

Photocatalytic activity in solid-solid interface

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Abstract- The present work investigates the photocatalytic activity of sol-gel derived TiO₂ thin films for methyl stearate (MS- as a fatty compound layer) oxidation. The prepared TiO₂ thin films were characterized by X-ray diffraction (XRD) and UV-vis transmittance spectra, while the photocatalytic activities of the TiO₂ thin films were evaluated in the oxidation of MS- as a fatty compound layer with the help of Contact Angle meter. The XRD results revealed that the sol-gel derived TiO₂ thin films were contained anatase phase only with small grain size in the range of 12 -15 nm. The activity of prepared TiO₂ thin films appreciably higher than those of a reference commercial Pilkington® Activ™ Glass (PAG) used in this studies. The results also indicates that the if concentration of methyl stearate increases, the photocatalytic oxidation of methyl stearate on TiO₂ thin films were decreases, it is due to blocking of light by thick layer of methyl stearate.

Keywords- Titanium dioxide, Thin film, Photocatalytic oxidation, Methyl stearate.

1. Introduction:

Titanium dioxide (TiO₂) has been largely employed as a photocatalyst (in thin film or powder form) in advanced oxidative processes (AOPs) due to its favourable environmental and economic properties (low toxicity, relatively high photocatalytic efficiency and low cost). Recent studies have revealed that the pure forms of the most common polymorphs of TiO₂ (anatase and rutile) exhibit lower photocatalytic activity than their mixtures. A mixture of approximately 80% anatase and 20% rutile has presented the best photoactivity in comparison with other fractions [1-3]. The TiO₂ is known as wide energy gap

materials. The absorption of radiation energy of certain wavelengths by a semiconductor (semiconductor excitation process) promotes electron transfer from the VB to the CB, leaving vacancies in the VB called holes. The photogenerated electron/hole (e⁻/h⁺) pair promotes the reduction and oxidation of species adsorbed at the surface of the photocatalyst materials and induces oxidative degradation of species in the present medium through radical reactions [4]. TiO₂ is widely employed in field of pollution, e.g wastewater treatment (solid-liquid interface), Reduction of gases pollution (solid-gas interface) and Reduction of solid layer (solid-solid interface), although TiO₂ has some shortcomings such as a wide energy gap (approximately 3.2 eV) and high number of e⁻/h⁺ pair recombination events [5-7].

In the present work, photocatalytic activities was examined by monitoring the water contact angle (CA) values upon UV irradiation for that the degradation of a methyl stearate layer, was chosen to study the sample activity, since it provides a reasonable model for a characteristic fatty contamination of exterior glass surfaces, such as house or office windows [8-11]. To this aim, a commercial Pilkington® Activ™ Glass was used as a reference standard self-cleaning material [9], since it is the ideal benchmark for photocatalyst films, as in the case of Degussa P25 used as a standard for powdered materials.

2. Experimental methods:

Titania sols were made from a modified, Ti(OiPr)₄ was added to HCl (n(HCl)/n(Ti(OiPr)₄) = 3.84) at room temperature under vigorous stirring. After 5 min, the prepared solution was dissolved in a solution of absolute ethanol (n(EtOH)/n(Ti(OiPr)₄) = 15.37) and the resulting solution was subsequently aged at room temperature for 30 min under stirring to get a transparent titania sol. The surfactant weight percentages are given with

respect to the total weight of solution reported in previous work [12]. The films were dip-coated onto SiO₂ pre-coated glass slides (25 mm × 70 mm × 2 mm) at a withdrawal rate of 10 cm/min. The all films were aged at room temperature for 10 min and calcined at 500 °C for 30 min to remove the organic species and induce crystallization of TiO₂. Silica sol was prepared from a tetraethoxysilane (TEOS, Aldrich) precursor, ethanol (Si/EtOH=0.15), HNO₃ (HNO₃/Si=0.265) and water (H₂O/Si=8.1). After two hours of mixing, the resulting solution was used for silica film deposition by the dip-coating technique with pulling speeds 10 cm/min.

The X-ray diffraction (XRD) patterns were obtained on a PANalytical X'Pert PRO high-resolution diffractometer with an alpha 1 configuration using CuK1 radiation (1.5406Å) in a wide-angle range (2θ) from 20° to 60° with a step angle of 0.033 using a fully opened X'Celerator detector while the UV-Vis transmittance spectra of the films were recorded on a UV-1800 Shimadzu spectrophotometer. The photocatalytic oxidation of methyl stearate on TiO₂ thin films were evaluated by examining the contact angle between the thin films and water droplets. The water contact angles were measured at ambient room temperature, using a CAM 100 FireWire horizontal video camera module with a protractor eyepiece. For this purpose, the Contact Angle Meter (CAM 100), KSV Instrument, Ltd. Finland, was used.

For the determination of the photocatalytic activities, the all glass slide were exposed with the above UV light source (125W medium pressure UV lamp, Intensity= 1.320x10⁻³ W/cm² determined by International light IL-1700 research radiometer with a UV detector SED-005 range 200 - 400 nm) in order to start from a “clean” hydrophilic surface and subsequently dip-coated with a solution of 0.1M methyl stearate in n-hexane (withdrawal speed=10 cm min⁻¹).

3. Results and discussion:

3.1 UV-Vis transmittance spectra:

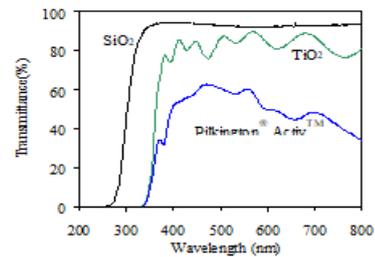


Fig. 1 UV-Vis transmittance spectra of SiO₂ film on glass slide, TiO₂ films on SiO₂ coated on glass slide by dip-coating technique and Pilkington® Activ™ Glass.

Fig.1. Shows the UV-vis transmittance spectra of the SiO₂ film prepared on glass slide, TiO₂ film prepared on SiO₂ precoated glass slide and reference commercial Pilkington® Activ™ Glass used in this study. Fig.1. also depicts that the absorption of light in the UV-vis range for reference commercial Pilkington® Activ™ Glass more than TiO₂ and SiO₂ film, further after 650 nm wavelength it gradually fall down. However SiO₂ film clearly showing more than 90% transmittance above 280 nm wavelength. It is interesting that up to 350 nm wavelength, the absorption of light for TiO₂ film and Pilkington® Activ™ Glass same. After 380 nm to 800 nm wavelength the TiO₂ film showed averagely 85 % transmittance. Nevertheless in case of reference commercial Pilkington® Activ™ Glass averagely only 45 % transmittance showed from range 380 nm to 800 nm wavelength. This results indicating prepared TiO₂ film good transmittance in visible region and can become the good candidate for UV light absorption and photocatalytic self cleaning coating.

3.2 X-ray diffraction (XRD) pattern:

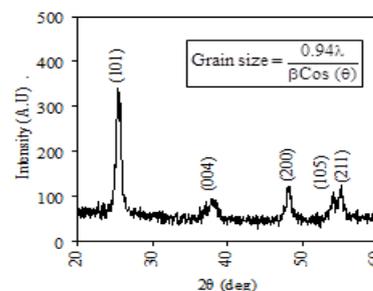


Fig. 2 X-ray diffraction pattern of TiO₂ film prepared on Si wafer by dip-coating technique.

Fig. 2 depicts XRD patterns of sol-gel derived TiO₂ film on Si wafer calcined at 500 °C for 30 min. Evidently, all the reflections belong to anatase phase (peaks appeared at $2\theta = 25.4^\circ, 38.1^\circ, 48^\circ, 54.1^\circ$ and 55.2° correspond to (101), (004), (200), (105) and (211) reflections, respectively) and no additional reflections belonging to rutile or brookite phases are observed. The average crystallite size was determined from the Scherrer's equation using the broadening of the (101) anatase peak and it is found in the range of 12 to 15 nm wavelength.

3.3 Photocatalytic oxidation:

Fig.3 (a,b) showed the photocatalytic oxidation of methyl stearate was investigated by water contact angle measurement during UV irradiation, immediately after application of the fatty compound layer on films.

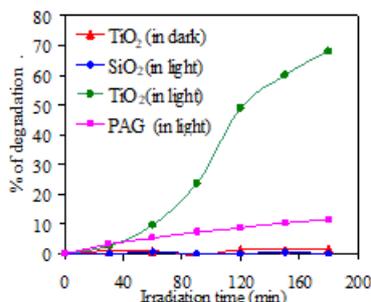


Fig.3(a) Photocatalytic activity of TiO₂ films with comparison of Pilkington® Activ™ Glass: % of degradation of methyl stearate as a function of irradiation time.



Fig.3(b) Photocatalytic activity of TiO₂ films with comparison of Pilkington® Activ™ Glass: Water contact angle as a function of irradiation time

In Fig. 3(a), both films, SiO₂ in UV light and TiO₂ in dark revealed that the methyl stearate is stable within 3 h and there is no oxidation of methyl stearate found. As can be noticed in Fig. 3(a), for an initial induction time was required before the methyl stearate oxidation took place (TiO₂ in light). This “incubation” period may be tentatively attributed to the lack of oxygen electron acceptor species in contact with TiO₂ film in light at the beginning of the experiment and, in

particular, to the relatively slow diffusion of oxygen species, whose presence is crucial role for the photocatalytic oxidation process, through the organic coating towards the surface of TiO₂ film. Nevertheless, it is interesting to observe that in Fig. 3(b) upon UV irradiation the water contact angle values for TiO₂ film sample undergo a considerably dropdown (from ~93° to ~30°) than those of the reference Pilkington® Activ™ Glass (from ~95° to ~84°) photocatalytic self cleaning active. In particular, after 3 h irradiation, while the Pilkington® Activ™ Glass presents a contact angle of ~84°, TiO₂ film shows a ~29°. Such a result indicates that the oxidation of methyl stearate over TiO₂ film considerably faster than reference Pilkington® Activ™ Glass.

4 Conclusions:

The present work was dedicated to the study of photocatalytic activity of TiO₂ film with comparison Pilkington® Activ™ Glass. In particular, the photocatalytic oxidation of a standard fatty compound, methyl stearate, was followed in an inexpensive and simple way by measuring its photocatalytic oxidation and water CA values as a function of UV irradiation time. The present results illustrated a significant photocatalytic activity of the derived TiO₂ film, which resulted considerably higher than that of a reference Pilkington® Activ™ Glass. The high transparency, photocatalytic activity, good adhesion with the substrate displayed by anatase TiO₂ film make it a good candidate to be considered in new emerging engineering applications.

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