RESULTS AND DISCUSSION

CHAPTER IV

RESULTS AND DISCUSSION

Structural, optical, surface and photoluminescence characterization of as-deposited, annealed and dye sensitized TiO_2 thin films are discussed in this chapter. The annealed samples used for dye sensitization.

4.1 NATURE OF THIN FILM

In thin film, thickness of a film plays an important role in determining its properties. There is often a considerable deviation from that of the bulk behavior and sometimes-new phenomena are observed in the thin film states [74]. In the present work, thin films of TiO_2 are deposited by SILAR method by varying the thickness (Table 4.1). Thickness of the film indicates that the films deposited in the present work belong to the category of "Thin film" [74]. Thickness of the film deposited in the present work ranges from .2μm to 1.3 μm and it is dependent on the adsorption and reaction time.

4.2 OPTICAL CHARACTERIZATION

Optical transmission data is recorded using UV-Vis spectrophotometer. Optical constants such as transmittance, absorption co-efficient, and band gap are calculated.

4.2.1 TRANSMITTANCE

Optical transmittance spectra of TiO_2 thin films of different thickness are shown in Fig.4.1. Transmittance of the films gradually decreases in the NIR region. There is a rapid decrease in the transmittance of the film at 302nm. As thickness increases, transmittance of the film decreases (Fig 4.1). Transmittance of the film decreased upon annealing. There is a drastic reduction in the transmittance of the films upon dye sensitization (Fig 4.2-4.9). The as-deposited film of thickness 0.2101μm exhibited maximum transmittance of 68% at 850nm.

Toshihiro Miyata [75] et al. (2006) reported an optical transmittance of 85% at 500nm for TiO_2 films deposited by vacuum arc plasma evaporation method. **Yang feng[76] et al. (2003)** have also observed an optical transmittance of 80% in UV region for as-deposited and annealed TiO_2 films deposited by chemical bath deposition method. Optical transmittance of the film deposited by SILAR method is found to be lower than the reported values.

4.2.2 ABSORPTION CO-EFFICIENT

Optical absorption co-efficient spectra of TiO_2 film of different thickness are shown in Fig 4.10.Absorption co-efficient increases gradually in the NIR region. There is rapid increase in absorption co-efficient of the films at 824nm. As thickness increases, absorption co-efficient of the film decreases (Fig 4.10). Absorption co-efficient of the film decreased upon annealing. The absorption co-efficient of the films is increased after dye sensitization (Fig 4.11-4.18).

4.2.3 BANDGAP

The $(\alpha h\nu)^2$ Vs $h\nu$ plots of as-deposited, annealed and dye sensitized TiO_2 films are shown in fig 4.19-4.30.Optical transition involved in the films are found to be direct and allowed. The band gap of as-deposited films is higher when compared to annealed and dye-sensitized films. TiO_2 film of thickness 0.2101μm exhibited a direct band gap of 3.7 eV, 3.6eV and 3.5eV for as-deposited, annealed and dye sensitized.

V.Senthilkumar[77] et al., (2010) and R.S.Mane[78] et al. (2005) observed direct band gap of as-grown TiO_2 thin film to be 3.5eV and 3.65eV respectively. These results agree well with direct band gap values obtained in the present work. Yangfeng **Gao[76] et al. (2003)** also observed a reduction in the band gap of the TiO_2 film upon annealing.

4.2.4 ABSORBANCE OF DYE EXTRACT

The natural dye of *Eugenia Jambolana* is extracted using ethanol as the solvent. Optical absorbance spectrum of *Eugenia Jambolana* is shown in the Fig 4.31. The anthocyanin dye exhibited maximum absorbance at 626nm.

4.3 STRUCTURAL CHARACTERIZATION

The as-deposited films exhibited amorphous nature and the annealed film of higher thickness (1.3058 μm) is found to be polycrystalline in nature (Fig 4.32-4.4.39). The annealed (450˚C) films of thickness 1.3058 μm exhibited prominent peaks corresponding to anatase phase of TiO_2 (JCPDS card no: 89-4203). The film exhibited preferred orientation along (101) direction.

V.Senthilkumar[77] et al. (2010) and Toshihiro Miyata[75] et al. (2006) reported the amorphous nature of TiO_2 thin films. **Tran Chien Dang[79] et al. (2010) and Yunxia Jin[80] et al. (2002)** observed polycrystalline nature for annealed (450˚C) TiO_2 thin film. These results agree well with the present work.

4.4 SURFACE MORPHOLOGY

The surface morphology of the TiO_2 film (1.3058μm) annealed at 450°C was investigated by scanning electron microscopy. Fig 4.40 shows SEM images of annealed TiO_2 films. From SEM images, it is observed that the deposited TiO_2 film consisted of particles with a uniform spherical grain size.

4.5 ENERGY DISPERSIVE X-RAY ANALYSIS

The elemental analysis of TiO_2 thin film was done by using energy dispersive X-ray analysis (EDAX). The EDAX spectra of TiO_2 thin film annealed at 450°C are shown in Fig 4.41.The atomic weight percentage of Ti and O in the film is 30.68% and 69.32% respectively. The EDAX data confirmed that the films are stoichiometric.

4.6 PHOTOLUMINSCENCE CHARACTERIZATION

Photoluminescence spectra of annealed (450°C) and dye sensitized TiO_2 thin film of thickness 1.3058 μm with the excitation wavelength of 350nm is shown in Fig 4.42-4.43.Photoluminescence spectra of TiO_2 film posses peak at 416nm(2.98eV) and 672nm (1.84eV).

According to the report of **T. S. Senthil [81] et al. (2009)** the broad band in the range of 350nm-550nm in the PL spectrum of anatase TiO_2 can be attributed to the

recombination of electron via self trapped excitons located or trapped on TiO_6 octohedral which originated from the defect states present in the film.

4.7 FTIR CHARACTERIZATION

In the present work, FTIR spectroscopy is used to analyze the functional groups present in *Eugenia Jambolana*. The FTIR spectrum is recorded in the wave number range of 3600-600 cm^{-1}. FTIR spectrum for *Eugenia Jambolana* powder is shown in Fig 4.43. The functional groups identified are listed in table 4.2.A thorough analysis of the FTIR data indicates the presence of anthocyanin pigment (cyanidin 3-O-glucoside) in the dye extracted from *Eugenia Jambolana.*

T. S. Senthil[81] et al. (2009) also reported the presence of anthocyanin pigment (cyanidin 3-O-glucoside) in dye extracted from Eugenia Jambolana.

Table 4.1

Optical band gap of TiO_2 thin film

Samples	Thickness (μm)	E_g(eV)	
		Before Dye Sensitization	After Dye Sensitization
1	0.2101	3.6	3.5
2	0.4202	3.5	3.45
3	0.6536	3.85	3.6
4	1.3058	2.7	2.5

Table 4.2

Functional groups present in *Eugenia Jambolana*

S.No	Wavenumber (Cm^{-1})	Functional groups
1	3446.79,3402.43,3379.29 3323.35,3300.20,3273.20	O-H stretch
2	1726.29 1624.06	C=O stretch of the ester group, C=O stretching vibration is conjugate
3	1549.91	C=O stretching vibration is conjugate
4	1359.82	OH in plane bending
5	918.12,896.90,867.97,817.82	β-glycosidic linkage
6	777.31	Liberation of H_2O
7	621.08	Out of plane vibration of the =C-H group

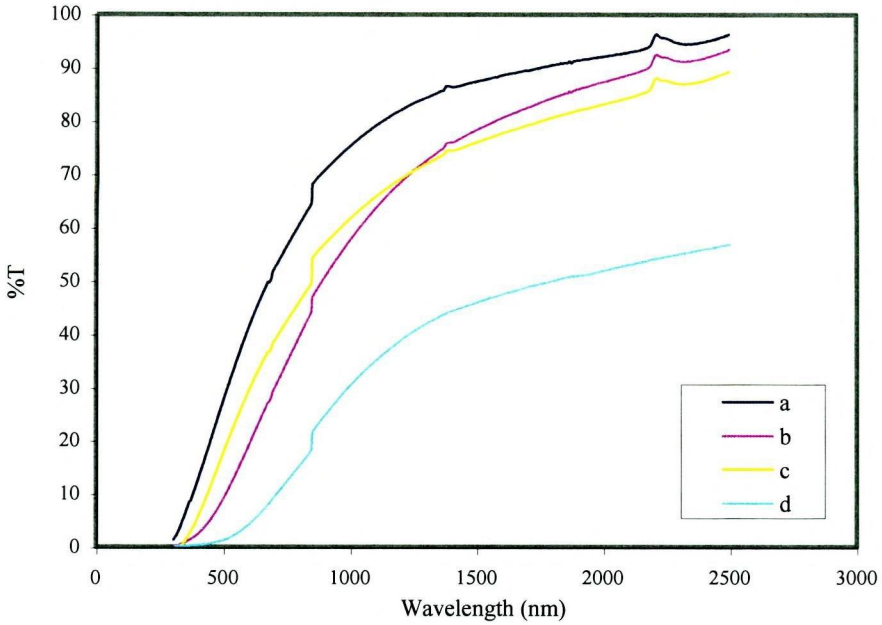

Fig 4.1 Transmittance spectra of TiO_2 film a) Sample1 b) Sample 2 c) Sample 3 d) Sample 4

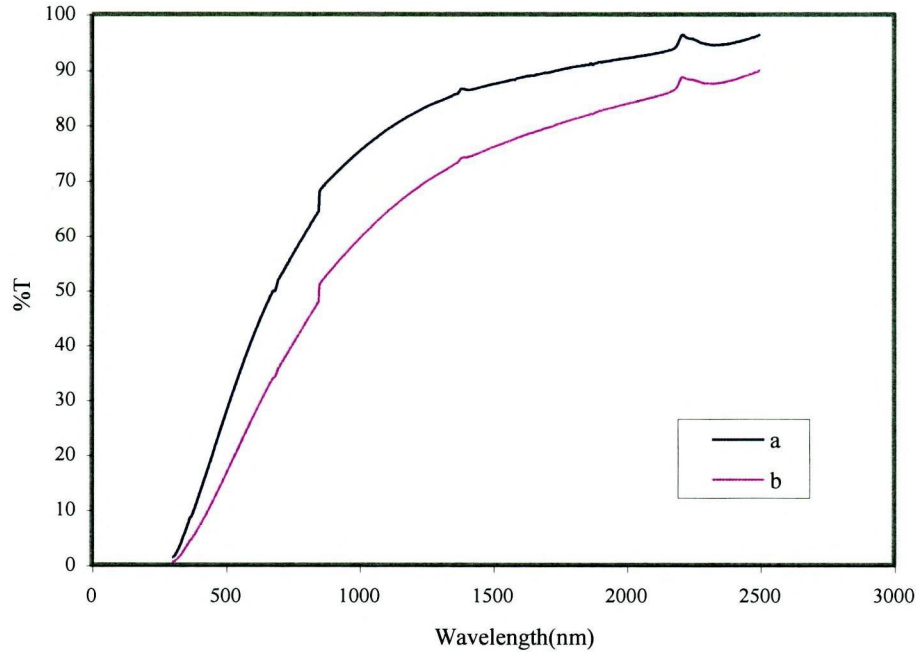

Fig 4.2 Transmittance spectra of TiO_2 film (sample 1) a) As-deposited b) Annealed at 450°C

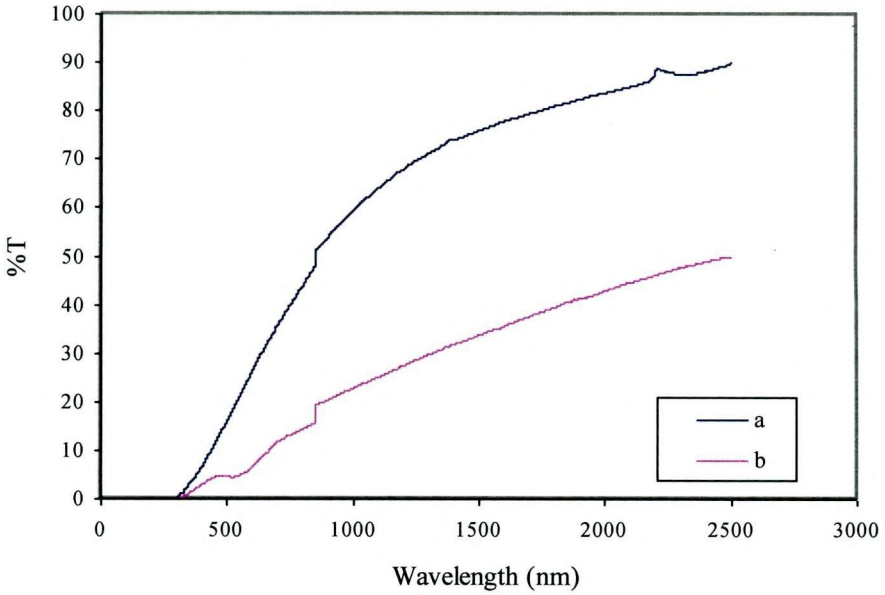

Fig 4.3 Transmittance spectra of TiO_2 film (sample 1)
a) Before dye-sensitization b) After dye sensitization

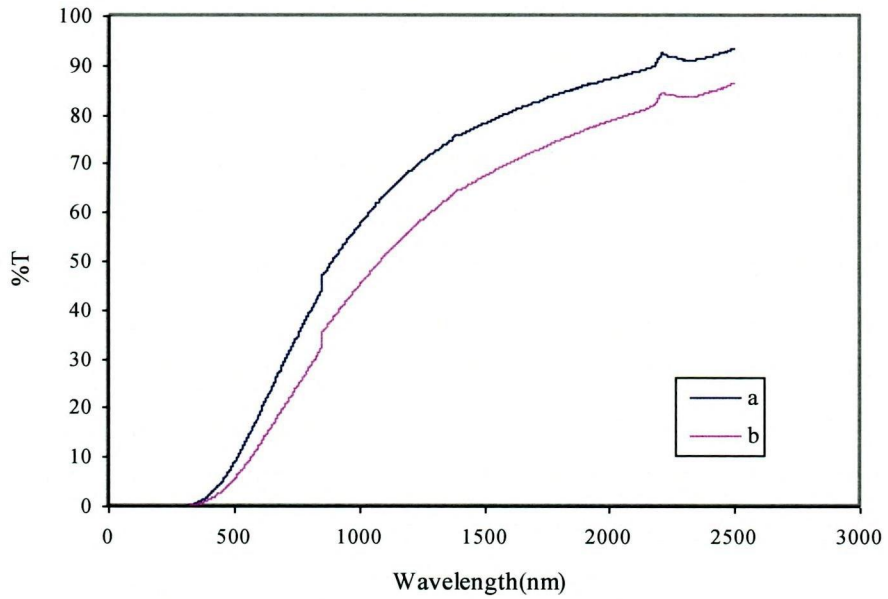

Fig 4.2 Transmittance spectra of TiO_2 film (sample 2)
a) As-deposited b) Annealed at 450°C

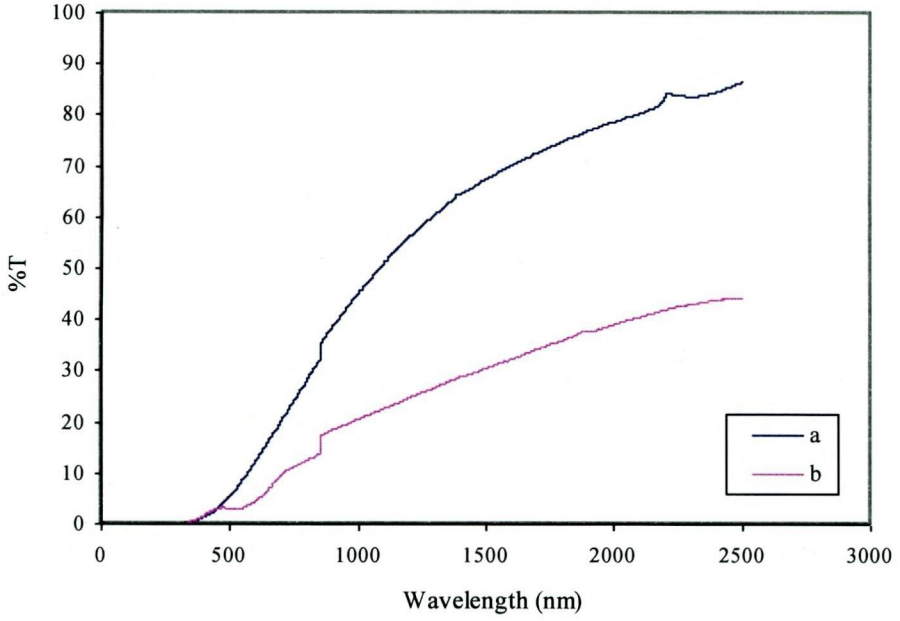

Fig 4.5 Transmittance spectra of TiO_2 film (sample 2)
a) Before dye-sensitization b) After dye sensitization

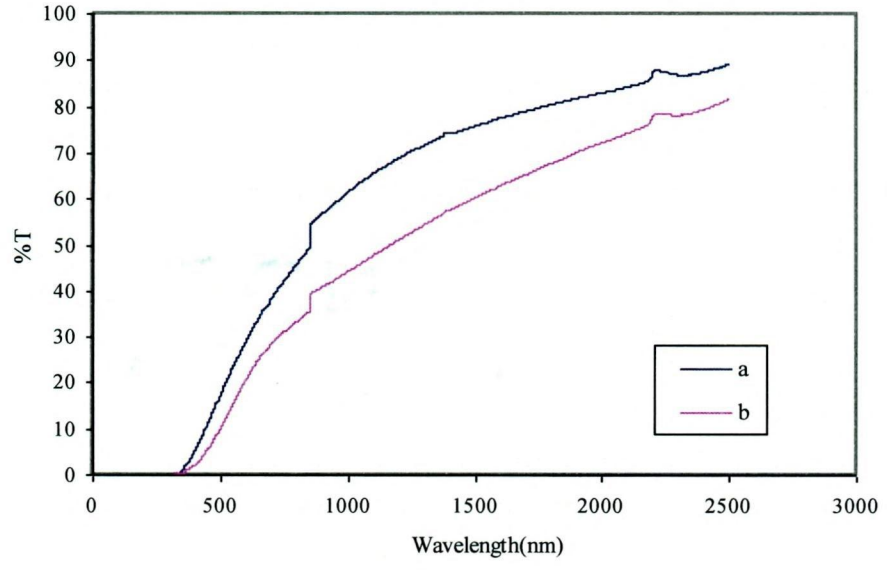

Fig 4.6 Transmittance spectra of TiO_2 film (sample 3)
a) As-deposited b) Annealed at 450°C

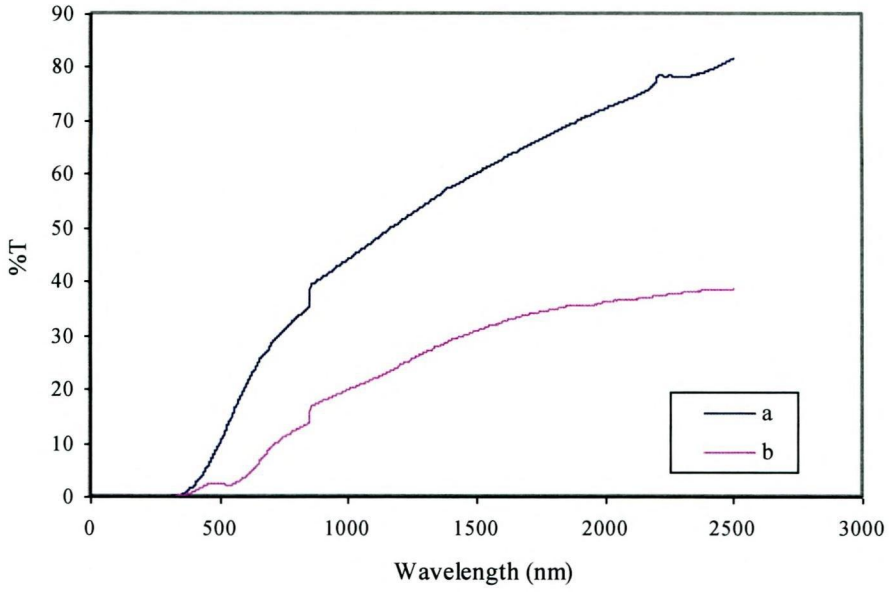

Fig 4.7 Transmittance spectra of TiO_2 film (sample 3)
a) Before dye-sensitization b) After dye sensitization

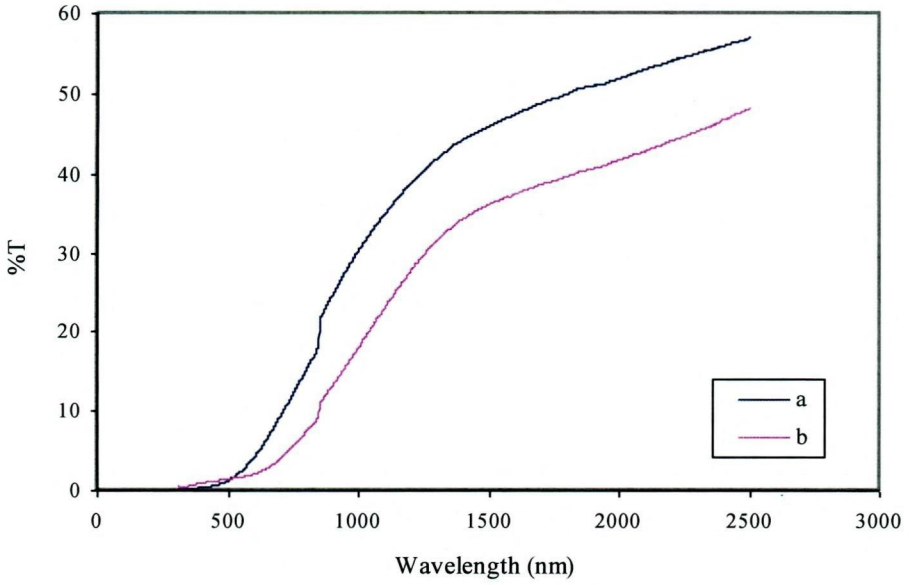

Fig 4.8Transmittance spectra of TiO_2 film (sample 4)
a) As-deposited b) Annealed at 450°C

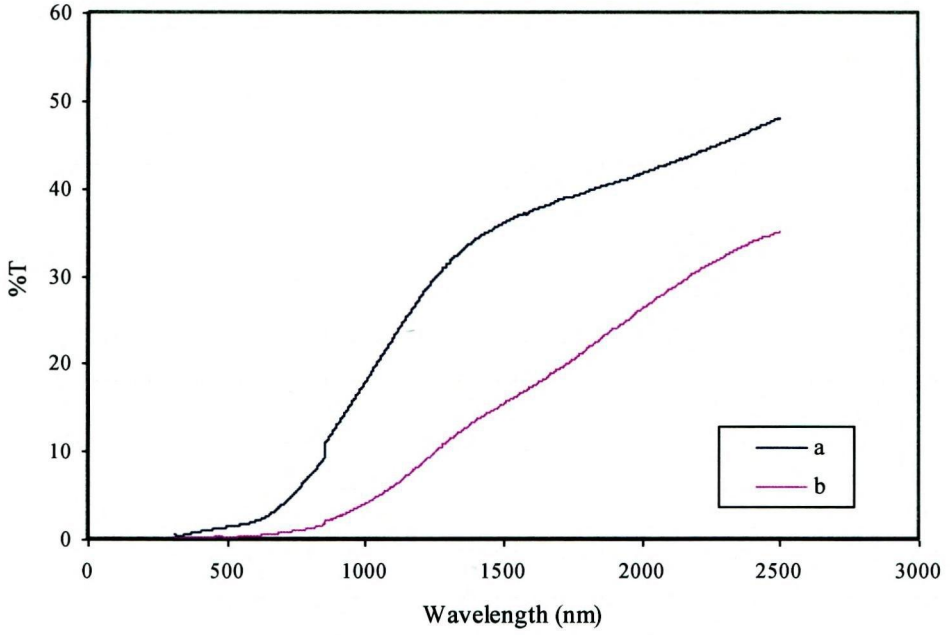

Fig 4.9 Transmittance spectra of TiO_2 film (sample 4)
a) Before dye-sensitization b) After dye sensitization

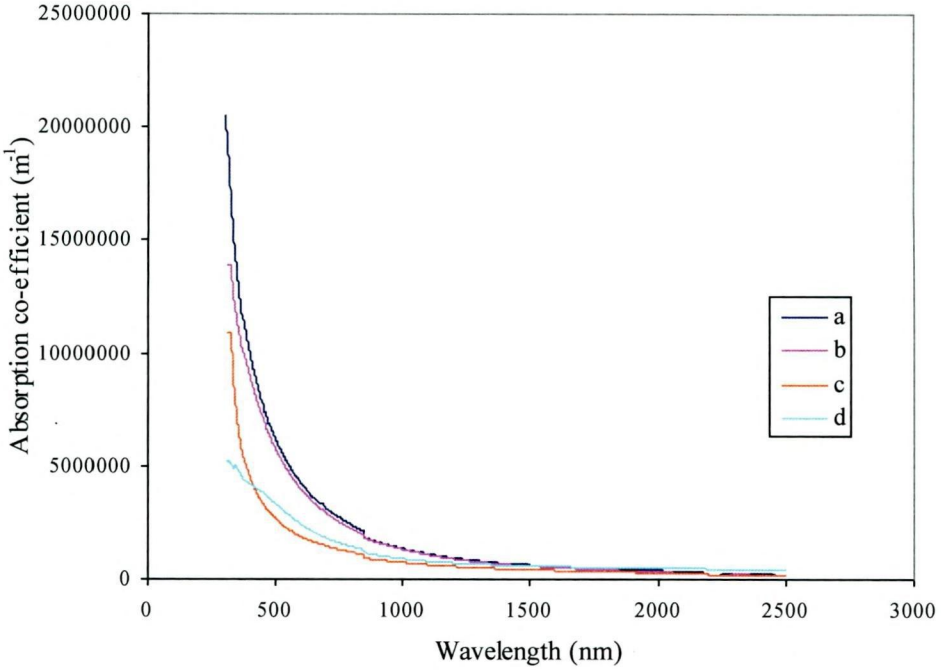

Fig 4.10 Variation of absorption co-efficient of TiO_2 film with wavelength a) Sample1 b) Sample 2 c) Sample 3 d) Sample 4

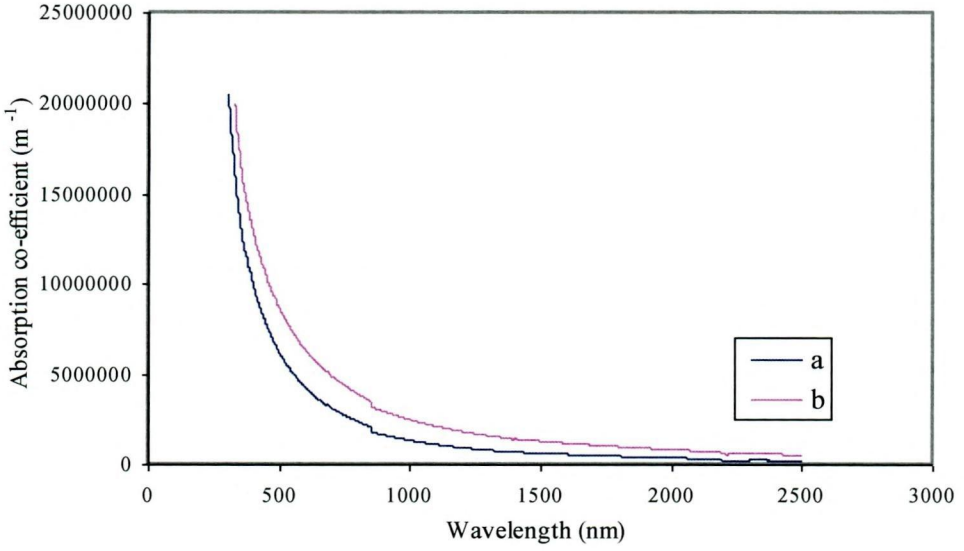

Fig 4.11 Variation of absorption co-efficient of TiO_2 film (sample 1) with wavelength a) As-deposited b) Annealed at 450°C

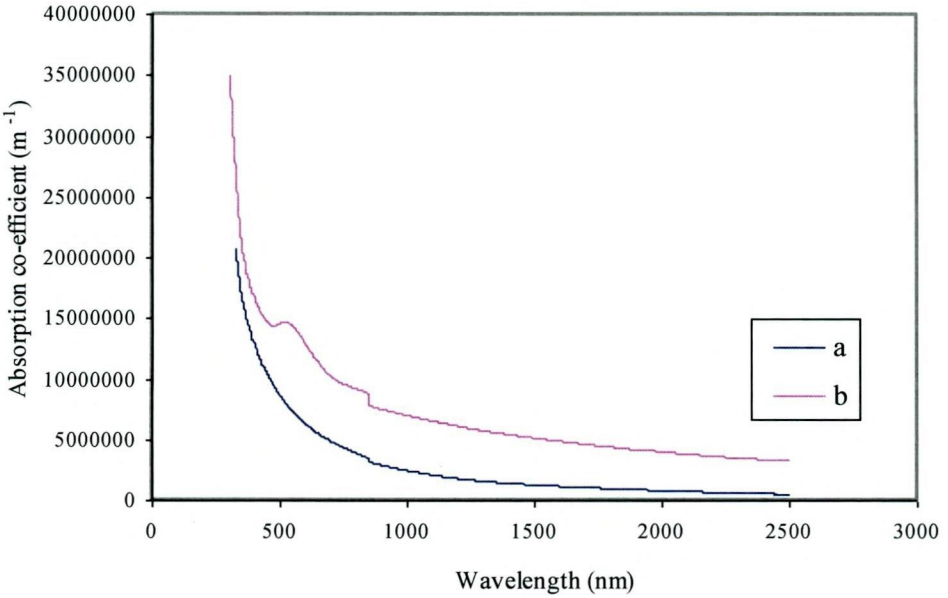

Fig 4.12 Variation of absorption co-efficient of TiO_2 film (sample 1) with wavelength a) Before dye-sensitization b) After dye sensitization

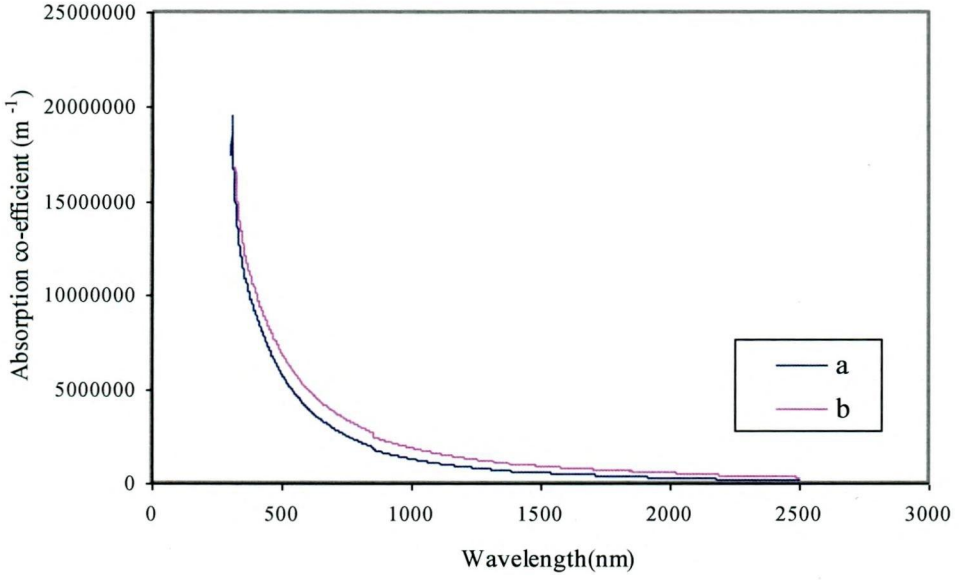

Fig 4.13 Variation of absorption co-efficient of TiO_2 film (sample 2) with wavelength a) As-deposited b) Annealed at 450°C

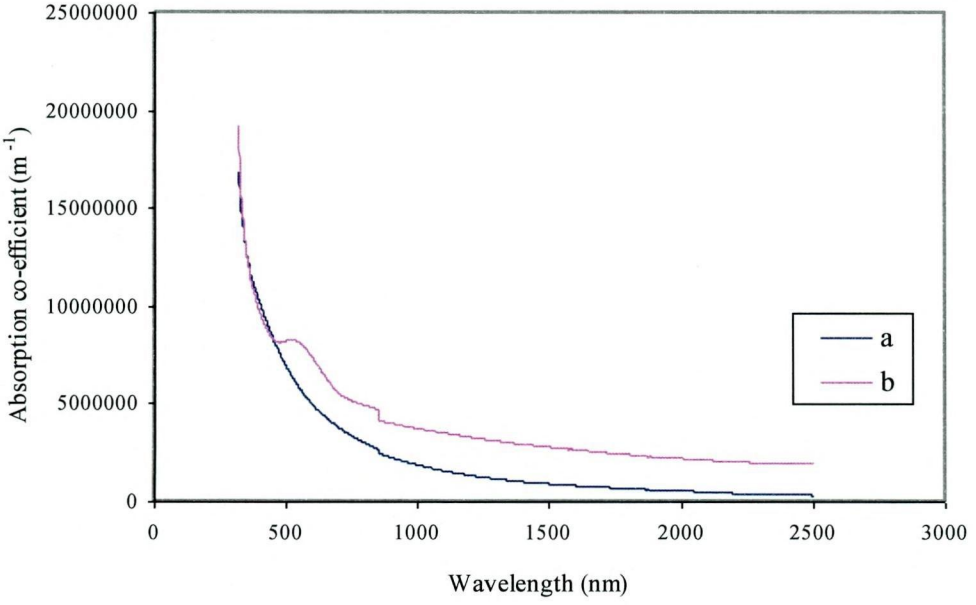

Fig 4.14 Variation of absorption co-efficient of TiO_2 film (sample 2) with wavelength a) Before dye-sensitization b) After dye sensitization

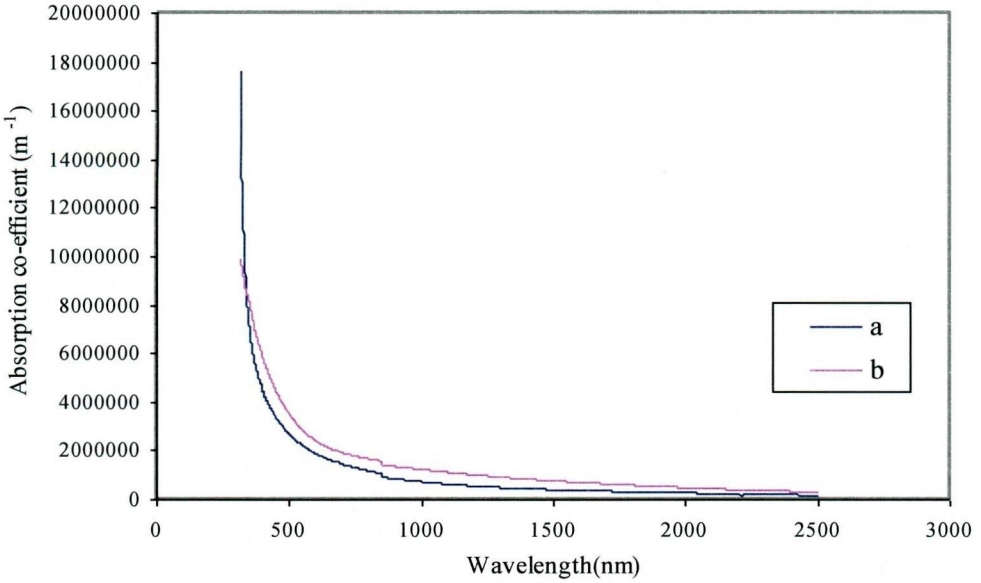

Fig 4.15 Variation of absorption co-efficient of TiO_2 film (sample 3) with wavelength a) As-deposited b) Annealed at 450°C

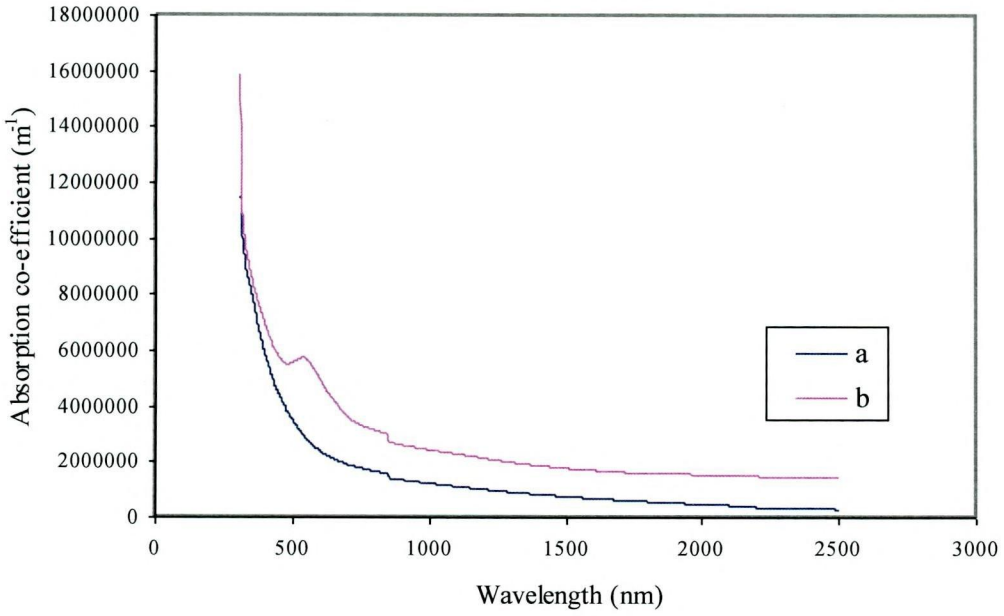

Fig 4.16 Variation of absorption co-efficient of TiO_2 film (sample 3) with wavelength a) Before dye-sensitization b) After dye sensitization

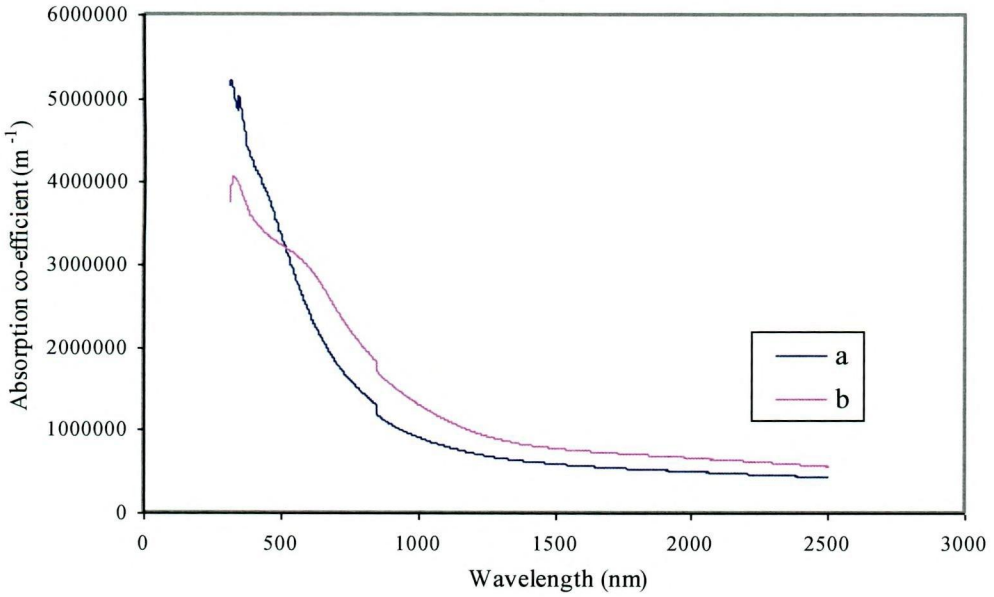

Fig 4.17 Variation of absorption co-efficient of TiO_2 film (sample 4) with wavelength a) As-deposited b) Annealed at 450°C

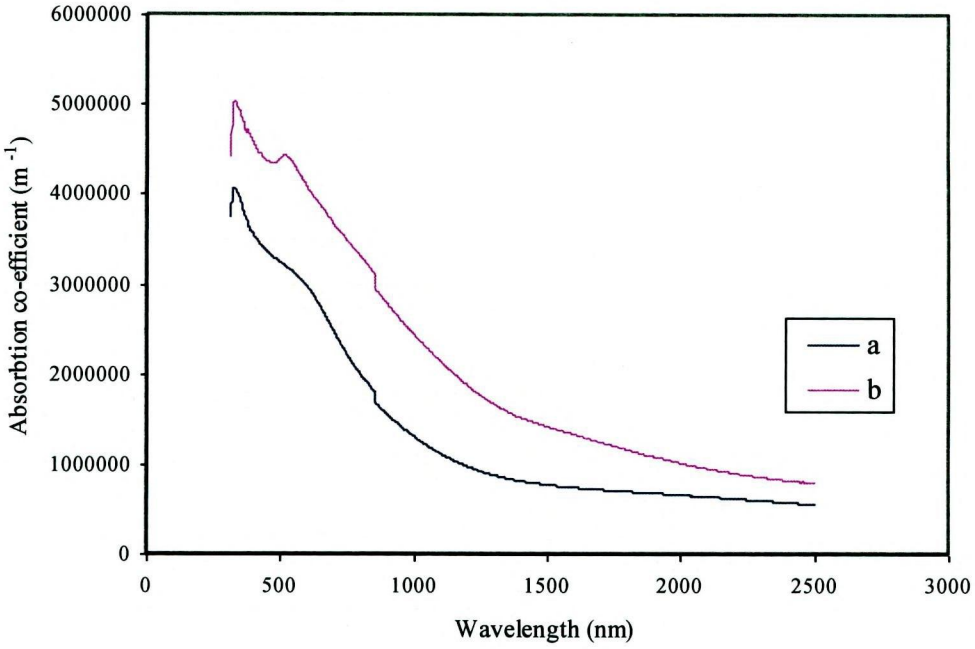

Fig 4.18 Variation of absorption co-efficient of TiO_2 film (sample 4) with wavelength a) Before dye-sensitization b) After dye sensitization

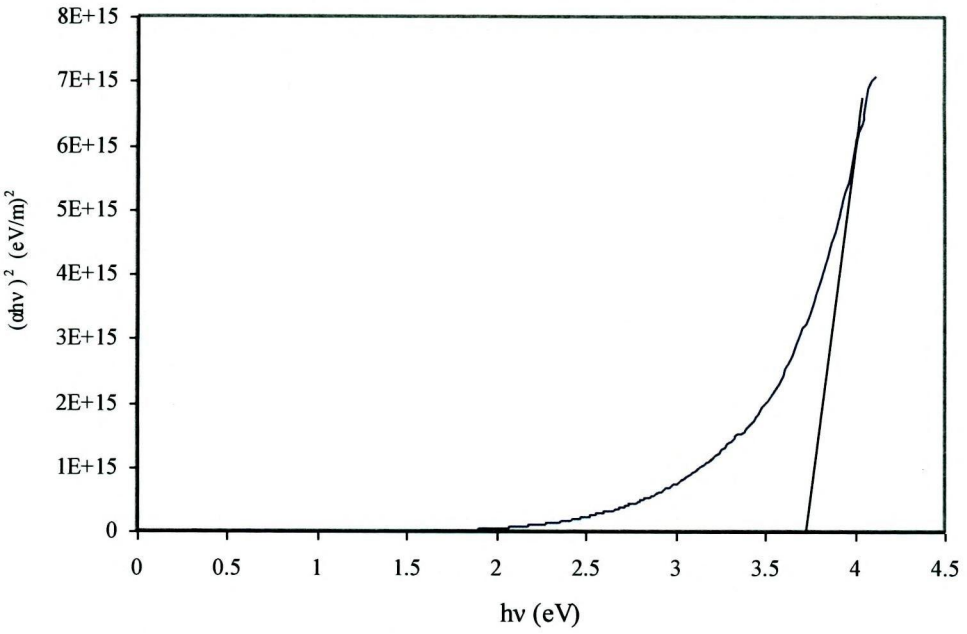

Fig 4.19 $(\alpha h\nu)^2$ Vs hν plot of as-deposited TiO_2 film (Sample 1)

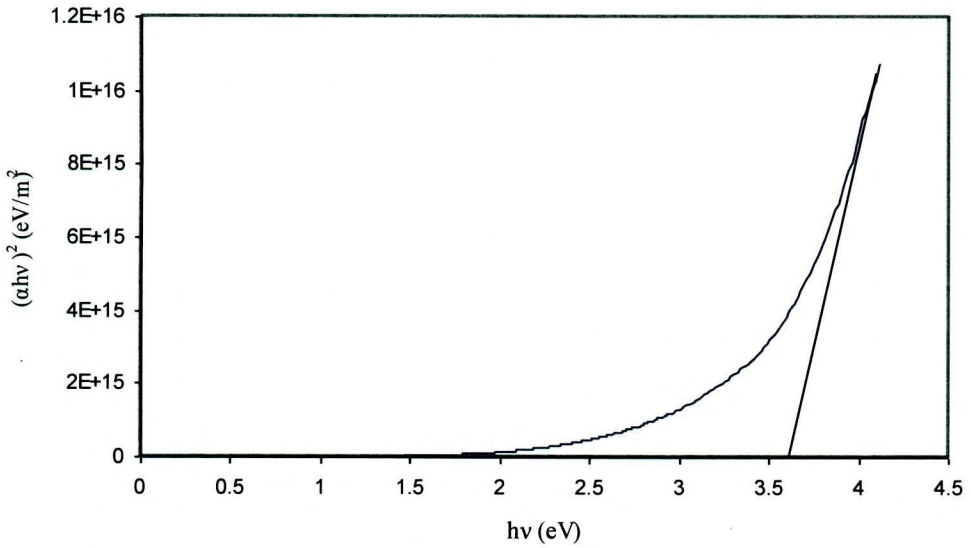

Fig 4.20 $(\alpha h\nu)^2$ Vs hν plot of annealed (450°C) TiO_2 film (Sample1)

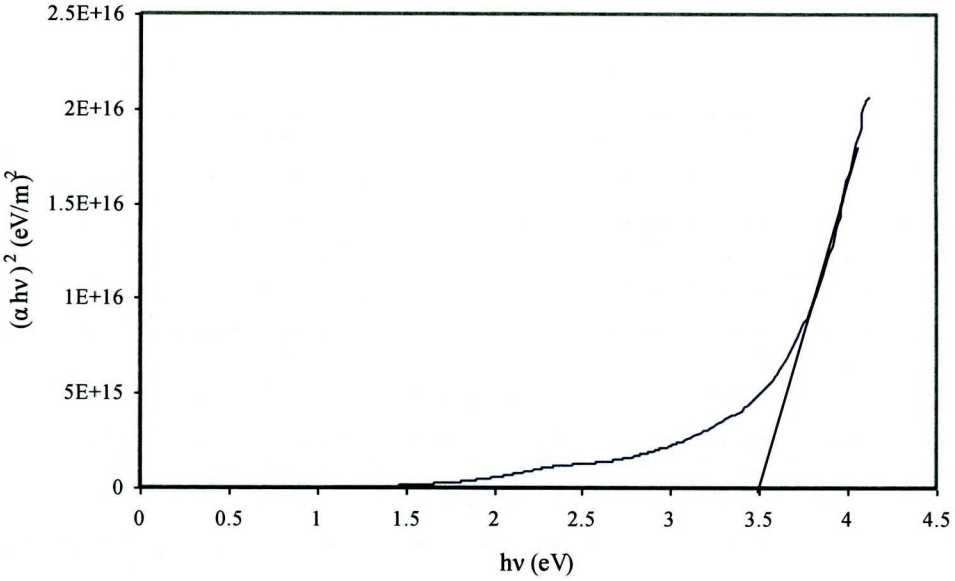

Fig 4.21 $(\alpha h\nu)^2$ Vs hν plot of dye sensitized TiO_2 film (Sample1)

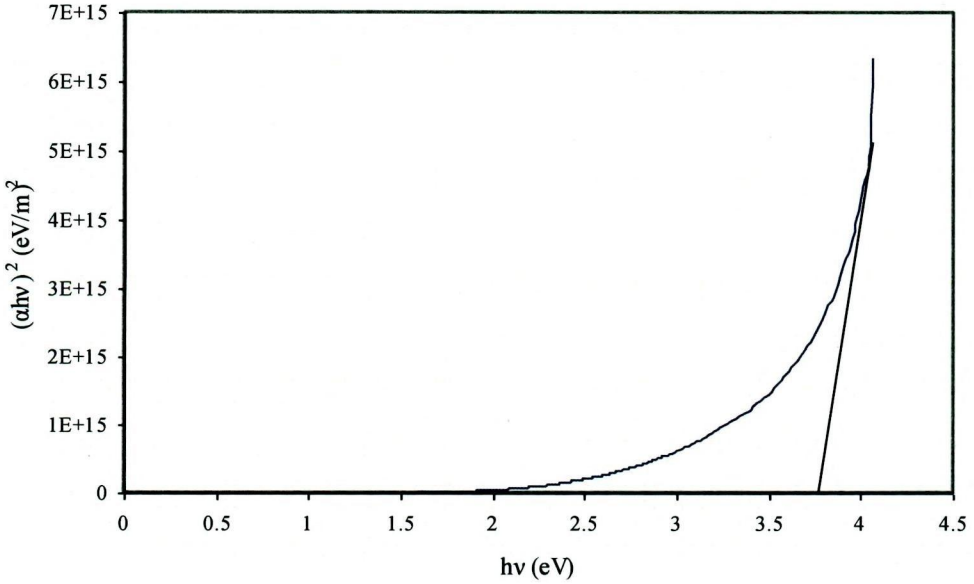

Fig 4.22 $(\alpha h\nu)^2$ Vs hν plot of as-deposited TiO_2 film (Sample 2)

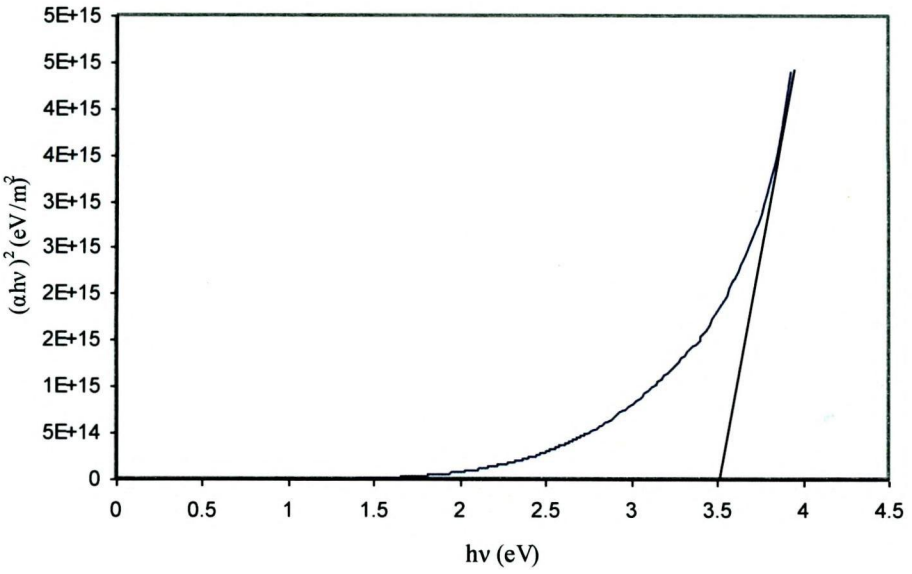

Fig 4.23$(\alpha h\nu)^2$ Vs hν plot of annealed(450°C)TiO_2 film (Sample 2)

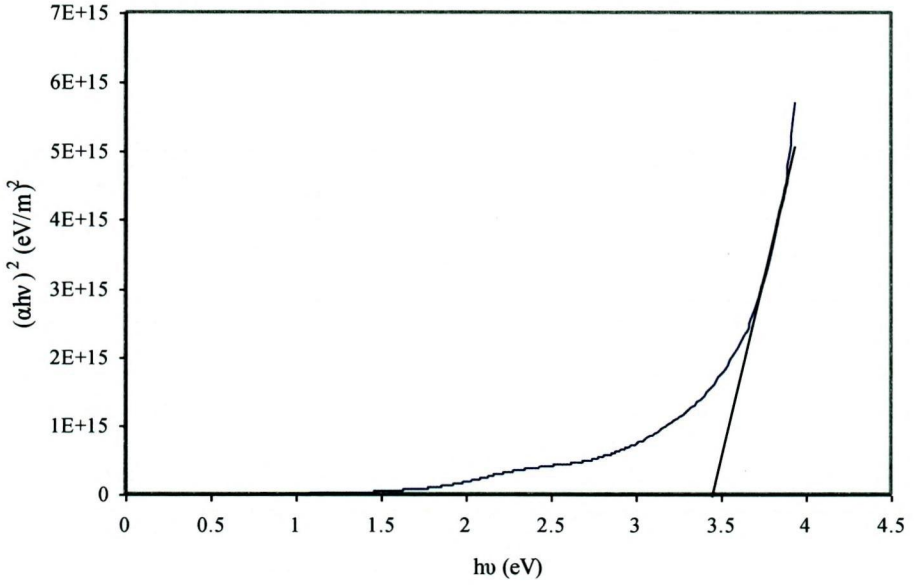

Fig 4.24 $(\alpha h\nu)^2$ Vs hν plot of dye sensitized TiO_2 film (Sample 2)

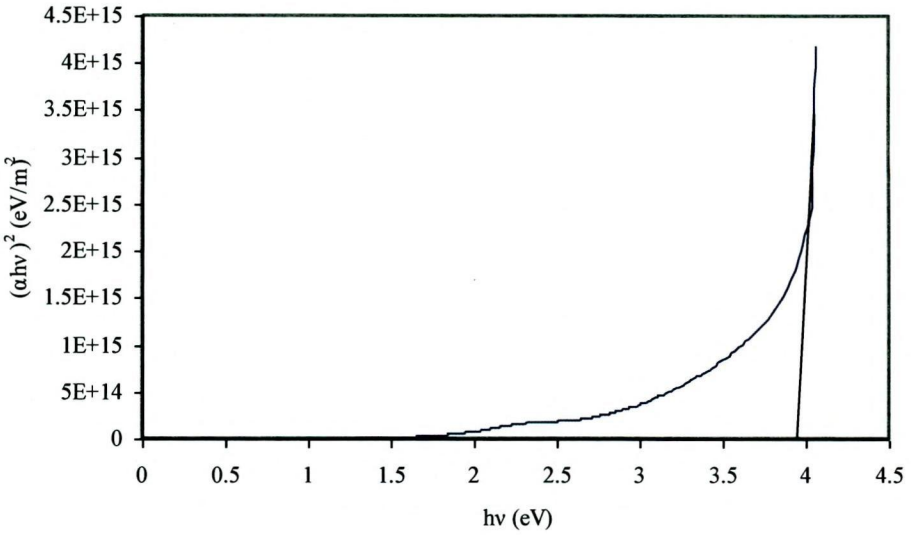

Fig 4.25 $(\alpha h\nu)^2$ Vs hν plot of as-deposited TiO_2 film(Sample3)

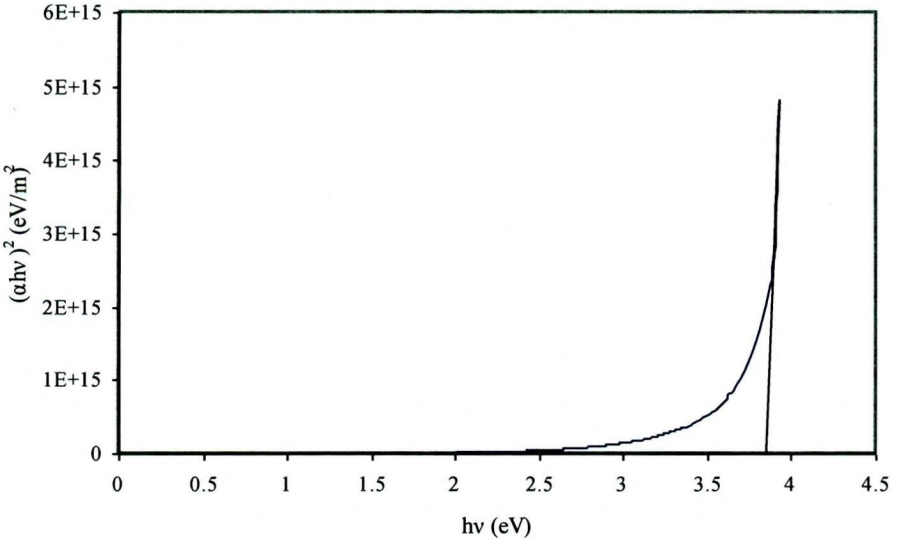

Fig 4.26 $(\alpha h\nu)^2$ Vs hν plot of annealed (450°C)TiO_2 film (Sample3)

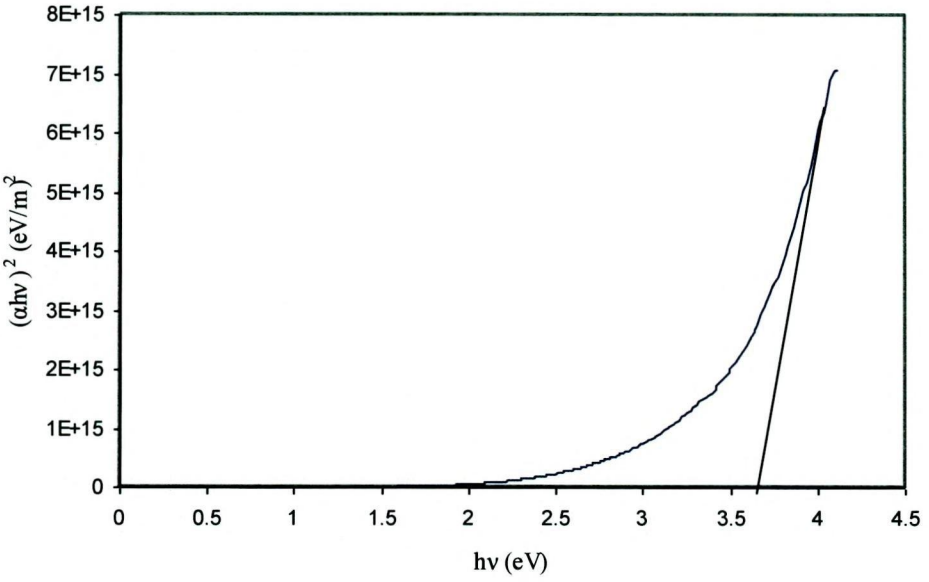

Fig 4.27 $(\alpha h\nu)^2$ Vs hν plot of dye sensitized TiO_2 film(Sample 3)

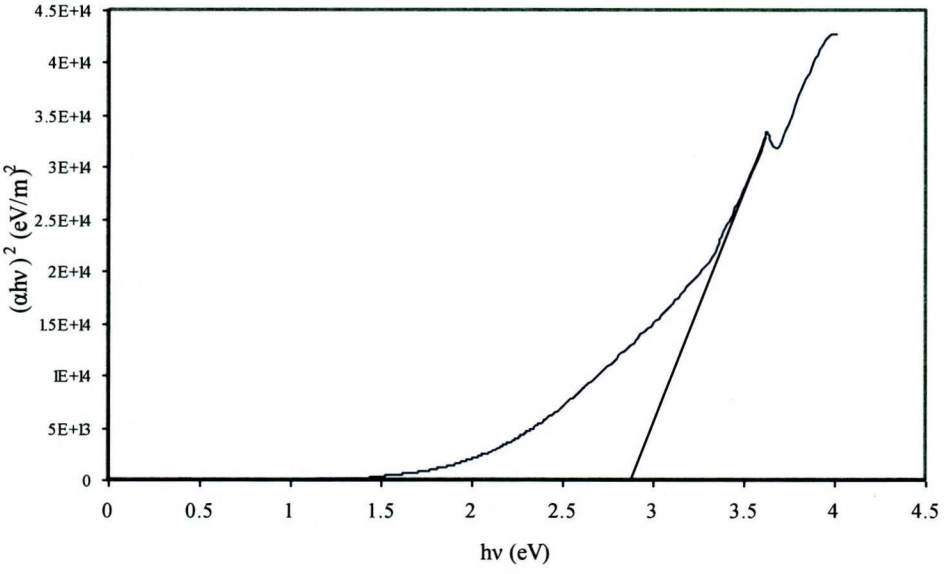

Fig 4.28 $(\alpha h\nu)^2$ Vs hν plot of as-deposited TiO_2 film (Sample 4)

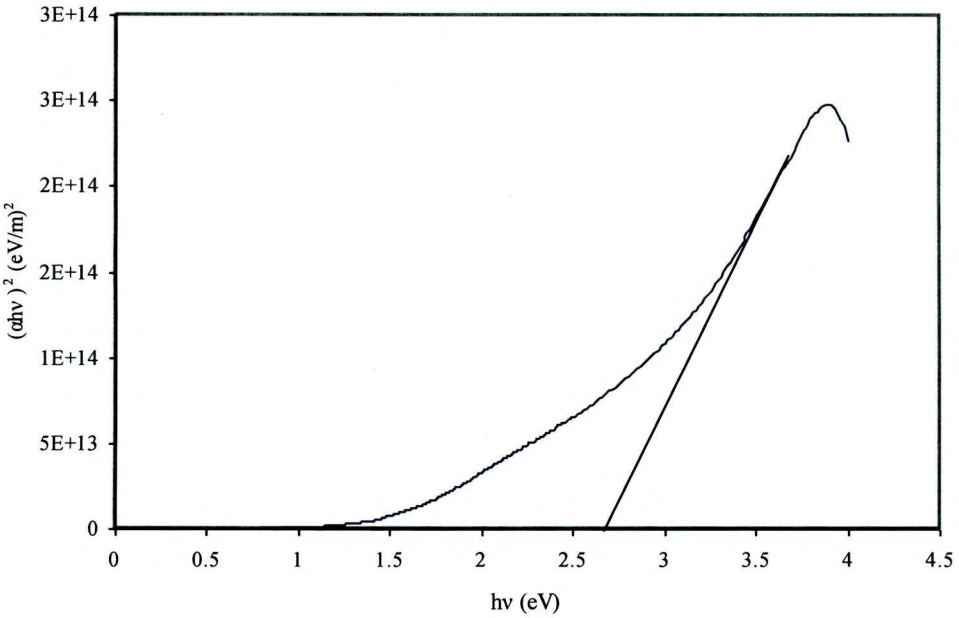

Fig 4.29 $(\alpha h\nu)^2$ Vs hν plot of annealed (450°C) TiO_2 film (Sample 4)

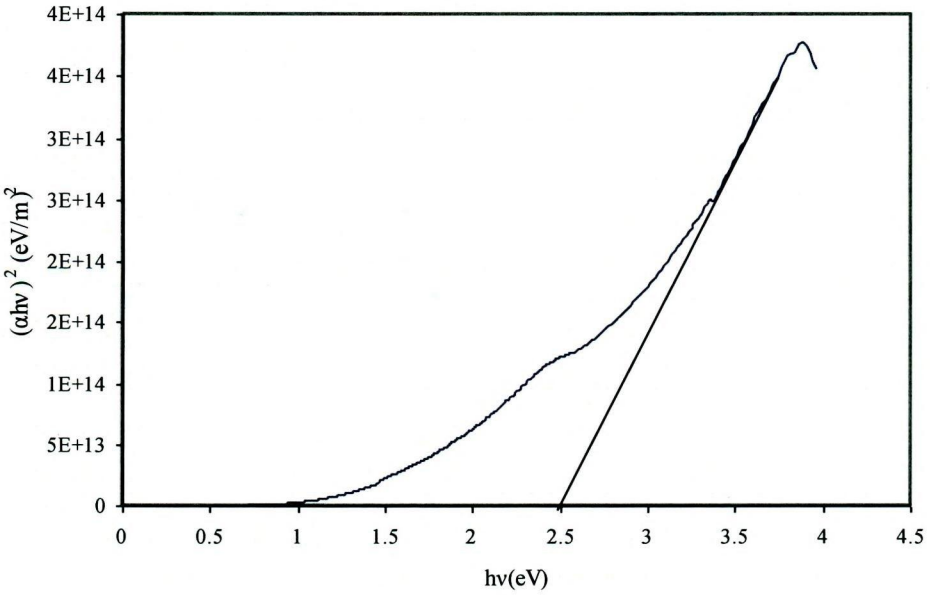

Fig 4.30 $(\alpha h\nu)^2$ Vs hν plot of dye sensitized TiO_2 film (Sample 4)

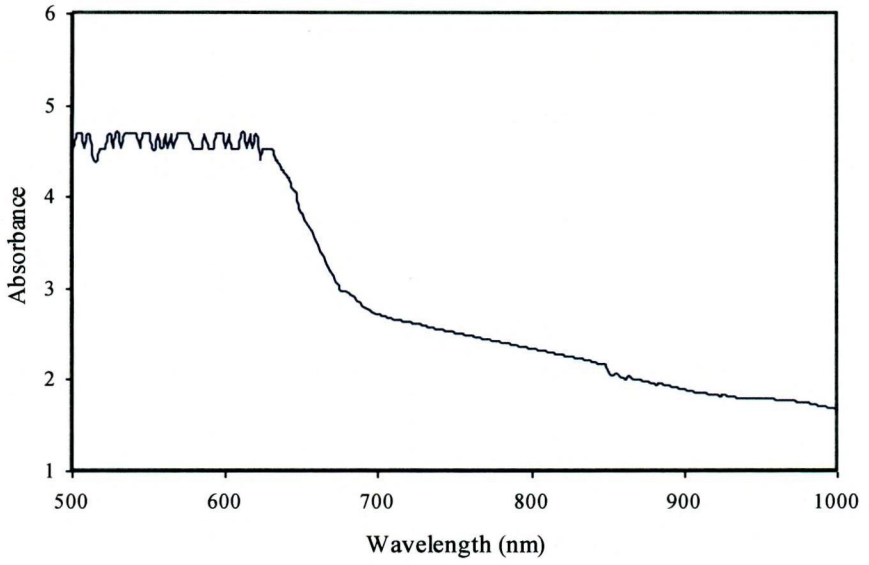

Fig 4.31 Optical absorption spectra of *Eugenia Jambolana* dye

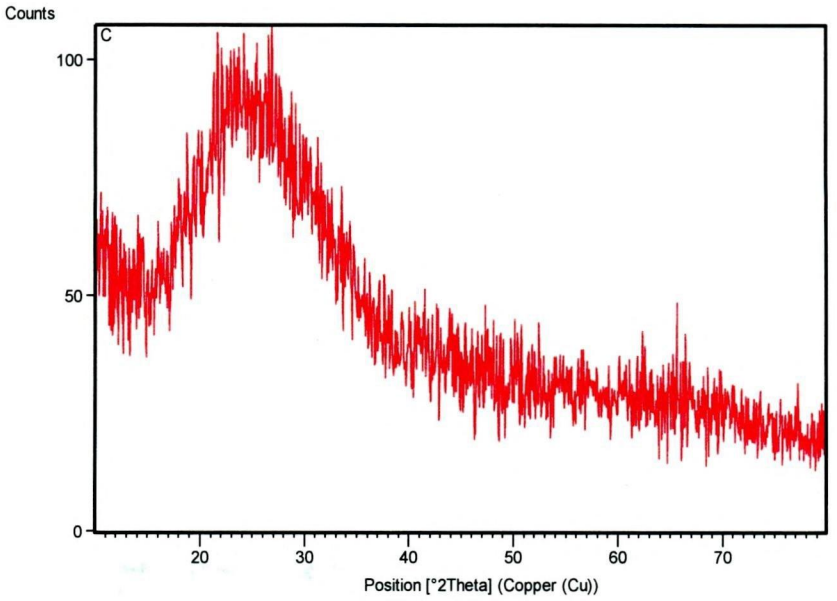

Fig 4.32 X-ray diffraction pattern of as-deposited TiO_2 Thin film (Sample 1)

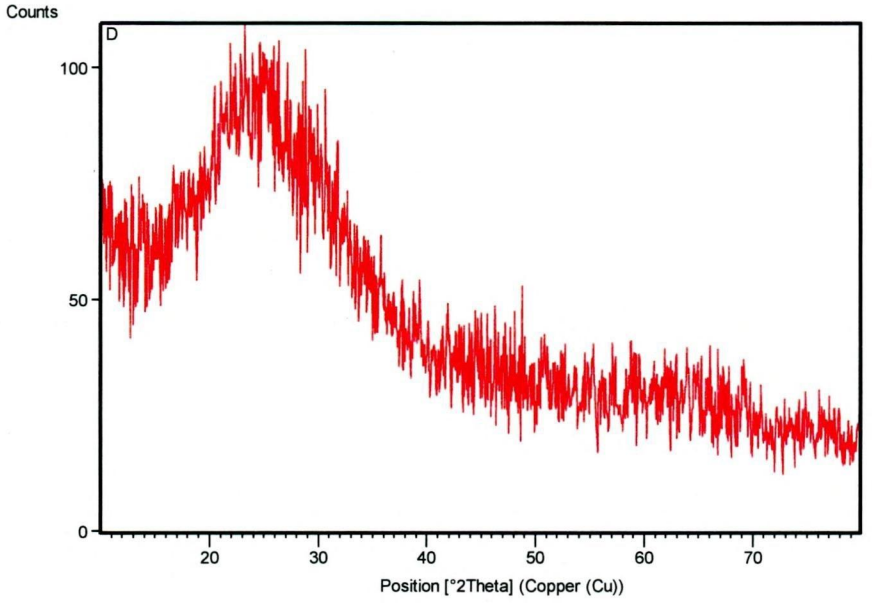

Fig 4.33 X-ray diffraction pattern of annealed (450°C) TiO_2 thin film (Sample 1)

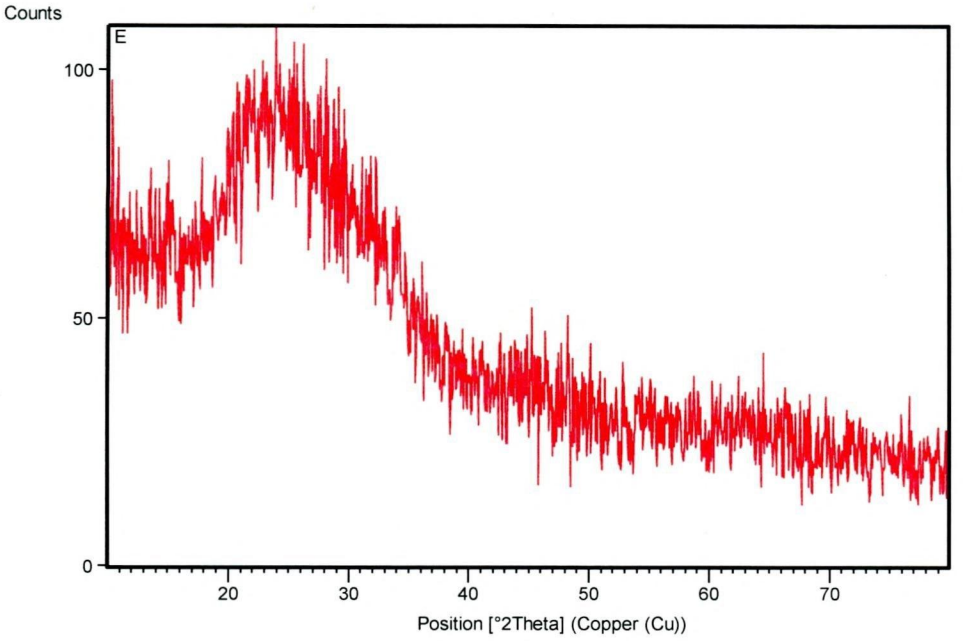

Fig 4.34 X-ray diffraction pattern of as-deposited TiO_2 Thin film (Sample2)

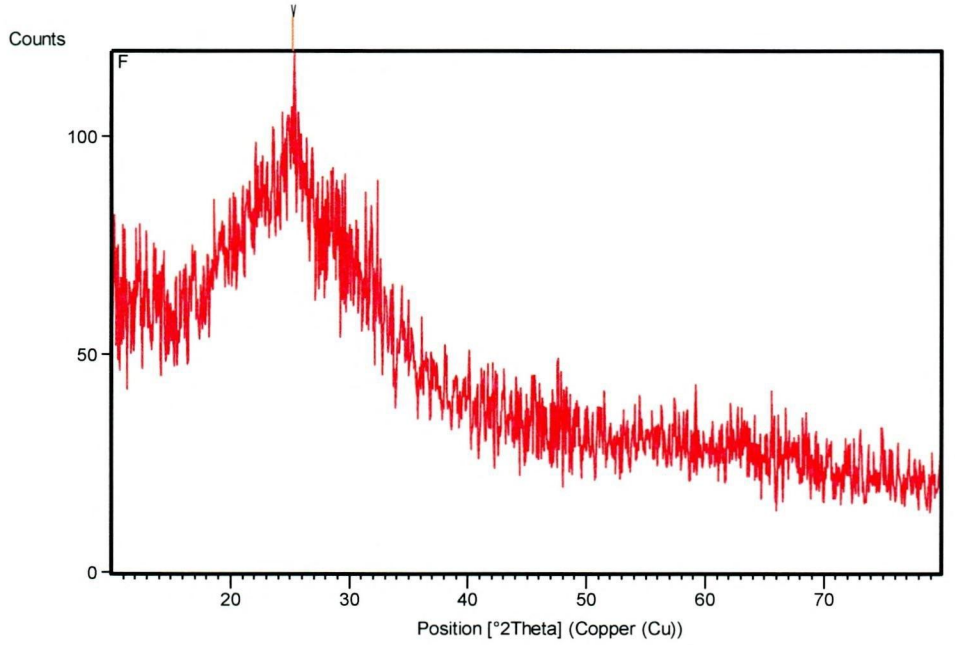

Fig 4.35 X-ray diffraction pattern of annealed (450°C) TiO_2 thin film (Sample 2)

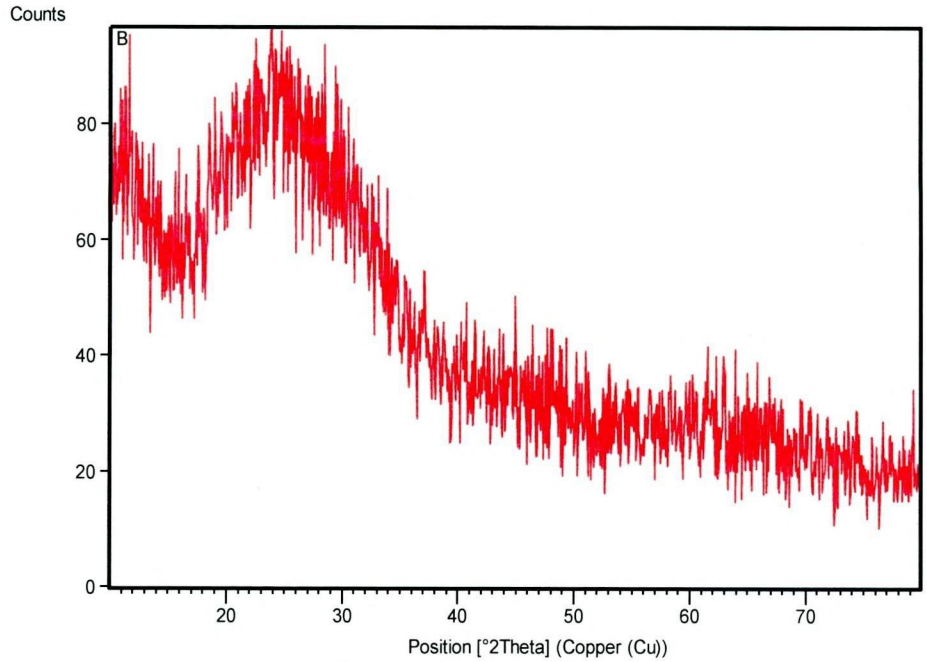

Fig 4.36 X-ray diffraction pattern of as-deposited TiO_2 Thin film (Sample 3)

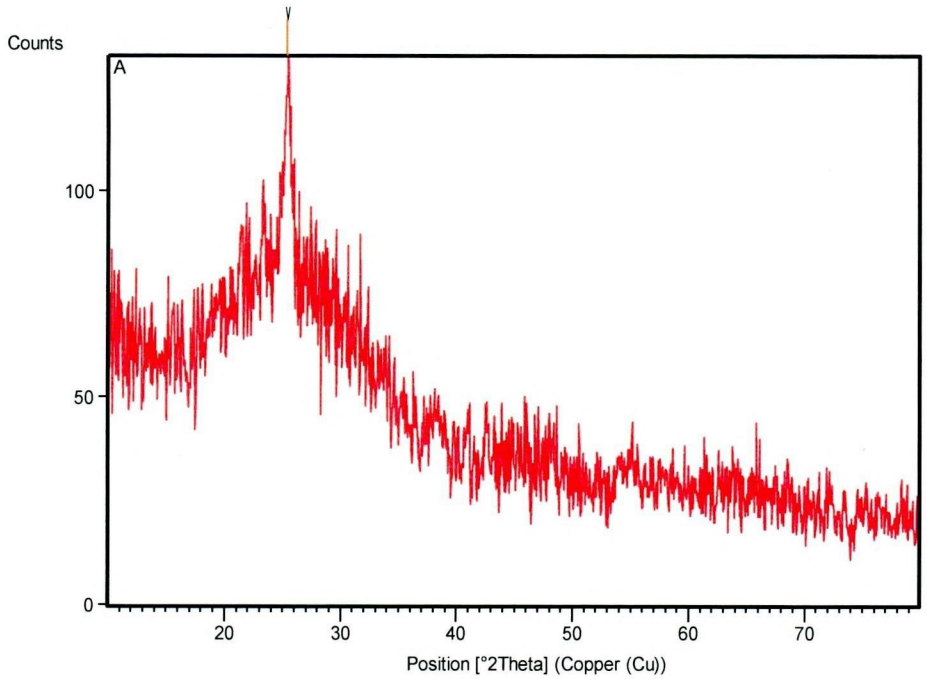

Fig 4.37 X-ray diffraction pattern of annealed (450°C) TiO_2 thin film (Sample 3)

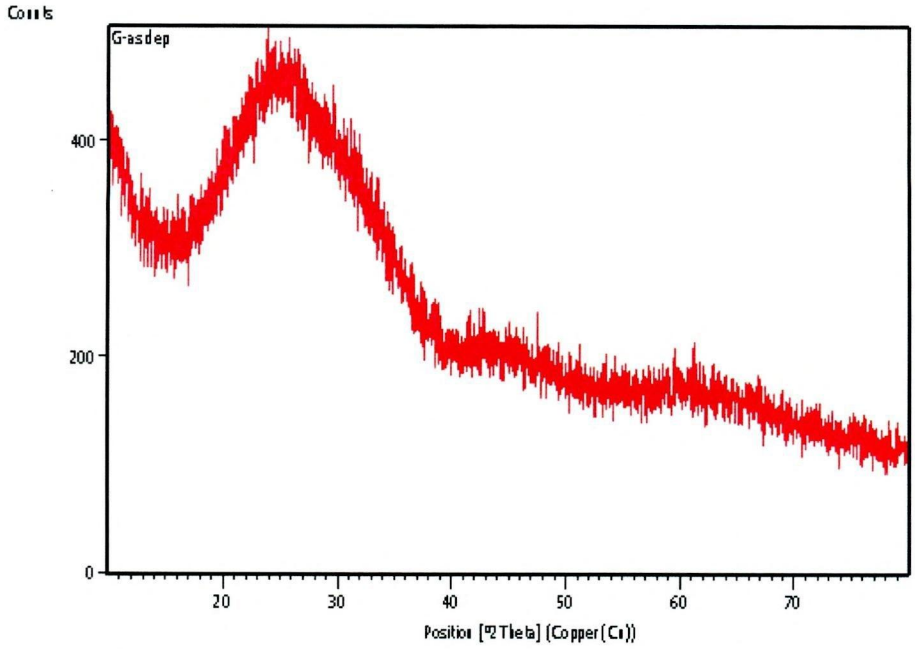

Fig 4.38 X-ray diffraction pattern of as-deposited TiO_2 Thin film (Sample 4)

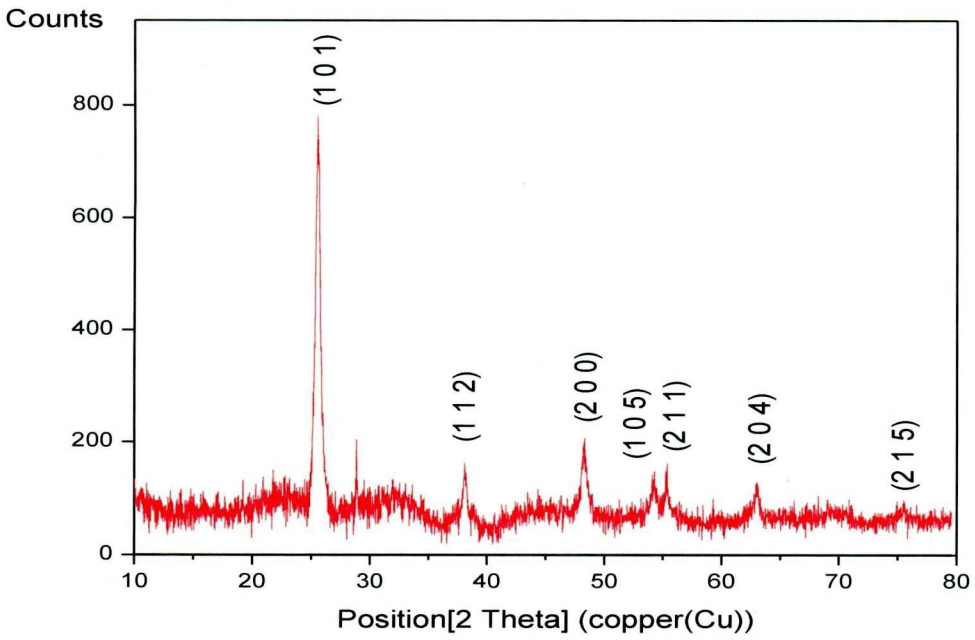

Fig 4.39 X-ray diffraction pattern of annealed (450°C) TiO_2 thin film (Sample 4)

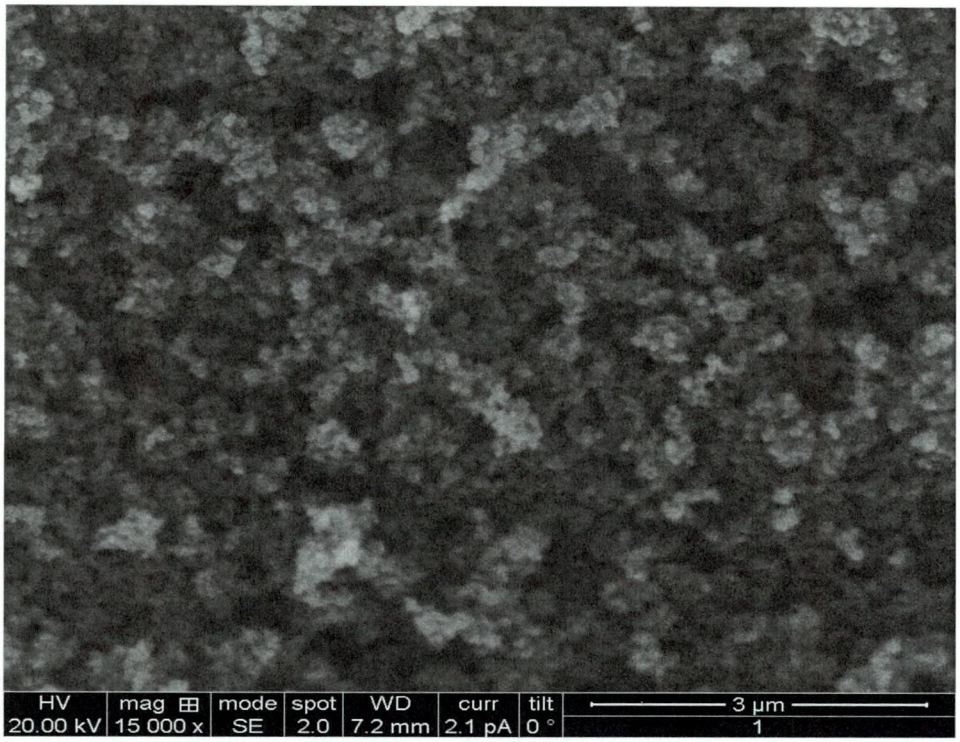

Fig 4.40 SEM image of TiO_2 thin film annealed at 450°C (Sample 4)

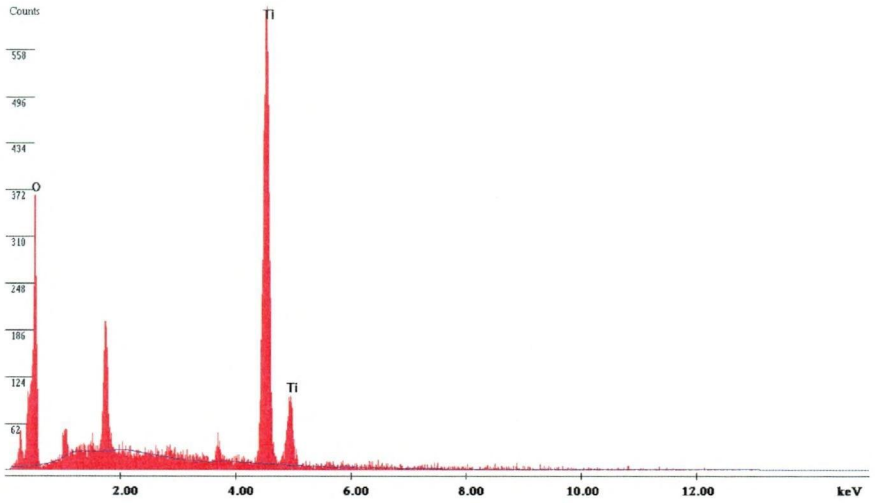

Fig 4.41 EDAX spectrum of TiO_2 thin film annealed at 450°C (Sample 4)

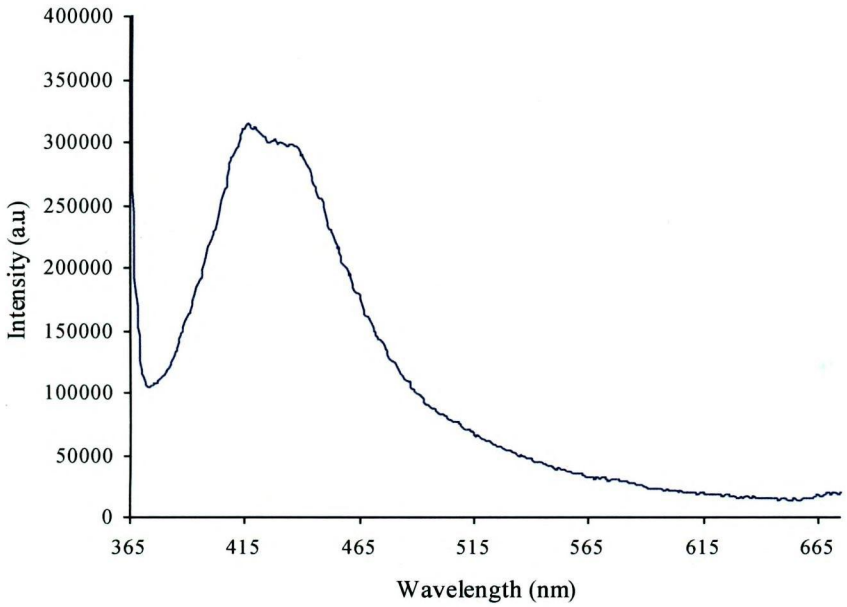

Fig 4.42 PL spectrum of TiO_2 thin film annealed at 450°C (Sample 4)

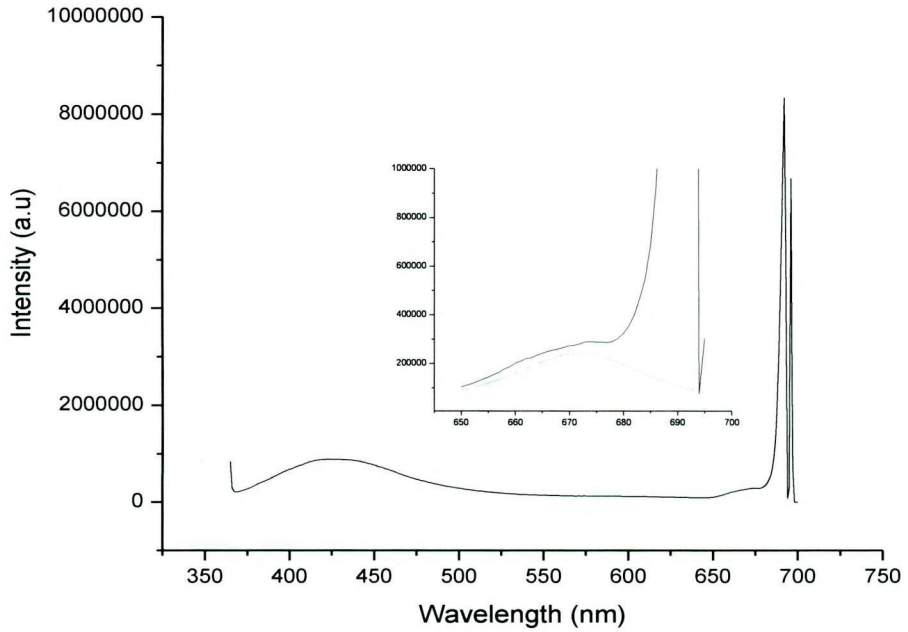

Fig 4.43 PL spectra of dye sensitized TiO_2 thin film (Sample 4)

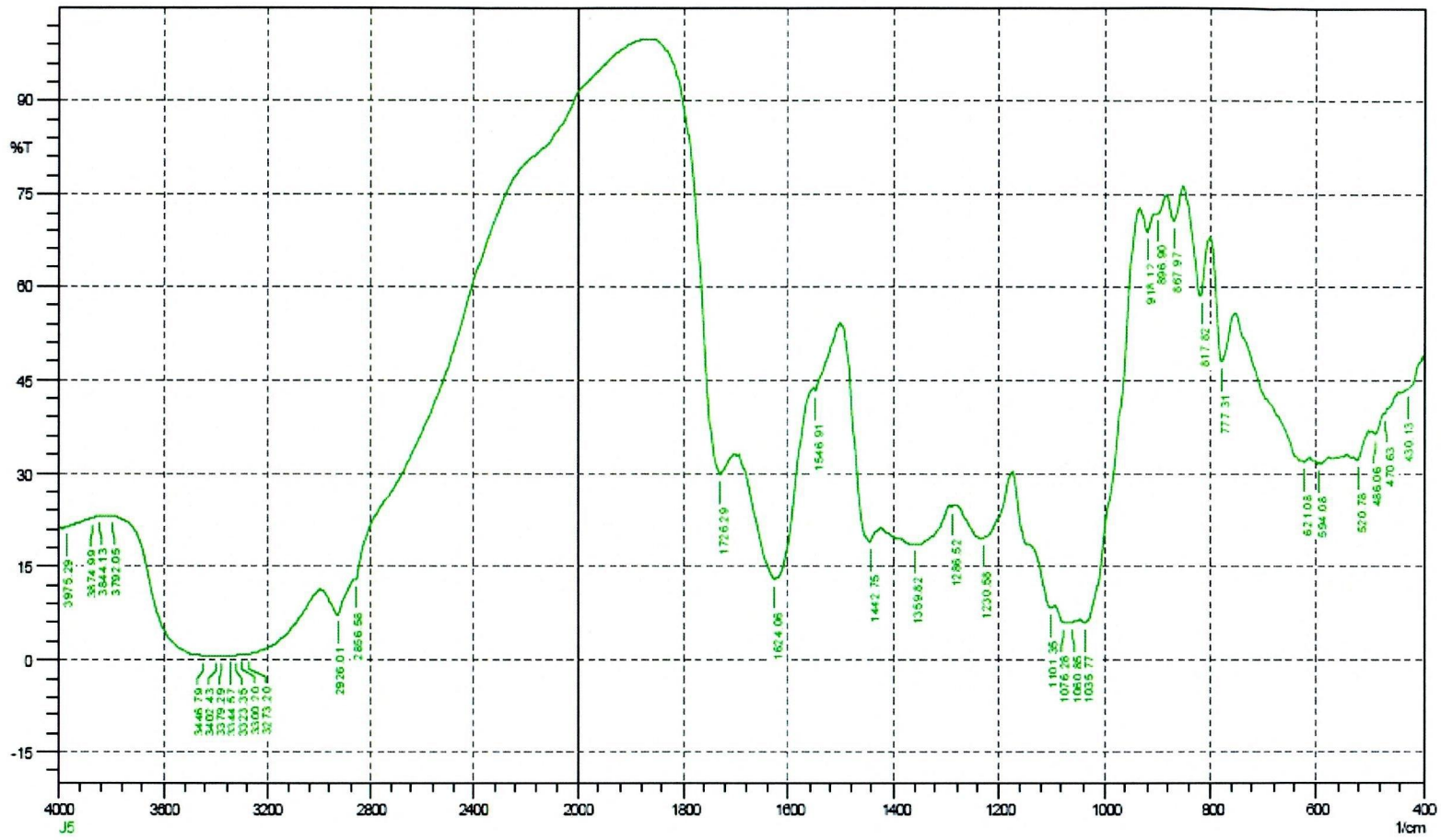

Fig 4.44 FTIR spectrum of *Eugenia Jambolana* powder