Effects of diethylene glycol on TiO\textsubscript{2} thin film properties prepared by sol–gel process

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Abstract

A technological approach for the sol–gel processing of stabilized thin film titanium dioxide on the stainless steel has been extensively investigated in this paper. Diethylene glycol was used as a drying control additive agent. The transformation of a titanium dioxide thin film was studied by X-ray diffraction. The surface morphology was observed by scanning electron microscope (SEM). As results, this substance helped in stabilizing the solution and improving the adhesive property of the film. Without diethylene glycol, the thin film peeled off. Substantially improvement of film was seen with the high amount of diethylene glycol applied. This effect was confirmed by adhesive test and the morphology of stainless steel surface. In addition, adding diethylene glycol to the sol–gel solution exerted less effect on transformation of anatase to rutile phase in titanium dioxide structure. Thus, the nanocrystalline anatase phase of thin film TiO\textsubscript{2} can be controlled and the high photoactivity of the film is secure.

Keywords: TiO\textsubscript{2}; Titanium dioxide; Sol–gel; Photocatalysis; Photocatalytic; Thin film; Chromium; Heavy metal

1. Introduction

The progress in development of TiO\textsubscript{2} thin films is of particular interest due to the numerous technological applications of this inorganic oxide. A number of methods have been employed to fabricate TiO\textsubscript{2} films, including sputtering, chemical vapor deposition, and sol–gel process [1–3]. The sol–gel process is one of the most appropriate technologies to prepare thin oxide coating. This technique offers many advantages over other deposition techniques due to the use of very simple equipment. In addition, the stochiometry and the high homogeneity of the final film can be controlled [4]. The film deposition can be performed by dip-coating technique. In this method, the substrate to be coated is immersed in a liquid and then withdrawn at a well-defined speed under controlled temperature and atmospheric conditions. The chemical reactions involve the formation of non-crystalline (amorphous) titanium dioxide by hydrolysis and condensation of titanium alkoxide. The reactions written in a very simplified manner can be presented as follows:

\[ \text{hydrolysis} \]

\[ \equiv\text{Ti} - \text{OR} + \text{H}_2\text{O} \rightarrow \equiv\text{Ti} - \text{OH} + \text{ROH} \quad (1) \]

\[ \text{and condensation} \]

\[ \equiv\text{Ti} - \text{OR} + \text{HO} - \text{Ti} \rightarrow \equiv\text{Ti} - \text{O} - \text{Ti} \equiv +\text{ROH} \quad (2) \]

This is followed by the transformation of amorphous titanium dioxide to either anatase or rutile crystalline by calcinations temperature.

The TiO\textsubscript{2} film properties tend to be the function of the sol–gel processing conditions including the kind and concentration of the solvent, the sol additive, and the heat treatment [5]. To obtain the high quality of TiO\textsubscript{2} thin film used in photocatalysis process for contaminant removal for air and water purification, it is necessary for us to investigate in detail the factors which may have important effect on the film properties.

In this study, we investigate the preparation and characterization of sol–gel TiO\textsubscript{2} thin films dip coated on the stainless steel plate. The important and useful details for thin film preparation reported in this paper are the effects of diethylene glycol (DEG) on thin film properties. The X-ray
diffraction (XRD) and scanning electron microscopy (SEM) are used to characterize the properties of the thin films.

2. Experimental

2.1. Materials

All chemicals in this research were analytical grade and were used as received. Nanocrystalline titanium dioxide was prepared via sol–gel hydrolysis and condensation of ethanol solutions (Merck Chemicals) of titanium tetraisopropoxide (Ti(OC\textsubscript{3}H\textsubscript{7})\textsubscript{4}, Aldrich Chemicals) or TTiP. The diethylene glycol (DEG) was obtained from Merck Chemicals.

2.2. Thin film preparation

The thin nanostructured film of TiO\textsubscript{2} was deposited on stainless steel plate with the surface cleaning prior to use. The synthesis of various sols of TiO\textsubscript{2} was as follows. The TiO\textsubscript{2} precursor solutions were prepared first by stabilizing titanium tetraisopropoxide, dissolved in ethanol, with or without diethylene glycol, and stirred for 30 min at room temperature. The varied molar ratios of TTiP to ethanol in this study were 1:20 and 1:40. The diethylene glycol was changed at the desired value following the TTiP concentration. The substrates were dipped into the sol and withdrawn at a constant speed to make a gel coating film. The TiO\textsubscript{2} gel films were heated to temperatures 500 °C for 30 min in air. The samples were put directly into a furnace, which was maintained at a given temperature.

2.3. Characterization of TiO\textsubscript{2} thin film

The coating mass of TiO\textsubscript{2} per surface area was determined by X-ray diffraction (XRD) and scanning electron microscope (SEM). The crystal phase of thin film was analyzed by thin film XRD analysis which were recorded on a Philip diffractometer using Cu Kα radiation and a step size of 0.02° in the range of 10–80°. The step time was 1 s, adequate to obtain a good signal-to-noise ratio in the mean reflections of the two studied TiO\textsubscript{2} crystalline phases, (101) anatase (2θ ∼ 25.17°) and (110) rutile (2θ ∼ 27.35°). Scanning electron microscope (Philip) was used to examine the smoothness of thin film surface.

3. Results and discussion

3.1. Robustness enhancement

It has been known that the resultant morphology of gels can be modified by adding chemical compounds to sol–gel process. The physical effects of external additives are to modify the surface tension and volatility of the solvent phase in the gel, and to vary the compatibility among the oligometric alkoxide, solvent mixture, and additionally incorporated materials such as organic polymers [6,7]. On the other hand, the chemical reactions in the sol–gel processes, such as hydrolysis and condensation, can be directly modified by the functional groups of chemical additives. Here, the DEG exhibits the resistant to peeling with adhesive Scotch Tape\textsuperscript{TM}. Sol solutions without DEG were unstable. As represented in Table 1, with the low concentration of ethanol and in the absence of DEG, the thin film was peeled off and failed in the adhesive test. The adherence of thin film on stainless steel was substantially improved even when small amount of DEG was applied to the sol. Moreover, the TiO\textsubscript{2} thin films were not removed from the stainless steel substrate even with 1 M NaOH and concentrated HNO\textsubscript{3}.

This robustness enhancement of TiO\textsubscript{2} thin film due to DEG addition is also reported by the other research group [8]. In addition to the adherence improvement, the TiO\textsubscript{2} films were also resistant to scratching with pencil points of 2H hardness as well.

3.2. Thin films surface morphology

Fig. 1 shows the original macroscopic morphology of stainless steel without any deposition of TiO\textsubscript{2} on the surface. The grain boundary of stainless steel was clearly seen.

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**Table 1**

| Experiment set | Molar ratio of TTiP:EtOH:-DEG | Pass (√) or failed (x) | Molar ratio of TTiP:EtOH:-DEG | Pass (√) or failed (x) |
|----------------|-------------------------------|------------------------|-------------------------------|------------------------|
| 1              | 1:10:0                        | x                      | 1:10:0.5                     | √                      |
| 2              | 1:20:0                        | x                      | 1:20:0.5                     | √                      |
|                |                               |                        | 1:20:1                      | √                      |
|                |                               |                        | 1:20:1.5                    | √                      |
| 3              | 1:30:0                        | x                      | 1:30:1.5                    | √                      |
| 4              | 1:40:0                        | √                      | 1:40:1.5                    | √                      |

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Fig. 1. Scanning electron micrographs of the stainless steel surface without TiO\textsubscript{2} thin film.
The macroscopic morphology of TiO₂ thin film deposited on stainless steel plate in the absence of DEG are shown in Fig. 2(a) with 1000× magnifications. It is noteworthy that the morphology was quite similar to the original stainless steel plate. With a higher magnification in Fig. 2(b), there were some particles left on the surface of the thin film. Because the organic components of the unfired coatings were decomposed during the heat treatment, it is anticipated that the nano-particle remaining on the surface of the thin film was the developed TiO₂. These particles disappeared in the presence of DEG in the sol solution. The flat and smoothness of TiO₂ thin film with the thickness 50 nm in average was obtained as seen in Fig. 3. Although the TiO₂ films became obviously thicker by this DEG addition, our experiments on photocatalytic activity remained rather unchanged. This SEM analysis shows that DEG does not only play an important role in stabilizing the dipping solution but also help in increasing the smoothness of the film.

3.3. Crystallization

Fig. 4 shows the X-ray diffraction patterns of the TiO₂ thin films. They were prepared by dipping the stainless

![Fig. 2](image1)

![Fig. 3](image2)

![Fig. 4](image3)
steel plate in the sol solution with different amounts of DEG. The molar ratios of TTIP to ethanol to DEG were varied from 1:20:0 to 1:20:1.5 using the method described previously. As shown in previous sections, DEG enhanced the thin film properties in a variety of physical characters such as adherence on the substrate, robustness, and surface smoothness. To investigate the effect of DEG on the crystalline TiO₂ thin film, the films were analyzed by XRD. Apparently, the DEG did not exhibit the significant effect on the crystallization of the films. The thin film originally consisted mainly of anatase crystalline. Even when high amounts of DEG were applied; the same crystalline structure still remained. The sharp peaks of anatase with the same intensity were obtained. This unchanged pattern might be explained by the fact that DEG is the organic component, which is easily removed during the heat treatment process. This might be presumed that adding diethylene glycol in the sol–gel solution exerted less effect on transformation of anatase to rutile phase in titanium dioxide structure. Thus, the nanocrystalline titania anatase film can be controlled and the high photoactivity of the film is secure. This statement might be supported by the experiments on photoreduction of chromium (VI) from aqueous using the obtained thin films. Results of this experiment are illustrated in Fig. 5. Comparatively, the photoactivity of the thin film obtained from the DEG addition exhibited the similar chromium (VI) removal pattern with the thin film obtained in the absence of DEG. This finding leads to the advantage of DEG in securing the photoactivity while enhancing the adherence, robustness, and smoothness of the TiO₂ thin film.

4. Summary

The effects of diethylene glycol (DEG) in the dip-coating solutions on the properties of the resultant TiO₂ coating films were studied. It was found that the addition of DEG to the sol solutions significantly enhances the adherence on the stainless steel substrate, film robustness, and surface smoothness. This sol additive exerted less effect on the crystallization of the TiO₂ thin film. The acquiring anatase is maintained which results in the high photoactivity of the film for application in environmental abatement.

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