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Comparison of the Photocatalytic activity of TiO₂ with the TiO₂:SiO₂ thin film

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Abstract

Nanocrystalline films of TiO₂ and TiO₂:SiO₂ with high photocatalytic activity was prepared on glass substrate via the sol-gel method. The films were subjected to high temperature treatment at 500°C for growing TiO₂ crystals. Energy Dispersive X-ray Spectroscopy (EDS) was used to indicate the elements in the films. The EDS result showed that besides Ti, O and Si elements, there were small amounts of Ca, Na and Mg presented in the film that were diffused from the glass substrate. X-ray diffraction (XRD) analysis indicated that TiO₂:SiO₂ films contain only anatase phase. Scanning electron microscopy (SEM) was used to study the films surface morphology. The TiO₂:SiO₂ films that were contacted with methyl orange (MO) in the aqueous solution (10 mg.L⁻¹) and irradiated with UV showed a high photocatalytic activity. UV spectrophotometry technique was used to monitor the degradation of methyl orange (MO) by the reduction of main absorbance peak at 464 nm. The results showed that complete degradation was achieved after 1.5 hr.

Keywords: Sol-gel; Dip coating; TiO₂; SiO₂; Doping; Photocatalytic activity

1. Introduction

Photocatalysis is the result of interaction of electrons and holes generated in an activated solid (semiconductor) with its surrounding medium (electrolyte) [1-3]. Recently, the application has



been focused on purification and treatment of water and air, which are concerned in the protection of environment, such as nature and life space [4, 5]. Utilization of conventional powder catalysts results in disadvantages of employing stirring during the reaction and separation after the reaction, but coating the material as a thin film on the substrate can solve these problems [4, 5]. Activation is the consequence of light absorption; therefore, electron-hole pairs are formed in the semiconductor that may recombine or participate in reductive and oxidative reactions [1]. Various metal oxide semiconductors such as: TiO₂, ZnO, MoO₃, CeO₂, ZrO₂, WO₃, α -Fe₂O₃, and SnO₂ are used as catalysts in the photocatalytic reactions [1, 6]. Mechanical stability, non-toxicity and high photoactivity of TiO₂ are reasons for favorability of this material as a photocatalyst [1]. TiO₂ has been prepared by several techniques such as chemical vapor deposition (CVD), physical vapor deposition (PVD), and magnetron sputtering. But, these techniques are complex and control of conditions is very difficult. The sol-gel method is easier to use and more economic in comparison with the other techniques [1]. In the present study, nanocrystalline thin film of TiO₂:SiO₂ was prepared by the sol-gel method. The sol-gel process is a wet chemical technique based on the hydrolysis/polycondensation of metal precursors, which leads to a variety of oxide materials. The thin films were prepared and their photocatalytic activities were then measured by the degradation of methyl orange (MO). Also, the effect of SiO₂ addition to the matrix of TiO₂ on its photocatalytic activity was investigated.

2. Experimental

2.1. TiO₂:SiO₂ film preparation

For the preparation of the target solution, Tetraisopropoxy titanium (TTIP), tetraethyl orthosilicate (TEOS), ethanol, hydrochloric acid, and acetylacetonone (ACAC) were commercially obtained and used without further purification [1-4]. The starting solution for sol-gel film preparation was obtained by adding ACAC and water in ethanol, followed by dropping in required amount of TTIP, TEOS and hydrochloric acid under stirring [1-3]. The volume fractions of TTIP, TEOS, ethanol, hydrochloric acid, ACAC, and water in the prepared solution are 8.8:1:143:0.5:2:1 [1, 2]. At last, the sols were aged in a sealed beaker for 24 h [1].

TiO₂:SiO₂ thin films were prepared by dipping the glass slides in the aged solutions at a drawing speed of 70 cm min⁻¹. These films were dried at room temperature for 15 min, followed by calcinations at 500 °C for 4 h and finally cooled in the oven to room temperature. The double- and multi-layer films are obtained by repeating the above procedures properly.

2.2. Film characterization

Grain size and crystallinity of the TiO₂ films was studied by X-ray diffraction using Cu K α ($\lambda=1.5406$ Å) radiation in the region of $2\theta=20^{\circ}-75^{\circ}$. In addition, the grain or crystalline size (L) was estimated by Scherrer's formula [1, 7] as:

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where L is the crystallite size of pure TiO₂, k is a constant (=0.94), λ is the wavelength of X-ray (CuK α = 1.54065 Å), β is the true half-peak width, and θ is the half diffraction angle of the centroid of the peak in degree.



The surface morphology of the films was studied using a Scanning Electron Microscope (SEM, Leo 1450 VP, Zeies, Germany). Energy Dispersive X-ray Spectroscopy (EDS, 7353, Axford, England) was used for elements analysis.

2.3. Photocatalytic activity measurement

Methyl orange (MO) powder ($C_{14}H_{14}N_3NaO_3S$) dissolved in distilled water at 10 mg.L^{-1} concentration. The TiO_2 film ($2 \text{ mm} \times 2 \text{ mm}$) was settled in 5 mL MO solution and a high pressure mercury lamp (125 W) was used as a light source. One face of TiO_2 thin film was irradiated with UV lamp. The averaged intensity of UV irradiance was 6.8 mW.cm^{-2} by measuring with a UV irradiance meter. The solution was bubbled with air during irradiation. The photocatalytic decolorization of MO is a pseudo-first order reaction and its kinetic may be expressed as follows [5, 9]:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (2)$$

Where k is constant rate of reaction, C_0 and C are initial and final concentration of methyl orange. The photocatalytic reaction involves the presence of oxygen and moisture on the photocatalyst surface to activate the photoreaction during light irradiation. From the fundamental photocatalytic kinetics, the reaction equation can be expressed as [9-11]:



Where *ads* represented the adsorbed state of species on the TiO_2 surface. The mechanism of the photocatalytic reaction can be described as the TiO_2 photocatalyst at first absorbed the light to generate free electron-hole pairs on the TiO_2 surface. The electrons reacted with oxygen to generate superoxide ion (O_2^-); while the holes redox with H_2O to produce OH radicals [9, 10].

3. Results and discussion

3.1. Characterization of the film

Fig. 1 shows the EDS pattern of TiO_2 and $TiO_2:SiO_2$ films. EDS results indicated the main peaks of Ti, Si and also small amounts of Na, Ca, Mg elements diffused from the substrate. Diffusing Si element from the glass substrate is the reason for vigorous Si peak. Moreover, the presence of SiO_2 in the thin film can destroy the linkage of Ti-O-Ti and change it to Ti-O-Si. This can shift the binding energy of Si to higher value [7].

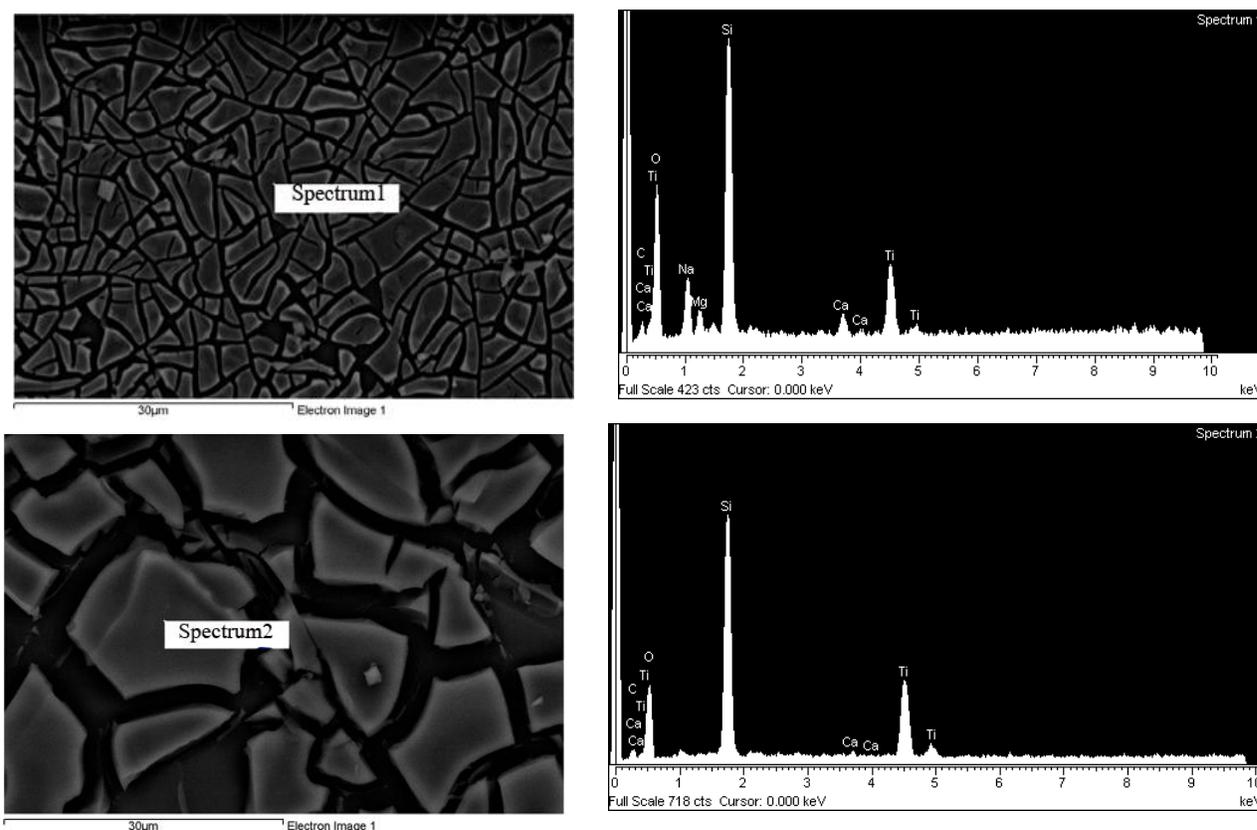


Fig. 1. EDS analyses of the films: Spectrum 1 = TiO_2 , Spectrum 2 = $\text{TiO}_2:\text{SiO}_2$

Fig. 2 shows XRD patterns of thin film at 500°C . The crystalline size of TiO_2 can be deduced from XRD line broadening using the Scherrer equation [1, 7]. Accordingly, the average grain size of TiO_2 , $\text{TiO}_2\text{-SiO}_2$ is 33 and 10 nm, respectively. The results indicate that high content of SiO_2 restrain the crystallization of TiO_2 and effectively suppress the phase transformation of TiO_2 from anatase to rutile. This strong retarding has been often ascribed to a good chemical homogeneity of the starting gels, i.e., to a high degree of Si–O–Ti bonding, which is believed to be reason of restricting the growth of grains during heat treatment [7, 11-15].

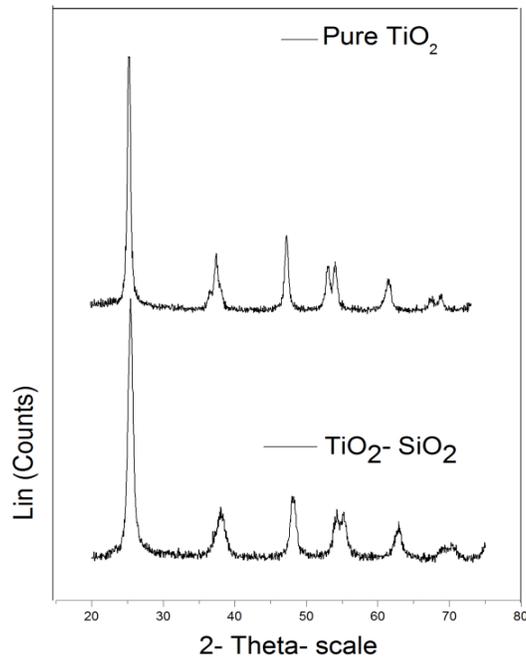
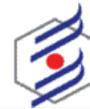


Fig. 2. XRD patterns of the obtained films with different SiO₂ content at 500 °C for 4 h.

3.2. Surface morphology of TiO₂ and TiO₂:SiO₂ films

The surface morphology of films can be observed in Fig. 3 which shows SEM micrographs of 10 layers of TiO₂ and TiO₂:SiO₂ films. The films produced by this technique indicate fractured morphology. During the drying and annealing processes of the films, crack formation takes place as a result of contraction, stress and different thermal coefficients of expansion of the overlayer and substrate. The fractured surface morphology of the films produced by this technique resulted in a large surface area that would suggest a higher photocatalytic activity. In fact, higher photocatalytic activity with smaller crystalline size of TiO₂ was observed [16].

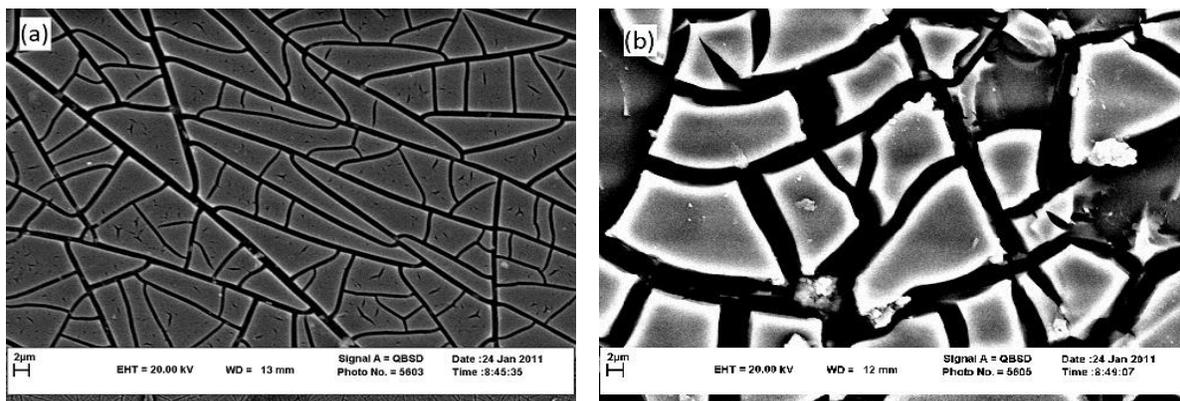




Fig. 3. SEM images of films: (a) TiO_2 , (b) $\text{TiO}_2:\text{SiO}_2$

3.3. Determination of photocatalytic activity of $\text{TiO}_2:\text{SiO}_2$ films

The photocatalytic activity of the $\text{TiO}_2:\text{SiO}_2$ films was investigated from the degradation of 5 mL of $10 \text{ mg}\cdot\text{L}^{-1}$ MO solution under UV irradiation. Fig. 4 shows degradation of MO solution in contact with $\text{TiO}_2:\text{SiO}_2$ films under UV irradiation. Fig. 5 also shows change of concentration of MO during irradiation time. A comparison of the photocatalytic activity of the films gives the following order: $\text{TiO}_2:\text{SiO}_2 > \text{TiO}_2$. The lowest degradation rate is shown by pure TiO_2 and that is because of lower surface area with higher crystalline size. When mole percent of SiO_2 is very high, crystals of TiO_2 cannot grow and photocatalytic activity is very low.

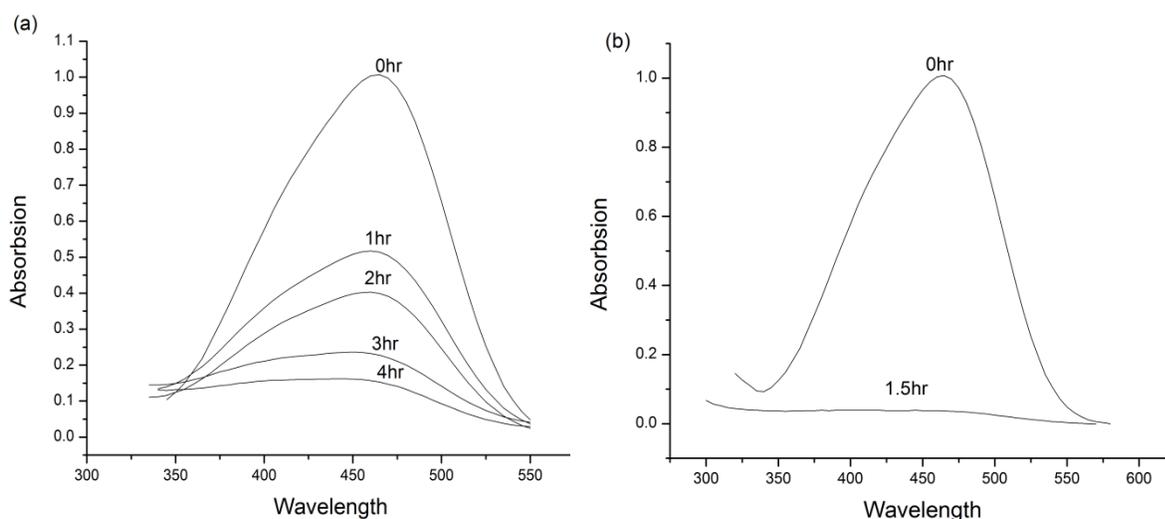


Fig. 4. Degradation of MO in contact with: (a) Pure TiO_2 (b) $\text{TiO}_2:\text{SiO}_2$

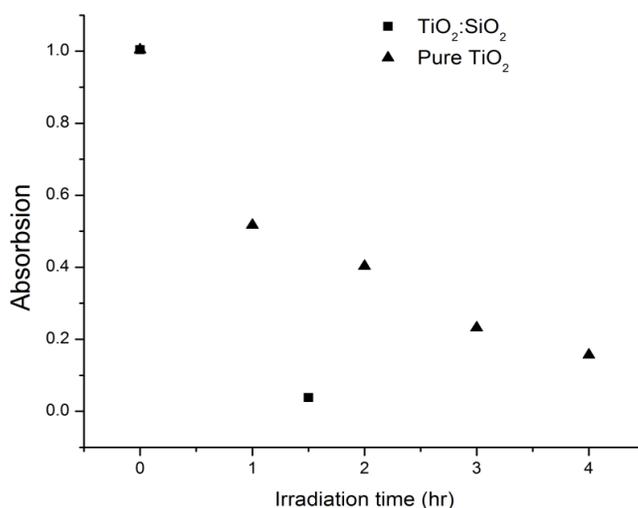


Fig. 5. Concentration of MO in contact with TiO_2 , $\text{TiO}_2:\text{SiO}_2$ films during the time



The photocatalytic activity of TiO₂ and TiO₂:SiO₂ film and powder precipitant is primarily attributed to the surface area of the catalyst. In the case of TiO₂ film, the surface area depends on TiO₂ particle size and substrate. This could be explained by the formation of film with higher total surface area as a result of fractured surface morphology and exposed sublayers as discussed in the SEM analysis (Figure 3). On the other hand, higher photocatalytic activity was observed by the films that produced by smaller TiO₂ crystals.

4. Conclusions

TiO₂ and TiO₂:SiO₂ films with high photocatalytic activity were prepared on glass substrate with the sol-gel method using TiO₂ solution from TTIP with different mole percent of SiO₂ where the TEOS was source of SiO₂. XRD patterns indicate that with higher mole percent of SiO₂, the TiO₂ grain size becomes smaller, therefore TiO₂ crystallines have more active surface area and this can enhance the photocatalytic activity of TiO₂. The SEM image illustrated the fractured morphology and sublayers exposed by micro-fractures in the final layer which contribute to larger total surface area and consequently greater photocatalytic activity.

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