Influence of catalyst on structural and morphological properties of TiO₂ nanostructured films prepared by sol–gel on glass

Mehdi Alzamani, Ali Shokuhfar, Ebrahim Eghdam, Sadegh Mastali

Mechanical Department, Advanced Materials and Nanotechnology Research Lab, K.N. Toosi University of Technology, Tehran, Iran
Faculty of Metallurgical and Materials Engineering, Semnan University, Semnan, Iran

Received 22 August 2012; accepted 6 October 2012
Available online 28 February 2013

Abstract  Transparent TiO₂ thin films have been prepared by the sol-gel method using titanium alkoxides as precursors. Thin films were deposited on glass supports by the dip-coating technique. The TiO₂ layer acts as a self-cleaning coating generated from its photocatalysis and photoinduced superhydrophilicity. The crystalline structure of TiO₂ films was dominantly identified as the anatase phase, consisted of uniform spherical particles of about 14–50 nm in size, which strongly depends upon catalyst-type and heat treatment temperature. Increasing heat treating temperature can lead to an increase in crystalline size. The results indicated that the sample S.S (sample derived from sol containing sulfuric acid as catalyst) exhibits superhydrophilic nature and better photocatalytic activity, which can be attributed to its higher anatase content and lower crystalline size. Morphological studies, carried out using Atomic Force Microscopy (AFM), confirm the presence of crystalline phase with such a grain size and low surface roughness. Thus, the applied films exhibiting high photocatalytic activity, superhydrophilic behavior, and low surface roughness can be used as an efficient self-cleaning coating on glass and other optical applications.

1. Introduction

In recent decade, thin TiO₂ photocatalytic films have been intensively studied because of their wide potential application in photocatalysis [1], self-cleaning [2,3], air cleaning [4], wastewater treatment [4,5], etc.; for their high photocatalytic efficiency [6]; wide band gap and chemical and physical stability
under the reaction conditions [7,8]. One promising application is represented by the self-cleaning properties of glasses in automotive industry. TiO$_2$ thin film possesses a unique two-fold task: the first is the photocatalytic function, in which there is a high recombining ratio of photoinduced electron–holes in the film that move to the surface [4] and interact with daylight to breakdown the organic dirt. The second is the hydrophilic function which means that instead of forming droplets, rainwater hits the glass and spreads evenly, running off in a “sheet” and taking the loosened dirt with it, also drying quickly without leaving streaks [9].

The sol–gel technique, among the practical methods, is one of the versatile methods to prepare metal oxide thin films even at low temperatures and has been properly used to make TiO$_2$ films because of appropriate homogeneity, ease of composition control, moderate equipment cost, and good optical properties [10]. The dip-coating method, as a widely adoptive methodology in the production of anti-reflection and self-cleaning films, is a time-saving, low-cost, suitable method for TiO$_2$ films [2,3].

The microstructure and properties of TiO$_2$ films depend upon details of deposition parameters which determine nucleation and growth of the crystal phase [11]. The properties of titania films depend not only on the preparation technique, but also on the deposition conditions. In the sol–gel synthesis, the formation of thin films depends on parameters such as sol reactivity, viscosity, water alkoxide ratio and metal precursor concentration. However tetragonal [6] anatase is known as the metastable form [11]; highest photocatalytic properties of TiO$_2$ thin films are obtained in this form [12]. Thus, conditions must be controlled in a way that offers anatase as the final structure. In addition to temperature, particle size can influence anatase-to-rutile phase transformation [13]. It has been reported that photocatalytic activity increased as the size of the TiO$_2$ particles became smaller than ~10 nm [14].

In this study, several TiO$_2$ thin films were prepared from diverse solutions, which differ due to varying catalyst-type (diethanolamine (DEA) as alkaline catalyst and hydrochloric acid (HCl), nitric acid (HNO$_3$) and sulfuric acid (H$_2$SO$_4$ as acidic catalysts) added to the sol. Then, structural and photocatalysis properties of thin films are discussed.

2. Experimental

2.1. Sample preparation

The XRF analysis of the windshield used as substrate is given in Table 1. TiO$_2$ thin films were deposited on windshields pre-coated with a SiO$_2$ layer (100 mm × 20 mm × 2 mm) by the sol–gel dip-coating technique and synthesized as follows. The procedures for the silica layer preparation and its characteristics are presented in detail elsewhere [15]. Titanium tetraisopropoxide (TTIP, Panreac) was used as a precursor to prepare TiO$_2$ sol. The sol consisted of a molar ratio of 1:25:0.3:1 of TTIP to isopropanol (i-PrOH) to X (X is the used catalysts and can be DEA, HCl, HNO$_3$, and H$_2$SO$_4$ to de-ionized water and was prepared as follows. TTIP was dissolved in 15 M i-PrOH, stirring vigorously at room temperature. After 2 h, a mixture of 10 M i-PrOH, X, and deionized water was added drop wise to the above solution under continuous magnetic agitation in laboratory atmosphere at room temperature. Fig. 1 illustrates schematic flowchart of the procedure used in this study. The two-step heat treatment (drying) can improve the adhesion of film on substrate and release residual stresses through slow solvent evaporation and condensation reactions.

2.2. Characterization of TiO$_2$ films

X-ray diffraction (XRD) was used for crystal phase identification. XRD patterns were obtained with a Bruker D8 Advance diffractometer using Cu-K$_\alpha$ radiation at 40 kV and 30 mA at a scan speed of 0.02 s per step with an increment of 0.02° per step and the crystallite size of TiO$_2$ thin films was estimated from X-ray line broadening analysis by the Scherrer equation. The nanoparticle size and morphology of films were characterized by scanning electron microscopy (SEM; Tescan model Vega-II) and field-emission-scanning electron microscopy (FE-SEM, Hitachi S-4160). Glass chemical composition was determined by X-ray Fluorescence (XRF; ARL model 8410) with ASTM C 982-97 reference standard. The surface morphology and the nano-scale roughness of TiO$_2$ films were studied by means of AFM (Veeco model CP Research).

Finally, the effect of catalyst-type on the hydrophilicity of the TiO$_2$ films was investigated by measuring contact angle of water droplet on the film under an ambient condition at room temperature in dark and 1 and 2 h after UV radiation using an OCA 15-plus (Dataphysics).

2.3. Evaluation of photocatalytic activity

Photocatalytic activity of the TiO$_2$ films was evaluated by investigating degradation of methylene blue (MB) dye, used as a model pollutant. For the photodegradation investigation, the TiO$_2$ films on glass substrates were immersed in an aqueous solution of MB (6.25 × 10$^{-5}$ M), then irradiated with UV light for different time of 15, 30, 45, 60, 90, 120 and 150 min.

Next, degradation of MB was determined by measuring absorbance of MB of each decanted solution using a UV–vis spectrophotometer (CECIL SERIES CE-2040) at a maximum wavelength of $\lambda_{\text{max}}$ = 664 nm, as the strongest MB absorption peak. The kinetics of the degradation of MB dye was described with the Langmuir–Hinshelwood (L–H) kinetic model.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The XRF analysis of glass substrate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>wt%</td>
<td>72.5</td>
</tr>
</tbody>
</table>
3. Result and discussion

3.1. Structural properties

XRD was used to investigate the phase constitutions and average crystalline size of the films derived from various solutions at two diverse heat treatment temperatures of 500 and 700 °C (Fig. 2). Studies indicated that the crystallinity of the films depends on their chemical composition; and the annealing temperature is known to be the most important factor influencing relative proportions of anatase to rutile phase and TiO\textsubscript{2} phase transformation from anatase-to-rutile. Factors such as preferential grain orientation, morphology, nucleation sites, and growth of rutile phase may influence XRD results.

Table 2 represents crystalline phases and their crystalline size identified by XRD measurements for the films derived from sols containing various kinds of catalysts. This table probably proves the nanometric crystalline size for all samples. As the heat treatment temperature increases, the TiO\textsubscript{2} crystallites continue to grow.

From Table 2, the crystallite size of TiO\textsubscript{2} thin films can be deduced from XRD line broadening using the Scherrer equation [16]:

\[ L = \frac{(K\lambda)}{(\beta \cos \theta)} \]  

where \( L \) is the crystallite size of TiO\textsubscript{2} thin films, \( K \) is a constant (=0.94), \( \lambda \) is the wavelength of X-ray (Cu-K\textsubscript{α} = 1.5406 Å), \( \beta \) is full width at half maximum (FWHM) of the peak, and \( \theta \) is the half diffraction angle of the peak in degrees (lattice strain and 10% error possibility in Scherrer’s equation are neglected).

Here, Spurr and Myers’ method [17] has been applied to determine anatase to rutile ratio which utilizes the ratio of (110) peak intensity of rutile phase in the angle (2\( \theta \)) of 27.355° to those of anatase phase in the (101) plane with the angle (2\( \theta \)) of 25.176°. While amorphous phase identification is not practical in this method, anatase and rutile phase’s proportions given in Table 2 are out of the total crystalline phase.

Fig. 2a–d shows the XRD pattern of films derived from different solutions at two different heat treatment temperatures of 500 and 700 °C. It is clear that increasing heat treatment temperature may lead to more rutile phase percent in all samples. The complete phase transition from anatase to rutile was not observed at 500 °C. Suppression of the anatase-to-rutile phase transformation may be due to dissolution of SiO\textsubscript{2} from substrate in anatase TiO\textsubscript{2} or vice-versa and diffusion barrier effect of SiO\textsubscript{2} in the TiO\textsubscript{2}–substrate interface. The films obtained from the solution containing DEA (Fig. 2a) consist of a mixture of anatase and rutile phases at 500 °C, while at 700 °C anatase phase completely transformed to rutile phase. Therefore, it can be concluded that DEA as alkaline catalyst keeps the sol stable and retards oxide precipitation in TTIP hydrolysis, but exhibits poor ability to make anatase stable at a relatively high temperature. So, it can
be supposed that photocatalytic property of TiO₂, due to lower photocatalytic activity for rutile is decreased at 700 °C. Hashimoto et al. [18] reported that rutile peaks appeared at 650 °C when diethanolamine (DEA) was used as a catalyst. Therefore, crystalline phase transition temperature depends on the catalyst used in the sol preparation.

On the other hand, samples obtained from sols with acidic catalysts mainly consist of anatase at 500 °C. As the heat treatment temperature increases to 700 °C, anatase relative crystalline size increases and some changes in phases occurs. Wang and Ying [19] suggested that critical size of 40–50 nm is required for the phase transition from anatase to rutile. In the S.CL (sample derived from sol containing hydrochloric acid as catalyst) and S.S samples (Fig. 2b and d), the anatase phase shortly transforms into the rutile phase; however S.N (sample derived from sol containing nitric acid as catalyst) shows anatase (Fig. 2c). This indicates that presence of HNO₃ as catalyst in the sol would cause the highest stability of the anatase phase.

The results show that catalyst-type can affect structure and crystalline size of the final layer. Acidic catalysts such as H₂SO₄, HNO₃, and HCl play effective roles in controlling hydrolysis and condensation reactions. Increasing heat treatment temperature to a value more than 500 °C may also result in a destructive effect on the final phases and therefore on film properties.

### 3.2. Surface morphology

The surface morphology of the TiO₂ films was examined using SEM. SEM images of different films derived from dissimilar sols and heat treated at 500 °C are very similar to each other, the surface being very smooth with only few irregularities. For example, SEM image of S.S is shown in Fig. 3a. One can observe from Fig. 3a that the coating is crack-free, porosity-free, transparent and uniform. Increasing the temperature for all samples may lead to non-uniform and cracked coating and reduce coating lucidity and transparency (as can be seen in Fig. 3b). This is perhaps due to substrate plasticity and softening or crystalline size increase or film structure variation at the temperature of 700 °C. In a sol–gel process of transition metal alkoxides, hydrolysis and condensation reactions occur very rapidly, so uniform and ultrafine products are difficult to obtain. With the use of bulky, branched alkoxy groups (i.e., isopropoxides), the hydrolysis and condensation rates can be reduced to favor the formation of nanometric clusters, yielding a more uniform particle size [20].

The well-defined crystallinity and size of TiO₂ films were confirmed by the FE-SEM studies (Fig. 4). The images report nano-scale spherical particles for all films, as can be considered in Fig. 4. These values are much larger than that obtained from XRD measurements because SEM tends to show the overall aggregates rather than individual

### Table 2  XRD results for coatings derived from different sols.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment temperature (°C)</th>
<th>Anatase phase (%)</th>
<th>Anatase relative crystalline size (nm)</th>
<th>Rutile phase (%)</th>
<th>Rutile relative crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.DEA (sol containing DEA as catalyst)</td>
<td>500</td>
<td>91</td>
<td>20.7</td>
<td>9</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>6</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>S.CL (sol containing HCL as catalyst)</td>
<td>500</td>
<td>96</td>
<td>25.9</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>89</td>
<td>51.7</td>
<td>11</td>
<td>34.6</td>
</tr>
<tr>
<td>S.N (sol containing HNO₃ as catalyst)</td>
<td>500</td>
<td>92</td>
<td>25.8</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>91</td>
<td>33.7</td>
<td>9</td>
<td>–</td>
</tr>
<tr>
<td>S.S (sol containing H₂SO₄ as catalyst)</td>
<td>500</td>
<td>92</td>
<td>14.1</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>82</td>
<td>34.5</td>
<td>18</td>
<td>34.6</td>
</tr>
</tbody>
</table>

Fig. 3 SEM images of the S.S film annealed at (a) 500 °C and (b) 700 °C.
3.3. Photocatalytic activity

When the content of Na\(^+\) exceeds the limiting value, the anatase structure is no longer stable and this may finally lead to the formation of brookite or rutile structure [9]. Table 1 shows XRF analysis of glass substrate, in which much sodium ions exist. The prepared TiO\(_2\) films contained Na\(^+\) ions diffused from the glass substrate into the films during the heat treatment resulting in an obvious decrease in the photocatalytic activity [21]. To prevent the negative effect of Na\(^+\) ions, a SiO\(_2\) layer was pre-coated on the glass by the sol–gel method. MB (methylene blue, C\(_{16}\)H\(_{18}\)ClN\(_3\)S.3H\(_2\)O), used in textile industry, often serves as a model compound (dye) for the photocatalytic activity measurement of TiO\(_2\) thin films. So, the coated samples with the dimension of 3 cm \(\times\) 1 cm in the aqueous solution were exposed to UV irradiation by two 12 W lamps. Next, solution decomposition was measured using UV–vis spectrophotometer with respect to time. It has been reported that in the degradation mechanism of MB, MB is first adsorbed on the sample surfaces and then oxidized to a radical MB\(^+\) by photoinduced holes produced by irradiation. The latter reacts further with O\(_2\) to form a radical [MBOO\(^+\)]\(^+\) and then to thionine (C\(_{12}\)H\(_9\)N\(_3\)S) and 4-nitroaniline (C\(_6\)H\(_5\)NH\(_2\)\(-\)C\(_6\)(NO\(_2\))\(_2\)). Finaly, the poly-aromatic ring is broken and aniline (C\(_6\)H\(_5\)NH\(_2\)) and 4-nitroaniline (C\(_6\)H\(_5\)NH\(_2\)\(-\)C\(_6\)(NO\(_2\))\(_2\)) are formed [22].

As can be seen in Fig. 5, in the absence of films, there was no direct photolysis of MB and MB concentration is constant. In fact, the photocatalytic activity of the films might lead to the decomposition process. MB decomposition in all samples follows the Langmuir–Hinshelwood kinetics model [23] given by

\[
-(dC/dr) = (kKC)/(1 + KC)
\]  

where C is the MB concentration (mg L\(^{-1}\)) at a time t (min), K is the adsorption coefficient of MB (L mg\(^{-1}\)) and k is the reaction rate constant (mg L\(^{-1}\) min\(^{-1}\)). After integration, Eq. (2) is transformed into

\[
t = [(\ln(C_0/C)/(Kk)] + [(C_0 - C)/k]
\]  

As the initial concentration (C\(_0\)) is a millimolar solution (C\(_0\)<0.1 mmol L\(^{-1}\)), the second term on the right-hand side of Eq. (3) is relatively negligible. Therefore, Eq. (3) can be further simplified to give an apparent first-order equation:

\[-\ln(C_0/C) \approx kKt = K't\]  

where K' is the pseudo-first order rate constant in min\(^{-1}\). This constant is evaluated through the linear regression of

![Fig. 4](image-url)  

FE-SEM images of the TiO\(_2\) thin film annealed at 500 °C, (a) S.DEA, (b) S.CL, (c) S.N, and (d) S.S.

![Fig. 5](image-url)  

Photodegradation of MB solution in the presence of samples coated with different catalyst-type sols.
$-\ln \left(\frac{C_t}{C_0}\right)$ versus $t$. The values of the determination coefficient $R^2$ are given in Fig. 5. The results show that the photocatalytic decolorization of the MB dye can be described by the pseudo-first order kinetic model.

Decreases of MB concentration in samples S.DEA, S.CL, S.N and S.S are 56%, 65%, 61% and 70%, respectively. One can deduce that S.S exhibits the highest decrease and therefore the highest photocatalytic activity. On the other hand, S.DEA shows the lowest reduction and so the lowest photocatalytic activity, among all the samples.

This phenomenon can be attributed to higher anatase phase proportion in S.S compared to S.DEA and its high hydrophilicity. Hence, the crystalline structure and surface morphology of films influence the photocatalytic efficiency of TiO$_2$. The weak photocatalytic activity of S.DEA possibly can be explained by the formation of rutile crystalline, which has a small band gap for photocatalytic reaction. In particular, it has been shown that anatase is more photocatalytic than other common titanium dioxide-based phases including amorphous titanium dioxide, rutile, and brookite phases.

3.4. Surface wettability of TiO$_2$ films

A superhydrophilic surface favors the spread of water and the contaminant on the surface can be removed easily by rainwater. Table 3 shows the contact angle of 4 µL water on the TiO$_2$ films. The contact angles less than 10$^\circ$ are recorded as zero, as the OCA 15-plus was not able to accurately measure contact angles below 10$^\circ$. This table gives the contact angles of water for all the samples studied in dark, after 1 and 2 h of irradiation. The measurement over the whole area of the films (five points) has shown that the films are uniform, the standard deviation of the contact angle being 3–5$^\circ$.

In dark, the surface wettability of the films is much different. Regardless of the catalyst type, the films are hydrophobic and the water contact angles tend to reach to the saturation contact angle values of about 60–80$^\circ$ without any clear dependence on the kind of catalyst. This is ascribed to the fact that the surface is contaminated by adsorbing some gaseous contaminants from air and the surface defect sites can be healed or replaced gradually by oxygen atoms.

It is well known that the contact angle of the TiO$_2$ films decreases gradually to almost zero when it is irradiated by UV light. It can be seen that the hydrophobic $\leftrightarrow$ hydrophilic interconversion rates of the films are obviously different, depending on catalyst-type. After 1 h UV irradiation, S.S, S.N and S.CL with 25$^\circ$ angle were hydrophilic, whereas S.DEA with 45$^\circ$ exhibited less hydrophilic nature. However, after 2 h illumination by UV, owing to the special photoinduced superhydrophilicity of TiO$_2$, the wettability of the films with acidic catalysts became almost the same. These films showed superhydrophilic nature with contact angle less than 10$^\circ$. But S.DEA with 21.5$^\circ$ angle showed less hydrophilicity, even after 2 h irradiation.

The self-cleaning property has been known to be a mutual effect of photocatalysis and hydrophilicity [24,25]. So, the best self-cleaning property is devoted to one which shows better photocatalytic activity. Combination of Fig. 5 and Table 3 indicates that the lowest photocatalytic activity of S.DEA may cause poor surface wettability.

3.5. AFM analysis

All prepared films were highly transparent and visually smooth. The surface roughness was generally very low with the Ra parameter in the range of 1–5 nm. A summary of the results represents that, hitherto, the sample S.S revealed the best properties among others. So, this specimen is chosen for topographic studies. Fig. 6 shows 3D-views of height data and the characteristic vertical profiles of S.S. Its surface topography, Fig. 6a, demonstrates homogenous granular surface and crack-free, porous-free and smooth film with low roughness variation that can be emphasized by symmetric distribution. This value of surface roughness can give monotonous thickness. Therefore, the results can be universalized to the entire surface.

Also, the TiO$_2$ film properly follows SiO$_2$ pre-coated unevenly and probable surface defects such as porosities and improves the final quality of thin films. The well-defined crystallinity and size of TiO$_2$ particles were confirmed by the AFM analysis.

Height profile is plotted in Fig. 6c which is mapped from the line shown in Fig. 6b. The Ra value for this film is 1.435 nm which can be proved by anatase small crystalline size (14.1 nm) for sample S.S, indicating a possibility that the films are optically smooth. The lower roughness value represents good homogeneity of the TiO$_2$ particles on the surface. It should be mentioned that surface roughness decreases with self-cleaning improvement.

4. Conclusion

In this study, TiO$_2$ films were prepared from titanium precursor solution with different catalysts. We successfully fabricated self-cleaning TiO$_2$ thin films on the windshield by sol–gel dip-coating, having desired structural, morphological, photocatalytic and wettability properties. The results showed that increasing heat treatment temperature from 500$^\circ$C to

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle for water in dark ($^\circ$)</th>
<th>Contact angle for water after 1 h irradiation ($^\circ$)</th>
<th>Contact angle for water after 2 h irradiation ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.DEA</td>
<td>64.9</td>
<td>45.2</td>
<td>21.5</td>
</tr>
<tr>
<td>S.CL</td>
<td>79</td>
<td>25.1</td>
<td>0</td>
</tr>
<tr>
<td>S.N</td>
<td>62.9</td>
<td>21.5</td>
<td>0</td>
</tr>
<tr>
<td>S.S</td>
<td>70.1</td>
<td>22.3</td>
<td>0</td>
</tr>
</tbody>
</table>
700 °C have led to more rutile phase percent and larger particle size in all samples. Also, it has been revealed that the S.S sample (sample obtained from sol containing H2SO4 as catalyst) with the lowest particle size, among other samples, has the best potentiality of self-cleansing surface with the highest photocatalytic activity. On the other hand, S.DEA showed the lowest reduction and so the lowest photocatalytic activity, among the samples.

Combination of AFM and wettability investigation indicated that such an average of rough coating (less than 10 nm) could have been easily predicted for the samples and proved the crack-free and uniform feature of films.

Acknowledgments

The authors are thankful to the SAPCO (Supplying Automotive Parts Co.) for their kind help and financial support.

References

[16] S. Pabisch, B. Feichtenschlager, G. Kickelbick, H. Peterlik, Effect of inter-particle interactions on size determination of zirconia and


