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Research

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Synthesis and characterization of Eu^{3+} doped TiO_2 thin films deposited by spray pyrolysis technique for photocatalytic application

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Abstract:

In this study, nanocrystalline TiO_2 : Eu^{3+} thin films are successfully formed by spray pyrolysis technique deposited on glass substrate. Optical, electrical, structure, surface morphology, and photocatalytic degradation of Methylene blue have been examined. The optical properties of the films are analyzed using transmittance and reflectance spectra, which are measured using UV-Vis-NIR double-beam spectrophotometer. Optical properties such as refractive index (n), extinction coefficient (k), optical conductivity (σ) and Urbach energy (E_u) have been calculated as a function of Eu^{3+} concentration. Film thickness were evaluated using the refractive index dependence on wavelength. The films thickness were determined as 97.13, 122.62, 123.24, 117.14 and 128.25 nm, respectively, for Eu doped TiO_2 at 0,4, 6, 8 and 10 wt % doping concentration. The band gap values raised from 3.29 to 3.42 eV with increasing the Eu^{3+} dopant concentration. The highest electrical conductivity was found to be $3.01 \times 10^{-2} (\Omega \cdot \text{cm})^{-1}$ at high doping level with 10 wt% Eu^{3+} . The XRD analysis illustrate the tetragonal crystal structure of films with anatase phase and reduces crystallite size

linearly with increasing Eu^{3+} concentration. Scanning electron microscopy (SEM) analysis indicated consistent allocation of irregular and spherical shaped grains covering the substrate surface. The average grain size in range of 82.5 – 51.1 nm is observed and films show porous nature. The photocatalytic effect of TiO_2 : Eu^{3+} thin films is predicted from the degradation of methylene blue (MB) at room temperature under UV light irradiation. An enhancement in photocatalytic degradation observed by increasing the amount of Eu^{3+} due to increase in the e/h pair production and increase of film thickness. These results make TiO_2 : Eu^{3+} thin films as attractive candidate for photovoltaic cells and other optoelectronic device applications

Keywords: , TiO_2 ,europium, doping, spray pyrolysis, photocatalytic .

Introduction:

Research on TiO_2 has drawn a lot of interest due to its unique characteristics. TiO_2 is a wide band gap semiconductor, nontoxic material, high hardness, displays a large range of electrical conductivity, shows mechanical and chemical stability, low cost materials with high light conversion efficiency and high dielectric constant. ¹⁻³ It is suitable for many applications such as gas sensor, solar cell, bio-medical product, water treatment and optoelectronic device. ⁴⁻⁵ Many studies have been focused to improve the optical, electrical and photocatalytic activity of TiO_2 by dye sensitizing and surface deposition with rare earth metals doping.

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Rare-earth doped semiconductor has been used in several applications including cathode ray tube (CRT) displays, solid-state lasers, sensors, fluorescent markers, radiation detection and medical applications.⁶ The motivation for the use of rare earth dopants in these applications arise from the bright, spectrally narrow emissions, largely irrespective of the host material. Rare earth ions display a robust release due to 4f–4f movement of electrons from top to bottom level.⁷ RE ions doped semiconductor collect the organic impurities on the surface due to the formation of lanthanide ions complexes with Lewis centers (e.g., organic acids, amines, aldehydes and alcohols). The interaction between functional groups and f-orbital increase the efficiency to separate electrons and holes.⁸ In trivalent rare earth ions the 4f orbital is incomplete while the 5s and 5p orbitals are filled, resulting in 4f orbital comprises the 5s and 5p orbitals consequences electron transitions within the incomplete 4f orbital and shielding of the 4f states from the electric field of the host. Titanium oxide can construct complexes of f-orbitals that absorb external ions near the surface and tune the band gap by improving photocatalytic movement.⁹ Among the rare earth elements, Eu^{3+} (Erbium) ions are more suitable for doping with TiO_2 due to its excellent Optical, properties, high photocatalytic activity and chemical performance. Eu^{3+} has unique luminance properties because of sharp emission of radiation in visible range attributed to intra 4f and 4f-5d transition.¹⁰

There are several approaches to prepare Eu^{3+} doped TiO_2 in variant forms due to its strong dependence on preparation technique, doping concentration, films thickness and particles size. Leostean et al. (2013)⁴ prepared nanoparticles of Eu doped TiO_2 using some organic additives such as polyethylene glycol 600 and methacrylic acid (MA). They found TiO_2 : Eu nanoparticles shows high

capacity to absorb organic additive lead to red luminescence which associated with XRD and TEM results. Zhu et al.(2014).¹¹The electroluminescence effect of TiO₂/p+-Si heterostructure devices has been investigated by TiO₂:Eu films and annealing temperature. It has been reported, the high Eu concentration and annealing temperature, the transfer of energy TiO₂ host to Eu³⁺ ions display red electroluminescence from TiO₂:Eu/p+-Si heterostructures. The influence of particle size and Eu-doped TiO₂ nanophosphor on optical behavior has been studied by Raman spectra and photoluminescence. The films demonstrate the PL discharge $^5D_0 \rightarrow ^7F_J$ (J=0, 1, 2, 3, 4, 5) due to changing within Eu³⁺ ions at wavelength 393nm in the near visible region.¹² A high photocatalytic activity response with a rise in Eu content was observed. However, Amorphous titania particles doped with Eu(III) acetylacetonate with atypical molar Eu/Ti ratios are elaborated at concentration of Eu = 0.125, 0.5, 2.0 and 5.0 using sol gel method was studied.¹³It was observed that ideal Eu/Ti value (0.5) that displayed greatest luminescence. Moreover, the Eu (acac)³ doping is suitable for optoelectronic, organic, and environmental purposes.

Moreover, to modify optical and biological findings of TiO₂ thin films by doping with rare earth element, researchers are trying to change the synthesis process. Among the mostly used process magnetron sputtering,¹⁴ plasma oxidation,¹⁵ sol gel,¹⁶ spray pyrolysis,¹⁷ electrospinning,¹⁸ hydrothermal method and pulsed laser deposition (PLD).¹⁹ The spray pyrolysis method is considered as a simple and low cost method. It has capability to produce wide variety of nanostructured materials with high quality, and homogenous films of different doping elements on different substrates, which can be used as sensors and other application.

In this article, we concern on investigation the effects of dopant concentration on physical findings of Eu^{3+} doped TiO_2 thin films. The purpose of present work is focused on synthesise of TiO_2 : Eu^{3+} thin film nanostructures by spray pyrolysis method and studied its optical, electrical, structural, surface morphology and photocatalytic properties at different doping concentration.

Experimental:

i. Preparation of pure TiO_2 solution:

First 1.6 ml Titanium (IV) isopropoxide $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (purity 98.0%,Sigma Aldrich) was dissolved with 4.5 ml of isopropanol and 5.15 ml of acetic acid (CH_3COOH) (Sigma Aldrich) was added. Then the solution stirred with a magnetic stirrer at 60 °C for 15 min. After stirring 12 ml of ethanol (purity 99.9%) mixed with the solution and then stirred for 2 hours at 60°C.

ii. Preparation of Eu^{+3} doped TiO_2 solution:

$\text{Eu}(\text{NO}_3)_3$ (purity 99.9%) was used as a Erbium source. To prepare the different rates (4, 6, 8 and 10 wt %), Eu^{3+} doped TiO_2 solutions were prepared by dissolved calculated amount of compound $\text{Eu}(\text{NO}_3)_3$ 3 ml of isopropanol and acetic acid then mixed at room temperature for 15 min. The resulting solutions were added dropwise to pure TiO_2 solution under constant stirring for 1hour at 60 °C. The final solutions were kept in the beakers and aged for 24 hours before films deposition.

iii. Films deposition:

The films deposited on glass substrates using spray pyrolysis method. Prior to the deposition of the thin film, the glass substrates were pre-cleaned with

an acetone, ethanol and distilled water using ultrasonic cleaner to improve their adhesion nature. The cleaned substrates were dried for 10 min before use. The pure and doped solution with different doping concentration (0, 4, 6, 8 and 10 wt %) of Eu^{3+} was backed-up in a spray container and dispersed the solution on the glass substrate to prepare uniform films. Deposition parameters such as spray time, nozzle diameter, substrate temperature, and spray nozzle- substrate distance were kept constant during the whole deposition process. The spraying time was about 15 s with the period between spraying processes was about 3 min to avoid cooling of the substrates and a nozzle diameter of 0.7 mm. The glass substrate temperature was 350 °C and air pressure was 1 bar. The height of spraying nozzle was 35 cm during the deposition process. After the deposition of the thin layers, the resulting thin films were annealed at 400 °C in air at a heating rate of 5 °C/min and cooled down to room temperature.

FIG.1. spray pyrolysis set up.

Characterization:

Optical properties of thin films obtained using UV-Vis-NIR double-beam spectrophotometer in 250–800 nm range at room temperature. The electrical characterizations of samples were investigated by four-point probe method (KIETHLEY Instrument). X-ray diffractometer (XRD) (Model JSDX-60PA) with monochromatic high- intensity Cu K α radiation ($\lambda = 0.154184$ nm) in the scanning range of (2θ) was between 20° and 80° with a slow scanning speed ($1^\circ/\text{min}$) and a minor time constant (1 s) used to study the structural properties of as-deposited films. The surface morphology of the films was investigated by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6500) at 10 kV. Photovoltaic characteristics of the samples were tested using Methylene Blue degradation at room temperature, which is used as a model contaminant. The photocatalytic degradation measured by UV-Vis double-beam spectrophotometer at an incident wavelength of 665 nm. The estimation done under UV light 50 W xenon lamp (Electro-Technic Products, USA) as a source of UV light.

Result and discussion:

i. Optical studies:

Transmittance :

Optical transmittance of undoped and various $\text{TiO}_2\text{: Eu}^{3+}$ thin films against wavelength were illustrated in Figure 2. The transmittance of light visible range for undoped TiO_2 thin films is over 65%. However the transparency of $\text{TiO}_2\text{: Eu}^{3+}$ films enhance up to 80% with increase the doping concentration. These results show that the highest transmittance at high doping concentration due to the minimized of light scattering with doping.²⁰

FIG.2. Transmission spectra of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Reflectance:

The reflectance spectra of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ films were shown in figure 3. It was observed that reflectance ability of undoped TiO_2 thin film is higher compared to reflectance ability of doped films. This is the consequence of structural disorder in TiO_2 lattice and change the films thickness.²¹

FIG. 3. Reflectance spectra of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Refractive index:

The refractive index for undoped and $\text{TiO}_2\text{:Eu}^{3+}$ thin films at different wavelengths were calculated using Eq(1):²²

$$n = \frac{(1+R)^{0.5}}{(1-R)^{0.5}} \quad (1)$$

Where n is the refractive index and R is the reflectance

The refractive index, n , of undoped and $\text{TiO}_2\text{:Eu}^{3+}$ films deposited at different doping concentration is depicted in Figure 4. The $n(\omega)$ values show a general decrease as the wavelength increases for all films and tend to decrease with increasing Eu^{3+} doping. The introducing of Eu^{3+} atoms may increase the films density. For this reason, the refractive index at high doping concentration, get smaller which can be explained by the tendency of Eu^{3+} nanoparticles to fully oxidize phase Eu_2O_3 . A similar behavior has been reported for Cr doped TiO_2 thin films are formed by magnetron co-sputtering process.²³

FIG. 4. Effect of doping concentration on refractive index of undoped and $\text{TiO}_2\text{:Eu}^{3+}$ thin films.

Thickness:

Films thickness can be evaluated by using the Eq(2) below: ²⁴

$$d = \frac{\lambda_1 \lambda_2}{(n_1 \lambda_2 - n_2 \lambda_1)} \quad (2)$$

Here λ_1 and λ_2 are the consecutive wavelength of maxima and minima while n_1 and n_2 are their refractive indices. Table I summarizes the thickness (d), refractive index (n) of the undoped, and TiO₂: Eu³⁺ prepared at different doping concentration. Where un doped films show lower thickness. Films thickness depends on the initial amount of solution spread on the substrate thus the thickness varies with doping concentration.

Table I. Thickness and refractive index of the undoped, and TiO₂: Eu³⁺.

Sample	λ_1 (nm)	n_1	λ_2 (nm)	n_2	d (nm)
TiO ₂	312	3.796	798	1.494	97.13
TiO ₂ :Eu ³⁺ 4 wt%	313	3.181	699	1.403	122.62
TiO ₂ :Eu ³⁺ 6wt%	314	3.183	687	1.390	123.24
TiO ₂ : Eu ³⁺ 8 wt%	312	3.180	791	1.310	117.14
TiO ₂ : Eu ³⁺ 10wt%	311	2.92	797	1.269	128.25

Extinction coefficient:

The extinction coefficient (k) is calculated by Eq(3): ²⁵

$$k = \frac{\alpha \lambda}{4\pi} \quad (3)$$

Where α was determined using the relation(4): ²⁶

$$\alpha = 2.303 \times \left(\frac{A}{d}\right) \quad (4)$$

Where A is the absorbance and d is the films thickness.

Figure 5 shows the change in extinction coefficient of $\text{TiO}_2:\text{Eu}^{3+}$ thin films with wavelength. It's clear from the figure that the extinction coefficient at 280 nm decrease for un doped and $\text{TiO}_2:\text{Eu}^{3+}$ films. This may be attributed to energy loss because of scattering and dispersion with increasing wavelength. These results confirm what we mentioned before that $\text{TiO}_2:\text{Eu}^{3+}$ films are transparent for visible light.

FIG. 5. Effect of doping concentration on extinction coefficient of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Optical band gap:

The optical band gaps for un doped TiO_2 and $\text{TiO}_2:\text{Eu}^{3+}$ has been computed by UV-vis spectra and presented in Figure 6 by Tauc Eq (5) below:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (5)$$

Where α is absorption coefficient, h is plank constant, ν is frequency, A and n are constant and E_g is optical band gap. For direct, forbidden, and indirect transitions the values of refractive indices are reported as $n=1/2$, $2/3$, and 2 , respectively.²⁷ The obtained band gap results are presented in Table II. The detected values were higher than the band gap of bulk TiO_2 in anatase phase which value is 3.18 e V. ²⁸ The Increment in band gaps of Eu^{3+} doping TiO_2 thin films oxygen partial pressure on it. This caused the extension of the band –tail into the band gap, ²⁹ growth defect, charge impurities, disorder at the grain boundary and Burstein Moss effect. Where the bottom states of conduction band are stopped transition occur in levels higher energy than Fermi energy. In contrast, Camps et al.(2017).¹ has been reported that the presence of Eu doping with TiO_2 thin films prepared through laser-assisted technique reduces the band gap because of creation of impurities and new energy states within TiO_2 band gap.

FIG. 6. Direct band gap plot of undoped and $\text{TiO}_2: \text{Eu}^{3+}$ thin films.

Urbach energy:

The Urbach energy E_u for undoped and $\text{TiO}_2: \text{Eu}^{3+}$ thin films was calculated formula(6):³⁰

$$\alpha = \alpha_0 + e^{\frac{h\nu}{E_u}} \quad (6)$$

Where α is absorption coefficient and α_0 indicates the a constant. Urbach energy is determined for undoped and $\text{TiO}_2: \text{Eu}^{3+}$ thin films from the slope of $\ln(\alpha)$ versus energy graph (See Figure 7). as shown in figure (7). The computed urbach energy is reported in Table II. It is noted that there was a significant decrease in the Urbach energy with doping. The undoped film had a value of 23.03 m eV compared to $\text{TiO}_2: \text{Eu}^{3+}$ films. The change in Urbach energy due to introduce impurity level and defect in the band structure after doping either on the conduction band or valence band or both conduction and valence bands. These results are very good agreement with literature.³¹

Table II. Variation of band gap and Urbach energy of the undoped, and $\text{TiO}_2: \text{Eu}^{3+}$ films

Sample	Energy gap E_g (eV)	Urbach energy E_u (meV)
TiO_2	3.29	23.03
$\text{TiO}_2: \text{Eu}^{3+}$ 4 wt%	3.33	21.23
$\text{TiO}_2: \text{Eu}^{3+}$ 6 wt%	3.37	19.63
$\text{TiO}_2: \text{Eu}^{3+}$ 8 wt%	3.40	17.35
$\text{TiO}_2: \text{Eu}^{3+}$ 10wt%	3.42	13.25

FIG. 7. Urbach plot of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Optical conductivity:

Optical conductivity, σ is found from the values of absorption coefficient α and the speed of light by using formula (7):²⁷

$$\sigma = \frac{\alpha n c}{4\pi} \quad (7)$$

The Figure 8 shows the plot between σ with photon energy of undoped and all $\text{TiO}_2:\text{Eu}^{3+}$ films for various concentrations. From the graph, it is noticeably clear that in the low-energy region, optical conductivity values of un doped and doped films were close to each other. However, at high-energy region the doped films are having high optical conductivity than un doped films due to electron excited by photon energy and also optical conductivity tend to increase with increasing Eu^{3+} doping. High optical conductivity of $\text{TiO}_2:\text{Eu}^{3+}$ that makes it suitable for optical device application.

FIG. 8. Optical conductivity of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

ii. Electrical studies:

To ascertain the electrical properties of the undoped and $\text{TiO}_2:\text{Eu}^{3+}$ films, the four-points probe method was used. The sheet resistance (R_{sh}) of the films were calculated using the following Eq (8):³²

$$R_{sh} = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \quad (8)$$

Where v is measurement voltage and I is applied current.

The electrical conductivity was measured for various Eu^{3+} concentrations by the following Expression (9):³³

$$\sigma_{el} = \frac{1}{d \cdot R_{SH}} \quad (9)$$

Where d is the films thickness. In Figure 9, we have reported the variation of the electrical conductivity in the undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films as a function of Eu^{3+} doping ratio. As clearly see, the increase in the amount of

Eu^{3+} causes a rapid increase in electrical conductivity reach it is a maximum conductivity value $3.01 \times 10^{-2} (\Omega \cdot \text{cm})^{-1}$ at high doping level 10 wt%. This related to increase the carrier concentration with increase of Eu^{3+} atoms percentage in TiO_2 thin films led to substitution of Eu^{3+} ions with oxygen ions. This substitution lead to reduce the potential barriers, resistance and promoted the conduction band. This behavior, already reported in the literature for the case of Fe doped TiO_2 ³⁴ and for Ni-doped ZnO thin films.³⁵

FIG. 9. Effect of doping concentration on electrical conductivity of undoped and $\text{TiO}_2: \text{Eu}^{3+}$ thin films.

iii. Structural studies:

X-ray diffraction pattern has been used to study the phase identification and structural properties of the prepared films. Figures 10 indicate the XRD arrangements of undoped and $\text{TiO}_2: \text{Eu}^{3+}$ thin films with distinct doping concentration. Undoped TiO_2 thin film illustrates is combination of anatase

and rutile phase is mostly the anatase with some amounts of rutile phase which is presented in figure (10 -a). In TiO_2 : Eu^{3+} samples anatase phase is kinetically favored over rutile, which is thermodynamically stable phase. From the XRD pattern figure (10 -b), it is observed that the 4 wt% TiO_2 : Eu^{3+} thin films have preferential orientation along (1 1 1) and (211) planes which corresponds to tetragonal crystal structure of anatase phase . These results is in good agreement with standard data JCPDS file and literature. ³⁶ There is not any diffraction peak found in the sample related to Eu^{3+} probably due to the small amount of Eu^{3+} doping. For 6 wt% and 8 wt% samples the (111) peaks corresponding to the anatase phase in general decreases in the intensity attributed to the reduction of crystalline quality. Additional peaks were also observed at Eu^{3+} 8 wt% sample along (101) and (110). Further increase of Eu^{3+} doping for 10 wt% sample the crystallization of TiO_2 film might have decreased due to the deformation in the lattice at especially high Eu^{3+} doping ratio.

FIG. 10. The XRD patterns of undoped and $\text{TiO}_2: \text{Eu}^{3+}$ thin films.

The average crystallite size of the films are evaluated using Debye–Scherrer’s formula as expressed below (10):³⁷

$$\text{crystallite size } D = \frac{K\lambda}{\beta \cos\theta} \quad (10)$$

Here, $k = 0.9$, λ , β and θ are shape factor, X-ray wavelength of Cu K α , full width at half maximum (FWHM) and Bragg angle, respectively. Table III shown that the average crystallite size decreased linearly by the increasing of the concentration of Eu³⁺. This can be attributed to the kinetic segregation of dopants and produce of nucleation centers on the surface at higher doping amount. Arunachalam et al(2015). found similar result for TiO₂: Zn thin films prepared by spray pyrolysis method.³⁸

Dislocations are imperfection in a crystal related with the misfit of the lattice in one part of the crystal with the other part. Dislocation density (δ) that describes the dislocation lines per unit volume of the crystals. The values ‘ δ ’ were calculated from the crystallite size (D) using the relation(11) below³⁹ and values are presented at Table III:

$$\delta = \frac{1}{D^2} \quad (11)$$

The calculated dislocation density shows that as the Eu³⁺ content enhance, the dislocation density which can be credited to the large discrepancy of ionic radii of Eu⁺³ and Ti⁺⁴ (Eu⁺³ = 0.95 Å and Ti⁺⁴ = 0.68 Å). Therefore, the lattice constants a and c values fluctuate around a mean value of TiO₂ single crystals (a = 3.785 nm and c = 9.513 nm). The degree of the crystal lattice distortion is established using the formula (12):²⁷

$$R = \frac{2a\sqrt{\frac{2}{3}}}{c} \quad (12)$$

The calculated results are listed in Table III. It is evident that the crystal lattice distortion rises with doping, as we predicated because of insertion of Eu⁺³ ions into the TiO₂ structure. Similar results were observed by Pal .et

al³⁹ The microstrain (ε) of the prepared un doped and TiO₂: Eu³⁺ thin films can be calculated from the relation (13):⁴⁰

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (13)$$

It is observed that microstrain decrease with increasing doping concentration, which imply decrease in defect, is due to the motion of the interstitial atoms from their grain boundary to the crystals.

The number of crystallites per unit surface area can be calculated using the following Eq (14):⁴⁰

$$N = \frac{d}{D^3} \quad (14)$$

Where d is the film thickness. Table III summarizes crystallites per unit area along diffraction planes for films. For high doping concentration 10 wt%, crystallites per unit area rises, which show dense surface.

Table III. Micro structural parameters of the undoped, and TiO₂: Eu³⁺ films

Sample	Average crystallites size (nm)	lattice distortion degree R	dislocation density (lines/m ²) x10 ¹⁴	Microstrain ($\varepsilon \times 10^{-3}$)	Cells number (N X 10 ¹⁵ /m ⁻²)
TiO ₂	56.70	0.50	3.11	5.81	53
TiO ₂ :Eu 4 wt%	12.68	0.55	6.22	4.25	60
TiO ₂ :Eu 6 wt%	9.81	0.59	10.39	3.97	130
TiO ₂ :Eu 8 wt%	8.95	0.65	12.48	3.75	163
TiO ₂ :Eu 10 wt%	6.94	0.66	20.76	3.36	383

iv. Surface Morphology studies:

Figure (11) (a-f) presents the SEM images of the prepared undoped and TiO_2 : Eu^{3+} thin films. The surface morphology for all samples is similar. SEM images exhibit that the films have the irregular shaped aggregates and spherical particles in small diameter cover the substrate surface uniformly. The average grain size values for undoped and (4, 6, 8 and 10 wt%) TiO_2 : Eu^{3+} thin films are found 82.5, 68.6, 61.2, 57.7, 51.1 nm, respectively. It can be observed that with the addition of Eu^{3+} atoms the grain size reduced significantly. The reduction of the grain size can be attributed to inhibition of grain growth induced by dissolution of Eu^{3+} ions into TiO_2 lattice. Moreover, dragging effect between Eu^{3+} ions and the grain boundaries can be responsible for grain size reduction. This is in well accordance with result observed by Hsiao .et al(20).⁴¹

FIG. 11. SEM images of (a) undoped and (b-f) $\text{TiO}_2: \text{Eu}^{3+}$ thin films.

v. Photocatalytic Studies:

The photocatalytic activity of all prepared films is measuring the degradation of methylene blue solution (MB) with different concentration of UV light irradiation multiple times. The concentration of methylene blue is in a linear relationship with absorbance as shown in Figure 12.

FIG. 12. MB concentration curve with absorbance.

The photocatalytic decomposition of MB using TiO_2 and $\text{TiO}_2: \text{Eu}^{3+}$ thin films under UV light versus irradiation period is illustrated in Figure 13.

FIG. 13. Degradation of MB using undoped and TiO₂: Eu³⁺ thin films under UV light as a function of time.

Figure 13 shows that MB dye decays constantly throughout the irradiation of samples. It is found that Eu³⁺ added in TiO₂ exhibit significantly enhanced in photocatalytic activity reaction under UV irradiation compared with undoped TiO₂. The photocatalytic activity is influenced by many factors such as crystal structure, defects and particle size, impurity, thickness, and surface area. Eu³⁺ doping provide electron traps to restrict recombination of photo-excited electron-hole pairs and produces impurity levels between conduction band and valence band of TiO₂ lead to change in absorption characteristics of TiO₂. High doping films 10wt% is appeared to give maximum performance because of small crystal size of anatase phase, large value of OH radicals and O₂ on TiO₂ surfaces.⁴²

Degradation efficiency (η) of photocatalyst was calculated as follows (15):²⁵

$$\eta = \frac{c_o - c_i}{c_o} \times 100\% \quad (15)$$

Where C_o initial concentration, C_i sample concentration. As shown in figure 14 the better results were observed at high doping concentration of TiO_2 : Eu^{3+} thin films. The variation in η values were attributed to the differences in physical properties of the films. The degradation efficiency of UV light improves by growing amount of Eu^{3+} due to increase the e/h pair production and film width that increases the mass. Results suggest that Eu^{+3} ions doping in TiO_2 thin films performs a vital role in the enhancement of photocatalytic efficiency under UV light. Eu^{+3} doped TiO_2 thin films is highly promising materials for photovoltaic cells, visible light photo-catalysis, and other photonic devices.

FIG. 14. Degradation efficiency undoped and TiO_2 : Eu^{3+} thin films under UV light.

Conclusion:

In present article, the consequence of Eu^{3+} doped TiO_2 thin films with varying Eu^{3+} concentrations deposited by Spray pyrolysis technique on glass substrates has been investigated. The fabricated TiO_2 : Eu^{3+} thin films show improvement in optical properties. The highest transmittance and lowest reflectance were observed at 10 wt % Eu^{3+} content . The thickness of the samples increases from 97.13nm to 128.25nm.. At the same time increasing the Eu^{3+} doping initially led to slight increase in the optical band gap which can be explained by growth defect, charge impurities, disorder at the grain boundary and Burstein Moss effect. Electrical properties have been estimated by four-point probe method it has been detected that maximum conductivity value $3.01 \times 10^{-2} (\Omega.\text{cm})^{-1}$ at high doping level 10 wt%. The XRD patterns revealed that TiO_2 : Eu^{3+} films show anatase phase with the tetragonal crystal structure and reduces the crystalline size by increasing Eu^{3+} concentration. In addition, dislocation density, lattice distortion degree, microstrain and cells number are also concluded.

SEM analysis show that the films have the irregular shaped particles in small diameter and the grain size decrease with doping concentration because of inhibition of grain growth and dragging effect. The photocatalytic activity of the doped samples for MB degradation under UV light irradiation was significantly improved by Eu^{3+} ratio. The increase in photocatalytic activity of the TiO_2 : Eu^{3+} thin films is due reduction of crystallite size, improvement of film thickness and avoid the photo-excited electron-hole pairs recombination.

Declarations:**Availability of data and materials:**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests:

The author declares that there is no conflict of interest regarding the publication of this paper.

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Figures

Figure 1

spray pyrolysis set up.

Figure 2

Transmission spectra of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 3

Reflectance spectra of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 4

Effect of doping concentration on refractive index of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 5

Effect of doping concentration on extinction coefficient of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 6

Direct band gap plot of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 7

Urbach plot of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 8

Optical conductivity of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 9

Effect of doping concentration on electrical conductivity of undoped and $\text{TiO}_2\text{:Eu}^{3+}$ thin films.

Figure 10

The XRD patterns of undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 11

SEM images of (a) undoped and (b-f) $\text{TiO}_2:\text{Eu}^{3+}$ thin films.

Figure 12

MB concentration curve with absorbance.

Figure 13

Degradation of MB using undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films under UV light as a function of time.

Figure 14

Degradation efficiency undoped and $\text{TiO}_2:\text{Eu}^{3+}$ thin films under UV light.