. Since *Indigofera arrecta* plant dye absorbs light of appropriate wave length, it can be used as photosensitizer for wide-band gap semiconductors, such as AZO ( $E_g$ = 3.16 eV), which cannot solely absorb reasonably in the visible light spectrum as shown in Fig. 6.



Fig. 6.Absorption spectrum of Indigofera arrecta plant dye in acetonitrile

#### 4. Photoelectrochemical studies

#### 4.1. Current-potential (I-V) curves

To investigate the photoelectrochemical activities of the synthesized AZO thin film electrodes in the present work, all experiments were performed in a single compartment cellinpolyiodide solution as the electrolyte. Photoelectrode (AZO thin film) area of 1 cm<sup>2</sup> was illuminated with an input power ( $P_{in}$ ) of 80 mW/cm<sup>2</sup> from a xenon arc lamp. The PEC solar cell fabricated in this work is depicted in Fig. 7.The I-V curves of AZO DSSCs with different Al contents (1, 2 and 5 at. %), sensitized by *indigifera arrecta* plant dye are depicted in Fig. 8. A careful perusal of these curves shows that in the dark, the current obtained at each AZO electrode was not zero however, showed insignificantly low values. The measurement of the dark current greater than zero here may be ascribed to the fact that the cell might be partially illuminated by the background light in the experimental room. Furthermore, when the electrodes were illuminated with white light, all photoelectrodes showed significantly high photocurrent densities though; higher photocurrent density was recorded for the AZO sample with Al: Zn of 2 at. %. These currents were comparatively higher than that recorded for undoped ZnO sample (as shown in the inset of Fig. 8a, 0.29 mA/cm<sup>2</sup>) under the same conditions. This confirmed that AZO semiconductor materials are better candidates for PEC solar cell application (Bhattacharya and Datta, 2005).



Fig. 7. DSSC using Indigofera arrecta dye-sensitized AZO photoelectrode

These increase in photocurrent densities of the electrodes upon dye-sensitization can be assigned exclusively to charge carriers injection by photoexcited dye molecules alongside the valence electrons excited by the white light which increases total charge carriers and hence higher photocurrent as observed (Fernando and Sendeera, 2008). This was in line with the expectation since white light consist of photons of energy  $hv \ge E_g$  of ZnO hence, can excite the electrons from the valence band to conduction band of the semiconductor to produce photocurrent(Taya et al. 2013; Fernando and Sendeera, 2008).

Table 3. PEC solar cell parameters of AZO thin f	ilm electrodes sensitized by	Indigofera arrecta plant dye
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AZO Electrodes with % Al	Photocurrent Density (I <sub>sc</sub> ) [mA/cm <sup>2</sup> ]	Photovoltage (Voc) [mV]	I <sub>max</sub> (mA/cm <sup>2</sup> )	V <sub>max</sub> (mV)
0	0.29	595.0	0.18	421.0
1	1.27	596.0	0.74	428.0
2	1.35	643.0	0.93	438.0
5	0.84	664.0	0.55	425.0

It was further observed that the photocurrent density increased with Al concentration, with the highest current recorded for Al: Zn of 2 at. %. Further increase in Al concentration beyond 2 at. %, current decreased rapidly; thus confirming the earlier assertion that 2 at. % Al concentration is the optimum doping level for AZO for PEC solar cell application. This enhanced performance at optimal doping concentration is probably due to optimal carrier concentration reached in the semiconductor which facilitates fast electron transport and consequent suppression of charge recombination activities (Bhattacharya and Datta, 2005).



Fig. 8.Current-potential curves for dye-sensitized nanocrystalline AZO electrodes with different Al dopings (a) 1 at. % (b) 2 at. % and (c) 5 at. %

*Indigofera arrecta* plant dye can effectively sensitize AZO because of their energy band gaps (Fernando and Sendeera, 2008) (1.91 eV estimated for indigofera and 2.80, 3.15 and 3.10 eV for AZO with Al: Zn of 1, 2 and 5 at. %).When *Indigofera arrecta* dye molecules absorb photons with energies greater than 1.91 eV, the electrons in the excited states of *Indigofera arrecta* plant dye can be quickly injected into the conduction bands of AZO nanostructures (Wolcott et al. 2009; Roy et al. 2008). This shows improvement in performance of the test dye on nanocrystalline AZO electrodes. The estimated photocurrent densities and photovoltages are presented in Table 3.

## 4.2. Electrochemical impedance spectroscopy (EIS) study

Electrochemical Impedance Spectroscopy (EIS) is a semi quantitative technique and is versatile for investigating the dynamics of the bound or mobile charges in the bulk or interfacial region of a PEC solar cell system (Mishra et al. 2009). In EIS measurements, the potential applied to the solar cell is perturbed by a small amplitude sinusoidal modulation and the resulting sinusoidal current response is measured as a function of the modulation frequency systems(Mishra et al. 2009). It is one of the most useful experimental techniques as it permits a simultaneous characterization of the different processes taking place in the cell; that is, at the semiconductor, in the electrolyte and at the counter-electrode (Kim and Honma, 2004; Rekha et al. 2013; Sekar and Ramasamy, 2013). The electrical current response is measured when a certain sinusoidal voltage is applied to the system. This current response will be a sinusoid at the same frequency, but shifted in phase (Kim and Honma, 2004).

EIS of AZO annealed at 673 K was carried out using a Frequency Response Analyzer coupled to a Potentiostat in a two-electrode mode (Yao et al. 2010; Kim and Honma, 2004). All the processes taking place in the entire cell were evaluated in the dark condition. The EIS data are commonly analysed by fitting into an equivalent electrical circuit model Rekha et al. 2013; Sekar and Ramasamy, 2013).

Fig. 9 (a-c), depicts the impedance spectra for *Indigofera arrecta* plant dye-sensitized AZO DSSCs with different Al contents(1, 2 and 5 at. %) measured at various bias potentials: 0.596, 0.643 and 0.664 V. In Fig. 9 ai and 9 ci, for Al contents of 1 and 5 at. %, the Nyquist plots showed relatively high impedance characteristics, contributed mainly by the photoelectrode and the ionic solution (ie the electrolyte). The charge transfer process at the platinum counter-electrode/electrolyte/photoelectrode interface, observed in the intermediate frequency range are low in each case due to relatively high charge transfer resistance of the electrolyte as observed in (aii) and (cii) (curve a, in each case)andTables 4 a and c, respectively.

The electron transport resistances  $R_t$  in the mesoporous layers (photoelectrodes) are low in these cases, due to low series resistances of the *Indigofera arrecta* dye-sensitized electrodes. Warburg impedance is observed in the high frequency range in the case of AZO of 1 at. % electrode as depicted in (aiii) which accounts for decrease in diffusion impedance of redox species in the electrolytethus, enhancing moderately high photocurrent density in the cell. Similar case is observed for AZO of 5 at. % electrode, where the low diffusion impedance of redox species in the electrolyte is represented by the CPE of low impedance(Rodríguez; 2011;Patil and Singh, 2011).





Fig. 9.Impedance spectra of *Indigofera arrecta* plant dye-sensitized AZO DSSCs with different Al contents: (a) 1 at. % (b) 2 at. % (c) 5 at. % obtained in dark for bias potentials of 0.596, 0.643 and 0.664 V

In Fig. 9b, for Al content of 2 at. %, the cell exhibits much lower impedance as compared to 1 and 5 at. % doping levels which results from overall decrease in cell impedance initiated by the CPE (Q as in biii) and the low ohmic resistances which lowers the charge transfer resistance and the diffusion impedance of redox species in the electrolyte system (Rodríguez; 2011; Patil and Singh, 2011). The zero series resistance of the photoelectrode also observed in (bi) reduces electron recombination processes in the photoelectrode and facilitate fast dye molecules injection and transfer thus, enhancing higher PEC cell performance as noted in Table 3 (Patil and Singh, 2011; Bisqquert and Vikhrenko, 2004; Zaban et al. 2010; Lopes et al. 2010; Jeong et al. 2003). Values of cell impedance elements estimated from the electrical analogs (circuit models) are shown in Tables 4 a-c, which are used to fit the EIS experimental data.

Table 4.Equivalent electrical circuit analog data estimated from the electrochemical cell measurement of *Indigofera arrecta* plant dyesensitized AZO (with different Cu contents) PEC solar cell measured in dark condition in a 2-electrode configuration at biaspotential of 0.596, 0.643 and 0.664 V (a) 1 at. % (b) 3 at. % and (c) 5 at. %

(a)			
Parameter	Value		
Rs	15.3622		
Rp	0.000911		
W	6.45E-05		
Cdl	2.22E-16		
(D)			
Parameter	Value		
Parameter Qy1	<b>Value</b> 4.49E-10		
Parameter Qy1 Qa1	Value 4.49E-10 1.400136		
Parameter Qy1 Qa1 R1	Value 4.49E-10 1.400136 767.9184		
Parameter Qy1 Qa1 R1 R2	Value 4.49E-10 1.400136 767.9184 51.70941		
Parameter Qy1 Qa1 R1 R2 Qy2	Value 4.49E-10 1.400136 767.9184 51.70941 7.17E-05		
Parameter Qy1 Qa1 R1 R2 Qy2 Qa2	Value 4.49E-10 1.400136 767.9184 51.70941 7.17E-05 0.752214		

(c)

Parameter	Value
Rs	33.815
R1	4720.164
Qy1	2.12E-05
Qa1	0.71399
R2	4720.118
Qy2	2.22E-16
Qa2	0.768824

#### 4.3. Power Conversion Efficiency $(\eta)$ and Fill Factor (FF)

Energy or power conversion efficiency ( $\eta$ ) of solar cell is the percentage of power converted from absorbed light to electrical energy and collected, when a solar cell is connected to an electrical circuit. The power outputs of the dye-sensitized AZO thin films PEC solar cells in the current work were determined in the dark and under illumination with an input power ( $P_{in}$ ), of 80 mW/cm<sup>2</sup>.

All the currents and potentials ( $I_{sc}$ ,  $V_{oc}$ ,  $I_{max}$  and  $V_{max}$ ) measured for the AZO thin film electrodes sensitized by *Indigofera arrecta* plant dye are shown in the I-V curve of Fig. 8 and the measured values are presented in Table 3, respectively. The light energy to electrical power conversion efficiency ( $\eta$ ) and fill factor (FF) were evaluated from the following Eqns (Lee et al. 2010):

$$\eta(\%) = \frac{I_{\max}(A/cm^2)V_{\max}(V)}{P_{in}(W/cm^2)} \times 100$$
(7)
$$I_{\min}(A/cm^2)V_{\max}(V)$$

$$FF = \frac{I_{\max}(A/cm^2)V_{\max}(V)}{I_{sc}(A/cm^2)V_{oc}(V)}$$
(8)

The estimated values of power conversion efficiencies and fill factors for all the ZnO film samples are presented in Table 5.

Table 5. Estimated values of power co	nversion efficiencies and fill fac	tors of <i>Indigofera arrecta</i> ]	plant dye-sensitized AZO PEC solar cells
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AZO Electrodes with % Cu	Efficiency (%)	Fill Factor (FF)
0	0.16	0.44
1	0.40	0.42
2	0.51	0.47
5	0.29	0.42

### CONCLUSION

A study of PEC solar cells of AZO thin film electrodes sensitized with a natural dye obtained from *Indigofera* arrecta plant has been carried out. In the study, chemically synthesized AZO electrodes were found to possess fibrous nanostructures that well favoured DSSCs application. Optical studies carried out on the AZO thin films

indicate red shifts in their absorption edges up to 450 nm wavelength. Energy band gap was found to vary from 2.80 to 3.15 eV and high transmittance of up to 88 % was achieved. Further with the use of *Indigofera arrecta* plant dye on AZO electrode, the spectral response of the wide band gap AZO (3.15 eV) was extended well into the visible region. *Indigofera arrecta* plant dye was seen to anchor well on nanocrystalline AZO thin film electrode. The use of the dye on AZO electrode shows significant enhancement in DSSC properties of the semiconductor. Photocurrent density and photovoltage of 1.35 mA/cm<sup>2</sup> and 0.643 V were measured for optimum doping level of AZO (2 at. %) which yielded light to electrical energy and fill factor of 0.51 % and 0.47, respectively. EIS study of the DSSCs also confirms good performance. It is clear from this study that AZO semiconductor materials are better candidates for PEC solar cells application than undoped ZnO.

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