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Alkannatinctoria Barks as Organic Photo Sensitizers for Dye Sensitized TiO_2 Thin Film Solar Cells

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ABSTRACT

Nano structured TiO_2 thin film dye-sensitized solar cells have been fabricated using TiO_2photoelectrode sensitized using the extracts of Alkannatinctoria barks as organic sensitizers and their characteristics have been studied. The organic extracts having Alkannin pigment, which have hydroxyl and carboxylic groups in the molecule can attach effectively to the surface of TiO_2 film. The UV-Vis absorbance spectra of organic extract found to be maximum of 692 nm. The solar cell constructed using the Alkannatinctoria barks sensitized TiO_2 photo-electrode exhibited a short-circuit photocurrent of 6.08 E-5A and a power conversion efficiency of 0.0971%. Organic dye sensitized TiO_2 photo electrodes present the prospect to be used as an environment-friendly, low-cost alternative system.

Keywords: AlkannaTinctoria; Organic dye sensitized; Power conversion efficiency; TiO_2.

1. INTRODUCTION

Dye sensitized solar cells (DSSCs) have attracted considerable interest as a low cost photovoltaic technology for building integration and indoor application (Liska *et al.* 1988; O'Regan and Graetzel, 1991; Graetzel, 2005; Maldonado, 2007). Sensitization of wide band gap semiconductor electrodes with dyes absorbing visible light has been a topic of continuous interest since its theoretical and experimental foundation by Gerischer, Tributsch and Calvin in the early '70s (Gerischer, 1971; Keis, 1991). The limited light harvesting efficiency of a dye monolayer on a semiconductor monocrystal lead to the advent of porous films consisting of nanometer sized semiconductor nanoparticles TiO_2 (O'Regan and Graetzel, 1991), ZnO (Keis, 1999; Martinson *et al.* 2009), SnO_2 (Bauer *et al.* 2002; Chappel *et al.* 2002), Nb_2O_5 (Sayama *et al.* 1998) that allowed for a dramatic enhancement of the effective surface area, thus making light absorption efficient in a single dye monolayer adsorbed on each particle.

The basic events of semiconductor sensitization can be schematized as follows,

$$S + hn/\ S^* \qquad (1)$$

$$S^* + TiO_2\ /\ S+ + e(TiO_2) \qquad (2)$$

$$S+ + I/\ S + I \qquad (3)$$

A schematic picture of the processes, which are at the basis ofthe functioning of sandwich type solar devices, is shown in fig.1.

In equation (1) the sensitizer (S), upon photon absorption, is promotedto an electronically excited state (S*). If this state lies energeticallyabove the conduction band of the semiconductor, electron injection to the empty states of the semiconductor can occur ona very fast time scale, equation (2), successfully competing with the otherexcited state deactivation pathways (radiative and non radiative processes).

The oxidized sensitizer (S+) is then regenerated by a redox electrolyte (usually the I/I3couple) according to process equation (3), inorder to prevent electron recapture as the following process,

$$S+ + e(TiO_2)\ /S \qquad (4)$$

The I/I_3 system, dissolved in organic solvents, has been almost universally used as a charge carrier in dye sensitized photo electrochemical cells, since oxidation of iodide by the photo oxidized dye is usually fast and effectively competes with equation (4). Recently much attention has also been devoted to the development of alternative redox couples based on non corrosive transition metal complexes (Sapp *et al.* 2002). Generally, synthetic organic dyes (Yum *et al.* 2007; Campbell *et al.* 2007; Tian *et al.* 2009) and transition metal coordination compounds [mostly ruthenium (Nazeeruddin *et al.* 1993;

Nazeeruddin *et al.* 2001) and osmium (Kuciauskas *et al.* 2001, Argazzi *et al.* 2004; Altobello *et al.* 2005) polypyridil complexes have been used as effective sensitizers, since they couple broad and intense charge transfer bands to favourable ground and excited state energetics for the electron transfer reactions in equation (2) and (3). However, the preparation routes for metal complexes are often based on multi step procedures involving tedious and expensive chromatographic purification procedures. Thus, for both practical and fundamental reasons, some groups have investigated the possibility of achieving solar energy conversion exploiting nanocrystalline TiO_2 sensitization with natural pigments. In nature, fruit, vegetable, leaves, flowers and algae contain several dyes which can be easily extracted and employed in dyesensitized solar cells. For example, Tennakone *et al.* (1997) investigated the use of tannins and related phenolic substances extracted from black tea, nuts and pomegranate, as well anthocyanins from flowers and leaves. Dai and Rabani, (2001; 2002), Sarto Polo and Murakami Iha, (2006; 1936), Zhang (2008), Calogero and Bignozzi (2008) investigated anthocyanins and betalain pigments extracted from a variety of vegetable species typical of mediterranean, tropical and subtropical areas. Kay and Graetzel (1993) were probably the first to elucidate the photo electrochemical behaviour of natural chlorophylls as well as anthocyanin dyes from California blackberrie (Cherepy *et al.* 1997). In this work we report, extracts of *Alkannatinctoria* barks used as sensitizer for nanocrystalline TiO_2 thin film for DSSC construction and their structural and optical and IV characteristics were studied.

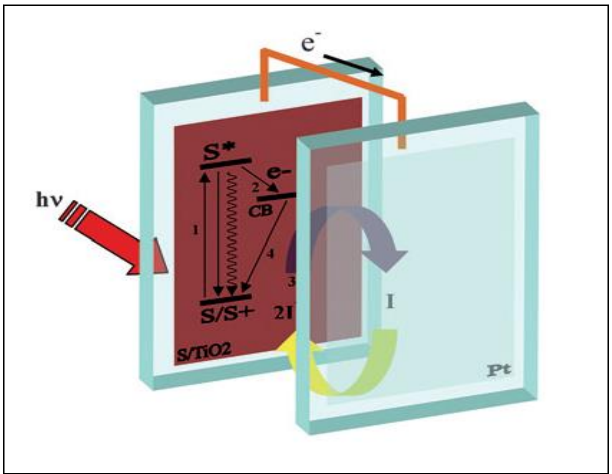

Fig. 1: Schematic representation of the working principle and assembly of a sandwich type cell

2. EXPERIMENTAL METHOD

The titania (TiO_2) nano powder was prepared using sol-gel and hydrothermal method. The precursor used for titania is Titanium tetra isopropoxide (TTIP) and the solvent was 2-propanal. The precursor TTIP of 7.7 mL is taken in a 250 mL beaker, later 105 mL of 2-propanal was added under stirring. The mixture was kept in stirring for one hour and later tiatanium tetra isopropoxide was added drop wise in continuous stirring until the solution mixture turns in to sol-gel homogenous state with moon stone yellow colour. The measured pH was 5.8 in sol-gel. Thus prepared sol-gel was transferred in to stirrer less stainless steel teflon coated autoclave and sealed with SS lid. The autoclave with sol-gel was aged in hot air oven at 120 °C for 24 hrs and later at elevated hydro thermal temperature of 150 °C for 48 hrs. The obtained white solids were centrifuged with deionised water at 4500 RPM for 15 min. The solid parts are dried in hot air oven for 12 hrs at 150 °C and motored to fine powder of titania (TiO_2).

Further the TiO_2 thin films were prepared in FTO substrates. The FTO substrates in 200 mm x 300 mm size and sheet resistance of 15 ohm per square were taken and washed in detergent, acetone and deionised water under ultrasonic bath. The washed substrates were dried and prepared for thin film coating. The sol-gel hydro thermally (Solvo thermal) prepared TiO_2 powder was mixed with surfactant binder Triton X100 in mortar pestle, until smooth paste formation. Then paste was applied on the FTO substrate, which was covered by scotch tape by four sides to form a slit opening of 1x1cm. The application of TiO_2 paste on the substrate was done using glass rod by doctor blade method to get even coating of TiO_2 on the FTO substrate.

For extraction of natural dyes from *Alkannatinctoria* the barks were taken and cut in to small pieces. The small pieces were soaked in 100 mL of ethanol and kept for 12 hrs in dark place. Then the residuals are filtered and washed with hexane for several times to remove oily substances in the filtrate. The pH measured was 5.1for the dye solution. This was used directly as dye solution for sensitizing TiO_2 thin films to act as photo anodes for the solar cell.

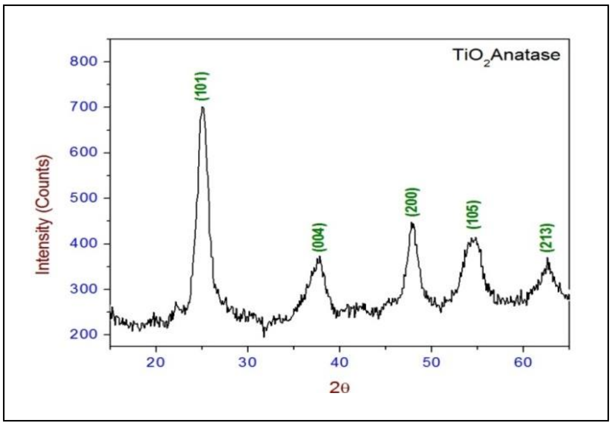

Fig. 2: X-ray diffraction patterns of as prepared TiO_2 thin film

Crystalline and phase analysis of the films were carried out by X-ray diffraction method (RigakuRint

2000 series). The optical properties of thin film and dye were studied using the absorbance spectra of UV-Vis spectroscopy (Jasco V-570). The surface morphology of the samples was studied using scanning electron microscopy. The J-V characteristics for the solar cell are studied using Keithley 2400 and solar simulator of AM1.5.The chemical composition of TiO_2 thin films and dye were studied using Fourier Transform Infra-red spectroscopy (Bruker).

3. RESULTS AND DISCUSSION

Fig. 2 shows the XRD patterns of the as-preparedTiO$_2$ samples. In the XRD pattern, all the reflections correspond to the tetragonal pure phase of anatase TiO_2 (JCPDS card No. 84-1286). The shape of the diffraction peaks indicates that the product is well crystallized. No impurity phase is observed in the XRD pattern. The results clearly show that the XRD pattern has relatively sharper and narrower high-intensity reflections and this is due to the good crystallinity observed in the film. The average crystallite size was calculated from the x-raydiffraction pattern using Scherer's formula (Vetrivel *et al.* 2014). The calculated average value of grain size is 6.470 nm. The calculated lattice to tetragonal cell are a =3.801 and c = 9.502. The obtained values are in good agreement with the standard card values and the previously reported data for anatase TiO_2 (Vetrivel *et al.* 2016).

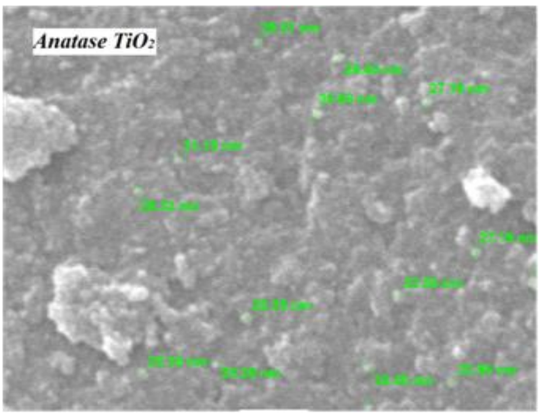

Fig. 3: SEM image of nanocrystalline TiO_2

The morphology of the synthesized product was examined by SEM images. Fig. 3 shows the SEM image of the synthesized anatase TiO_2 particles. The image clearly shows that the synthesized samples have nanoparticles with sphere-like structure with a diameter in the range of 20-35 nm.

Fig.4 shows the absorption region with the edge extending to 341.91 nm. The sphere-like structured nanoparticles with a rough surface morphology are responsible for reduced transmission and thereby higher absorption. The band gap energy could be estimated using the formula Eg=hc / λ, where h and c are the Planck's constant and velocity of light, respectively, and the calculated value is 3.6 eV. However, the obtained value is at the UV part of the solar spectrum, indicating that the synthesized structures have a very good application prospect in the field of photovoltaic conversion. Therefore, photoanodes were fabricated by coating TiO_2 paste as the bottom layer and prepareddye particles as the sensitizing layer to compare the sensitizing abilities.

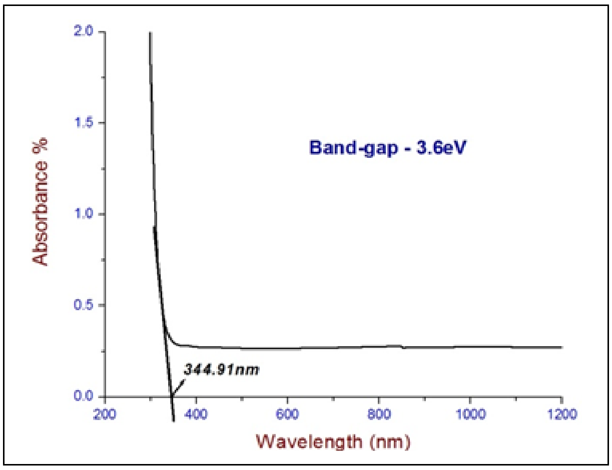

Fig. 4: UV-visabsorption spectra ofanatase TiO_2

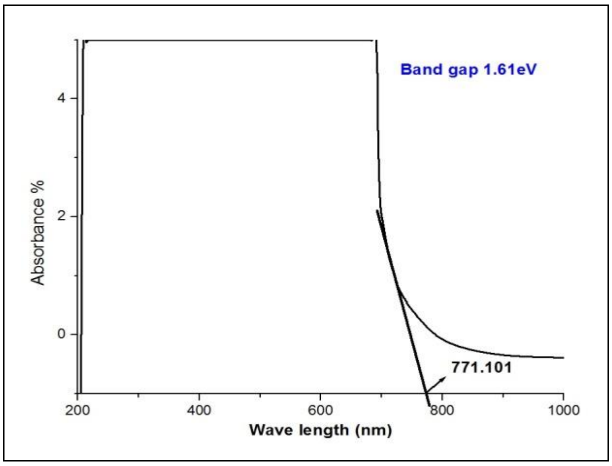

Fig. 5: UV-vis absorption spectra of *Alkannatinctoriadye*

The optical properties of the prepared dye have been evaluated by means of optical absorption spectroscopy. Fig.5 shows the broad absorption region with the edge extending to 771 nm. The band gap energy could be estimated using the formula E_g= hc⁄λ, where h and c are the Planck's constant and velocity of light, respectively, and the calculated value is 1.61 eV. However, the obtained value is at the red part of the solar spectrum, indicating that the dye structures have a very good application prospect in the field of photovoltaic conversion (Senthil *et al.* 2014).

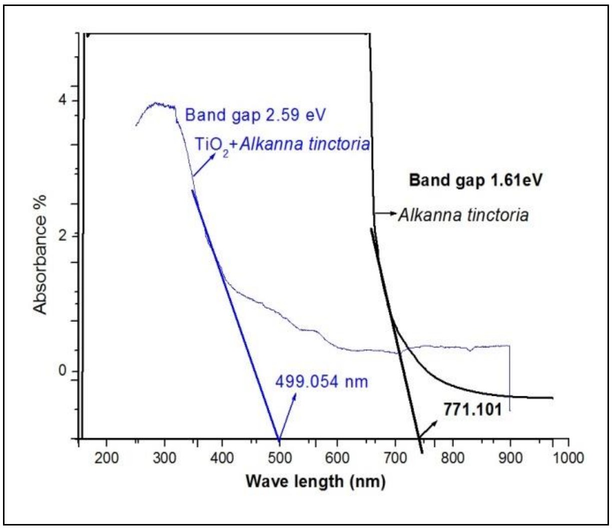

Fig. 6: Comparision of UV-vis absorption spectra of Alkanna tinctoria dye sensitized TiO2thin film and as prepared TiO_2 thin film

Fig. 6 shows the absorbance spectrum of TiO_2 and TiO_2 thinfilm sensitized with *Alkanna tinctoria*. The broad spectrum of *Alkanna tinctoria* from 400-700nm, which might indicate the extract contains chlorophyll mixture which shows an absorption peak in between 400-500 nm and 600-700 nm (Hernandez-Martınez *et al.* 2012) the extract also has spectrum between 476 and 545 nm and around 520 nm which could be associated with the presence of betalains (Al-Alwani *et al.* 2015) and anthocyanins (Kevin Gould and Winefield, 2009) respectively. Anthocyanin is the core component of some natural dyes and is often found in the fruits, flowers, and leaves of plants (Wongcharee *et al.* 2007). The spectrum of TiO_2 thin film sensitized with *Alkanna tinctoria* was less compared to original dye spectrum. This is due to the ratio of dye absorbance in TiO_2 thin film. The *Alkanna tinctoria* sensitized TiO_2 thin film shows broad spectrum till 500nm and little peak in around 550nm. This confirms betalains and anthocyanin presence in the sensitized TiO_2 thin film. The major compound present in the *Alkanna tinctoria* is Alkannin pigments, which is rich in corboxyl and hydroxyl groups. This corboxyl and hydroxyl will enable adherence of dye to TiO_2 molecules in thin film. The absorved band gap of dye is 1.61 eV and dye sensitized TiO_2 thin film is 2.59 eV. Whereas the band gap observed for TiO_2 thin film is 3.6 eV. This shows the sensitization of dye makes the TiO_2 thin film to open up few more area in the region of visible light spectrum. After dye absorption the absorbance band of TiO_2 is broadned and red shifted.

The I–V characteristics of TiO_2 nanocrystalline thin films sensitized with *Alkannatinctoria* dye is shown in Fig. 7. The solar cell sensitized with *Alkannatinctoria* dye extract exhibit a power conversion efficiency of 0.097 %, with a short circuit current density (Jsc) of 6.08E-5A/cm2, open circuit voltage (Voc) of 1.62E-1V and fill factor (FF) of 0.35. Based on investigation on the structure and properties of dye molecules, it was found that the *Alkannatinctoria* extract possesses photosensitization effect. This is due to the better interaction between the carbonyl and hydroxyl groups of anthocyanin molecule in dye extract and the TiO_2 film. Monzir Abdel-Latif*et al.* (2013) have prepared extracts from ten different plant seeds. *Alkannatinctoria* fabricated dye sensitized solar cells resulting in a power conversion efficiency of 0.02. The obtained power conversion efficiency for *Alkannatinctoria* barks extracts of 0.097 % is the best efficiency reported here for TiO_2 nanocrystalline thin film based dye sensitized solar cells.

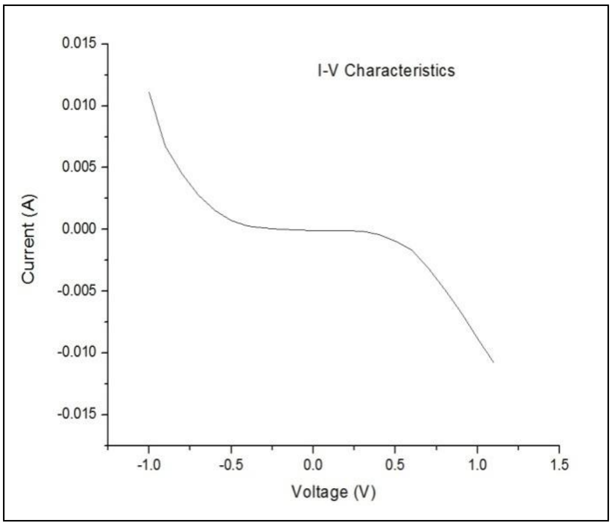

Fig. 7: I-V graph of Alkannatinctoriadye sensitized TiO_2 thin film solar cell.

5. CONCLUSION

The nanocrystalline TiO_2 thin films have been prepared by sol–gel, hydrothermaland doctor blade coatingmethod. X-ray diffraction analysis reveals that the TiO_2 nanocrystalline thin films exhibit anatase phase. The dye extracted from *Alkannatinctoria* barks strongly absorb visible light and have been found to be suitable for the use as sensitizer in solar cells. The efficiency of the fabricated dye sensitized solar cell using *Alkannatinctoria* barks extract is 0.097 %. The use of natural dyes in dye sensitized solar cells is of environmentally friendly, renewable, low cost and green source of energy.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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