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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF Tio2 THIN FILM FOR PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE EFFLUENT

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ABSTRACT

In this work the preparation of TiO_2 was synthesized by sol-gel spin coating method by using TTIP as precursor solution with DEA and ethanol. The prepared samples were annealed at various temperatures. Crystallinity, phase formations and structures of the annealed samples were examined by XRD, SEM and UV-Vis spectra studies. Surface morphological studies obtained from SEM micrograph showed that the particles with spherical shapes are anatase in nature. Estimated optical band gap showed shifts with increasing annealing temperatures. The prepared thin film were used for photo catalytic degradation of methyl blue dye to identify the best photo catalyst to degrade textile dye effluent under ultraviolet light irradiation. Among the prepared samples TiO_2 thin film annealed at 450°c produce the maximum decoloration during the testing time.

INTRODUCTION

TiO_2 has been exhaustively investigated due to its unique properties and wide range of well-known applications most of the work has been focused on anatase TiO_2 made by Fujishima Honda in 1972 (Brinker *et al*, 1990), soon led to the usage photo catalytic properties of certain materials to convert photon energy into chemical energy to oxidize or reduce materials (Patrocinio *et al* , 2008; Homoudi *et al* 2007). Their usage in wide range of ever expanding applications, including air and water purification systems, photovoltaic cells, self-cleaning coating, sensors, sterilizations ,hydrogen evolution, and antifogging devices, continued to attract the interests of large number of researchers over the decades(Hoffmann *et al* 1995; Cheng *et al* 2003; Mechiakh *et al* 2007).

Among the large number of photo catalytic materials, Titania (TiO_2)is the most extensively studied and used semiconductor material due to its physical and chemical properties such as strong oxidizing abilities for the decomposition of organic pollutants, superhydrophilicity ,transparency to light stability, durability, and low cost (Jeong *et al* 2004; CFolin *et al* 2006). In fact photo activity of $TiO_2$was reported way back in 1938 as per recorded scientific works (Carp *et al* 2004). Titania exists in three main phases, namely anatase, rutile and brookite. Among the three phases, anatase and rutile phases have been widely employed in various photo catalytic studies [10]. Recently it has been reported that stability of these Titania phases in nanometer scale are connected to particle sizes. Formation of particle sizes and shapes depend on many factors, including on various parameters involved in the synthesis processes (Takikawa *et al* 1999; Zhao *et al* 2001). Therefore, extensive researches are being carried out on nano-TiO_2 photo catalysts in an endless manner by tailoring various physical parameters to achieve improved photo catalytic performance.

Being a semiconductor with band gap energies in the range of 3.0-3.4 eV, TiO_2 is easy to be irradiated especially by UV light to create the excited electron –hole pairs which could separate and the resulting charge carriers might migrate to the surface where they react with adsorbed water and oxygen to produce radical species. These radicals strike any adsorbed organic molecules, resulting in complete or selective decomposition. The sufficient photo generation of electron-hole pairs and the prevention of recombination of them are two key factors in increasing the efficiency of photo catalytic activity. The specific surface area presented by a catalyst also plays a significant role in increasing the efficiency of photo catalytic activity (Liu *et al* 2003; BinZhou *et al* 2009).

Experimental Methods

Thin Film Preparation

Titanium Tetra Isopropoxide (TiO_2,), Diethanolamine (DEA), and Ethanol were used as starting material, stabilizer, and

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solvent to prepare the sol-gel with ratio 3:1:20. All the chemicals used in this experiment were of analytical grade and were used without further purification The starting solution was prepared by mixing DEA with 10ml of ethanol (C_2H_5OH) followed by the addition of TTIP After stirring this solution for 30mins, additional 10ml of ethanol was added and the stirring was continued for 3hrs at room temperature. Finally a smooth, homogeneous, stable solution sol-gel was obtained and aged under ambient temperature. The resultant solution was stable for period of 7days. The TiO_2 thin films were prepared on glass substrates by spin coating method. The prepared sol-gel was coated on to well cleaned glass substrates by spin coater (Model SPU2008C-Apex instruments) at 3000rpm for 20sec.In order to get multilayer the process was repeated for the required number of cycles. After each coating the films were heated (pre-heat) at 250°c for 5mins to evaporate the solvent and the organic residues. The spin coating and pre-heating process were repeated for required number of times. For improved crystallization, films were annealed at 350°C, 450°C, and 550°C for one hour and allow to cool to room temperature gradually for 24hours.

Photocatalysis

Photocatalysis is the acceleration of photoreaction in the presence of catalyst. In photo catalysis, the photo catalytic activity (PCA) depends on the ability of the electron-hole pairs, which generate free radicals(e.g. hydroxyl radicals: ·OH) and able to undergo secondary reactions. The resulting reactions· OH radical, being a very strong oxidizing agent(standard redox potential +2.8V) can oxidize most azo dyes to the mineral end products. According to this, the relevant reaction at the semiconductor surface causing the degradation of dyes can be expressed as follows:

TiO_2 + hv (UV) $\rightarrow TiO_2(e_{CB}^- + h_{VB}^+)$ (1)
$TiO_2 (h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^·$ (2)
$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^·$ (3)
$TiO_2(e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{·-}$ (4)
$O_2^{·-} + H^+ \rightarrow HO_2^·$ (5)
Dye + $OH^·$ $\rightarrow$ degradation products (6)
Dye+ h_{VB}^+ $\rightarrow$ oxidation products (7)
Dye + e_{CB}^- $\rightarrow$ reduction products (8)

Where hv is the photon energy required to exite the semiconductor electron from valance band (VB) to conduction band(CB). The film was annealed at different temperatures 350°C, 450°C and 550°C and the activities of TiO2 samples on degradation of azo dyes under UV lamp irradiated were evaluated.

RESULTS AND DISCUSSIONS

Structural analysis

The X-ray diffraction patterns of TiO_2 samples annealed at different temperatures are shown in Fig.1. Since no obvious diffraction peaks are observed for the as prepared sample, it can be concluded that the TiO_2thin films are still amorphous. The diffraction pattern of the samples annealed at 350°C,450°C,550°C shows higher intensity and narrower diffraction lines with the increasing the annealing temperature. It denotes that the TiO_2 crystallites grow, as the annealing temperature increases. No impurity peaks were detected in the XRD patterns of the annealed samples.

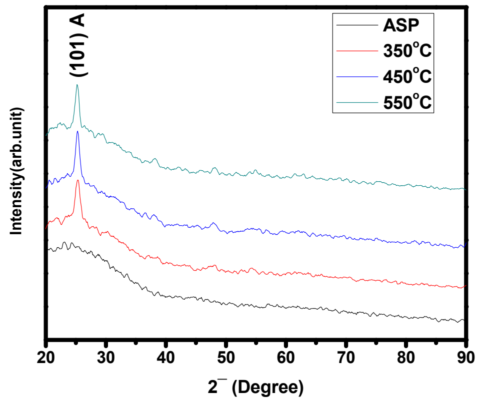
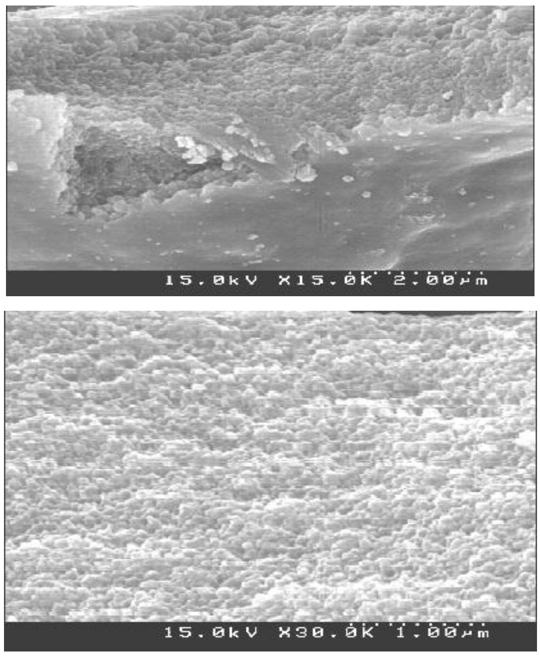


Fig 1 XRD pattern of TiO_2 thin film un annealed and annealed at 350°C, 450°Cand 550°C.

The characteristic peaks in the XRD graph exhibit tetragonal structure and matches with the JCPDS number 84-1285;and all the peaks correspond to TiO_2 anatase crystal phase . Crystallite sizes were estimated by the Scherrer formula and the sizes were8.5nm, 13.4nm, and 21.3nmfor the samples annealed at 350°C, 450°Cand 550°C respectively. The crystallite size gradually increases with the increasing annealing temperature.

Morphology

Figure 2 shows the texture and morphology of the TTIP samples annealed at different temperatures (350°C,450°C,550°C respectively).SEM images show granular morphology which could be due to agglomeration of tiny spherically shaped crystals, evenly distributed regular shaped fine particles are formed at 450°C.Thus this sample has larger exposed surface area than the other samples.



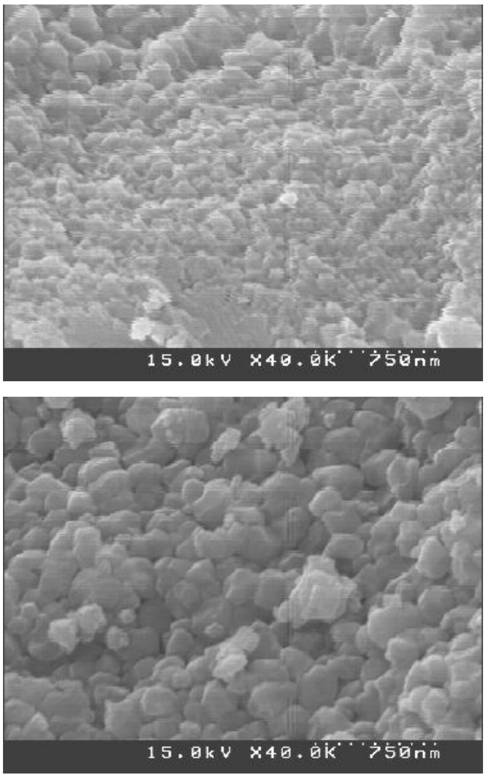


Fig: 2 SEM images of TiO_2 thin film un annealed and annealed at 350°, 450°C, 550°C.

UV-Vis Absorption Spectra

The results of the UV-Vis studies carried out to investigate the optical absorption properties of the prepared TTIP samples are shown in Fig 3.All the samples are characterized by sharp absorption edges around 388nm-420nm and the absorption varies with annealing temperature. Results show stronger absorption for the TTIP annealed at 450°C in anatase phase than that for other samples.

The absorption edge of TTIP annealed at 450°C (in anatase phase) shows a red shift into the visible region. The estimated optical band gap energy for the thin film annealed at 450°C is 3.24 eV and small variations in band gap energies were observed with annealing temperaturee.

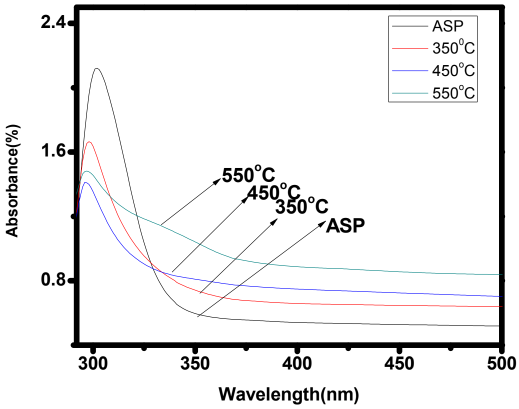


Fig 3 Absorption spectra of TiO_2 thin film un annealed and annealed at temperatures (350°C,450°C,550°C)

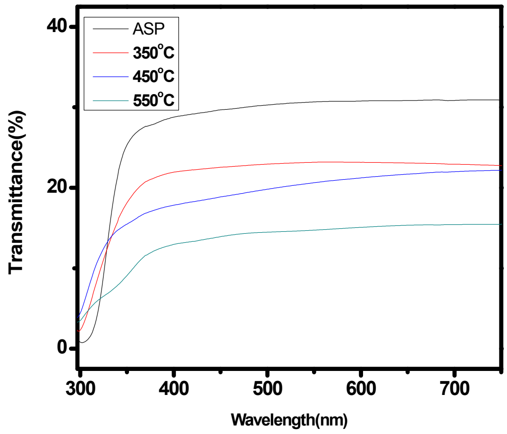


Fig: 4 Transmittance spectra of TiO_2 thin film annealed at temperatures350°C, 450°C, 550°C

Photocatalysis

Photo catalytic degradation

In order to study the photo catalytic degradation of the textile dye effluent under UV light irradiation, an indigenously designed reaction chamber fitted with an 8w mercury vapour UV light source. The lamp was installed inside a double walled quartz chamber to protect it from direct contact with aqueous solution.

Photocatalytic Degradation Experiment Results And Discussions

The results of photo catalytic degradation tests on methylene blue dye by the prepared TiO_2 thin film photo catalysts in anatase phase. The sharp reduction of adsorption peaks around 664nm shows the photo catalytic degradation of methylene blue dye under the irradiation of UV light for different durations.The UV-Vis adsorption spectra clearly indicate the best photo catalytic degradation efficiency for the TiO_2 annealed at 450°C, which is in anatase phase. The efficiencies of other samples decrease with higher annealing temperatures. Smaller size particles have larger specific surface area. Also spherical shapes offer larger specific surface area. Both these properties increase the number of active sites. This is beneficial to attain better absorption to methylene blue in the aqueous solution, and this enhances the redox reactions and thus the degradation of dye effluents.

The TiO_2 thin film surface reacts with any dye adsorbed on the surface to decompose them. This photodecomposition process involves intermediate species such as $O_2^{-\cdot}$ $HO_2^{\cdot}$, OH^+, OH^-, O^2 which play important roles in the photo catalytic degradation reaction mechanisms. Degrading capabilities of the best photo catalyst on the textile dye, based on the above test results, the best photo catalyst anatase Titania annealed at 450°C was employed to degrade textile dye effluent collected from one of the textile factories. The textile effluent was diluted with distilled water at 1:10 ratios to obtain and they were tested separately.

The anatase TiO_2 annealed at 450°C produces faster decolouration of the textile dye effluent diluted with distilled water at1:5 and 1:10 ratio and achieves 89% and 78% of decolouration in 4 hours.for all samples in the same duration of UV light irradiation. This indicates that the highly diluted dye provides better transparent medium for wider penetration of UV light and which in turn enhance the photo catalytic decolouration rate at a given duration. It was also noted that the degradation rates are slightly accelerated with time, and this could be due to increased transparency of reaction medium for the UV light with the decolouration process.

Photo catalytic degradation

In order to study the photo catalytic degradation of the textile dye effluent under UV light irradiation, an indigenously designed reaction chamber fitted with an 8w mercury vapour UV light source and a magnetic stirrer was setup inside a dark enclosure. The lamp was installed inside a double walled quartz chamber to protect it from direct contact with aqueous solution.

CONCLUSION

TiO_2 thin films were successfully synthesized by cost effective sol-gel route. XRD analysis confirmed the synthesis of nano crystalline TiO_2 thin film for annealing temperature up to 450°c. The surface morphological studies with SEM micro graph showed spherically shaped nano particles. UV-Vis spectra revealed absorption edge only in the UV region for the samples and demonstrated strong absorption width for TiO_2 annealed at 450°c and the same demonstrated the highest photo catalytic efficiency in the degradation of methylene blue under UV light.

The same photocatalyst employed in the degradation of textile dye at different dye concentrations produced better degradation efficiency for less concentrated dye. The surface morphology, crystallite size and concentration of dyes have significant effects on the photo catalytic degradation process.

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