

OPTICAL PROPERTIES OF ORGANIC LUMINESCENT HYBRID THIN FILMS

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ABSTRACT

Hybrids semiconductor is very important in term of developing displays with huge industrial applications. In this study, titanium dioxide (TiO_2), which is well known in capability of emitting light is used as a host to synthesize hybrids. TiO_2 thin films doped with Eu(III)-phen, Er(III)-phen, and Tb(III)-phen complexes were prepared by sol-gel dip-coating process on the glass substrate. Synthesis parameters such as annealing temperature and percentage of doped ions (europium, erbium and terbium) on the highly oriented crystal growth were studied in detail. The bond configuration of the lanthanide organic complex was analyzed by using FTIR. X-ray diffraction measurements were carried out to determine the crystallinity of the resultant thin films, whereas FESEM and EDX were performed to observe morphology and elemental composition of the films, respectively. Besides, the bandgap energies of both undoped and doped TiO_2 thin films were measured from diffused reflectance analysis.

INTRODUCTION

Organic-inorganic hybrid materials have great potential for many applications due to the synergy between the properties of these two different building blocks the concept of 'hybrid organic-inorganic materials' emerged over the past decade with the expansion of soft inorganic networks to exhibit their extraordinary properties such as luminescent materials in lighting and displays, optical amplifier and lasers [1]. The development of sol gel derived hybrids where luminescent centers are incorporated in organic or inorganic hosts is a recent theme in the field of luminescent materials [2]. For technological applications, these luminescent lanthanide organic complexes have to be incorporated into a stable solid matrix. Lanthanide complexes are generally incorporated into different substrates or matrixes, including sol gel materials, supramolecules and porous materials [3].

The approach of using rare-earth ions as activators and semiconductors as host offers the advantage of combining the optical properties of rare-earth ions and the unique qualities of the semiconductors. Among these hosts, titanium dioxide (TiO_2), a very important n-type semiconductor, is a technologically important material and is widely used as photocatalysts, transparent conductors, dielectrics, electrochromic films and 'self-cleaning' coatings on windows and tiles [4] for its fine physical, chemical and optical properties. TiO_2 has been extensively used for solar energy conversion, photocatalysis and gas sensing because of its high photo-catalytic activity, stability with

suitable band gap. TiO_2 has three main crystal phases: anatase, rutile and brookite. Among these phases, anatase phase, which is a metastable phase, is also chemically and optically active and suitable for photocatalyst. TiO_2 gives better solar cell efficiency compared to other crystal structures [5]. Because of its wide usefulness, a number of techniques have been used to prepare TiO_2 thin films, such as thermal oxidation [6], sputtering [7,8], pyrolysis [9,10], chemical vapour deposition (CVD) [11,12] and sol-gel process [13-15].

Rare earth organic complexes constituted by an excitation harvesting ligand attached to an emitting ion (Tb^{3+} , Eu^{3+} , Er^{3+}) have been subject of much research since the first demonstrations of their reliability as active layer in Vis and near-IR organic light emitting diodes [16,17]. These molecular systems strongly absorbing in the UV and possessing a consistent Stokes shift of their emission towards the region of the maximum conversion of the solar radiation. Low temperature encapsulation of a solar cell with a coating doped light harvesting complex is supposed to allow an improvement of the quantum efficiency of a commercial photovoltaic system without modification of the industrial process leading to the fabrication of the solar modules [18]. In this work, we present a technique of TiO_2 thin film preparation on glass substrates by co-doping of Eu(III), Er(III), Tb(III) and 1,10-phenanthroline in the TiO_2 sol-gel matrix.

METHODOLOGY

Preparation of Coating Solution

The polymer hybrids will be prepared by the sol-gel technique and solvent cast into flat sheets. Titanium dioxide is chosen as the metal oxide semiconductor. Chemically extra pure Titanium (IV) isopropoxide (TIP) and HNO_3 (65% w/w) are utilized as starting materials without further purification. Distilled water (H_2O) is used for hydrolysis. The TiO_2 precursor sol will be prepared by mixing 400 mL of H_2O and 3.8 mL of HNO_3 (65% w/w). Then 36 mL of TIP will be added dropwise to the H_2O - HNO_3 solution under continuous stirring. After stirring for 24 hours, the resultant solution (sol) will be aged for 6 hours at room temperature.

Deposition of TiO_2 Films

The glass substrates will be dipped into the coating solution, withdrawn at a regulated speed of 100mm/min and then undergo drying process at 150 °C for 5 min. Finally, the gel films obtained will successively heat-treated at 300-600 °C for 4 hours. The effect of the films structure on preparative stages will also being investigated. The flow chart showing the preparation process of coating films is illustrated in Figure 1.

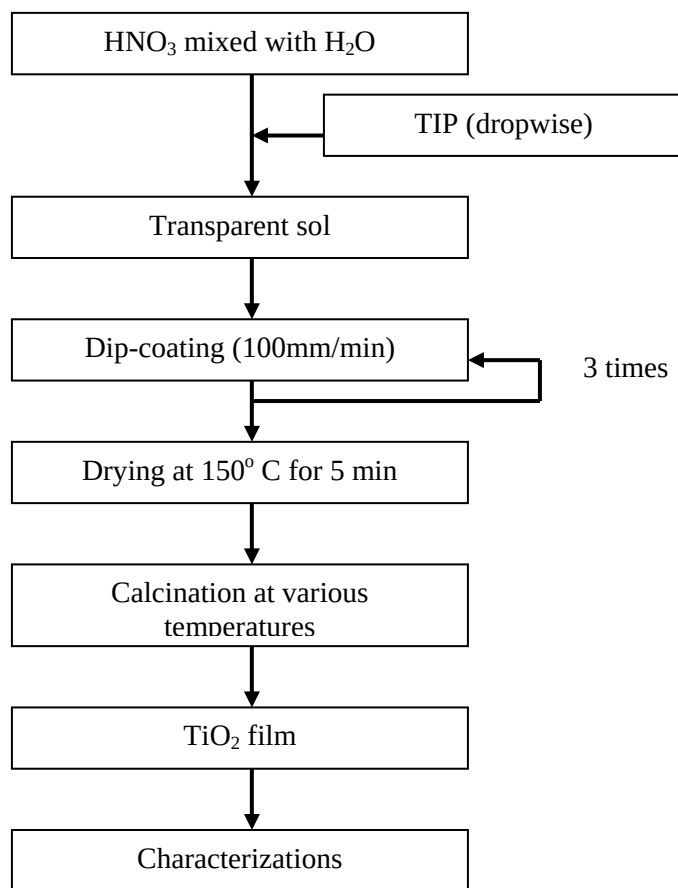


Figure 1: Flow chart of the preparation process of TiO₂ film

Deposition of Lanthanide Complexes of nc-TiO₂ Films

[Er(phen)₂](NO₃)₃ (phen = 1,10 phenanthroline) = ErPN Synthesis :

A solution of ortho-phenanthroline (4 mmoles) in 50 mL of absolute ethanol and 2 mmoles of erbium nitrate salt in 10 mL of deionized water was heated to boiling, filtered, and treated with 150 mL of boiling acetone. The solution was allowed to stand at room temperature for two days and deposited the crystalline, analytical pure chelate (Melby *et al.*, 1964). [Eu(phen)₂](NO₃)₃ = EuPN and [Tb(phen)₂](NO₃)₃ = TbPN complexes were synthesized using the same procedure.

Synthesized lanthanide complexes (ErPN, EuPN, TbPN) will be dissolved in dimethyl formamide (DMF) solvent and 1, 3, 5, 7 and 10 wt % solution will be prepared for all complexes, respectively. The transparent TiO₂ layers will then being immersed for 2 days in that solution separately. The complex-coated TiO₂ films will be rinsed with DMF and dry under nitrogen flow.

Deposition of Semiconducting Polymer Layer on Complex-coated TiO₂ Films

The two types of semiconducting organic polymers (n and p type) will be used. Several semiconducting organic polymers like poly (benzimidazobenzophenanthroline), poly

(3-octylthiophene-2,5-diyl), or poly (3-methylthiophene) will be dissolved in toluene according to the ratio of 10 mg polymer in 1 mL toluene. Hole transport layer will then be coated by spin-coating.

Characterizations

FTIR spectra of TiO_2 and synthesized lanthanide organic complexes were measured in the wavenumber range from $4000\text{--}400\text{ cm}^{-1}$ by using a spectrometer (Spectrum One, Perkin Elmer, USA). The crystallinity and the structure of TiO_2 thin films were examined using X-ray Diffraction (XRD) method (Bruker Diffractometer D5000, Germany). The surface morphology of the prepared films was investigated from the magnified images of the films surface by field emission scanning electron microscopy (FESEM) (Philips, model XL 40) incorporated with energy dispersive X-ray analysis (EDX) (EDAX Inc. USA). The absorption spectrums of lanthanide complexes and TiO_2 thin films were monitored by UV-Vis DR spectroscopy technique. UV-Vis DR spectra were recorded under ambient conditions on a Perkin Elmer Lambda 900 UV VIS/ NIR spectrometer.

RESULTS AND DISCUSSIONS

Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of synthesized complexes have been investigated in the region $4000\text{--}400\text{ cm}^{-1}$. The infrared spectra of ligand (1, 10-phenanthroline) and synthesized complexes were selected for comparison. Similar types of peaks are observed for the complexes synthesized in the present investigation as depicted in Figure 2.

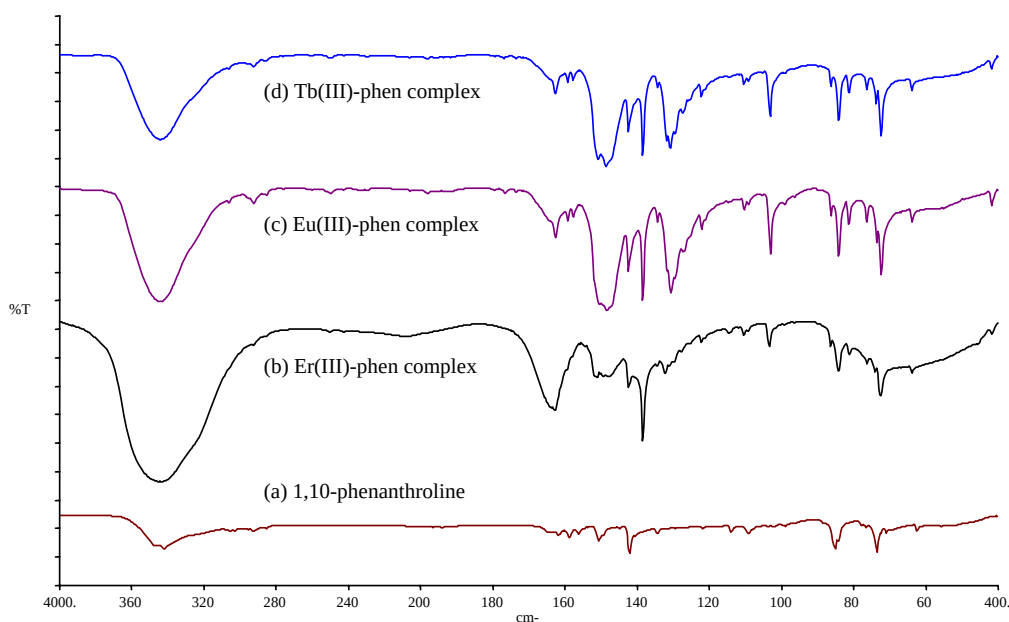


Figure 2: FTIR spectra of the samples; (a) ligand 1,10-phenanthroline, (b) Er(III)-phen complex, (c) Eu(III)-phen complex and (d) Tb(III)-phen complex

All the complexes exhibit a very strong band between 1300-1700 cm^{-1} and a medium band at 1000-1200 cm^{-1} . These absorptions are principally ring stretching vibrations at 1627 cm^{-1} (C=N) and 1487 cm^{-1} (C=C) are similar to the bands at 1618 cm^{-1} and 1505 cm^{-1} in the free ligand. All the complexes possess very intense absorptions at 724-727 cm^{-1} . New bands are observed for the complexes at 1300-1500 cm^{-1} , 800-1250 cm^{-1} and 400-450 cm^{-1} . The results tend to indicate that 1,10-phenanthroline molecules are chelated to the metals. The spectra of all 1,10-phenanthroline complexes show strong and broad absorption bands in the water stretching region (3200-3600 cm^{-1}).

X-Ray Diffraction (XRD) Analysis

XRD was used to characterize the structure and for identification of the crystalline phases of the prepared samples. Figure 3 shows the XRD patterns of undoped TiO_2 thin films deposited on glass substrates calcined at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C.

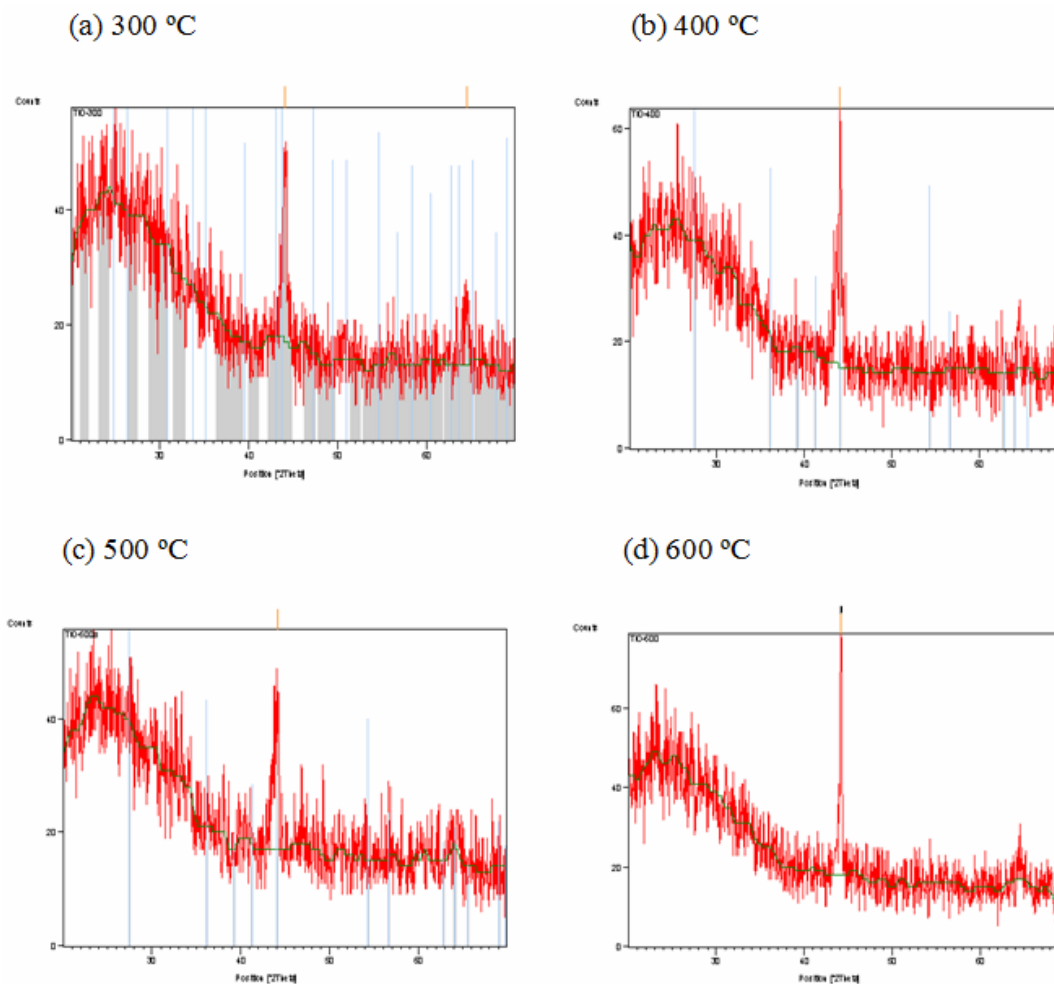


Figure 3: X-ray diffractogram of undoped TiO_2 thin films deposited on glass substrates calcined at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C

It can be seen that all TiO_2 films show similar XRD patterns and have tendency to semicrystalline oriented and exhibit the mixed phases of rutile and anatase. However, as the films are calcined at higher temperatures, the peaks appeared more intense. Figure 3 (a) and (b) show the peak intensity increases when the annealing temperature increased from 300 °C to 400 °C, respectively. It is also similar when the film is annealed from 500 °C up to 600 °C as illustrated in Figure 3 (c) and (d). All XRD spectra indicate that the crystallinity of TiO_2 thin films improved upon calcination at higher temperatures.

Field Emission Scanning Electron Microscopy (FESEM)

Surface morphology, one of the prime factors that govern the physical as well as the electro-optical properties of the TiO_2 thin film materials, has been studied by means of FESEM analysis. Besides, to confirm the presence of TiO_2 attained on the films, EDX analysis was carried out.

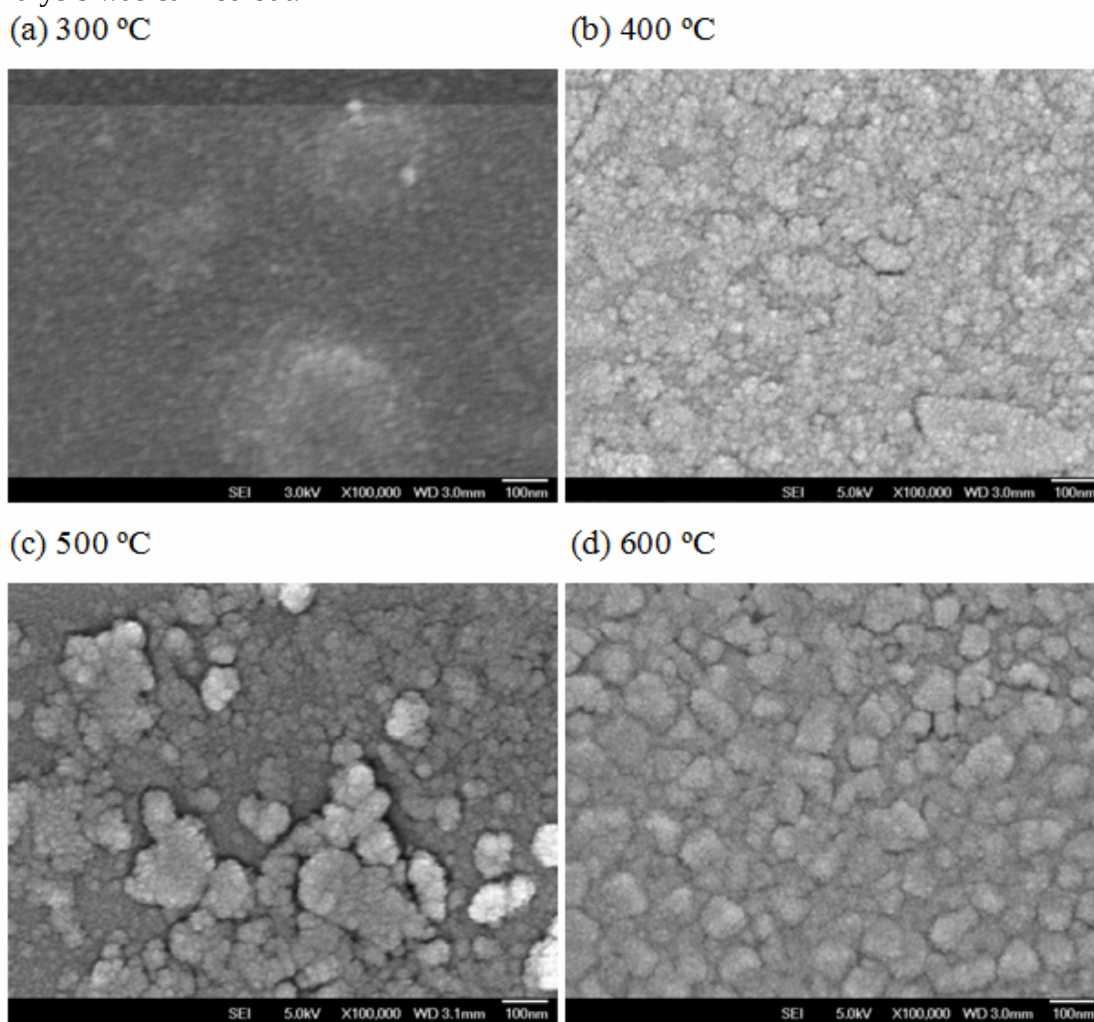


Figure 4: FESEM micrograph of TiO_2 thin films deposited on glass substrates calcined at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C

Figure 4 shows the FESEM micrograph of the surface of TiO_2 thin film deposited on glass substrate with different annealing temperature, respectively. Figure 4 (a) shows the FESEM micrograph of the surface of TiO_2 films annealing at 300 °C. The film shows a plain and smooth surface. This indicates that the TiO_2 thin film layer has been successfully coated on the glass substrates and uniformly distributed. With increasing annealing temperature up to 600 °C, the surface morphology shows the grains of TiO_2 thin film tends to agglomerate, thus become larger and denser as illustrated in Figure 4 (c) and (d). The grains grow larger with the increase in annealing temperature. Therefore, the particle size increased and more voids are present in the films. Ranga Roa *et al.* [5] suggested that at higher temperature, TiO_2 particles have a strong tendency to agglomerate to larger particles, which lead to a decrease in the surface area, thus reduce its applicability.

Energy Dispersive X-ray Spectroscopy (EDX)

EDX is a chemical microanalysis technique used in conjugation with FESEM and used to characterize the elemental composition of the TiO_2 thin films. A typical EDX pattern of the coated TiO_2 film is shown in Figure 5. An elemental composition of the thin film was found to be 47.94% O, 45.09% Si and 6.97% Ti where the presence of TiO_2 on the film was confirmed.

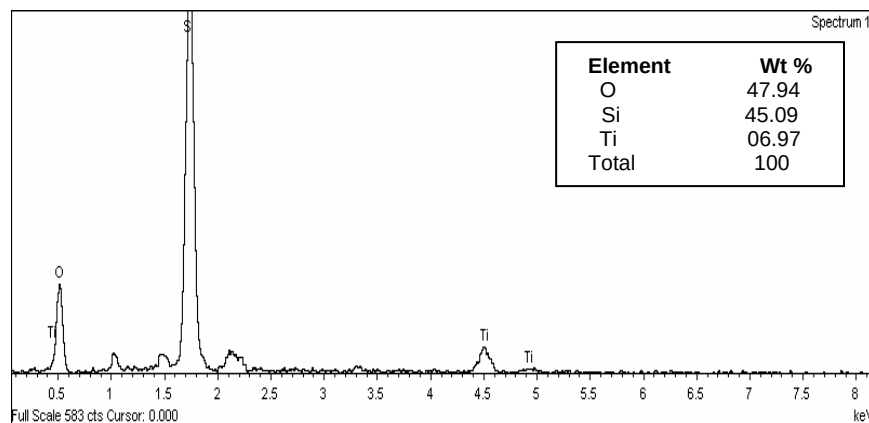


Figure 5: EDX spectrum of TiO_2 thin film coated on glass substrates

UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DR)

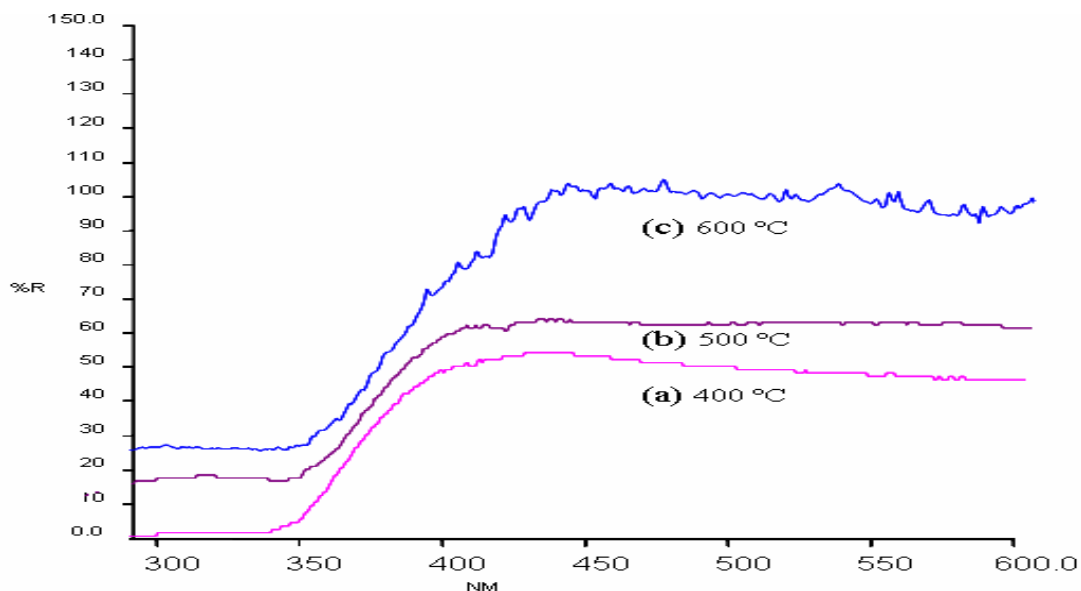


Figure 6: Diffuse reflectance spectra of TiO_2 thin films deposited on glass substrate with different annealing temperatures; (a) 400 °C, (b) 500 °C and (c) 600 °C

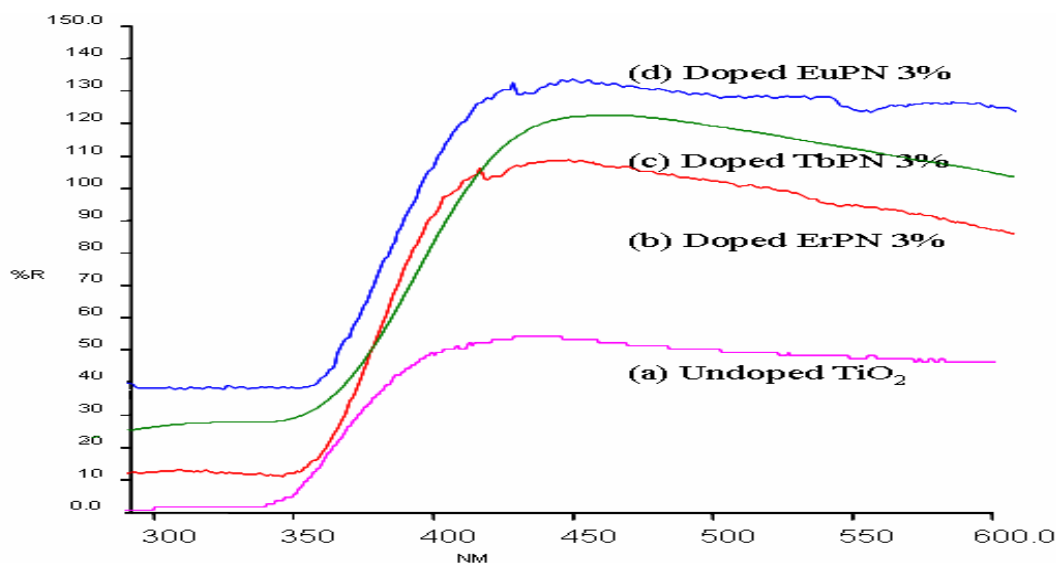


Figure 7: Diffuse reflectance spectra of TiO_2 thin films with annealing temperature at 400 °C; (a) undoped TiO_2 , (b) doped ErPN 3%, (c) doped TbPN 3% and (d) doped EuPN 3%

Diffuse reflectance spectra of the TiO_2 thin films investigated can be seen in Figure 6 and Figure 7. Based on these reflectance spectra the absorption edge for each sample was determined. Using these absorption edge values, the band gap energy was calculated as shown in Table 1.

Table 1: Absorption edges and band gap energies of the prepared TiO₂ thin films

Sample	Absorption Edge (nm)	Band Gap Energy (E _g ; eV)
undoped TiO ₂ films calcined at:		
(a) 400 °C	348	3.57
(b) 500 °C	352	3.52
(c) 600 °C	355	3.49
doped TiO ₂ films calcined at 400 °C:		
(a) ErPN 3%	355	3.49
(b) TbPN 3%	354	3.50
(c) EuPN 3%	359	3.46

Table 1 shows that the values of bandgap energy of TiO₂ films deposited on the glass substrate decrease when the annealing temperatures are increased. The decrease in the bandgap is due to the increase in the particle size due to agglomeration during calcination process. From Figure 6, it is clearly seen that the absorption edge shifts to higher wavelength values for higher deposition temperatures. The result agrees with the FESEM images (Figure 4 (c) and (d)) where particles grow larger with the increase in annealing temperature. This suggest that the bandgap values for TiO₂ can vary depending on particle size of the material, with smaller bandgap values indicative of relatively densely packed crystalline structures. Besides, the introduction of dopants also shows the decreasing in bandgap value of TiO₂ thin film as illustrated in Table 1. This trend, again being consistent with the literature.

CONCLUSION

In this study, titanium dioxide (TiO₂) thin films have been successfully deposited on glass substrates. The Eu (III)-phen, Er (III)- phen and Tb (III)-phen complexes can be doped in TiO₂ sol-gel matrix to form homogeneous coating solution. The formation of lanthanide (III)-phen complexes was confirmed by FTIR spectroscopy. XRD and FESEM illustrate the structural and morphology, when the annealing temperature was increased from 300 °C to 600 °C, where the films tend to crystalline and the grain size of the films are increased due to the agglomeration of TiO₂ particles. The optical properties of the thin films show the bandgap value of TiO₂ semiconductor films decreased upon the introduction of dopants and increasing in the heat treatment temperatures.

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REFERENCES

- [1]. Q.M. Wang, B. Yan and X.H. Zhang (2006). *Journal of Non-Crystalline Solids*. **352**, 4136-4141
- [2]. C.R. Neri, P.S. Calefi, Y. Iamamoto and O.A. Serra (2003). *Materials Research*. **6**, 1516-1523.
- [3]. Y. Wang, L. Wang, H. Li, P. Liu, D. Qin, B. Liu, W. Zhang, R. Deng and H. Zhang (2008). *Journal of Solid State Chemistry*. **181**, 562-566.
- [4]. S.J. Bu, Z.G. Jin, X.X. Liu, L.R. Yang and Z.J. Cheng (2005). *Journal of the European Ceramic Society*. **25**, 673-679.
- [5]. A.R. Roa and V. Dutta (2007). *Solar Energy Materials and Solar Cells*. **91**, 1075-1080.
- [6]. G.P. Burns (1989). *Journal of Applied Physics*. **65**, 2095.
- [7]. S. Schiller, G. Beister, and W. Sieber (1981). *Thin Solid Films*. **83**, 239.
- [8]. M.H. Suhail, G.M. Rao and S. Mohan (1992). *Journal of Applied Physics*. **71**, 1421.
- [9]. K. Okimura, N. Maeda and A. Shibata (1996). *Thin Solid Films*. **281/282**, 427.
- [10]. G.W. Rice (1987). *Journal of the American Ceramic Society*. **70**, C117.
- [11]. S. Zhang, Y.F. Zhu and D.E. Brodie (1992). *Thin Solid Films*. **213**, 265.
- [12]. K.S. Yeung and Y.W. Lam (1983). *Thin Solid Films*. **109**, 169.
- [13]. J.P. Lu, J. Wang and R. Raj (1991). *Thin Solid Films*. **204**, L13.
- [14]. K.A. Vorotilov, E.V. Orlova, and V.I. Petrovsky (1992). *Thin Solid Films*. **207**, 180.
- [15]. V.J. Nagpal, R.M. Davis and S.B. Desu (1995). *Materials Research*. **10**, 3068.
- [16]. R.G. Curry and W.P. Gillin (2000). *Applied Physic Letters*. **77**, 2271.
- [17]. J. Kido, K. Nagay, Y. Okamoto and T. Skotheim (2000). *Chemical Letters*. 1267.
- [18]. S. Marchionna, F. Meinardi, M. Acciarri, S. Binetti, A. Papagni, Pizzini, V. Malatesta and R.
- [19]. Tubino (2006). *Journal of Luminescence*. **118**, 325-329.