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Sol-Gel mediated synthesis of tri-doped TiO_2Nanoparticles towards application of photo catalysis and its kinetic study

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Abstract: Rare earth (RE) ion (RE = La, Ce, Y) doped TiO_2 catalysts were successfully synthesized by the sol-gel method. The particle size were reducing while increasing doping concentration (x= 0.2, 0.4, 0.6) in the 2nd order reaction and it was strongly reflected inX-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy(TEM). The resulted images indicated that the particles were binded. While increasing the concentration of dopents particle size also increases. The average particle size of TiO_2 with dopant said to 70±2 nm. In FTIR spectrum comparing all compositions peak between 400-4000 cm^{-1} were shifted and also Ti-O-RE stretching band, which attributed to formed pure and doped TiO_2 nanoparticles. The reflectance spectra reveal that the RE-doped TiO_2resulted in red shifts. Optical band gap (Eg) was reducedin high doping concentration (0.6) due to highadsorptionon the surface of RE-doped TiO_2 (3.02 eV) and pristine TiO_2 (3.2 eV). It causes that the separation of TiO_2 particles through UV radiation in recycling process were in environment treatment applications. Further tri doped TiO_2 nanoparticles were used as applicant in photocatalytic degrdation of industrially toxic dye methylene blue. Hence, these results indicate that the Tri- doping of the rare earth ions can extensively improve the photocatalytic activity of TiO_2 doped rare earth contrast with the pristine TiO_2.

Keywords: Rare earth elements, Sol-Gel, optical band gap, photocatalytic activity, kineticstudy.

Introduction

To keep the clean environment is now a day's big challenging for us and one of the photocatalytic based titanium dioxide (TiO_2) plays a vital role in the environment pollute treatment applications, and it represents an efficient photocatalyst for water and air purification in the environment. TiO_2nanocrystalline powder has still impasse of photocatalytic studies because of its strong oxidized ability, non-toxicity, and long thermal photostability.[1] TiO_2 have a three phase in nature depending upon the thermal behavior it can be dividedinto anatase, rutile, and brookite phases. Among this three phase, anatase phase TiO_2 has been widely used on environmental applications because of its high activity, chemical stability, robustness against photo-corrosion, low toxicity and availability at low cost so far, especially for the detoxification of water and air.[2] In the view of commercial applications, TiO_2 nanoparticles have some limitations because of TiO_2 powder have fine particles which effects separation in recycling process during treatment and also its have low photo-efficiency. To overcome limitations in recent years researchers have focused on dopant based TiO_2 which enhanced photo-efficiency and catalyst properties. From the earlier reports, the metal – doped TiO_2 have very low photocatalytic degradation on the surface of TiO_2nanoparticles, because of high recombination rate of photogenerated electron–hole pairs. In few reports based on rare earth and transition metal ion doped with TiO_2

nanoparticles still researchers are refinement the preparation of rare-earth-doped TiO2 nanoparticles and their properties. Rare earth doped TiO_2 shows a better photocatalytic activity and also it has relatively high photo-efficiency and chemical stability under UV radiation. Concurrently, the higher order in photocatalytic activity compared to pure TiO_2 due to higher absorptionon the surface of TiO_2 in the presence of rare earth and also red shift absorption in the UV region.[3] From the complexion structure 3d-4f plays asignificant role in the property absorb foreign ion on the surface and leads to photocatalytic activitywere illustrated in (Figures 1)[4-8]

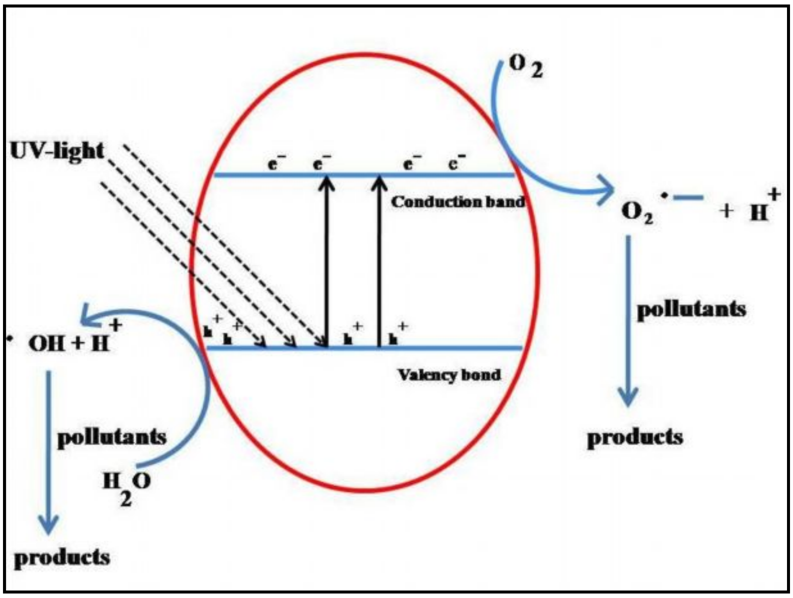


Figure 1.Schematics diagram of the electron-hole generation in a photocatalyst

The currentinvestigation states that improving the photocatalytic efficiency of rare earth doped TiO_2 synthesized by sol-gel technique and clearly indicates catalytic behavior which efforts through rare earth ion in detailed below.

Experimental

Synthesis

All the starting materials were taken in 99.99% purity in Alfa Aesar company chemicals. The pristine ansate phase and rare earth (La, Ce, Y) doped TiO_2 were synthesized by a sol- gel technique. Titanium-iso-propoxide and acetic acid were taken in the stoichiometric ratio of 1:2 and mixed stock solution in a 200 mL beaker. Then the mixture solution was stirred vigorously for 5 mins and then added 150 mL of Millipore water in a dropwise (Solution A) and maintain 60°C to gel formation.Once gel formed, the mixture of TiO_2 sol and water subsequently kept at room temperature in anticipation of white powders were found at the bottom of the beaker. Then the beaker was kept in the oven at 80°C and resulting pure white color powders were harvested and calcinated at 400°C for 5 h through the restive furnace to extract pristine anatase phase TiO_2. Similarly, The same procedure was followed by RE-doped TiO_2 but intermediate Solution B was prepared by mixing each (0.2) Lanthanum (III) nitrate hexahydrate,cerium(III) nitrate hexahydrate, Yttrium(III) nitrate hexahydrate with 150 mL of water and B solution was stirred until rare earth ion dissolve. Then Solution B was slowly added to solution A (TiO_2) with stirring in the presence of 60°C heat. The experiment was continued until obtaining agel. After the completion of the experiment, the solution was dried at 80°C in a hot air oven to obtain salt. Now the saltswere ground into powder by using agate mortar and followed by calcination in the furnace at 400°C for 5 h and repeat the process for other concentration 0.4 and 0.6 respectively.

Characterization

The structure analysis was carried out using powder XRD pattern using BRUKER X-Ray Diffractometer with the CuKα radiation (λ = 1.540598 Å) and FTIR pattern by SHIMADZU instrument for all composition. The surface morphology and particle size analysis were carried out using SEM by using Hitachi

SU-70 ultra-high-resolution analytical and TEM by JEOL JEM 2100F. The photo catalytic activity and photoefficiency were carried using UV Diffuse Reflectance Spectroscopy by ELICO,UV- Vis reflectance Spectroscopy ELICO SL No. 218 double beam UV-Vis Spectrophotometer by and all the characterization were explained in depth in below sections.

Results and discussion

Catalyst Characterization

The powder XRD pattern showed that only anatase phase structure was found in all compositions of rare earth doped TiO_2 (0.2,0.4,0.6)and in pristine TiO_2 without any rutile impurities. These patterns all peaks are well matched with earlier reports and existed JCPDS card no.: 84-1286. The lattice parameters are extractedfrom powder X software, and all composition are exhibited tetragonal crystal system as well as minor changes in lattice parameters. The highest relative intensity peaks near $2\Theta = 25°$ were broadened in the plane of (101) as well as intensity is high in pure and while increasing the composition of rare earth ion reduced is shown in (Figures 2).

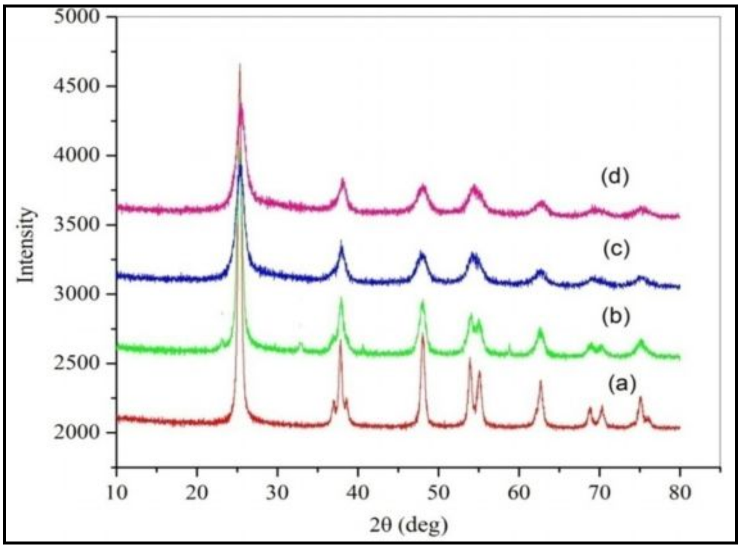


Figure 2.XRD pattern of doped TiO_2 sample denoted as (a) pure TiO_2 (b) TiO_2 doped (0.2) La, Ce, Y, (c) TiO_2 doped (0.4) La, Ce, Y, (d) TiO_2 doped (0.6) La, Ce, Y

There is two doublet peaks near 39° and 55° respectively in pristine TiO_2 can be reduce increasing doping level which indicates that reducing crystalline nature monotonously. Hence, the RE-doped TiO_2 have small photo degradation effect which have high significant for particle applications.

Theoretical values of particle size were calculated through Scherrer formula by following equation (1)

$$\tau = K(/\beta\cos\theta \qquad \text{--------} (1)$$

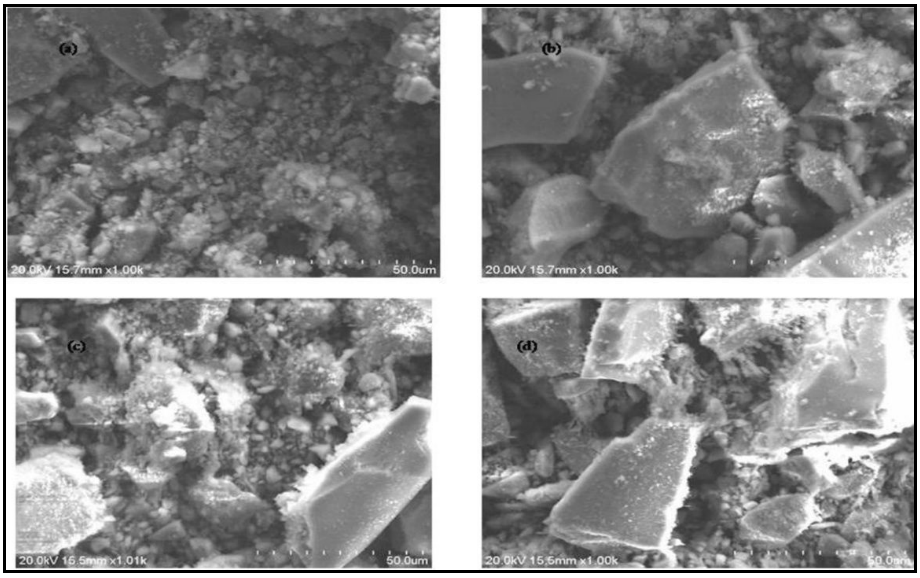
Where, τ - particle size, K- dimensionless shape factor (0.9- the shape of the crystallite), λ- X-ray wavelength, and θ- Bragg angle respectively. The extracted particle size was reduced (Table 1) while increasing RE doping level due presence of small complex ionic radii in the system. Hence, the particles are a tendency to move fine nanoparticle to ultra-finenanoparticlewhich have overcome defects of separation the titled compounds in recycling process in water treatment application.[9]

Table 1.Characteristics of Pure TiO_2 and Rare earth (La, Ce, Y) – doped TiO_2 with Different Doping Contents

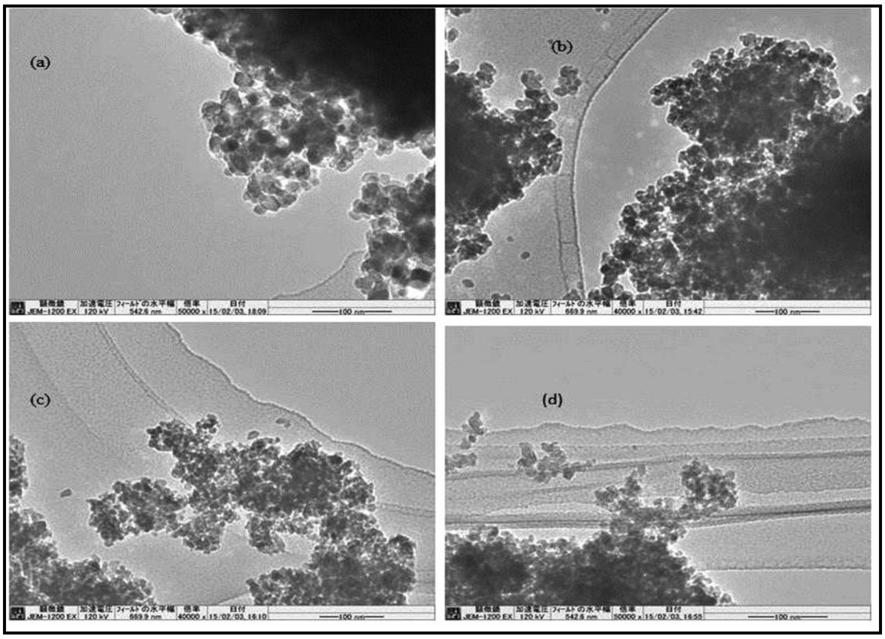
Catalyst	Particle Size (nm)
Pure TiO_2	18.3
(0.2) La, Ce, Y doped TiO_2	13.34
(0.4) La, Ce, Y doped TiO_2	9.67
(0.6) La, Ce, Y doped TiO_2	7.2

Morphology

The surface morphology of synthesized powder of pristine TiO_2 and RE-doped TiO_2 (0.2,0.4,0.6) are shown in (Figures3(a),(b),(c),(d)) and (Figures4(a),(b),(c),(d)) respectively.



Figures 3.SEM image(a) pure TiO_2 (b) TiO_2 doped (0.2) La, Ce, Y, (c) TiO_2 doped (0.4) La, Ce, Y , (d) TiO_2 doped (0.6) La, Ce, Y.

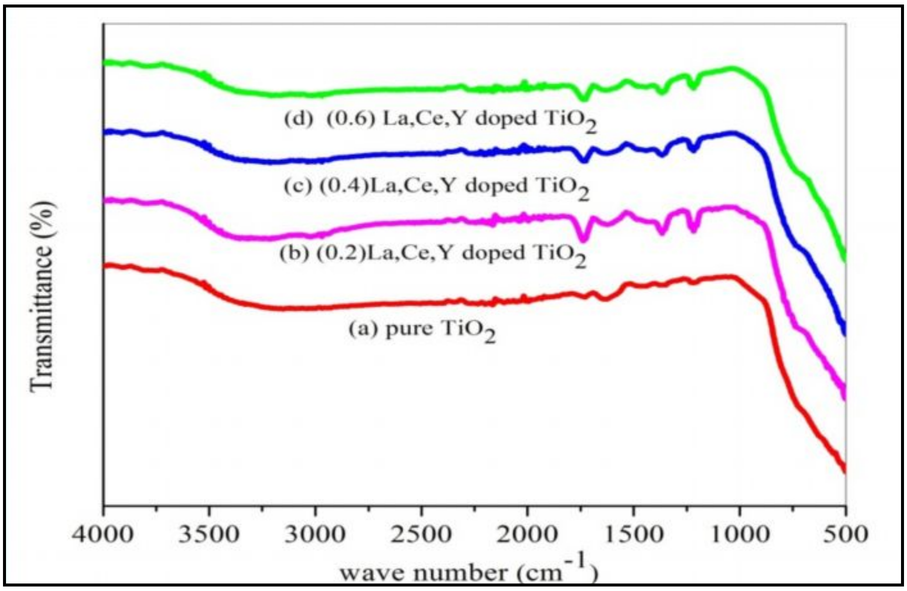


Figures 4.TEM images (a) pure TiO_2 (b) TiO_2 doped (0.2) La, Ce, Y, (c) TiO_2 doped (0.4) La, Ce, Y , (d) TiO_2 doped (0.6) La, Ce, Y.

Figures3 represents that micrograph images of all composition indicate particles are a sphere in shapes and also 5 to15 particles combined and shows large particle in view. As results, it refelts in TEM images like aggregation in few areas of all the compositions. The particle size was estimated in both SEM and TEM images it seem to decrease particle size 70 nm for pure TiO_2 to 13 nm for 0.6 RE-doped TiO_2 and collided particles have 65 nm respectively. These particle size results were a good agreement with the powder XRD results Table 1 and earlier reports.[6]The ultrafine particles were found to be about the ~13 nm, and it plays a vital role in the photocatalytic activity in environment treatment applications.

Fourier Transform Infrared Spectroscopy

FTIR spectrum of all the composition was shown in (Figures 5). Absorbed peaks are small shift while increasing doping level. The absorbed peak at 3600-3000$cm^{-1}$is assigned to H_2O and isopropanol weak O-H stretching vibrations[10] and also near 1720-1742 cm^{-1} range it clearly shows that the acetic acid and TTIP.[11]The peaks observed between1215-1235 cm^{-1} being v_1 vibration of rare earth ion which this not available in pure TiO_2[10] and also the peaks in the range of 1355-1365.60 cm^{-1} shows strong v_2(Ti-O-Ti) metal oxide vibration.[12]By comparing all compositions peaks between 400-450 cm^{-1} was assigned to the Ti-O-RE stretching band, which attributed to formed pure and doped TiO_2 nanoparticles and hence it would be beneficial for the photocatalytic process.[13]

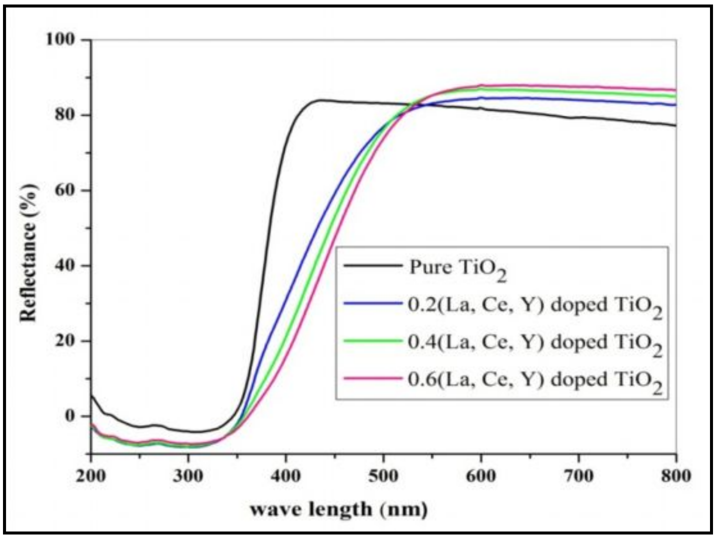


Figures 5.FTIR spectra of the sample with different rare earth doped photocatalysts

UV-Diffuse Reflectance Spectroscopy

The reflectance plot of pristine and rare earth doped $TiO_2$are shown in (Figures 6). The spectra reflect for rare earth doped TiO_2 shows red shifts in the band gap transition, but pure samples do not occur in any case due to Ti-O-Ti have complete fill in subshell. The absorption edge shift toa higher angle for high dopant concentration and it is gradually decreasing for decreasing dopant level and pure TiO_2. The optical bandgap energy were theoretically extracted by using the Kubelka-Munk relation.[14]

$$\alpha = \frac{(1-R)^2}{2R} \quad \text{---------(2)}$$



Figures 6.Diffuse reflectance spectra of pure TiO_2 and (0.2) La,Ce,Y- , (0.4) La,Ce,Y -and (0.6) La,Ce,Y – doped TiO_2 (from left to right ,with the different content)

Table 2. Band gap energy

Catalyst	Band gap (eV)
Pure TiO_2	3.2
(0.2) La, Ce, Y doped TiO_2	3.1
(0.4) La, Ce, Y doped TiO_2	3.07
(0.6) La, Ce, Y doped TiO_2	3.0

Where, α is reflectance changed according to Kubelka Munk and R is the reflectance of %. The optical band gap (E_g) of the TiO_2 can be related to absorption coefficient (α) using taut plot by below equations

$\alpha h\nu = const(h\nu - Eg)^2$ ----------(3)

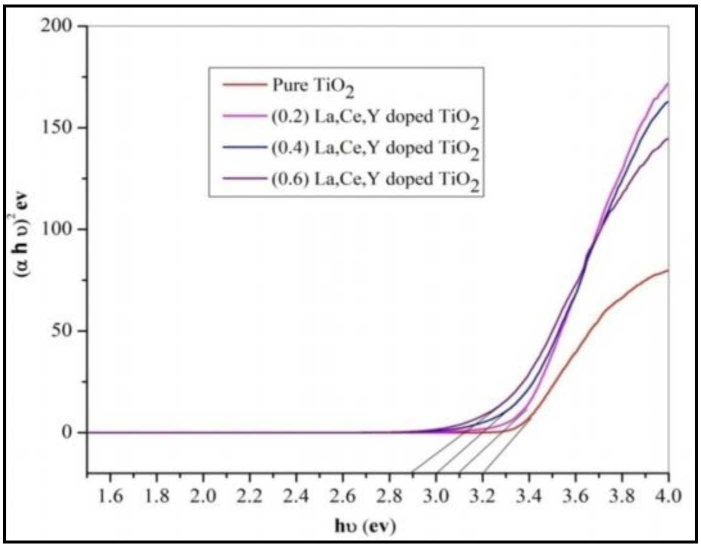


Figure7. Band gap spectra of pure TiO_2 and (0.2) La,Ce,Y- , (0.4) La,Ce,Y -and (0.6) La,Ce,Y – doped TiO_2 (from right to left ,with the different content)

Figures 7 shows that relationship of $(\alpha h\nu)^{1/2}$ versus photon energy(E) of anatase TiO_2 pure and dopant optical band gaps Eg by through linear fit. The Eg values were reduced(Table 2) from pure to high doping concentration (0.6) due to high adsorption in surface of RE-doped TiO_2 and pure TiO_2 occurs near 3.2 eV that is good agreement with earlier reports.[14]The optical band gap plays major role in photo degradation here reducing optical band gap due to mixed RE complexion have high ionic radii. Hence, TiO_2 particles were easily separated from UV radiation while recycling process and these RE-doped induced better results in environment treatment applications.

Photocatalytic Activity

Synthesized Nanoparticles are carried out to degradation process with Methylene blue dye at its cut-off value 641nm under UV –light it clearly observed in (Figures8a). About 1 mL of the Methylene blue dye ($1x10^{-4}$)m was stirred with 0.25mg of synthesized TiO_2, it was placed in the UV chamber at 641nm and subjected for the various time intervals.Its catalytic degradation spectra were recorded from 400-800nmshown in (Figure 8b). Same procedure was adopted for (0.2) La,Ce,Y-doped TiO_2, (0.4) La,Ce,Y-doped TiO_2, (0.6) La,Ce,Y-doped TiO_2 as well as same spectra were recorded are shown in(Figure8c, d, e). By observing the degradation spectra of all samples, Surface Plasma Resonance (SPR) band of Methylene Blue was recorded at 661nm.(Figures8b, c, d,e) shows clear absorbanceat 50 min SPR band was degraded in all the sample but especially, in (Figures8e) shows that higher degradation while compares to the (Figures 8 b, c, d). From the above research, it clearly stated that by increasing concentration of doping it can significantly improve the photocatalytic ability of TiO_2.

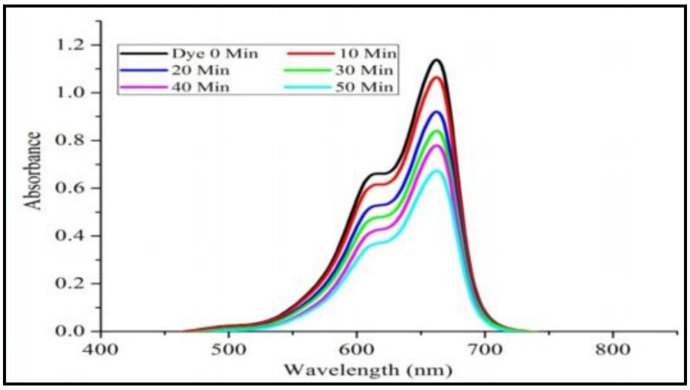


Figure 8.(a) UV-VIS spectra of Methylene blue dye

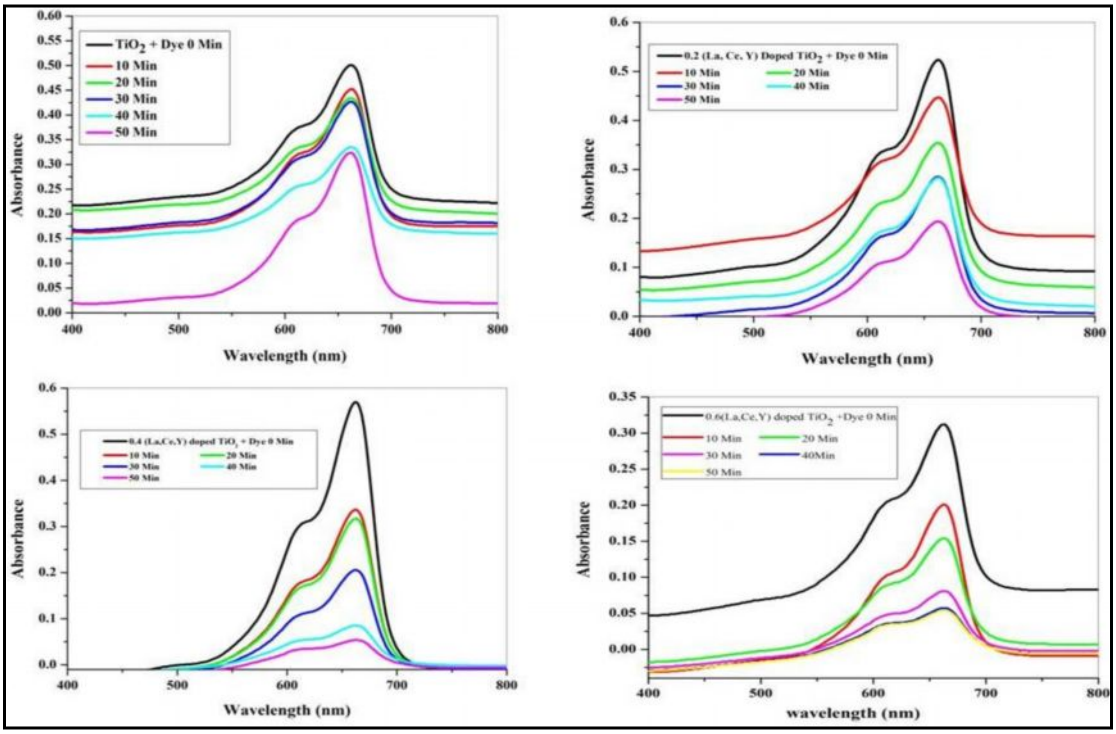


Figure 8.(b) UV-VIS spectra of pure TiO_2(c) TiO_2 doped (0.2) La, Ce, Y (d) TiO_2 doped (0.4) La, Ce, Y (e) TiO_2 doped (0.6) La, Ce, Y

In addition rate constants of Methylene Blue Dye degradation of kinetic data were carried out by thefirstorder kinetic reaction as follows.[15]

$\ln(C/C_0) = - kt$(4) $\longrightarrow$

Where:

C = final concentration of Methylene Blue Dye
C_0 = Initial concentration of Methylene Blue Dye
K = rate of reaction constant
t = time

By this study resulted in that percentage of the dye degradation of the blank Methylene blue dye and the synthesized nanomaterial's for different time intervals Shown in (Figures 9).

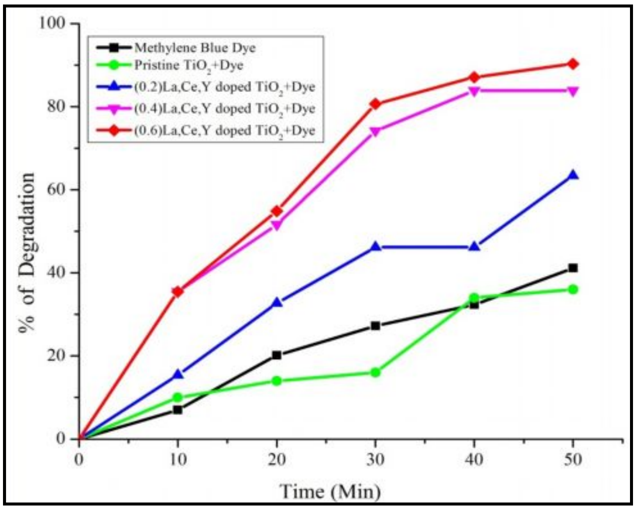


Figure 9.Time vs percentage of dye degradation

It reveals that enhancement of photocatalyst by varying the time from 0 to 50 min and concentration from 0.2 to 0.6 of Rare earth elements. The percentage of the dye degradation is given in(Table3).

Table 3. Percentage of Methylene Blue Dye Degradation at various Time intervals

Sample Label	0 Min	10 Min	20 Min	30 Min	40 Min	50 Min
Blank Methylene Blue Dye	0	7.01	20.17	27.19	27.19	41.14
Pristine TiO_2	0	10	14	16	16	36
(0.2)La,Ce,Y doped TiO_2	0	15.38	32.62	46.15	46.15	63.46
(0.4)La,Ce,Y doped TiO_2	0	35.48	51.61	74.19	83.87	83.83
(0.6)La,Ce,Y doped TiO_2	0	35.48	54.83	80.09	87.09	90.32

This clearly indicated that dye degradation percentage of (0.6) La,Ce,Y-doped TiO_2 shows the higher efficiency of degradation 90.32% at 50 min compare to all other concentration and time. Therefore clearly optimized time for photo catalyst is at 50 min is confirmed. (Figures 10)demonstrates that time increases in (C/C_0) decreases this is due to the phenomenon of dye degradation in all sample obviously at 0.6 shows the higher degradation at optimum time 50min under UV light. Along with that rate of constant of first order kinetic for 50 min and relative coefficient were estimated in (Table 4).

Table:4 Relative coefficient and first order rate constant for 50 Min as a function of Rare earth concentration

Sample	Rate of constant (k) for 50 Min(x10^3)	Relative coefficient (R^2)
Blank Methylene Blue Dye	10.6	0.990
Pristine TiO_2	8.92	0.919
(0.2) La,Ce,Y doped TiO_2	20.13	0.960
(0.4) La,Ce,Y doped TiO_2	36.49	0.962
(0.6) La,Ce,Y doped TiO_2	46.70	0.982

Table 4indicates the rate constant and relativecoefficient of all samples. The (0.6) La,Ce,Y-doped TiO_2 at 50 min has high value of k = 46.70 and R = 0.982. This concluded that it had thebetter Photocatalytic performance under the UV light irradiation for this concentration. This good result especially at this higher concentration because of barrier of the surface will become higher, and space charge region will become narrower, and huge electric field developed within the region resulted in separation of electron-holes pair before recombination were take place in this ratio.[16-18]

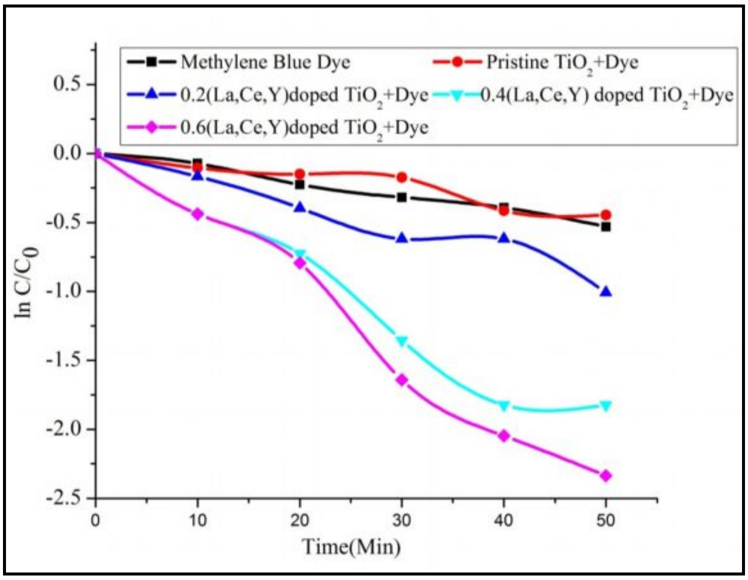


Fig. 10 Time vsln(C/C_0)

Conclusions

While compared to pristine TiO_2,RE-doped TiO_2have enhanced their photocatalytic activity. All the compositions were successfully synthesized in ultra-fine nanoparticles using the sol-gel method. The synthesized nanoparticle range (13 nm) and spherical in shape morphology were analyzed by SEM, TEM and powder XRD. The tri-doping RE ions gives high success rate in photocatalytic in the absorbance compared to pristine due to higher adsorption, red shifts, lower band gap energy and prevention of electron and holes recombination during UV radiation. Maximum enrichment of photoreactive had obtained near 0.6 % RE ion doped TiO_2, and it may be in favor of the more resourceful in the separation charge carriers the main reason behind science is large interfacial electron transfer rate.First order kinetic reveals that higher percentages of the degradation, as well as the rate of the constant and relative coefficient of better photocatalytic nanoparticles value, were estimated.

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