

Synthesis and Characterization of nano-Titania Phases for Photocatalytic Degradation of Textile Dye Effluent

N. Karthikeyan^{1,2}, V. Narayanan³ and A. Stephen^{1*}

¹Department of Nuclear Physics, University of Madras, Maraimalai Campus, Guindy, Chennai 600025, India

²Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda, Sri Lanka

³Department of Inorganic Chemistry, University of Madras, Maraimalai Campus, Guindy, Chennai 600025, India
*stephen_arum@hotmail.com

Abstract: Nano-Titania was synthesized by sol-gel method and the as prepared sample was annealed at various temperatures. Crystallinity, phase formations and structures of the annealed samples were examined by powder x-ray diffraction studies. The results revealed formation of pure anatase phase for annealing temperatures up to 600 °C and pure rutile phase at 900 °C. High resolution scanning electron microscope (HR-SEM) images showed granular morphology due to agglomeration of tiny spherically shaped particles. Energy dispersive x-ray (EDX) spectrometer analysis confirmed the expected elemental composition without any impurities. UV-Vis spectra revealed sharp absorption edges for all the samples in the UV region. Estimated optical bandgap showed shifts with the increasing annealing temperatures. The prepared photocatalysts were used for photocatalytic degradation of methylene blue dye to identify the best photocatalyst and then the best catalyst was employed for photocatalytic degradation of textile dye effluent under ultraviolet light irradiation. Among the prepared samples, Titania annealed at 450 °C produce the maximum decolouration during the testing time.

Keywords: Titania, Anatase, Rutile, sol-gel, photocatalytic degradation, textile dye effluent, nanomaterials

I. INTRODUCTION

The landmark break through made by Fujishima and Honda in 1972 [1], soon led to the usage photocatalytic properties of certain materials to convert photon energy into chemical energy to oxidize or reduce materials. Their usage in wide range of ever expanding applications [2-6], including air and water purification systems, photovoltaic cells, self-cleaning coating, sensors, sterilization, hydrogen evolution, and antifogging devices, continued to attract the interests of large number of researchers over the decades.

Among the large number of photocatalytic materials, Titania (TiO₂) 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, low cost and environmental friendliness. In fact photoactivity of TiO₂ was reported way back in 1938 as per recorded scientific works [7, 8].

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 photocatalytic studies. Recently it has been reported that stability of these Titania phases in nanometer scale are connected to particle sizes [5, 9, 10]. Formation of particle sizes and shapes depend on many factors, including on various parameters involved in the synthesis processes. Therefore, extensive researches are being carried out on nano-TiO₂ photocatalysts in an endless manner by tailoring various physical parameters to achieve improved photocatalytic performance.

Being a semiconductor with bandgap energies in the range of 3.2 - 3.4 eV [11-13], TiO₂ 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 efficient photo generation of electron - hole pairs and the prevention of recombination of them are two key factors in increasing the efficiency of photocatalytic activity. The specific surface area presented by a catalyst also plays a significant role in increasing the efficiency of photocatalytic activity. [14-18].

II. MATERIALS AND EXPERIMENTAL DETAILS

A. Preparation of photocatalytic materials

Titania (TiO₂) was synthesized by sol-gel method, by dissolving the precursor titanium (IV) isopropoxide (97%, Sigma Aldrich) in isopropanol (97%, Sigma Aldrich) under continuous stirring at room temperature, and then by adding citric acid as the chelating agent mixed with deionized water [19]. Addition of citric acid mixed with deionized water transformed the clear solution into pale-whitish gel. The gel was dried in air at room temperature for a few days and then grounded to obtain fine powder sample. The as prepared sample was in amorphous state, and it was annealed at 300 °C, 450 °C, 600 °C and 900 °C for 1 hour using an alumina crucible in a muffle furnace to refine the structure and also to obtain various phases.

B. Characterisation of materials

The structures of the annealed samples were determined by the powder XRD RICH SEIFERT diffractometer using Cu K₁ radiation ($\lambda = 0.154056$ nm). The averaged crystallite sizes were estimated using the standard Scherrer's formula:

$$D = (K \times \lambda) / (\Delta 2\theta \cos \theta)$$

where, K - shape factor (its 0.9 for sphere like particles)

- λ - wave length of incident X-ray (1.5406 Å)
- $\Delta 2\theta$ - full-width at half maximum of the peaks (in radians)
- θ - diffraction angle

Surface morphology and elemental analysis were carried out using QUANTA 200 FEG high resolution scanning electron microscopy. The light absorption property of all the powder samples was studied using CARY 5E UV-VIS-NIR spectro-photometer. The liquid samples collected at regular intervals of time during the degradation of methylene blue and chosen textile dye effluent were analyzed using CARY 5E UV-VIS-NIR UV-Vis spectrophotometer and Unico 2800 Single Beam UV/Vis Spectrophotometer respectively.

C. Photocatalytic degradation experiment

In order to study the photocatalytic 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. The experiment was carried out in two stages. First the degrading capabilities of the prepared samples were tested on a model organic dye, methylene blue. And then the identified best photocatalyst was employed to degrade the real textile dye effluent collected from a factory.

The methylene blue dye solution was prepared by dissolving 9.8 mg of methylene blue in 1000 ml of double-distilled water. Reaction suspensions were prepared by adding required amount of synthesized TiO₂ photocatalyst powders into 500 ml of methylene blue solution. The suspension was magnetically stirred under dark condition for 30 minutes to establish adsorption-desorption equilibrium condition.

Then photocatalytic decomposition study of methylene blue was carried out under UV light irradiation. The samples from the suspensions were collected at equal interval of time, centrifuged and filtered. The concentrations of methylene blue collected at regular time interval were analyzed by UV-Vis spectrophotometer at the wavelength of 664 nm. Degradation efficiencies were calculated using following equation:

$$(\%) = (1 - C_t/C_0) \times 100$$

where C_0 is the initial concentration and

C_t is the concentration of irradiated suspension at time t , taken at regular intervals.

The textile effluent was diluted with distilled water at 1:4 and 1:8 ratios to obtain two different concentrations of the effluent and they were tested separately. The effluent was diluted to ensure maximum spread of UV light throughout the container. Reaction suspensions were prepared by adding required amount of synthesized TiO₂ photocatalyst powders into 500 ml of diluted textile dye effluent solutions. Then the experiment was carried out as described above under same conditions.

The photocatalytic activity is largely controlled by (i) the light absorption properties, (ii) reduction and oxidation rates on the surface by the electron and hole, (iii) and the electron-hole recombination rate [20]. And these properties depend on many physical, morphological and chemical factors of the photocatalyst, medium and environment.

III. RESULTS AND DISCUSSIONS

A. Phase and structure confirmation

The X-ray diffraction patterns of TiO_2 samples treated 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_2 powders are still amorphous. The diffraction pattern of the samples annealed at 300 °C, 450 °C, 600 °C and 900 °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.

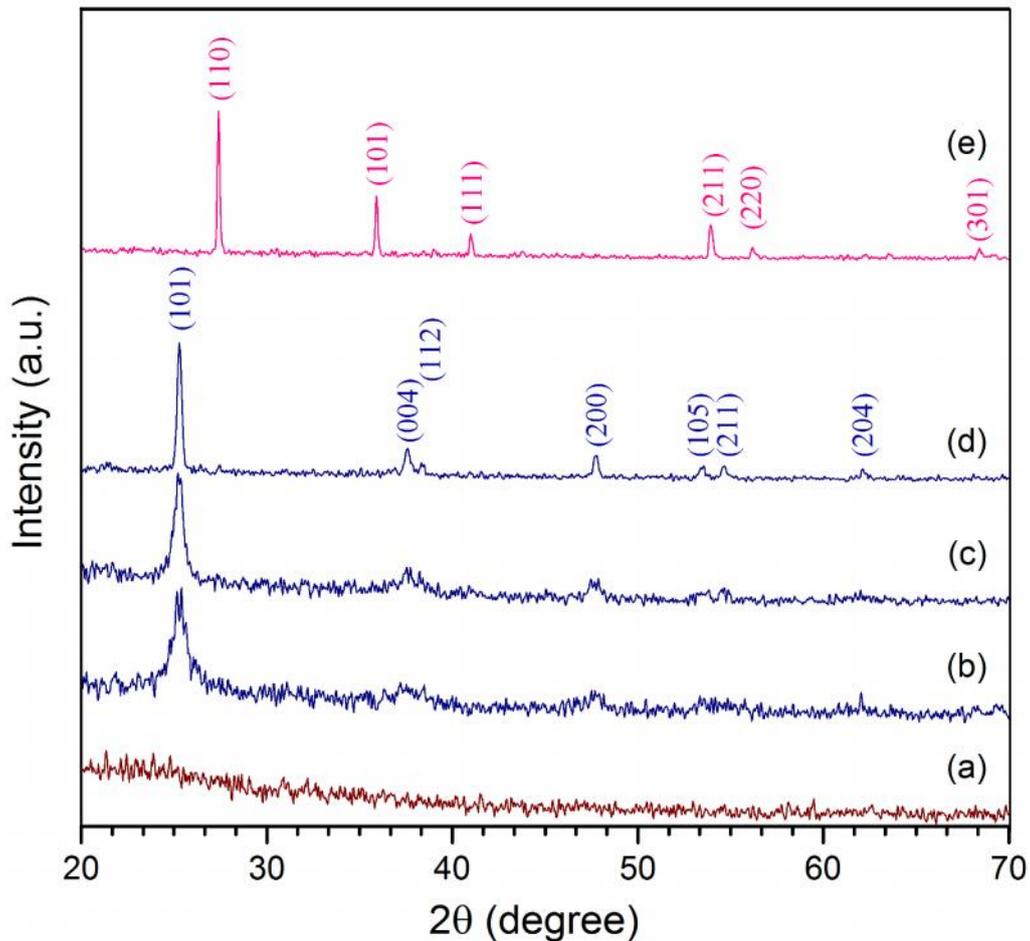


Figure 1: XRD patterns of Titania samples (a) as prepared and annealed at (b) 300 °C, (c) 450 °C, (d) 600 °C, and (e) 900 °C.

The characteristic peaks in the diffractograms 1(b), 1(c), 1(d) exhibit tetragonal structure and matches with the JCPDS number 84-1285; and all the peaks correspond to TiO_2 anatase crystal phase. Similarly the peaks in 1(e) exhibit tetragonal structure and they match very well with the JCPDS number 89-6975; and they correspond to TiO_2 rutile phase.

Crystallite sizes were estimated by the Scherrer's formula and the sizes were 10 nm, 14 nm, 25 nm, 41 nm for samples annealed at 300 °C, 450 °C, 600 °C and 900 °C respectively. The crystallite size gradually increases with the increasing annealing temperature.

B. Morphology

Figure 2 [(1) to (4)] shows the texture, morphology and elemental composition of the titania samples annealed at different temperatures (at 300 °C, 450 °C, 600 °C and 900 °C respectively). SEM images show granular morphology which could be due to agglomeration of tiny spherically shaped crystals. Agglomeration is one of the drawbacks of titania [21]. However, comparatively, evenly distributed regular shaped fine particles are formed at 450 °C. Thus this sample has larger exposed surface area than the other samples.

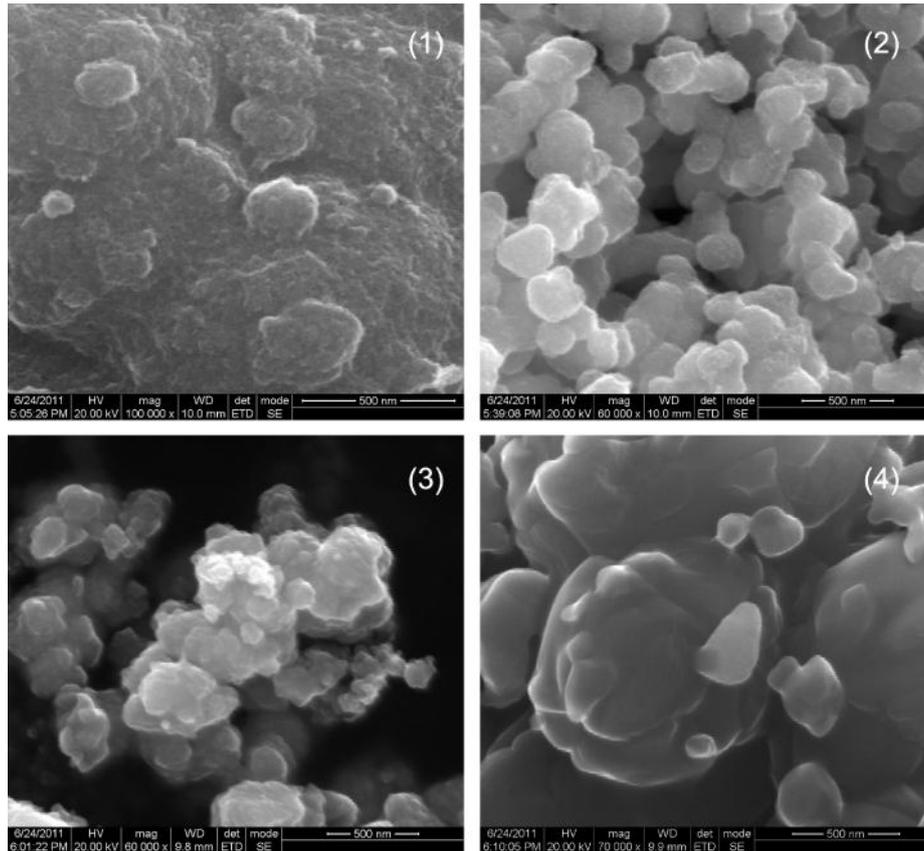


Figure 2: HR-SEM images of Anatase Titania annealed at (1) 300 °C, (2) 450 °C, (3) 600 °C, and Rutile Titania annealed at (4) 900 °C.

The elemental compositions of the samples annealed at different temperatures and their purity were confirmed by EDX and it establishes the presence of Ti and O, without any notable impurities in all the samples. EDX spectra are shown in Fig.3.

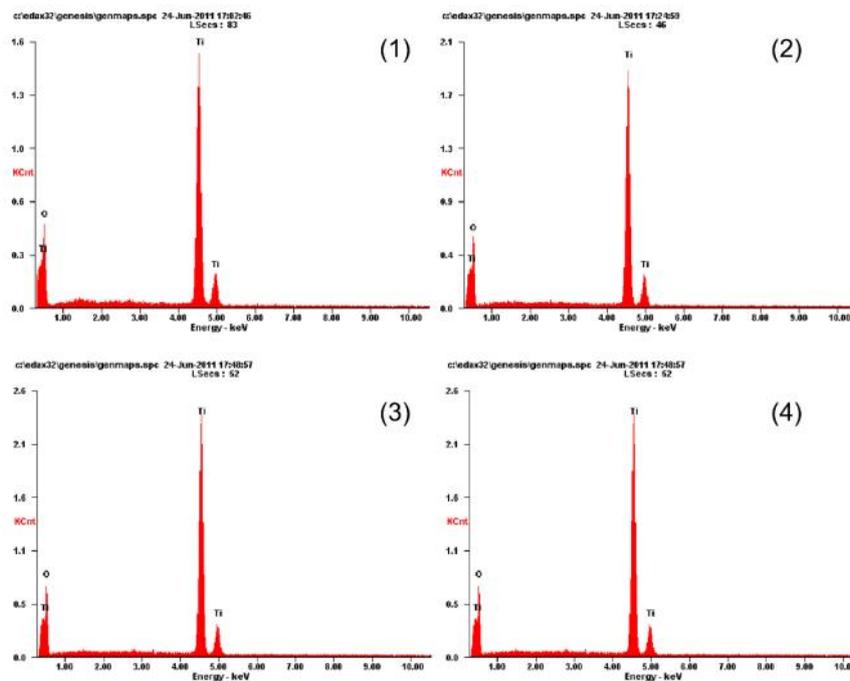


Figure 3: EDX spectra of Titania samples annealed at (1) 300 °C, (2) 450 °C, (3) 600 °C, and (4) 900 °C.

C. UV-Vis Absorption Spectra

The results of the UV-Vis studies carried out to investigate the optical absorption properties of the prepared titania samples are shown in Fig. 4. All the samples are characterized by sharp absorption edges around 388 nm - 420 nm and the absorption varies with annealing temperature. Results show stronger absorption for the Titania annealed at 450 °C in anatase phase than that for other samples in anatase and rutile phases. The absorption edge

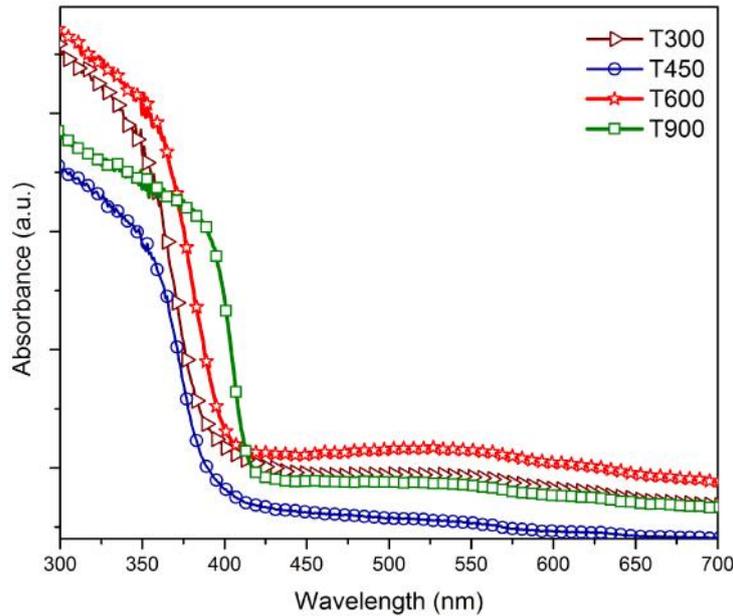


Figure 4: Diffuse Reflectance spectrum of all prepared samples

of Titania annealed at 900 °C (in rutile phase) shows a red shift into the visible region. The estimated optical bandgap energies of the samples vary between 2.95 eV and 3.20 eV and small variations in bandgap energies were observed with annealing temperature.

IV. PHOTOCATALYTIC DEGRADATION EXPERIMENT RESULTS AND DISCUSSIONS

A. Degrading capabilities of the prepared photocatalysts on a model dye

The results of photocatalytic degradation tests on methylene blue (MB) dye by the prepared nano-Titania photocatalysts in anatase and rutile phases are shown in Fig. 5. The sharp reduction of absorption peaks around 664 nm shows the photocatalytic degradation of methylene blue dye under the irradiation of UV light for different durations.

The UV-Vis absorption spectra clearly indicate the best photocatalytic degradation efficiency for the Titania 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 adsorption to methylene blue in the aqueous solution, and this enhances the redox reactions and thus the degradation of

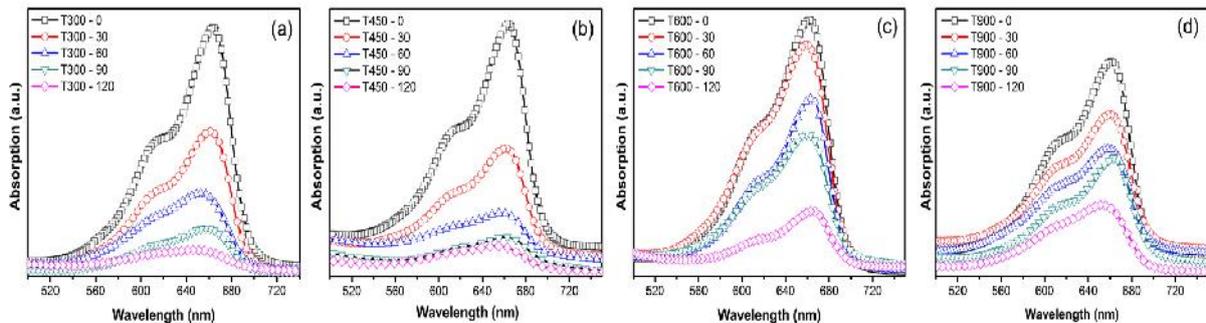


Figure 5: Degradation of MB by anatase Titania annealed at (a) 300 °C, (b) 450 °C, (c) 600 °C, and rutile Titania annealed at (d) 900 °C.

methylene blue. The obtained results are in agreement with these physical factors and the characterization results, with the exception of the Titania annealed at 300 °C. This variation could be due to strong agglomeration of tiny spherically shaped particles as evident from the HR-SEM images. Though the particle sizes are comparatively larger, the anatase Titania annealed at 450 °C shows regularly shaped fine particle morphology with less agglomeration. The sample also exhibited the strongest optical absorption property among the prepared samples.

Though the rutile phase Titania annealed at 900 °C, showed a significant reduction of bandgap and a redshift in optical absorption studies, it produced the least photocatalytic degradation efficiency among the prepared samples. HR-SEM images for this sample revealed intense agglomeration of irregular shape particles with fused like surface morphology, and this could be the major reason for drastic reduction in its photocatalytic degradation efficiency.

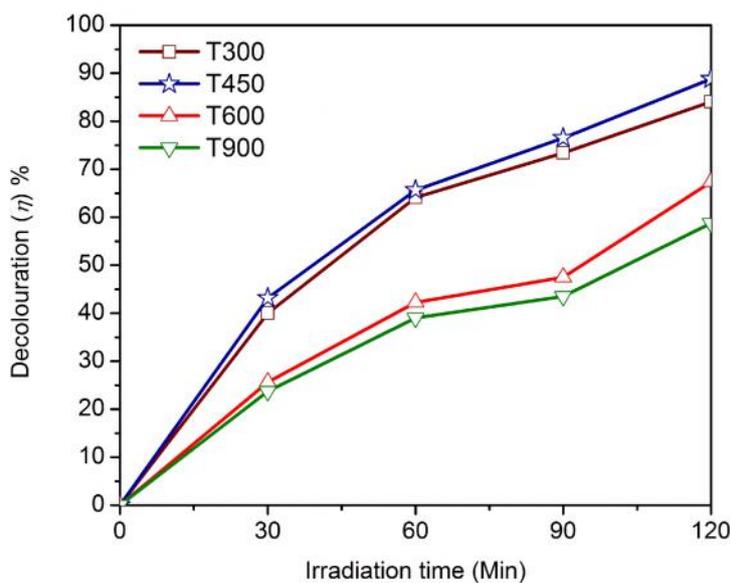


Figure 6: Decolouration profile of MB by anatase Titania annealed at (a) 300 °C, (b) 450 °C, (c) 600 °C, and by rutile Titania annealed at (d) 900 °C.

Fig. 6 shows the decolouration percentages of methylene blue as a function of UV irradiation time. Decolouration takes place due to photocatalytic degradation of methylene blue in the presence of photocatalytic nano-Titania. Anatase Titania annealed at 450 °C gives the maximum decolouration of 89 % in 2 hours. Then the other anatase Titania photocatalysts annealed at 300 °C and 600 °C and, rutile Titania annealed 900 °C gives 84, 67 and 59 percentages of decolouration respectively.

B. Photocatalytic degradation mechanism

A possible photocatalytic degradation mechanism for methylene blues is graphically shown in Fig. 7. When

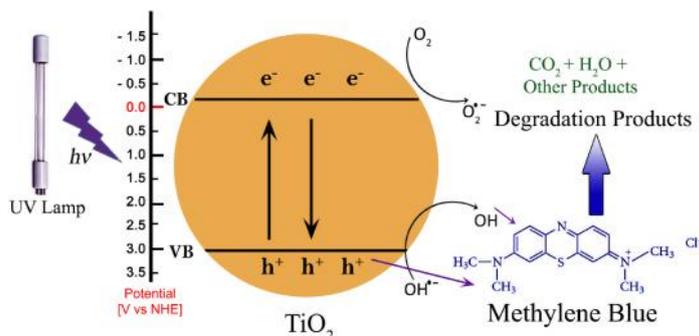


Figure 7: Photocatalytic degradation mechanism for methylene blue

irradiated with UV light with energy (h) larger than the band gap of Titania, electrons are excited from the valence band to the conduction band, creating electron-hole pairs. Thus electrons and holes are produced in conduction band and valence band respectively. The oxidizing potential possessed by these electron-hole pairs are sufficient to decompose the methylene blue or any other dye in aqueous media. These charge carriers migrate

to the surface and react 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^{\cdot} , OH^- , $O^{\cdot-}$ which play important roles in the photocatalytic degradation reaction mechanisms.

C. Degrading capabilities of the best photocatalyst on the textile dye

Based on the above test results, the best photocatalyst 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 1:4 and 1:8 ratios to obtain two different concentrations of the effluent and they were tested separately. Results of the photocatalytic degradation test are shown in Fig. 8 as decolouration profile.

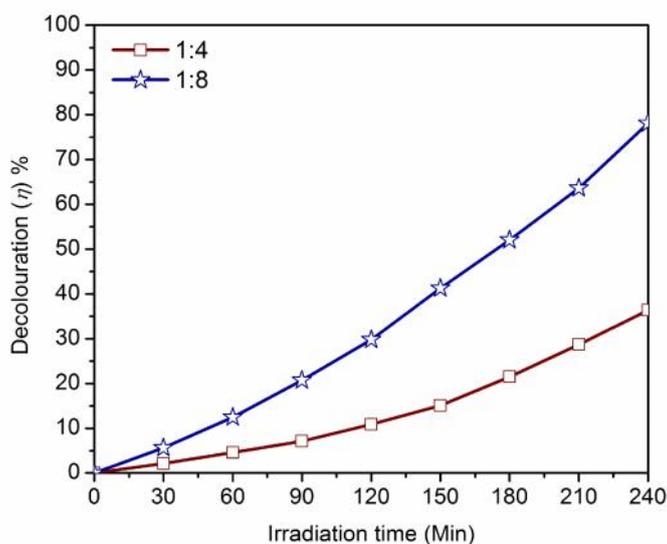


Figure 8: Decolouration profile of textile dye effluent by anatase Titania annealed at 450 °C.

The anatase Titania annealed at 450 °C produces faster decolouration of the textile dye effluent diluted with distilled water at 1:8 ratio and achieves 78 % of decolouration in 4 hours. Whereas the dye diluted with distilled water at 1:4 ratio undergoes only 36 % of decolouration 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 photocatalytic 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.

V. CONCLUSIONS

Titania powders were successfully synthesized by cost effective sol-gel route. XRD analysis confirmed the synthesis of nano-Titania powders and the formation of anatase crystalline phase for annealing temperatures up to 600 °C and then formation of pure rutile crystalline phase when annealed at 900 °C. It also confirmed the crystallite sizes from 10 nm to 41 nm for the prepared catalysts annealed at various temperatures. The surface morphological studies with HR-SEM micrographs showed irregular spherically shaped nanoparticles and especially with stout agglomeration for the samples prepared at 300 °C and 900 °C. Elemental composition and the purity of all the samples were established with EDX studies. UV-Vis spectra revealed absorption edges only in the UV region for all the samples and demonstrated strong absorption width for TiO_2 annealed at 450 °C and the same sample demonstrated the highest photocatalytic 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. Crystalline phases, particle sizes, agglomeration of particles and concentration of dyes have significant effects on the photocatalytic degradation process.

ACKNOWLEDGMENT

One of the authors, NK, thanks HETC project for the financial support. The authors are thankful to Centre for Nanoscience and Nanotechnology, University of Madras for FESEM and SAIF at IIT Chennai for the UV-Vis characterization of powder samples.

REFERENCES

- [1] A. Fujishima and K. Honda, "Electrochemical Photolysis of Water at a Semiconductor Electrode," *Nature*, vol. 238, pp. 37-38, 1972.
- [2] A. Fujishima, T. N. Rao, and D. A. Tryk, "Titanium dioxide photocatalysis," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 1, pp. 1-21, 6/29/ 2000.
- [3] A. Fujishima, T. N. Rao, and D. A. Tryk, "TiO₂ photocatalysts and diamond electrodes," *Electrochimica Acta*, vol. 45, pp. 4683-4690, 10/13/ 2000.
- [4] A. Fujishima, X. Zhang, and D. A. Tryk, "TiO₂ photocatalysis and related surface phenomena," *Surface Science Reports*, vol. 63, pp. 515-582, 12/15/ 2008.
- [5] H. Kazuhito, I. Hiroshi, and F. Akira, "TiO₂ Photocatalysis: A Historical Overview and Future Prospects," *Japanese Journal of Applied Physics*, vol. 44, p. 8269, 2005.
- [6] D. A. Tryk, A. Fujishima, and K. Honda, "Recent topics in photoelectrochemistry: achievements and future prospects," *Electrochimica Acta*, vol. 45, pp. 2363-2376, 5/3/ 2000.
- [7] C. F. Goodeve and J. A. Kitchener, "The mechanism of photosensitisation by solids," *Transactions of the Faraday Society*, vol. 34, pp. 902-908, 1938.
- [8] S.-i. Kato and F. Mashio, "Titanium Dioxide-Photocatalyzed Liquid Phase Oxidation of Tetralin," *The Journal of the Society of Chemical Industry, Japan*, vol. 67, pp. 1136-1140, 1964.
- [9] H. Zhang and J. F. Banfield, "Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: Insights from TiO₂," *Journal of Physical Chemistry B*, vol. 104, pp. 3481-3487, 2000.
- [10] M. R. Ranade, A. Navrotsky, H. Z. Zhang, J. F. Banfield, S. H. Elder, A. Zaban, *et al.*, "Energetics of nanocrystalline TiO₂," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 99, pp. 6476-6481, 2002.
- [11] K. Maeda and K. Domen, "New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light," *The Journal of Physical Chemistry C*, vol. 111, pp. 7851-7861, 2007/06/01 2007.
- [12] M. D. Hernandez-Alonso, F. Fresno, S. Suarez, and J. M. Coronado, "Development of alternative photocatalysts to TiO₂: Challenges and opportunities," *Energy & Environmental Science*, vol. 2, pp. 1231-1257, 2009.
- [13] X. Yan, C. Zou, X. Gao, and W. Gao, "ZnO/TiO₂ core-brush nanostructure: processing, microstructure and enhanced photocatalytic activity," *Journal of Materials Chemistry*, vol. 22, pp. 5629-5640, 2012.
- [14] M. Jakob, H. Levanon, and P. V. Kamat, "Charge Distribution between UV-Irradiated TiO₂ and Gold Nanoparticles: Determination of Shift in the Fermi Level," *Nano Letters*, vol. 3, pp. 353-358, 2003/03/01 2003.
- [15] A. Wood, M. Giersig, and P. Mulvaney, "Fermi Level Equilibration in Quantum Dot-Metal Nanojunctions[†]," *The Journal of Physical Chemistry B*, vol. 105, pp. 8810-8815, 2001/09/01 2001.
- [16] V. Anh Tuan, N. Quoc Tuan, B. Thi Hai Linh, T. Manh Cuong, D. Tuyet Phuong, and T. Thi Kim Hoa, "Synthesis and characterization of TiO₂ photocatalyst doped by transition metal ions (Fe³⁺, Cr³⁺ and V⁵⁺)," *Advances in Natural Sciences: Nanoscience and Nanotechnology*, vol. 1, p. 015009, 2010.
- [17] S. Rehman, R. Ullah, A. M. Butt, and N. D. Gohar, "Strategies of making TiO₂ and ZnO visible light active," *Journal of Hazardous Materials*, vol. 170, pp. 560-569, 10/30/ 2009.
- [18] R. Qiu, D. Zhang, Y. Mo, L. Song, E. Brewer, X. Huang, *et al.*, "Photocatalytic activity of polymer-modified ZnO under visible light irradiation," *Journal of Hazardous Materials*, vol. 156, pp. 80-85, 8/15/ 2008.
- [19] M. R. Vaezi, "Two-step solchemical synthesis of ZnO/TiO₂ nano-composite materials," *Journal of Materials Processing Technology*, vol. 205, pp. 332-337, 2008.
- [20] X. Chen and S. S. Mao, "Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications," *Chemical Reviews*, vol. 107, pp. 2891-2959, 2007.
- [21] L. You-ji and C. Wei, "Photocatalytic degradation of Rhodamine B using nanocrystalline TiO₂-zeolite surface composite catalysts: effects of photocatalytic condition on degradation efficiency," *Catalysis Science & Technology*, vol. 1, pp. 802-809, 2011.