

Photocatalytic Degradation of Acid Red 73 Using TiO₂ Nanoparticles Immobilized on Alumina Foam

Somayeh Alijani, Mohammad Vaez, and Abdolsamad Zarringhalam Moghaddam

Abstract—In this study, TiO₂ nanoparticles were synthesized by the P-25 powder modified sol-gel method and immobilized on alumina foam as support. The structural properties of the as-prepared film were characterized by XRD, SEM, and BET analysis. The XRD results show no discernible changes in the structure of TiO₂ as a result of the immobilization procedure. The formation of microcracks in the film, as observed in SEM images, may have a beneficial effect on the photocatalytic performance of the as-prepared film with respect to the exposure of TiO₂ nanoparticles within the inner layers to the solution. Comparing with the films synthesized by the sol-gel method and those made from the slurries of P-25 powder, the film prepared by the modified sol-gel method exhibit higher photocatalytic activity. The reasonable performance and sufficient stability of the TiO₂ nanoparticles on alumina foam leads to consider it as an effective and environmental friendly photocatalyst in the degradation of colored wastewater.

Index Terms—Alumina foam, Degradation of Acid Red 73, Immobilized titania nanoparticles, Modified sol-gel method.

I. INTRODUCTION

TiO₂ has been extensively used in the photocatalytic processes due to the chemical stability, non-toxic nature and low cost [1], [2]. However, investigations in this field are frequently performed with the suspension of fine powdered TiO₂ which limits the application of such catalysts in large-scale of wastewater treatment [3]. Therefore, the immobilization of TiO₂ nanoparticles on an appropriate support has been widely accepted since it could help to eliminate the costly phase separation processes and to promote the practicality of such catalysts as an industrial process. Recently, the photocatalytic activity of immobilized TiO₂ particles on macroporous ceramic alumina foams has been reported [4]. It was found that reticulated macroporous ceramic foam with an open three-dimensional structure and low flow resistance improving the light penetration and fluid flow is highly promising support for photocatalytic applications and water purification systems. However, Vargová *et.al* have recently reported that the TiO₂ films on such support prepared by the sol-gel method exhibit lower photocatalytic activity compared to the layers made of suspension containing commercial titania nanopowders [5]. This result limits the use of the derived sol-gel coatings on

alumina foam in water purification applications. Since the preparation of TiO₂ films using the sol-gel technology can lead to the formation of coatings with controlled morphology, high purity and durability [6], the current study has provided an effort for the enhancement of the performance of the derived sol-gel films on alumina foam. Some investigators have reported that incorporation commercial TiO₂ powder into the sol-gel precursor solution (i.e., defined as a P-25 powder-modified sol-gel method) can result in thicker films with improved photocatalytic activity as compared to those prepared by means of the unmodified sol-gel method [7], [8]. Therefore, in this study, for the first time, we immobilized TiO₂ film onto alumina foam via P-25 powder-modified sol-gel method to improve the structural properties and photocatalytic performance of the as-prepared film. In addition, the photocatalytic activity of the as-prepared films for degradation of Acid Red 73 was compared to the derived sol-gel TiO₂ films and those prepared using slurries of P-25 nanopowders.

II. EXPERIMENTAL

A. Synthesis of TiO₂ Nanoparticles and Immobilization on Alumina Foam

TiO₂ nanocrystals were prepared by the P-25 modified sol-gel method as follow: a solution of titanium tetraisopropoxide (TTIP, Ti(O-i-C₃H₇)₄, purity 98%, Merck) with a concentration of 0.3 M in anhydrous ethanol (98%, EtOH) was prepared and stirred at room temperature for 30 min. Then, a mixture of deionized water and dilute nitric acid was added dropwise to the above solution to adjust the pH<2. After stirring for 1 h, P-25 powder with a loading of 40 g/L was ultrasonically dispersed in the sol. The obtained white dispersion was then aged for 12 h followed by gelation at room temperature. The titania coating was carried out by dipping the alumina foam (10 PPI, 95mm×45mm×10mm, purchased from M.S.A company) into the TiO₂-powder modified sol for 10 min followed by a drying procedure at 80 °C for 10 min. The coating process was performed three-times. Subsequently, the coated samples were calcinated at 600 °C for 1 h with a heating and cooling rate of 1 °C/min. For comparison, the similar coating process was also carried out using slurries of P-25 nanopowders (40 g/L) and titania precipitated by unmodified sol-gel.

B. Characterization

The XRD patterns of the prepared titania nanoparticles and the coated samples were obtained using PHILIPS PW1800 analyzer with a Cu Ka X-ray source. The rutile content in samples can be calculated by following equation as used in

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our previous work [9]:

$$X_R = \frac{(I_R/I_A)0.79}{1+(I_R/I_A)0.79} \quad (1)$$

The main grain size (L) can also be determined according to the Scherrer's formula [10]:

$$L = \frac{0.89\lambda}{\beta \cos \theta} \quad (2)$$

Scanning Electron Microscopy (EM 3200) images of the coated samples were obtained after Au coating by a sputtering method. The specific surface area of samples was determined by the BET method, in which the N₂ adsorption at 77K using the device utilized for the measurement of specific surface area of TiO₂ nanoparticles (ASAP 2000, Micromeritics, USA).

C. Photocatalytic Activity Measurement

The photocatalytic activities of the samples were assessed by the photodegradation of Acid Red 73 as the model compound. Experiments were carried out in a batch-mode rectangular reactor made of Pyrex glass with total volume of 1 L. Four UV-A lamps (9W, Philips), positioned parallel to each other in the box, provided the artificial irradiation. The scheme of the employed photocatalytic reactor has been presented in our previous work [11]. The irradiation intensity of lamps measured by a UV radiometer (UVA 365 Lutron) was approximately 1.8 mW/cm². Two air pumps with a 1 L/min flow rate were used to bubble the dye solution. The reactor was cooled by a fan placed at the box. Before each experiment, the aqueous solution of acid dye was agitated with gentle air in the presence of TiO₂ sample in the darkness for at least 30 min to achieve the complete equilibrium of adsorption process. Photocatalytic degradation processes were performed at 298 K with 250 mL of solution and an initial Acid Red 73 concentration of 20 mg/L. At regular time intervals, samples were taken out and then analyzed by an Optizen 3220UV Double Beam spectrophotometer. Before the measurement of residual dye concentration, each sample was filtered (pore size < 0.22 μm) to remove any possible TiO₂ particles present in the solution. The maximum wavelength (λ_{max}) of Acid Red 73 is 545 nm.

III. RESULTS AND DISCUSSION

The XRD patterns of plain TiO₂ powder prepared by PPMSG method and immobilized titania nanoparticles on alumina foams are shown in Fig. 1. Despite the peak observed at 2θ = 66.5°, which is ascribed to alumina, almost no significant change in the crystal structure of the as-prepared samples can be noted due to immobilization process.

Furthermore, the size of the crystallites calculated using Scherrer's equation and the anatase content of the samples have been summarized in Table I.

The results show that the size of anatase crystallites of the as-prepared products, which was served as a measure of TiO₂

crystallinity, is practically the same and no significant variation of crystal size is observed due to the presence of P-25 powder and the immobilization process.

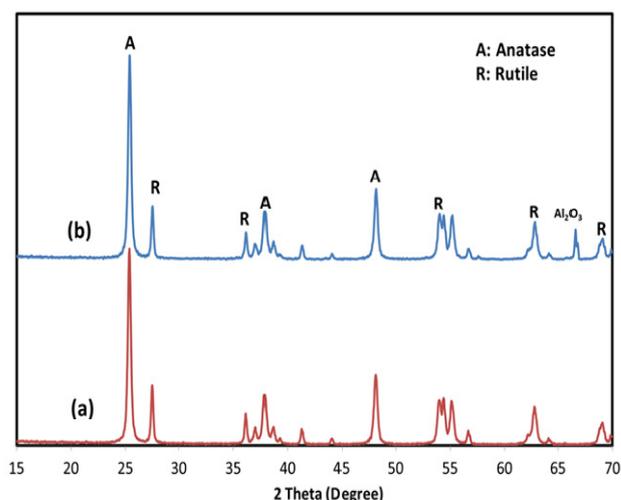


Fig. 1. XRD patterns of TiO₂ powders (a) Immobilized titania nanoparticles coated on the alumina (b)

However, by inspection of Table I, it is noticed that the incorporation of P-25 powder into film promotes formation of the rutile component in the crystal structure, which can influence the photocatalytic activity of catalyst.

TABLE I: PHYSICAL PROPERTIES OF TiO₂ POWDER AND FILMS OBTAINED FROM MODIFIED SOL-GEL METHOD AND THE TYPICAL SOL-GEL METHOD

Method	Crystal size (nm)	Anatase content (%)
Powders prepared by PPMSG method	43.06	78
Film prepared by PPMSG method	46.3	82
Film prepared by sol-gel method	39.2	91

SEM photographs of the TiO₂ films prepared by modified sol-gel and plain sol-gel (without P-25 in the sol) are shown in Fig. 2. SEM micrograph of alumina foam coated with modified titania films indicates the presence of microcracks in the film. The formation of microcrack can be attributed to the P-25 powder incorporated into the sol. Since P-25 powder has relatively large density and low porosity, its loading in the sol during the synthesis procedure lead to the formation TiO₂ gels with the decreased permeability. As reported by literature, the decreased permeability of the gels prepared with the PPMSG method is one of the important factors that results in the formation of microcrack in the films [7]. It is believed that the presence of microcracks in the film is beneficial to the exposure of titania nanoparticles within the inner layers to the solution and can improve the photocatalytic efficiency of the as-prepared films.

The surface area of the alumina foams before and after coating with the film made by modified sol-gel technique exhibit the values of 0.2 and 7.26 m²/g, respectively. These values indicate that good photocatalytic efficiency can be expected from the coated samples.

Since for the large application, the durability of the film is a very important parameter, the stability of TiO₂ film immobilized on the alumina foam was investigated for three types of film prepared by three different methods: 1)

suspension of commercial TiO₂ (P-25) 2) sol synthesized by a typical sol-gel procedure 3) TiO₂ sol made by PPMSG method. In order to provide slurry of P-25 powder in the first method, a solution of P-25 powder with concentration of 40 g/L was prepared. After the coating procedure, the calcination process was carried out at 600°C for 1 h with a heating and cooling rate of 1 °C/min. The preparation procedure in detail has been reported in our previous works [9], [11]. It is clear that sol synthesized in unmodified sol-gel was made without adding P-25. The initial dye concentration and volume of solution used in this experiment were 20 mg/L and 250 mL, respectively. TiO₂ films were immobilized on the substrate with three time of coating using each TiO₂ solution obtained as the above and the change of TiO₂ weight immobilized on the alumina foam was investigated after 2 h in the reactor under UV irradiation, where the stability was studied as the difference of TiO₂ weight immobilized on the foams before and after the photodegradation process, as suggested by literature [12].

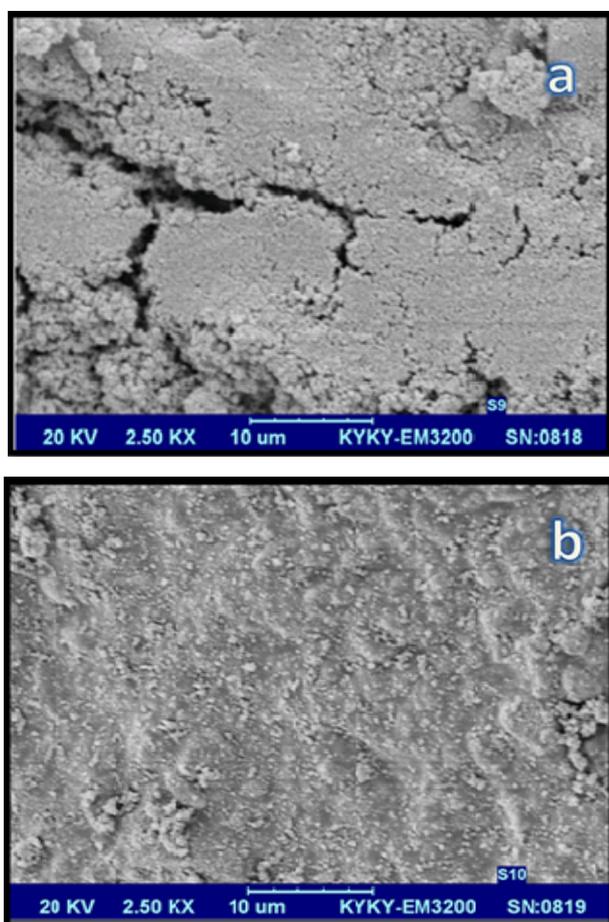


Fig. 2. SEM images of the surface of TiO₂ films made from the precursor sol with P-25 powder (a) without P-25 powder (b)

As shown in Fig. 3, TiO₂ nanoparticles synthesized by PPMSG method and immobilized on the alumina foam exhibit best stability among three types, where 88 wt.% of the initial weight remained. It indicates the bond force between the TiO₂ particles and alumina surface was high, even TiO₂ film was cracked. This result shows good adhesion of film prepared in the modified sol to the support and demonstrates good stability and durability of films obtained from modified sol-gel for applications in water treatment.

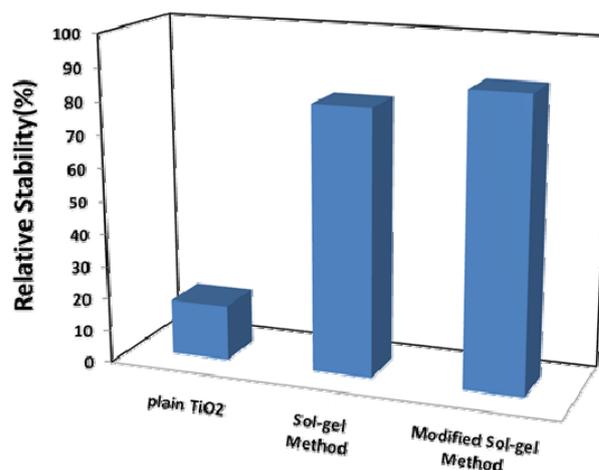


Fig. 3. Stability of film immobilized on the alumina foam for three methods: P-25, sol-gel method, and modified sol-gel method

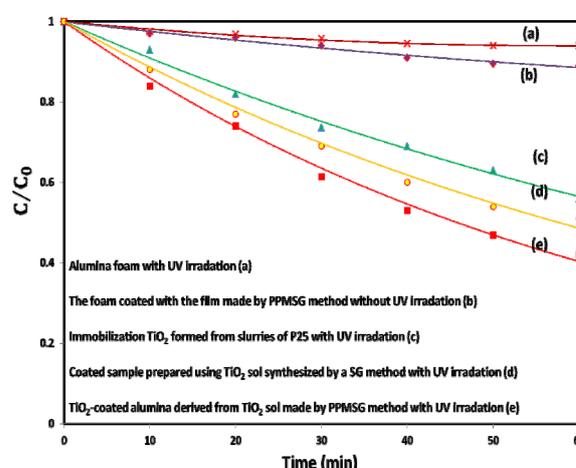


Fig. 4. Effect of photocatalyst on the degradation of Acid Red 73

To evaluate the photocatalytic activity of the immobilized TiO₂ particles on alumina foams, five decolorization processes were compared for Acid Red 73 (dye: 20 mg/L, pH: 6 and H₂O₂: 0.55 mg/L): alumina foam with UV irradiation (a), the foam coated with the film made by modified sol-gel technique without UV irradiation (b) immobilized TiO₂ formed from slurries of commercial TiO₂ (P-25) with UV irradiation (c) coated sample prepared using TiO₂ sol synthesized by a typical sol-gel procedure with UV irradiation (d) and TiO₂-coated alumina derived from TiO₂ sol made by PPMSG method with UV irradiation (e). It is pointed that for the preparation of the film in process (e), a slurry of P-25 powder (40 g/L) was prepared and then the alumina foam was dipped into the as-prepared slurry for coating the film on the foam. However, after the coating procedure, the calcination process was carried out as earlier implied. Experimental results show that the adsorption of Acid Red 73 on reticulated alumina foam becomes saturated after 60 min under UV light radiation, since the dye concentration does not change further with prolonged UV. This indicates that alumina foam does not possess any photocatalytic activity (curve (a) in Fig. 4) and the insignificant variation of dye concentration in this period can be attributed to the presence of UV-H₂O₂. The ceramic alumina foams coated with the film prepared by PPMSG procedure show a higher catalytic activity in the absence of

UV radiation, since the saturated adsorption capacity is higher in comparison with the uncoated alumina foams (curve (b) in Fig. 4). The deposition of TiO₂ nanoparticles on the foam may lead to the affinity of the alumina for acid dye. It can be also attributed to the increased surface area of the support after coating. By comparison of the acid dye removal with and without UV radiation (curves (b), (c), (d) and (e) in Fig. 4), it can be concluded that photocatalytic degradation is predominant in the disappearance of Acid Red 73 and the adsorption is insignificant.

In according to the data shown in Fig. 4 (curves (d) and (e)), the photocatalytic activity of films formed from sols containing P-25 powder is higher than that of films made by typical sol-gel technique. The microcracks formation in the films prepared from modified sol-gel can be responsible for the higher catalytic activity of the alumina coated with the as-prepared films. The presence of microcracks may have a positive effect on the photocatalytic performance of the film regarding to UV light penetration and availability of organic contaminates to TiO₂ particles which may be in the inner layers. In addition, the presence of P-25 powder in the resultant catalyst can increase the interface area between the TiO₂ catalyst and liquid and consequently improve the photocatalytic efficiency. Moreover, the films formed from the sol prepared via the modified sol-gel technique show higher activity than that made from the suspension of commercial TiO₂ (P-25), as shown in Fig. 4 (curves (c) and (e)). It is assumed that this difference can be caused by the difference in adhesion of TiO₂ film immobilized on the alumina foam. As results shown, better stability and durability is offered by the films obtained from the sol synthesized by the modified sol-gel method compared to that prepared by the slurries of P-25 powders.

IV. CONCLUSION

TiO₂ nanoparticles synthesized by the P-25 modified sol-gel method were immobilized on the alumina foam as support and their structural properties were characterized by XRD, SEM, and BET analysis. The high photocatalytic activity and good stability of the as-prepared films make to consider it as an alternative for wastewater treatment applications.

REFERENCES

[1] M. N. Chong, B. Jin, C. W. K. Chow, and C. Saint, "Recent developments in photocatalytic water treatment technology: A review," *Water Research*, vol. 44, pp. 2997-3027, May 2010.

[2] T. Ochiai, K. Nakata, T. Murakami, A. Fujishima, Y. Yao, D. A. Tryk, and Y. Kubota, "Development of solar-driven electrochemical and photocatalytic water treatment system using a boron-doped diamond electrode and TiO₂ photocatalyst," *Water Research*, vol. 44, pp. 904-910, February 2010.

[3] A. Y. Shan, T. I. M. Ghazi, and S. A. Rashid, "Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: A review," *Applied Catalysis A: General*, vol. 389, pp. 1-8, December 2010.

[4] G. Plesch, M. Gorbár, U. F. Vogt, K. Jesenák, and M. Vargová, "Reticulated macroporous ceramic foam supported TiO₂ for photocatalytic applications," *Materials Letters*, vol. 63, pp. 461-463, February 2009.

[5] M. Vargová, G. Plesch, U. F. Vogt, M. Zahoran, M. Gorbár, and K. Jesenák, "TiO₂ thick films supported on reticulated macroporous Al₂O₃ foams and their photoactivity in phenol mineralization," *Applied Surface Science*, vol. 257, pp. 4678-4684, March 2011.

[6] U. G. Akpan and B. H. Hameed, "The advancements in sol-gel method of doped-TiO₂ photocatalysts," *Applied Catalysis A: General*, vol. 375, pp. 1-11, February 2010.

[7] G. Balasubramanian, D. D. Dionysiou, M. T. Suidan, V. Subramanian, I. Baudin, and J. M. Lainé, "Titania powder modified sol-gel process for photocatalytic applications," *Journal of Materials Science*, vol. 38, pp. 823-831, February 2003.

[8] Y. Chen and D. D. Dionysiou, "TiO₂ photocatalytic films on stainless steel: The role of Degussa P-25 in modified sol-gel methods," *Applied Catalysis B: Environmental*, vol. 62, pp. 255-264, February 2006.

[9] M. Vaez, A. Z. Moghaddam, N. M. Mahmoodi, and S. Alijani, "Decolorization and degradation of acid dye with immobilized titania nanoparticles," *Process Safety and Environmental Protection*, vol. 90, pp. 56-64, January 2012.

[10] S. N. Hosseini, S. M. Borghei, M. Vossoughi, and N. Taghavinia, "Immobilization of TiO₂ on perlite granules for photocatalytic degradation of phenol," *Applied Catalysis B: Environmental*, vol. 74, pp. 53-62, June 2007.

[11] M. Vaez, A. Zarringhalam Moghaddam, and S. Alijani, "Optimization and Modeling of Photocatalytic Degradation of Azo Dye Using a Response Surface Methodology (RSM) Based on the Central Composite Design with Immobilized Titania Nanoparticles," *Industrial & Engineering Chemistry Research*, vol. 51, pp. 4199-4207, February 2012.

[12] C. S. Ryu, M.-S. Kim, and B.-W. Kim, "Photodegradation ofalachlor with the TiO₂ film immobilised on the glass tube in aqueous solution," *Chemosphere*, vol. 53, pp. 765-771, November 2003.



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