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Synthesis and Characterization of *Eugenia jambolana* Dye Sensitized TiO_2 Thin Films†

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Modified chemical bath deposition method is adopted for the deposition of TiO_2 thin films. *Eugenia jambolana* is used as the natural dye sensitizer. Systematic study on the structural and optical properties of the as-deposited, annealed and dye-sensitized TiO_2 thin films is carried out. The material is crystallized in anatase phase of TiO_2. The pigment present in *Eugenia jambolana* is identified as cyanidin 3-O-glucoside. An enhancement in the optical absorption of the films is observed upon dye sensitization. Band gap of the dye sensitized TiO_2 films is in the range of 2.5 eV-3.6 eV. The material exhibited photoluminescence which may be ascribed to the recombination of electrons *via* self trapped excitons located or trapped in octahedral TiO_6.

Key Words: TiO_2, Dye Sensitization, *Eugenia jambolana*.

INTRODUCTION

Dye sensitized solar cell converts solar energy into electrical energy by employing a photo anode, which is usually a wide band gap semiconductor. The main component in the functioning of the cell is the sensitizer which enables the absorption of photons having much lower energy than the band gap of anode material. Dye sensitized solar cells have emerged as a cost effective counter part of solid state photovoltaic devices. The progress of such devices occurred with the development of nanostructured porous semiconductor films onto which light absorbing dye molecules are adsorbed[1-4]. The use of natural pigments as sensitizers for sensitized solar cells is very interesting because, on one hand they enhance the economical aspect and on the other, produce significant benefits from the environmental point of view[5]. The most investigated wide band gap semiconductor for dye sensitized solar cell is titanium dioxide which is a non-toxic and inexpensive material with appropriate photoelectrochemical properties for solar cell application[6]. The effect of several natural dye sensitizers on the performance of the dye sensitized solar cell based on TiO_2 is well explored. In the present work an attempt has been made analyse the effect of natural dye extracted from *Eugenia jambolana* on the characteristics of TiO_2 thin films.

EXPERIMENTAL

Modified chemical bath deposition method also known as successive ionic layer adsorption and reaction method has been adopted for the deposition of TiO_2 thin films. Titanium trichloride and ammonium hydroxide are used as the cationic and anionic precursors respectively for film deposition. Deionized water is used for rinsing the substrates between successive immersion in the cationic and anionic precursors. To study the effect of adsorption/reaction time on the properties of the TiO_2 films, samples are deposited at different adsorption/ reaction times while other deposition conditions are maintained as constant (Table-1). In a typical deposition, the substrate was immersed in aqueous $TiCl_3$ for 20 s when the Ti^+ ions adsorbed to the substrate surface followed by a rinsing in deionized water for 5 s.The substrate was then immersed in ammonium hydroxide solution for 40 s and during which OH^- ions react with the Ti^+ ions preadsorbed on the substrate to form TiO_2 layer. Finally the substrate was rinsed in deionized water for 5 s to remove the loosely bound ions. This process completes one successive ionic layer adsorption and reaction cycle. The cycle is repeated untill film with a reasonable thickness get deposited. The deposited films were annealed at 450 ºC for 5 h. The annealed TiO_2 thin films are used for dye sensitization. TiO_2 films deposited by successive ionic layer adsorption and reaction method are sensitized by the natural dye obtained from *Eugenia jambolana*.

Fruits of *Eugenia jambolana* are collected, shade dried and powdered. Ethanol is used as solvent for the extraction of natural dye. The material of the film is characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, UV-visible. spectroscopy, photoluminescence

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spectroscopy and the dye extract is characterized by FTIR and UV-visible spectroscopy.

TABLE-1
FILM DEPOSITION CONDITIONS

Concentration of precursors (vol. %)		Adsorption time (s)	Reaction time (s)	Rinsing time (s)	Thickness (µm)
$TiCl_3$	NH_3OH				
0.5	5	20	20	5	0.2101
0.5	5	40	20	5	0.4305
0.5	5	20	40	5	0.6536
0.5	5	30	60	5	1.3058

RESULTS AND DISCUSSION

The as-deposited TiO_2 films exhibited amorphous nature and the annealed ones are polycrystalline in nature. The prominent peaks observed in the X-ray diffraction pattern (Fig. 1) of the material are indexed to the anatase phase of TiO_2 (JCPDS card no: 89-4203). The film exhibited preferred orientation along (101) direction.

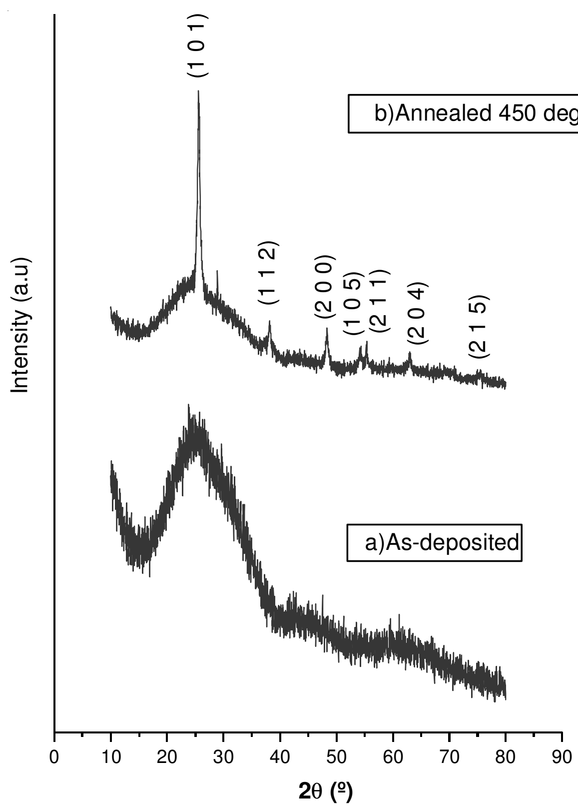

Fig. 1. XRD pattern of as-deposited and annealed TiO_2 thin films

The films are composed of fine grains and the scanning electron micrograph (Fig. 2) revealed the porous microstructure of the films. The elemental composition of TiO_2 films is analyzed by energy dispersive X-ray analysis (Fig. 3) and the composition of the films is found to match with the nominal stoichiometry.

The as-deposited film of thickness 0.2101 µm exhibited maximum transmittance of 68 % at 850 nm. Transmittance of the film decreased upon annealing (Fig. 4). Absorption coefficient of the films is of the order of 10^6 m^{-1}. Transmittance spectrum of the dye extract is shown in Fig. 5. The dye is

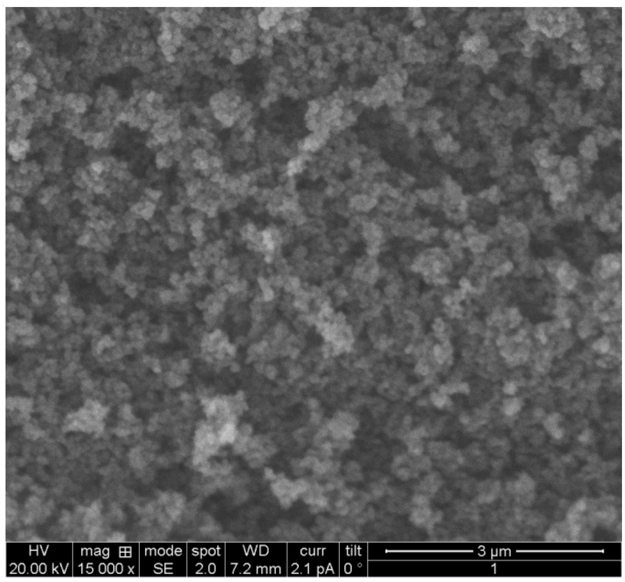

Fig. 2. Scanning electron micrograph of the film

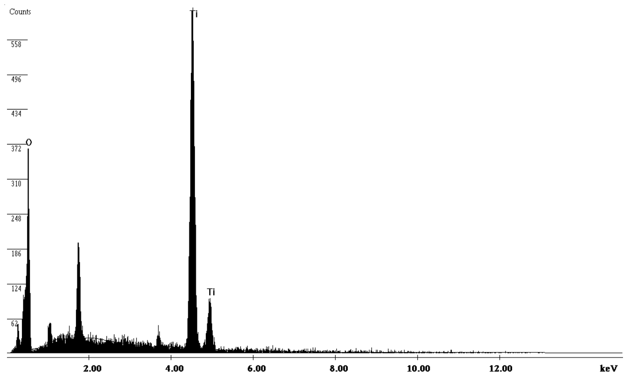

Fig. 3. EDAX spectrum of the TiO_2 thin films

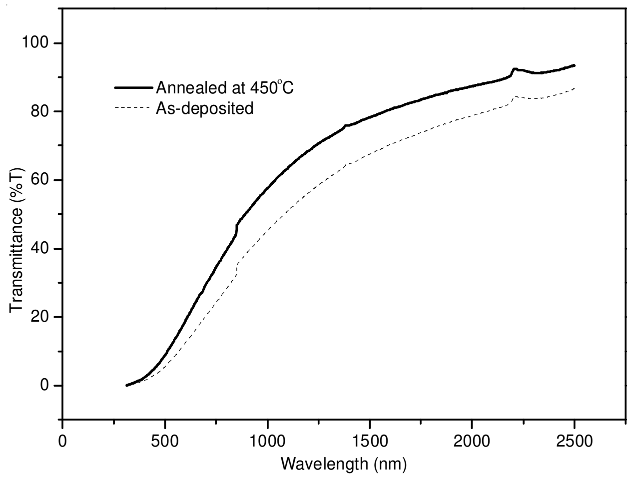

Fig. 4. Transmittance spectra of as-deposited and annealed thin films

highly absorbing in the visible region. FTIR analysis of the dye indicated the presence of anthocyanin pigment cyanidin-3-O-glucoside in the extract (Fig. 6, Table-2).

The sensitizaton of the film by the natural dye obtained from *Eugenia jambolana* is found to enhance the optical absorption of the material. The absorption coefficient of the film is increased by a factor of 1×10^6- 40×10^6 m^{-1} upon dye sensitizaton (Fig. 7).

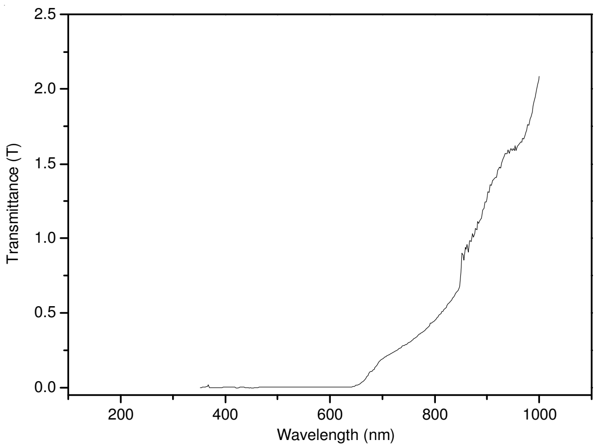

Fig. 5. Transmittance spectrum of the dye extract

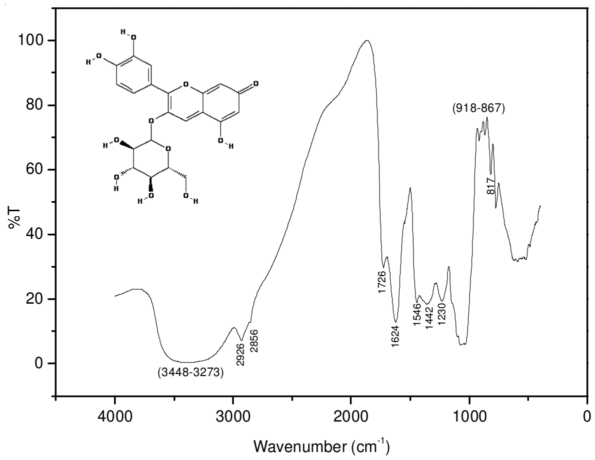

Fig. 6. FTIR spectrum of the dye extract (inset: molecular structure of cyanidin 3-O-glucoside)

TABLE-2 FUNCTIONAL GROUPS PRESENT IN *Eugenia jambolana*	
Wave number (cm^{-1})	Functional groups
3446-3273	O-H stretch
1726, 1624	C=O stretch
1549	C=O stretching vibration is conjugate
1359	OH in plane bending
918-817	β-Glycosidic linkage

Optical transition involved in the films are found to be direct and allowed. The band gap of as-deposited, annealed and dye sensitized films are given in Table-3. There is a red shift in the band gap of the films upon dye sensitization. And the band gap of the dye sensitized TiO_2 films is in the range of 3.3 eV-2.6 eV.

The material exhibited photoluminescence (2.98 eV and 1.84 eV) and according to the report of Senthil *et al.*[7] this is attributed to the recombination of electrons *via* self trapped excitons located or trapped in TiO_6 octahedral (Fig. 8).

Conclusion

TiO_2 thin films deposited by modified chemical bath deposition are amorphous in nature and crystallized in anatase upon annealing. The films are stoichiometric in nature consisted of spherical grains. The ethanol extract of the dye obtained from*Eugenia jambolana* is found to contain anthocyanin pigment, cyanidin-3-O-glucoside. The dye exhibited high

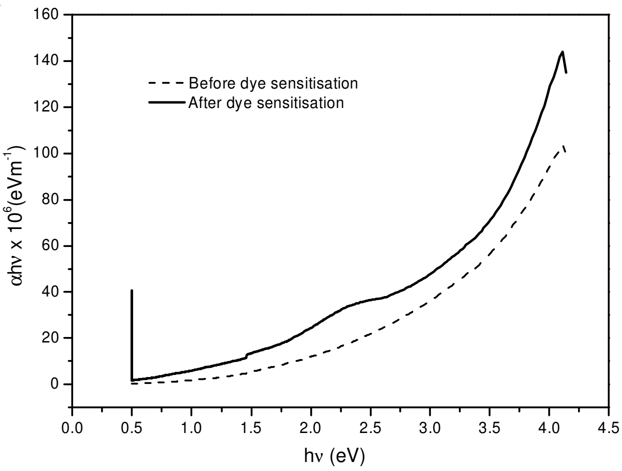

Fig. 7. Absorption spectra of films before and after sensitizaton

TABLE-3 OPTICAL BAND GAP OF TiO_2 THIN FILMS		
Thickness (μm)	E_g(eV)	
	Before dye sensitization	After dye sensitization
0.2101	3.40	3.25
0.4305	3.30	3.20
0.6536	3.28	3.16
1.3058	2.70	2.62

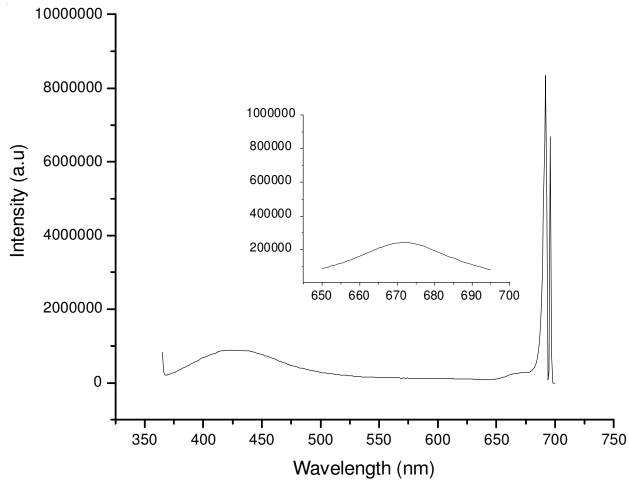

Fig. 8. Photoluminescence spectra of TiO_2 thin films

absorption in the visible region and sensitizaton has been effective improving the absorption coefficient of the films in visible region. Red shift is observed in the band gap of the dye sensitized film and the band gap of the dye sensitized films are in the range of 2.5 eV -3.6 eV.

REFERENCES

1. K. Kalyanasundaram and M. Grätzel, Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer Academic Publishers, Dordrecht (1993).
2. J.A. Bard and M.A. Fox, *Acc. Chem. Res*., **28**, 141 (1995).
3. P.V. Kamat, *Inter-Am. Photochem. Soc. Newslett.,* **19**, 14 (1996).
4. F.N. Castellano and G.J. Meyer, *Prog. Inorg. Chem.*, **44**, 167 (1997).
5. H. Zhou, L. Wu, Y. Gao and T. Ma, *J. Photochem. Photobiol. A*, **219**, 188 (2011).
6. A. Kay and M. Gratzel, *J. Phys. Chem.*, **97**, 6272 (1993).
7. T.S. Senthil, N. Muthukumarasamy, S. Agilan, M. Thambidurai, K.V.R. Murthy and R. Balasundaraprabhu, *J. Optoelectron. Adv. Mater.*, **11**, 831 (2009).