Available online at BCREC Website: http://bcrec.undip.ac.id

Bulletin of Chemical Reaction Engineering & Catalysis, 9 (3), 2014, 175-181

Research Article

Effect of Calcination Temperature on Surface Morphology and Photocatalytic Activity in TiO_2 Thin Films Prepared by Spin Coating Technique

K. M. Mothi[1], G. Soumya[2], S. Sugunan[2*]

[1] *Christ University, Hosur Road, Bangalore 560029, Karnataka*
[2] *Department of Applied Chemistry, Cochin University of Science and Technology, Cochin-22, Kerala, India*

Received: 21st November 2013; Revised: 18th March 2014; Accepted: 29th June 2014

Abstract

TiO_2 thin films were deposited on glass substrate using Sol-Gel derived precursor by Spin Coating technique at different calcination temperatures. Structural identity of the prepared films was confirmed by powder X-ray diffraction measurements. Morphology of the films was monitored using Atomic force microscopy and it was observed that calcination temperature of 400 °C favored TiO_2 nanofibers. Photocatalytic activity of the films was checked by observing the degradation of herbicide Atrazine in UV region and the percentage of degradation was analyzed by HPLC method.

Keywords: TiO_2; Thin film; Spin Coating; Sol-Gel; AFM

How to Cite: Mothi, K.M., Soumya, G., Sugunan, S. (2014). Effect of Calcination Temperature on Surface Morphology and Photocatalytic Activity in TiO_2 Thin Films Prepared by Spin Coating Technique. *Bulletin of Chemical Reaction Engineering & Catalysis*, 9 (3): 175-181. (doi:10.9767/bcrec.9.3.5733.175-181)

Permalink/DOI: http://dx.doi.org/10.9767/bcrec.9.3.5733.175-181

1. Introduction

Thin films of metal oxides have been emerged as one of the most significant topics recently due to its heavy applications in diverse fields. Among various metal oxide thin films, superior physical and chemical properties of TiO_2 thin films forced the researchers to concentrate more in this area. Deposited TiO_2 films on glass substrate are used in heterojunction solar cells, DSSC, gas detection, photo-oxidation, photocatalysis and electro-chromic devices [1-3]. Most of the semiconducting thin films act as electron selective layer in inverted heterojunction solar cells. A lot of methods have been adopted to prepare thin films including vacuum evaporation, CVD, spray pyrolysis, spin coating etc. Fabrication of thin films can be easily achieved by spin coating due to its simple working procedure, low cost, uniform film forming ability etc.

Contamination of the earth's environment by toxic chemicals from various sources to a larger extent is a serious threat to the entire world. Major part of the total environmental pollution is coming from contaminated aquatic environment [4]. Removal of these recalcitrant chemicals for a clean, vivid and salubrious environment is the main aim of Green chemistry. Among the various organic pollutants, herbi-

* Corresponding Author
E-mail: mothikrishnamohan@gmail.com (M.K. Mohan)
Tel.: +91 484 2862428/2575682;
fax: +91 484 2575804

cides are a major pollution source for both underground and surface waters. Contamination of herbicides in water due to agricultural, non-agricultural and industrial activities is a serious worldwide problem. The environmental fate of these pollutants depends a lot on their mobility in soils and their tendency to intrude into other environmental compartments, such as air and water [5]. The extensive use of herbicides in agriculture fields to control weedy plants and to increase the quality and quantity of crop productivity has become an important tool to the detriment of the environment. The herbicides and their degradation products may alter the natural habitats of different plant and animal species depending on how they are transported in the environment [6]. Due to its chemical stability, resistance to biodegradation, and sufficient water solubility, these organic pollutants penetrate deep into the ground water [7,8]. Ubiquitous use and improper disposal of herbicides cause serious ecological consequences. As a result, if these xenobiotic organic chemicals are introduced into water ecosystems, they can make water quality worse and threaten human health [9]. So it is very mandatory to curtail these recalcitrant and persistent chemicals for a hygienic environment. A lot of methods have been employed for this purpose and some are found to be effective. But most of these methods are ineffective for the removal of these stable chemicals. If the chemical is degraded by biological or chemical processes before it leaches, it never reaches the aquifer. If the chemical has high persistence, it is not degraded, and also does not bind with soil, it is very likely to leach into and contaminate the ground water.

Heterogeneous semiconductor photocatalysis is a highly effective technique for the degradation and mineralization of pollutants in water and waste water to environmentally harmless compounds. It has recently got immense significance due to its heavy application in environmental pollution control [10]. Titania crystallizes in three allotropic forms namely anatase, rutile and brookite out of which anatase is considered photocatalytically more active phase. TiO_2 coating with high photoactivity can be applicable for environmental clean-up by photocatalysis. Atrazine is a tri-azine based compound and it is found in the environment contaminating soil and water reserves [11]. This herbicide belongs to the persistent organic pollutants because of its poor biodegradability and long half-life in water. Atrazine, which has been found in both deep and superficial waters, presents a moderate solubility in water (1.6 x 10^{-4} M at 20 ^{o}C).

Several methods have been employed to remove atrazine from aqueous wastes, such as adsorption on activated carbon and its combination with ozone [12, 13], adsorption onto carbon nanotubes [14], etc. Due to the stability of the s- triazine ring, complete mineralization of atrazine could not be attained at shorter periods of time via oxidation, which only affects the lateral chains with 5 of the 8 carbons removed as CO_2. The photocatalytic oxidation of s-triazine herbicides and their pathway of degradation have been scrutinized by various researchers. But photocatalytic degradation of this herbicide using TiO_2 thin film is very rare.

Here very cost effective and environmentally benign TiO_2 thin films were employed for the effective degradation of Atrazine in aqueous medium. Fabrication of TiO_2 thin films by Spin Coating technique and the effect of different calcination temperature on surface morphology and photocatalytic efficiency are also reported in this work.

2. Experimental

2.1 Materials and methods

Titanium(IV) isopropoxide was purchased from Sigma Aldrich, Germany. All the solvents were purchased from Merck Pvt. Ltd. India. The powder X-ray diffraction of the sample was performed using a Bruker AXS D8 diffractometer with Ni filtered Cu Kα radiation source (λ= 1.5406 A°) in the range of 10-70^{0} at a scan rate of 0.5 ^{0}/min. Film deposition was done with a WS-650 Mz-23 NPP single wafer spin processor. Morphology of the film was monitored using a BT 02218 Nanosurf easyScan 2AFM/STM package with single controller. Thickness of the film was measured using Stylus Profilometer (Dektak-6M). Degradation studies were done using HPLC (Dionex Ultimate 3000) with photo diode array UV detector and a 5 µm Thermo Hypersil ODS-2 C-18 reverse phase column.

2.2 Preparation of Thin films

Desired amount of Titanium(IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$) was dissolved in a 1:1 volume mixture (v/v) of ethanol and acetic acid. The solution was stirred vigorously for about 3 hours to form a stable sol and then it was mixed with fixed amount of ethylene glycol in order to create viscosity. The whole solution was stirred and aged properly. Film deposition was done by using Spin coating technique by dropping about 0.5ml of this Sol-Gel derived precursor on the top of the glass substrate. The

spin coating was performed at a speed of 1400 rpm for about 40 s. After that, the prepared films were calcined at 350, 400, 500, and 600 °C for 2 h in a muffle furnace with limited supply of oxygen.

2.3 Photocatalytic Reaction

Photocatalytic reactions were done in an Oriel Arc lamp to have uniform illumination. The diameter of the collimated beam is around 1 inch (2.54 cm) from the lower end of the beam tuning assembly. In order to control the temperature for the lamp environment, uniform illuminator was equipped with fan cooled lamp housing. The light source of the system was 150 W Xe ozone free lamps with an average life of 1000 hours. A 280-400 nm dichoric mirror (cold mirror) filter was used in order to get UV radiation which gave an irradiance of 96.8 mW/cm^2 (150 W). The experiment was conducted in a beaker. To this desired amount of the herbicide solution was taken and TiO_2 film was immersed into it by using a steel holder. Before irradiation, the mixture was stirred in the dark for 30 minutes to attain an adsorption/desorption equilibrium. The mixture was placed under the photo reactor and the time of irradiation was limited to 1 hour. Then the filtrate was centrifuged and filtered using a Whatman filter paper. The percentage degradation was analyzed using HPLC technique.

3. Results and Discussion

3.1 Catalyst Characterization

XRD pattern of TiO_2 thin films calcined at various temperatures are shown in figure 1 and 2. Figure 2 represents the XRD pattern of the film calcined at 350 °C. Here the peak at 2θ = 30.8° indicates (121) plane of brookite. Normally brookite cannot be prepared in the pure form. (120) and (111) peaks of brookite at 2θ = 25.3° and 25.6° respectively cannot be differentiated due to the overlapping of these peaks with (101) peak of anatase [15]. Generally brookite phase was occurred along with some other phases of TiO_2. Normal brookite has a $I_{(121)} / I_{(120)}$ ratio of ~ 0.9 (JCPDS No. 29-1360), but many of the literature reports show that these ratios are lower than this value and the corrected ratio could be achieved by calcination at relatively high temperature [15,16]. Complete transformation of brookite to anatase was achieved at a calcination temperature of 400 °C. The characteristic peak of anatase at 2θ = 62.5° does not overlap with any diffraction peaks of brookite. XRD patterns of the films calcined at 350 °C and 400 °C was sharp and uniform which represent the crystalline nature of the TiO_2 thin film. Compared to powder form, the intensities of peaks are very less in film form due to the low concentration of TiO_2. The thickness of the film used here was around 200 nm which is very less compared to substrate concentration. But a calcination temperature of 500 °C results an irregular XRD pattern due to agglomeration of particles. Here along with anatase, a very less amount of rutile was also detected. Transformation of anatase to rutile started from this temperature. XRD pattern of the film calcined at 600 °C was also not uniform and showed thermodynamically stable rutile as the major phase.

Crystallite size of the prepared films were calculated by Scherrer equation and it was found to be 11, 13, 16, and 19 nm for films calcined at 350, 400, 500, and 600 °C, respectively.

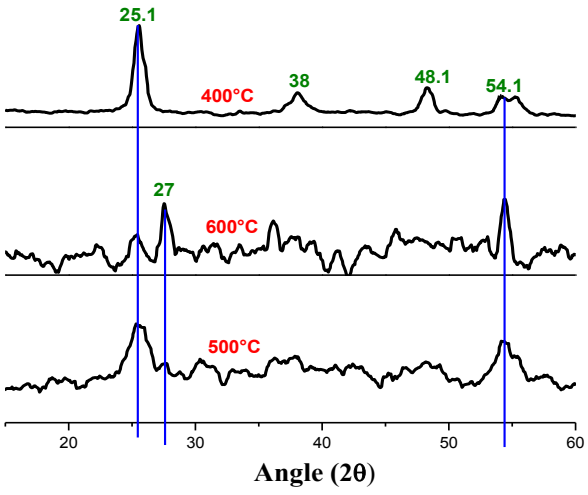

Figure 1. XRD patterns of TiO_2 thin films calcined at different temperatures

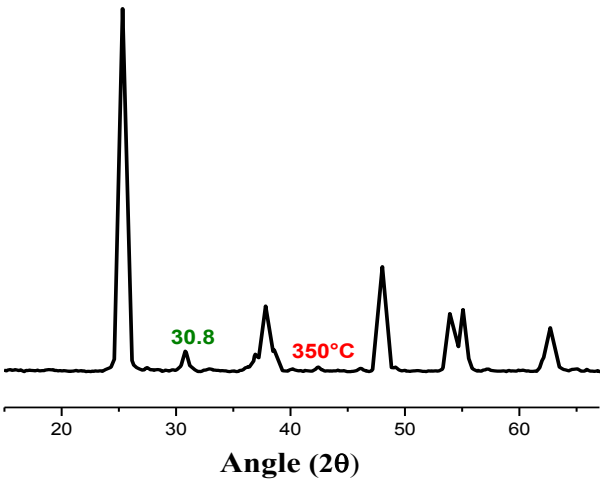

Figure 2. XRD pattern of the film calcined at 350 °C.

Effect of temperature on the transformation of various phases and variation of crystallite sizes can be evident from XRD analysis. Photocatalytically active anatase was formed at a calcination temperature of 400 °C which influences the reaction positively. Brookite was obtained at 350°C which is photocatalytically less active. Increase of temperature increases the particle size thereby reduces the specific surface area which influences the photo reaction adversely. So at 600 °C, the photocatalytic activity was found to be less.

Exactly similar volume of the precursor solution was spin coated for the fabrication of thin films. The thickness of the prepared film was analyzed by Stylus Profilometer and that was found to be around 200 nm in all the cases.

AFM image of TiO_2 film calcined at 350 °C along with its 3D map is shown in Figure 3 and it showed a uniform nature. The area roughness of the above film was found to be 252 nm. Here the possibility of adsorption is marginal due to reduced surface area which affects the photocatalytic activity of the system negatively. All the films were fabricated by Spin coating the precursor solution so that there is a chance for crystal growth during calcination. A calcination temperature of 400 °C facilitated the crystal growth towards nanofiber morphology. Fig-

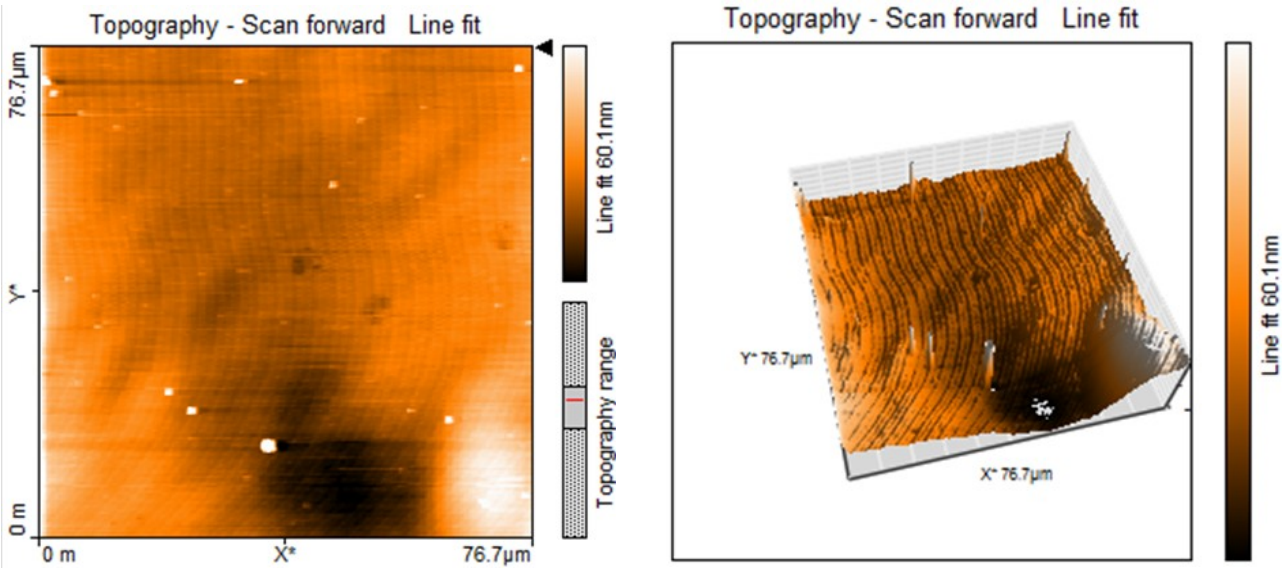

Figure 3. AFM image of film calcined at 350 °C about 2 h along with its 3D map.

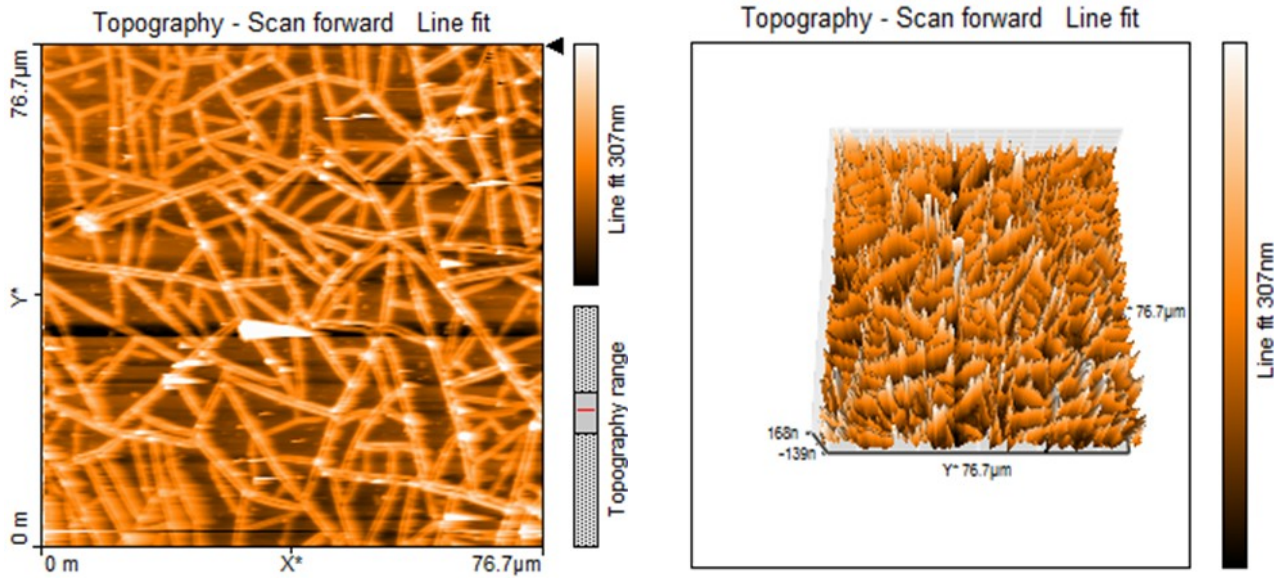

Figure 4. AFM image of 1 h calcined TiO_2 film along with its 3D map.

ure 4 and 5 represents the AFM images of the films calcined at 400 °C for about 1 h and 2 h respectively. The samples showed similar morphology at different duration of time. We have repeated the experiment 4-5 times and obtained the same morphology in this particular temperature. Area roughness is directly related to the surface area. Surface area is one of the major factors that affect photocatalysis. But photocatalysis depends on various other factors.

The film with nanofiber morphology is more amenable to photocatalysis due to its relatively higher surface area resulted from the surface roughness. Surprisingly the nanofiber morphology was disappeared at 500 °C and obtained TiO_2 nanoparticle dispersion (Figure 6), which reduced the photocatalytic ability of the system to a smaller extend. But higher temperature favored agglomeration of particles can be seen from the image, which is well in accordance with the crystallite size obtained from XRD results (Figure 7). Agglomeration results in an increase of particle size which reduces the photo activity due to poor adsorption of the substrate molecule. Area roughness of all the films except that calcined at 350 °C was found to be around 590 nm. Area roughness was less for

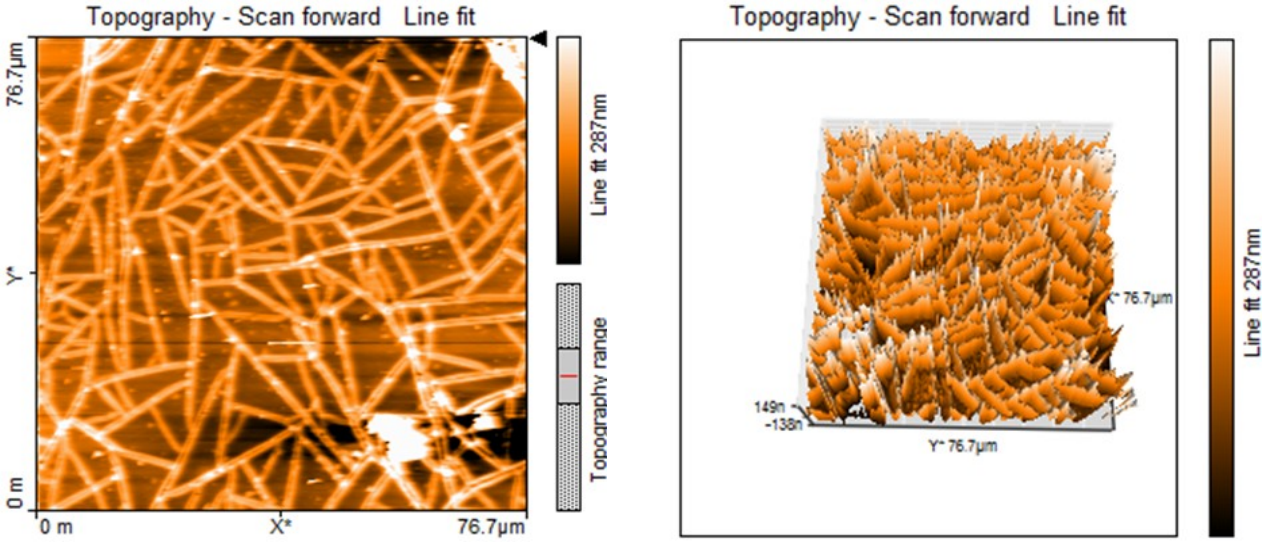

Figure 5. AFM image of 2 h calcined TiO_2 film along with its 3D map.

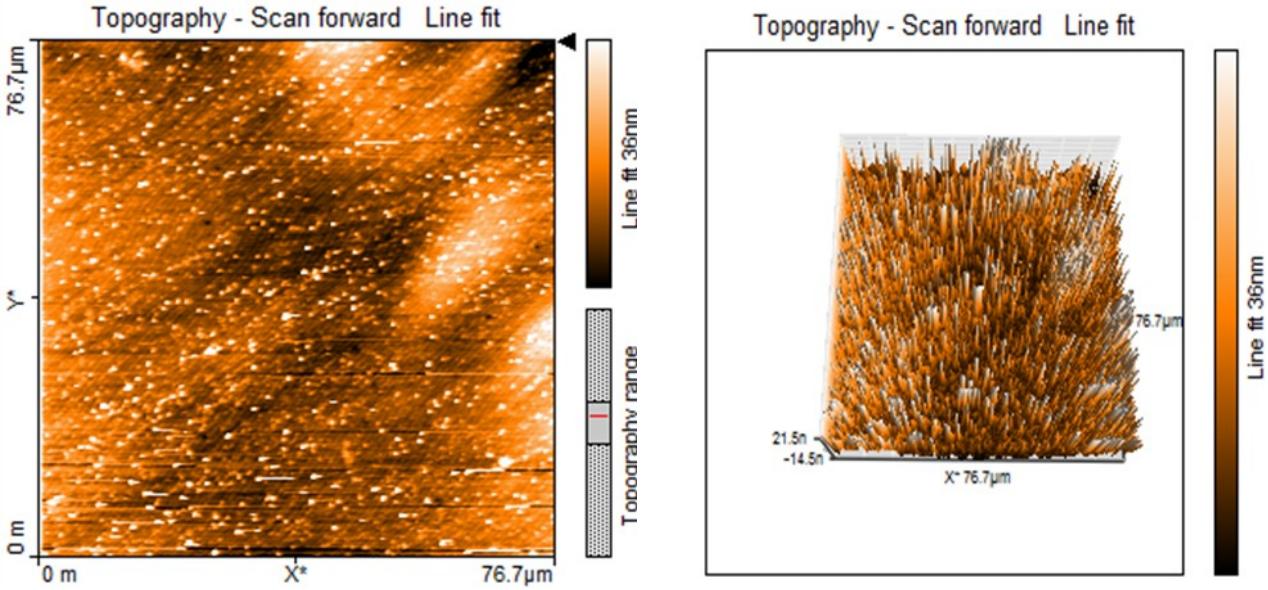

Figure 6. AFM image of 2 h calcined TiO_2 film at 500 °C and its 3D map.

uniform morphology, but high temperature destructed the uniform behavior so that area roughness was found to be higher. The shapeless structures in the image at 600 °C are mainly due to agglomeration which affects the photo reaction adversely.

3.2 Catalytic activity studies

Photocatalytic ability of the prepared films was evaluated by monitoring the degradation of herbicide Atrazine in UV region. About 20 ml of 10^{-4} M Atrazine solution was taken in a beaker. To this TiO_2 films having thickness around 200 nm was immersed with the help of a steel holder. Before irradiation the whole system was magnetically stirred for 30 minutes under dark to attain adsorption/desorption equilibrium. This mixture was placed under the photo reactor and the time of irradiation was limited to 1h. Then filtrate was centrifuged and filtered using a Whatman filter paper. The percentage degradation was analyzed by HPLC with photo diode array UV detector and a 5 µm Thermo Hypersil ODS-2 C-18 reverse phase column using UV detection at 226 nm. The mobile phase used was acetonitrile/water + 1 mmol Ammoniumacetate in the ratio 50:50. Maximum degradation of the herbicide was obtained with film calcined at 400 °C and that was found to be 91%. Calcination at 400 °C favored photocatalytically more active anatase phase as well as nanofiber morphology that positively influence the percentage of degradation by improving the adsorption of substrate on film surface. Photocatalytically less active brookite was formed at 350 °C that results a lower degradation. Crystallite size of the sample calcined at 500 °C was somewhat high that decreases the surface area thereby photocatalytic activity. The adsorption ability of rutile obtained at a calcination temperature of 600 °C is very low that in turn influences the photocatalytic activity adversely. The effect of temperature on degradation is shown in Figure 8.

4. Conclusion

Cost effective, benign and sustainable TiO_2 thin films having 200 nm thickness was fabricated by Spin coating technique. Phase transformation from brookite to rutile can be evident

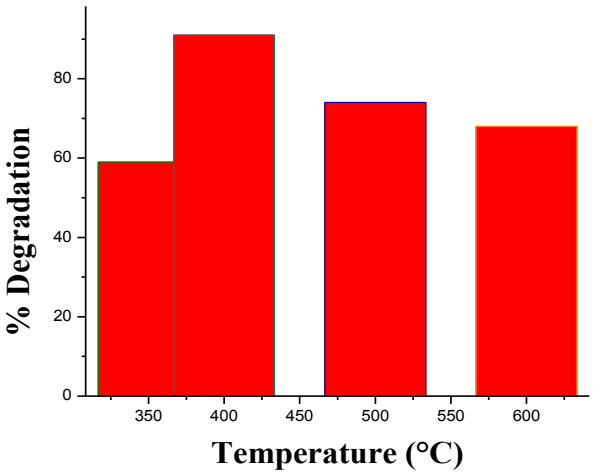

Figure 8. Effect of calcination temperature on photocatalytic degradation of Atrazine. Reaction Conditions: Concentration: 20 ml of 10^{-4} M Atrazine solution, Catalyst: TiO_2 films having thickness around 200 nm calcined at different temperatures, Time of irradiation: 1 h.

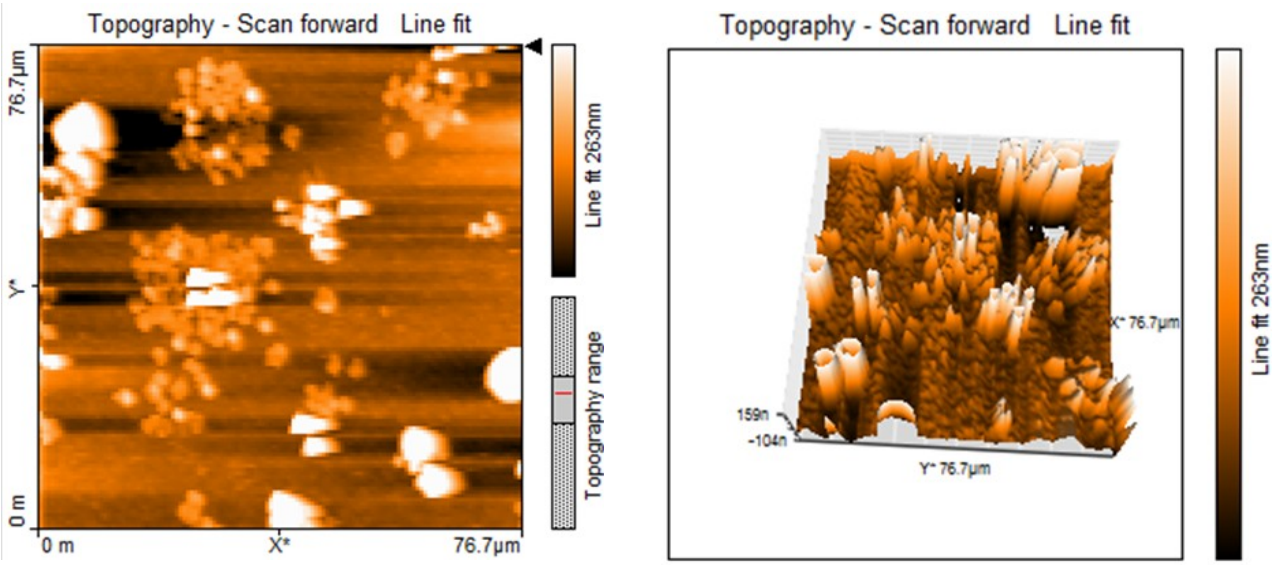

Figure 7. AFM image of 2 h calcined TiO_2 thin film at 600 °C along with its 3D map.

from XRD patterns calcined at various temperatures. Effect of temperature on morphology was observed from AFM images. Photocatalytic activity of the prepared films was measured by monitoring the degradation of recalcitrant and persistent herbicide Atrazine in UV region by HPLC technique. Maximum degradation of about 91% was obtained with sample calcined at 400 °C which showed nanofiber morphology.

Acknowledgments

One of the authors MKM is indebted to UGC-BSR for the fellowship. Help received from STIC, CUSAT during characterization is well acknowledged.

References

[1] Suciu, R. C., Rosu, M. C., Silipas, T. D., Biris, A. R., Bratu, I., Indrea, E. (2011). TiO_2 thin films prepared by spin coating technique, *Rev. Roun. Chim*. 56: 607-612.

[2] Viswas, M., Sharma, S. K., Rao, S., Mohan, K. N., Gowda, K. V. A., Chakradhar, R. P. S. (2010). Influence of surfactant and annealing temperature on optical properties of sol-gel derived nano-crystalline TiO_2 thin films. *Spectrochimica Acta Part A*. 75: 1073-1077.

[3] Chen, Y., Stathatos, E., Dionysiou, D. (2009). Sol–gel modified TiO_2 powder films for high performance dye-sensitized solar cells. *J. Photoch. Photobio. A*. 203: 192–198.

[4] Gomathi Devi, L., Krishnamurthy, G. (2011). TiO_2- and $BaTiO_3$-assisted photocatalytic degradation of selected chloroorganic compounds in aqueous medium: correlation of reactivity/orientation effects of substituent groups of the pollutant molecule on the degradation rate. *J. Phys. Chem. A.* 115: 460-469.

[5] Navarro, S., Fenollb, J., Velac, N., Ruizb, E., Navarro, G. (2009) . Photocatalytic degradation of eight pesticides in leaching water by use of ZnO under natural sunlight. *Journal of Hazardous Materials.* 172: 1303-1310.

[6] Quiroz, N. A., Gutierrez, D. J. R., Martínez, S. S., Bahena, C. L. (2011). Degradation of Gesaprim Herbicide by Heterogeneous Photocatalysis Using Fe-Doped TiO_2. *International Journal of Geosciences.* 2: 669-675.

[7] Graham, J. A. (1991). Monitoring groundwater and well water for crop protection chemicals. *Analytical Chemistry.* 63: 631–622.

[8] Blake, D. M. (2001). Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. *National Renewal Energy Laboratory, Cole Boulevard Golden, Colo, USA*.

[9] Rahman, M., Kim, T. H., Kwon, G.S. (2009). Removal efficiency of the herbicide oxadiazon in treatment processes for drinking water. *Journal of the Korean Society for Applied Biological Chemistry.* 52: 252-257.

[10] Kuvarega, A. T., Krause, R. W. M., Mamba, B. B. (2011). Nitrogen/Palladium-Codoped TiO_2 for Efficient Visible Light Photocatalytic Dye Degradation, *J. Phys. Chem. C.* 115: 22110-22120.

[11] Kalkhoff, S. J., Lee, K. E., Porter, S. D., Terrio, P. J., Thurman, E. M. (2003). Herbicides and Herbicide Degradation Pro- ducts in Upper Midwest Agricultural Streams during August Base Flow Conditions. *Journal of Environmental Quality.* 32: 1025-1035.

[12] Guzman-Perez, C. A., Soltan, J., Robertson, J. (2011). Kinetics of Catalytic Ozonation of Atrazine in the Presence of Activated Carbon. *Separation and Purification Technology.* 79: 8-14.

[13] Gupta, V.K., Gupta, Bina, Rastogi, Arshi, Agarwal, Shilpi, Nayak, Arunima. (2011). Pesticides removal from waste water by activated carbon prepared from waste rubber tire. *Water Research.* 45: 4047-4055.

[14] Chen, G. C., Shan, X. Q., Zhou, Y. Q., Shen, X. E., Huang, H. L., Khan, U. S. (2009). Adsorption kinetics, isotherms and thermodynamics of atrazine on surface oxidized multiwalled carbon nanotubes. *Journal of Hazardous Materials.*169: 912-918.

[15] Paola, A. D., Bellardita, M., Palmisano, L. (2013). Brookite, the Least Known TiO_2 Photocatalyst, *Catalysts.* 3:36-73.

[16] Li, J. G., Ishigaki, T., Sun, X. (2007). Anatase, Brookite, and Rutile Nanocrystals via Redox Reactions under Mild Hydrothermal Conditions: Phase-Selective Synthesis and Physicochemical Properties. *J. Phys. Chem. C.* 111: 4969-4976.