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Bandgap Tailored TiO_2 Thin Films by Addition of SiO_2 for Enhanced Photocatalytic Activity against Congo Red under Visible Light Illumination

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Colloidal solutions of SiO_2-TiO_2 mixed oxides having different SiO_2 contents were synthesized by sol-gel technique and thin films were deposited over glass slides by using dip coating technique. The films were subjected to high temperature at 400 °C for growing TiO_2 crystals. Energy dispersive X-ray spectroscopy was used to indicate the elements in the films. X-ray diffraction analysis indicated that SiO_2-TiO_2 films contain only anatase phase. Scanning electron microscopy was used to study the films surface morphology. The SiO_2-TiO_2 films that were contacted with congo red (5 ppm) and irradiated with visible light showed a high photocatalytic activity. UV spectrophotometry technique was used to monitor the degradation of congo red by the reduction of main absorbance peak at 497 nm. Complete degradation was achieved after 2 h for 3 mol % SiO_2-TiO_2 thin film.

Keywords: TiO_2, SiO_2, Dip coating, Congo red, Photocatalytic activity.

INTRODUCTION

Photocatalysis is a "green" technique, which offers great potential in environmental remediation such as the photo-degradation of the organic pollutants in the wastewater from industrial drains. Photocatalysis is the result of interaction of electrons and holes generated in an activated solid (semi-conductor) with its surrounding medium (electrolyte) [1-3]. The purification of water by semiconductor photocatalysis is an area of interest for both researchers and water purification companies [4]. The use of powder catalyst results in disadvantages of stirring during the reaction and separation after the reaction [5]. Preparation of catalyst as a thin film will make it possible to overcome these disadvantages and to extend it for industrial applications. Photocatalytic oxidation and reduction reactions over metal oxide semiconductors like TiO_2, ZnO, MoO_3, CeO_2, ZrO_2, WO_3 and SnO_2 have been extensively reported in literature. Among these TiO_2 is the most commonly used semiconductor metal oxide having sufficient chemical stability, high photocatalytic efficiency, non-toxicity and low cost [6,7]. Various types of TiO_2 such as aerosols, aerogels, nanorods, nanotubes, nanocrystals and mesoporous materials that show promising photo reactivity are synthesized in the recent years [8-10]. Crystal structure and particle size are important factors in determining photo activity [11]. Anatase TiO_2 has a higher activity than rutile ones [12]. The doping of metal is considered as the most efficient way, which enhances the photocatalytic activity by the prevention of electron-hole pair recombination [13]. The addition of La_2O_3, CeO_2, CuO, Fe_2O_3, SiO_2 or other oxides into anatase TiO_2 can improve the thermal stability and prevent the growth of titania grains [8,10]. SiO_2-TiO_2 composites offer low cost, high thermal stability and high wear resistance. The photocatalytic activity of SiO_2-TiO_2 mixed oxide is enhanced by enlarged surface area and porosity [14]. SiO_2-TiO_2 thin films are prepared by several methods such as metal organic chemical vapour deposition [15,16], sputtering [17], chemical vapour deposition [18], sol-gel [19] and spray pyrolysis [20]. These techniques produce transparent and highly conducting films. Among these sol-gel is the cost efficient technique used for the deposition of thin films [19]. In the present study, nanocrystalline SiO_2-TiO_2 thin films were prepared by the sol-gel dip coating method. The photocatalytic activities of prepared thin films were then measured by the degradation of congo red (CR). Also, the effect of SiO_2 addition to the TiO_2 on its photocatalytic activity was investigated.

EXPERIMENTAL

All the chemicals were of analytical reagent grade and used directly without any further purification. TiO_2 and SiO_2

precursors were titanium tetra isopropoxide (TTIP) and tetraethyl orthosilicate (TEOS). Ethanol and acetic acid were selected as solvent and stabilizer of TTIP. Congo red (CR) dye was used without further purification.

Preparation of SiO_2-TiO_2 thin films: Nano structure SiO_2-TiO_2 thin films were prepared by the following steps. 4 mL of TTIP was mixed with 30 mL ethanol. Then 1 mL of acetic acid was added drop wise to the solution. Finally TEOS (1, 2 and 3 mol %) was mixed rapidly and the whole solution was magnetically stirred for 1 h. The pure TiO_2 sol was prepared by the same procedure without adding TEOS. Finally, the prepared sol was deposited on glass slides [25 mm × 75 mm × 2 mm] by dip coating method with a speed of 50 mm/30 s followed by calcination at 400 °C for 3 h.

Characterization of thin films: Grain size and crystallinity of the films were studied by X-ray diffraction method (XRD) using (XPERT PRO) X-ray diffractometer which was operated at 40 KV and 30 mA with Cu K_α (1.5406 Å) radiation in the region of 2θ = 20-80°. The thickness of the films were measured using (Surfest SJ-301) stylus profilometer. UV-visible spectra and photoluminescence spectra of the prepared thin films were recordered by using (Shimadzu 1800) UV-Vis-NIR spectrometer and (Shimadzu RF-5301) photoluminescence spectrometer respectively. The surface morphology and elemental analysis of the films were studied using (Quanta SEG-200) scanning electron microscope and (Bruker) EDAX respectively. Degradation process of congo red was observed by (Shimadzu 1800) UV spectrophotometer.

Photocatalytic activity of SiO_2-TiO_2 thin films: For visible light photocatalysis, an immersion type photo reactor with a 300 W tungsten lamp fitted on to double walled quartz immersion well of 40 mm outer diameter with inlet and outlet for circulation of water was used. The TiO_2 and SiO_2-TiO_2 films were settled in 100 mL of 5 ppm congo red dye solution and placed inside the visible light chamber. The photo catalytic decolorization of congo red is a pseudo-first order reaction and its kinetic energy is expressed as follows

$$\ln\left(\frac{C_o}{C}\right) = Kt \quad (1)$$

where K is the rate constant of a reaction, C_o and C are initial and final concentration of congo red.

RESULTS AND DISCUSSION

X-ray diffraction analysis: The crystalline phase and the crystallite size of the prepared films were studied by XRD analysis, which is shown in Fig. 1.

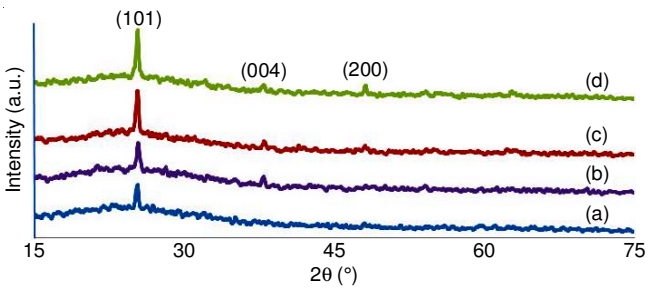

Fig. 1. XRD pattern of (a) Pure TiO_2 (b) 1 mol % SiO_2-TiO_2 (c) 2 mol % SiO_2-TiO_2 (d) 3 mol % SiO_2-TiO_2 thin films

The diffraction peaks can be indexed to tetragonal phase and it is matched with the standard JCPDS card no (89-4203). The most intense diffraction peaks occur at 2θ regions of 25.5°, 37.87° and 48.11° which corresponds to (1 0 1), (0 0 4) and (2 0 0) reflections planes respectively. The sharp and narrow XRD pattern suggests that synthesized films have high crystalline nature. The crystallite size (D) was calculated for the characteristic reflection of plane (1 0 1) using the following Scherer's formula and the calculated crystallite sizes are shown in Table-1.

$$D = \frac{k\lambda}{\beta\cos\theta}(nm) \quad (2)$$

where D is the crystallite size, K is the constant (0.94), λ is the wavelength of X-ray (CuK_α = 1.54065 Å), β is the true half-peak width and θ is the half diffraction angle of the centroid of the peak in degree.

TABLE-1
STRUCTURAL AND OPTICAL PARAMETERS FOR THE PREPARED THIN FILMS

Samples	Thickness (μm)	Crystallite size (D, nm)	Band gap values (eV)
TiO_2	1.0	68	3.10
1 mol % SiO_2-TiO_2	1.5	54	2.75
2 mol % SiO_2-TiO_2	2.0	41	2.50
3 mol % SiO_2-TiO_2	2.5	33	2.10

Table-1 presents that the crystallite size of TiO_2, 1 mol % SiO_2-TiO_2, 2 mol % SiO_2-TiO_2 and 3 mol % SiO_2-TiO_2 thin films are 68, 54, 41 and 33 nm respectively. The results indicated that high content of SiO_2 restrain the crystallization of TiO_2 and effectively suppress the phase transformation of TiO_2 from anatase phase to rutile phase [21].

Optical analysis: Band gap energy of the photocatalyst is a very important parameter for the selection of light source to excite the electrons from the valance band to the conduction band to generate electron hole pairs and to degrade the dyes [22]. Tauc's relationship for optical band gap calculations for the photocatalysts is described by using the following equation:

$$\alpha = \frac{A}{h\nu(h\nu - E_g)^{-1/2}} \quad (3)$$

where α is the absorption coefficient of the semiconductor at a certain value of wavelength, h is Planck's constant, ν is the frequency of light, A is the constant which is related to the effective masses associated with valance band and conduction band and E_g is the gap between bottom of conduction band and top of valance band.

From the Tauc's plot the band gap energy is calculated. All the samples exhibited bandgap energy between 2.1 to 3.1 eV.

Tauc's plot for the TiO_2 and SiO_2-TiO_2 thin films is shown in Fig. 2, where $(\alpha h\nu)^2$ is plotted against the photon energy (hν). The band gap energies are estimated from the extra polated lines and the values are given in Table-1. The energy gap of TiO_2 films decreases when the mol ratio percentage of SiO_2 increases. This implies that the band gap tailored with increase

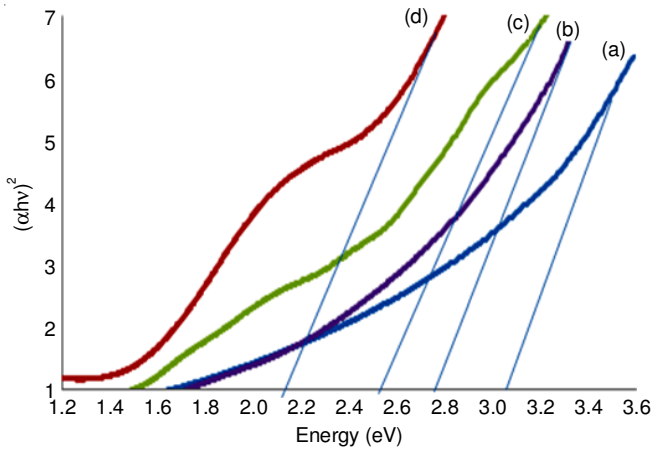

Fig. 2. Band gap of (a) Pure TiO_2 (b) 1 mol % SiO_2-TiO_2 (c) 2 mol % SiO_2-TiO_2 (d) 3 mol % SiO_2-TiO_2 thin films

in SiO_2 concentration to TiO_2 improves the minimum energy required for excitation of electrons.

Fig. 3 shows the room temperature photoluminescence emission spectra of pure TiO_2 and SiO_2-TiO_2 thin films. It can be seen that there are two different emission bands in the photoluminescence spectrum centered at 485 and 560 nm corresponding to the blue and green emission bands. The blue emission is due to electron excitations and the green emission is due to the deep level effects [23]. But in case of SiO_2-TiO_2 thin films, the intensities were negligible which is due to the prevention of electron-hole pair recombination in TiO_2 by SiO_2. Due to the restricted recombination, the holes and the electrons were freely available for the generation of OH and OOH radicals, which are responsible for the enhanced photo catalytic degradation.

Surface morphology and EDX analysis of SiO_2-TiO_2 film: The surface morphology of films can be observed in Fig. 4(a) and (b) which shows SEM micrographs of pure TiO_2 and 3 mol % SiO_2-TiO_2 films respectively.

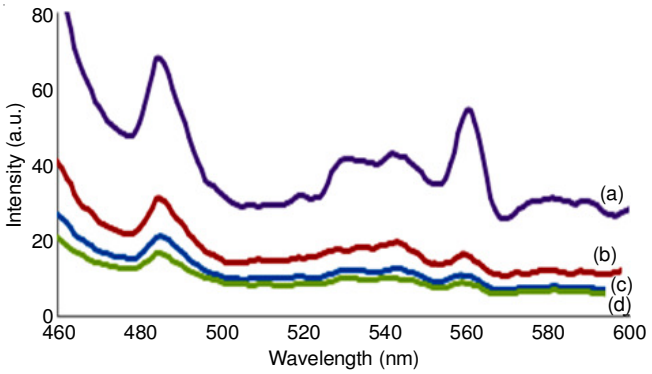

Fig. 3. Photoluminescence spectra of (a) Pure TiO_2 (b) 1 mol % SiO_2-TiO_2 (c) 2 mol % SiO_2-TiO_2 (d) 3 mol % SiO_2-TiO_2 thin films

Images obtained for the thin films by this analysis indicate fractured morphology. During drying and annealing process of the films, crack formation takes place as a result of contraction stress and different thermal coefficient of expansion of the over layer and substrate. The fractured surface morphology results in enlarged surface area, which suggests high photocatalytic activity [24]. In the present study, high photocatalytic activity with smaller crystalline size of SiO_2-TiO_2 films was observed.

Fig. 5(a) & (b) shows the EDX pattern of pure TiO_2 & 3 mol % SiO_2-TiO_2 films respectively. EDX results indicated the main peaks of Ti, Si and O. Moreover the presence of SiO_2 in the thin film can destroy the linkage of Ti-O-Ti and change in to Ti-O-Si. This can shift the binding energy of Si to higher value [8].

Photocatalytic activity of SiO_2-TiO_2 thin films: The photocatalytic reaction involves the presence of oxygen and moisture on the photocatalyst surface to activate the photo reaction during light irradiation. From the fundamental photocatalytic kinetics, the reaction equation is expressed as [25-27]. In photocatalytic activity photons are absorbed by a photocatalyst, which excites electrons from valance to conduction bands to generate electron-hole pairs.

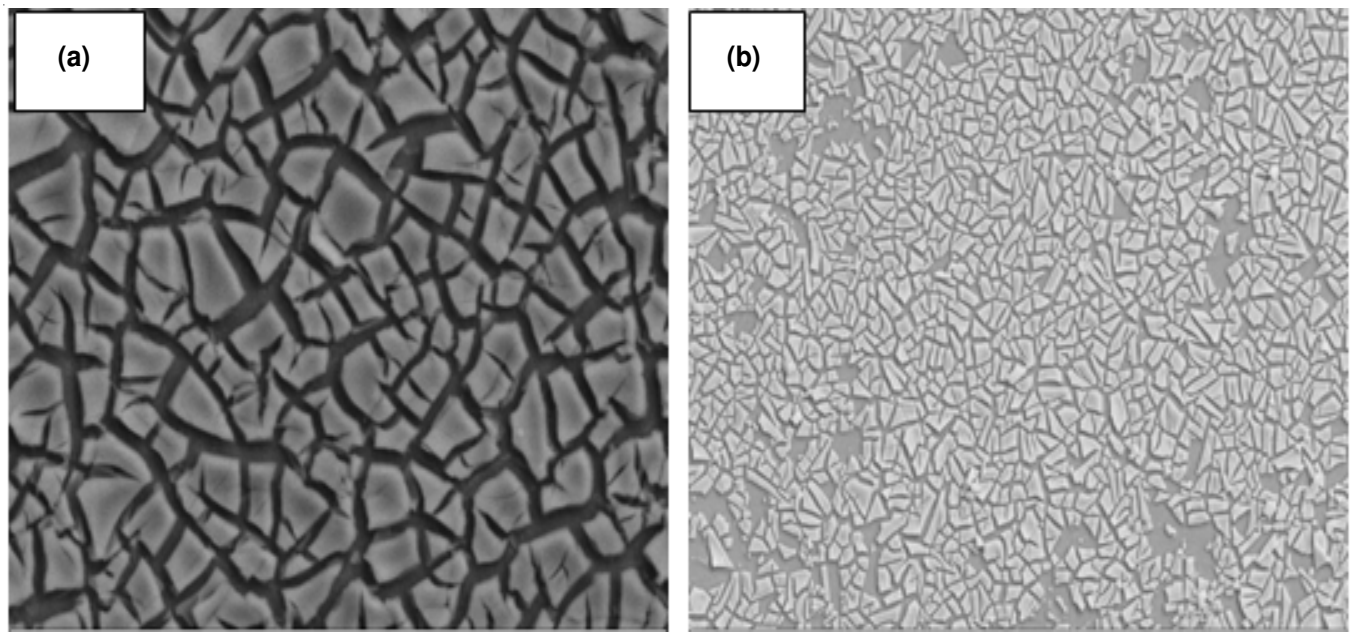

Fig. 4. SEM micrographs of (a) Pure TiO_2 (b) 3 mol % SiO_2.TiO_2 thin films

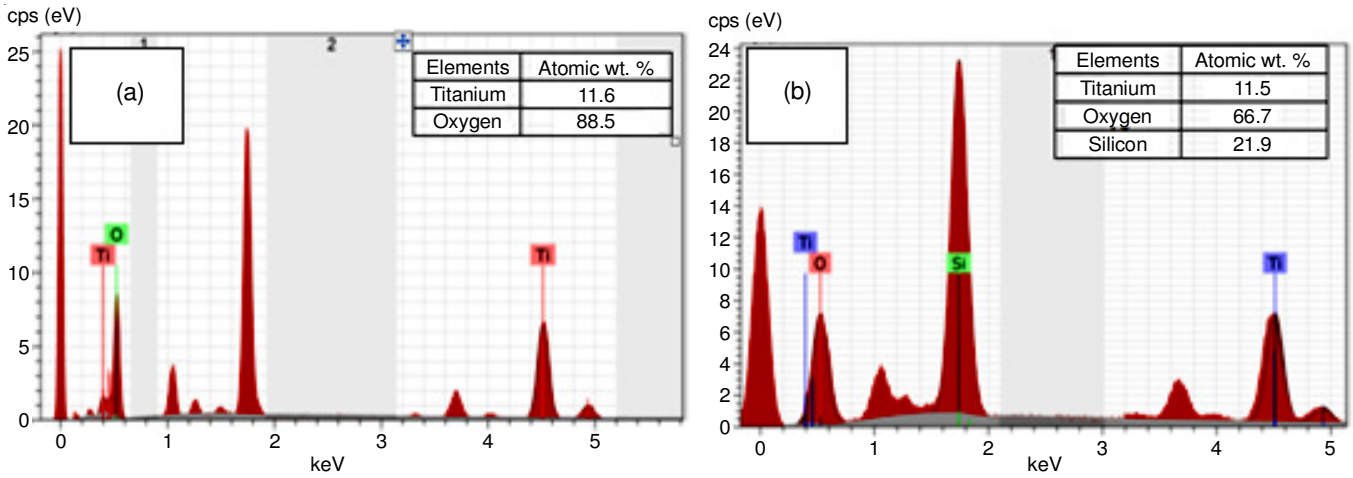

Fig. 5. EDX pattern of (a) Pure TiO_2 (b) 3 mol % SiO_2-TiO_2 thin films

$$SiO_2\ (e^- + h^+) / TiO_2\ (e^- + h^+) \rightarrow TiO_2\ (e^-) + SiO_2\ (h^+) \quad (4)$$

Electrons are reacted with oxygen to form superoxide radical ion.

$$e^- + O_2 \longrightarrow {}^{\bullet}O_2^- \quad (5)$$

Superoxide radical ion is reacted with water to form peroxide radical and hydroxyl ion.

$$H_2O + {}^{\bullet}O_2^- \longrightarrow {}^{\bullet}OOH + OH^- \quad (6)$$

The peroxide radical form oxygen and hydrogen peroxide which further react with superoxide radical ion to form $^{\bullet}OH$, OH^- and O_2.

$$2{}^{\bullet}OOH \longrightarrow O_2 + H_2O_2 \quad (7)$$

$$H_2O_2 + {}^{\bullet}O_2^- \longrightarrow {}^{\bullet}OH + OH^- + O_2 \quad (8)$$

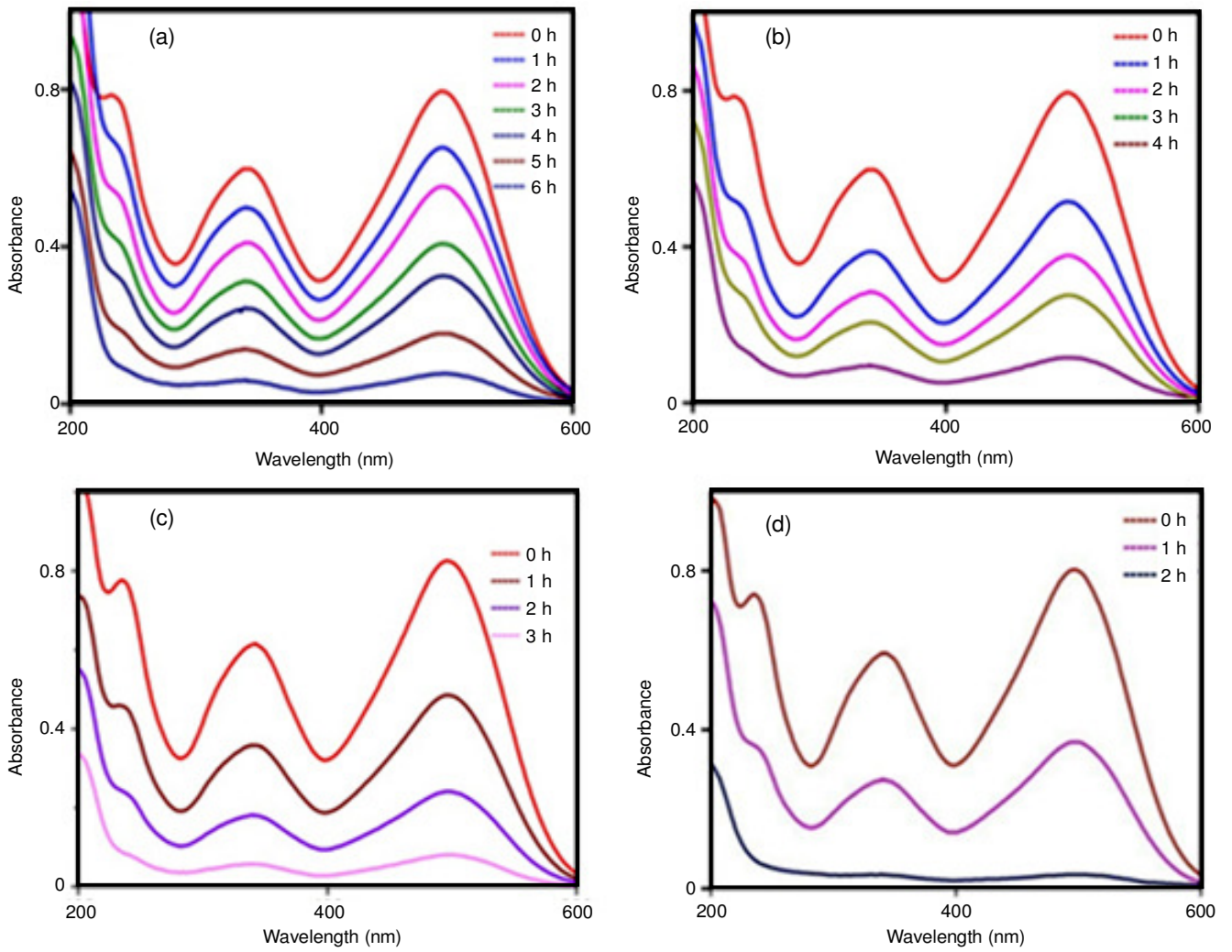

Fig. 6. Degradation of congo red in contact with (a) Pure TiO_2 (b) 1 mol % SiO_2-TiO_2 (c) 2 mol % SiO_2-TiO_2 (d) 3 mol % SiO_2-TiO_2 thin films

The pollutant was degraded by hydroxyl radical, superoxide radical ion and holes, which are further decomposed into CO_2 and H_2O.

$$^{\bullet}OH + {}^{\bullet}O_2^- + h^+ + \text{Pllutants} \longrightarrow$$
$$\text{Degradaded pllutant} \longrightarrow CO_2 + H_2O \quad (9)$$

The photocatalytic activity of the synthesized TiO_2 and SiO_2-TiO_2 film was evaluated towards the degradation of congo red dye solution under visible light irradiation. The photocatalytic degradation was monitored using main absorption peak of the congo red solution (λ = 497 nm) under visible light illumination in the presence of TiO_2 and SiO_2-TiO_2 thin films at different time intervals is shown in Fig. 6. For photocatalytic mechanism to occur both the catalyst and light source are necessary for the photocatalysis reaction to occur. Photodegradation was not observed in absence of light as well as catalyst. It implies that both are needed for the degradation of congo red. The colour of the dispersed solution disappeared after 2 h and the main absorption peak of congo red disappeared at 497 nm and the intensity of other small peaks also decreased for 3 mol % SiO_2-TiO_2 thin films.

Fig. 7 shows the change of concentration of congo red during irradiation time for pure TiO_2 and various concentration of SiO_2 doped TiO_2 thin films. A comparison of the photo catalytic activities of four films gives the following order.

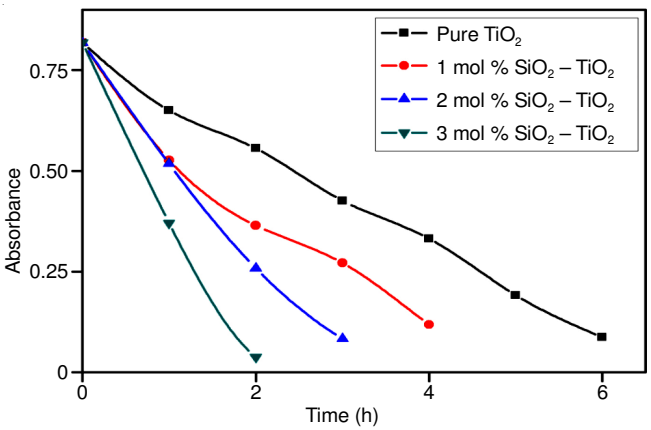

Fig. 7. Concentration of congo red in contact with TiO_2 and SiO_2 –TiO_2 thin films during the time

3 mol % SiO_2-TiO_2 > 2 mol % SiO_2-TiO_2 > 1 mol % SiO_2-TiO_2 > TiO_2. Calculation of rate constant K for photo degradation of congo red is shown in Fig. 8.

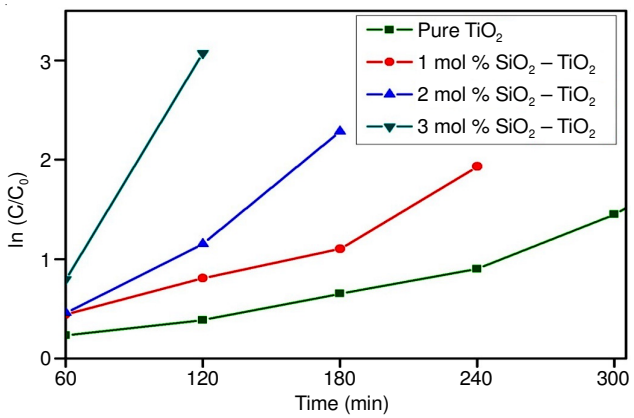

Fig. 8. Evaluation of the rate constant (K) for TiO_2 and SiO_2 –TiO_2 thin films

The lowest degradation rate is shown by pure TiO_2, which is due to lower surface area with higher crystalline size. Highest degradation rate is shown by 3 mol % SiO_2-TiO_2 thin film which indicates that doping of SiO_2 in TiO_2 is an important factor for high photocatalytic activity. The photocatalytic activity of SiO_2-TiO_2 films is primarily attributed to the surface area of the catalyst. In the case of TiO_2 film, the surface area depends on TiO_2 particle size and substrate. This is explained by the formation of film with higher total surface area as a result of fractured surface morphology as discussed in the SEM analysis. On the other hand, the higher photocatalytic activity was exhibited by the films produced by smaller TiO_2 crystals [21].

Conclusion

TiO_2 and SiO_2-TiO_2 thin films were successfully synthesized by the sol-gel dip coating technique. The structural, morphological and optical properties were investigated. The photocatalytic activity of the synthesized thin films was tested against the environment hazardous congo red dye solution under visible light irradiation. The results show that the higher efficiency up to 99 % was obtained with 3 mol % SiO_2-TiO_2 which is attributed due to the tailored band gap and small crystallite size which correspond to increased surface area and greater photo catalytic activity.

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