Journal of Materials Science Research and Reviews

5(4): 46-51, 2020; Article no.JMSRR.59863

Effect of Stabilizer on Structural, Optical and Photocatalytic Properties of Sol-Gel Dip-Coated TiO_2 Films

Romy Dwipa Y. Away[1], Chika Takai-Yamashita[1], Takayuki Ban[1] and Yutaka Ohya[1*]

[1]Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan.

Authors' contributions

This work was carried out in collaboration among all authors. Author RDYA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors CTY and TB managed the analyses of the study and literature searches. Author YO initiated the research and supervised. All authors read and approved the final manuscript.

Article Information

Editor(s):
(1) Dr. Suraya Hani Bt Adnan, Universiti Tun Hussein Onn Malaysia, Malaysia.
(2) Dr. Yong X. Gan, California State Polytechnic University, USA.
Reviewers:
(1) Adawiya J. Haider, University of Technology, Iraq.
(2) Ajit Behera, National Institute of Technology, India.
Complete Peer review History: http://www.sdiarticle4.com/review-history/59863

Short Research Article

Received 15 May 2020
Accepted 30 July 2020
Published 04 August 2020

ABSTRACT

Thin films of titanium dioxide (TiO_2) were prepared through sol-gel routes and dip-coating technique, employing titanium isopropoxide (TTIP) in 2-propanol as precursor, and three stabilizing agents i.e. diethanolamine (DEA), lactic acid, and citric acid. The optical properties, crystallinity, and morphology of the samples were evaluated using UV-Visible (UV-Vis) Spectrophotometry analysis, X-Ray Diffraction (XRD) analysis, and Scanning Electron microscope (SEM). Homogeneous crack-free thin films with uniform size were obtained. All the samples showed the formation of anatase phase TiO_2 with no impurities. It was found that TiO_2 with all samples has excellent photocatalytic performance on methylene blue degradation.

**Corresponding author: Email: ohya@gifu-u.ac.jp;*

Keywords: TiO_2; anatase; sol-gel; stabilizer; photocatalyst.

1. INTRODUCTION

Titanium dioxide (TiO_2) is one of the most efficient semiconductors as a results of its chemical and physical properties. It has been used in a great variety of applications, such as degradation of pollutants in water, soils, and the atmosphere [1-3], material for smart windows [4], antireflective coatings [5], optical filters [6], solar cells [7] and as a support for catalysis and photo-electrochemistry [8]. Titanium oxide (TiO_2) films are achievable from numerous techniques such as sol–gel process [4,9], hydrothermal [10], ion beam sputtering [11], chemical vapor deposition [12], activated reactive evaporation [13], etc. Tailor making of the film properties, chemical and mechanical stability of films, introduction of porosity in films, low process cost and possible processing at low temperature are some of the few advantages offered by the sol–gel method [14-16]. Sol–gel process which involves hydrolysis and condensation of the metal alkoxides followed by treatment at an elevated temperature causing polymerization to produce the oxide network formation, has led to a great deal of investigations.

The present study reports the preparation of TiO_2 coatings by sol–gel dip-coating technique based on three different precursor solutions employing diethanolamine (DEA), citric acid and lactic acid as the stabilizing agents to prevent precipitation of titanium isopropoxide. Metal alkoxides are susceptible to nucleophillic attack and are highly reactive due to electronegative OR groups stabilizing the metal in its highest oxidation state. DEA is used as a stabilizing agent and inhibitor for the precipitation of oxides on hydrolysis of the alkoxides. Citric acid and lactic acid acts as a catalyst and chelating agent in addition to acting as a modifier of the molecular structure of coating sol. Y. Ohya et al. reported that the fabrication of oxide films using DEA as sol stabilizers in 2-propanol solvent resulted in dense TiO_2 films [17]. While, T. Ohya et al. reported that lactic acid has brown colored film and citric acid has poor film uniformity in water solvent [18]. Based on this knowledge, our study focused on preparing the best sol composition by three precursor sols and investigating their influence on the microstructure. Photocatalytic activity of the obtained films was evaluated through degradation of methylene blue.

2. MATERIALS AND METHODS

2.1 Synthesis of TiO_2 Thin Films

Titanium isopropoxide (TTIP) as precursor, diethanolamine (DEA), citric acid monohydrate, and l-lactic acid as stabilizing agents were purchased from Wako Pure Chemical Industries. The substrates used were a sapphire (0001) single crystal. First, the substrates were ultrasonically cleaned in acetone, dried at 110^{o}C for 10 minutes and then heated at 700^{o}C for 30 minutes in order to remove impurities. The starting reagent used in the present experiment was titanium tetraisopropoxide (TIP). A sol with long-term stability against ambient humidity was obtained by adding stabilizing agents (DEA or citric acid monohydrates or l-lactic acid) to a 2-propanol solution of TTIP. The molar ratios of added additive to TTIP were 1. An appropriate amount of water was also added to each solution. The TiO_2 sols were deposited onto sapphire substrate using dip-coating method. Because photocatalytic properties also depend on the film thickness [16], the film thickness was controlled by withdrawing the substrate at a rate of 6 cm/min to achieve the same thickness. The sol concentration used in the present study was 0.3 M. After deposited, they were dried at 110^{o}C for 10 minutes and annealed at 700^{o}C for 30 minutes. In order to achieve same crystallinity phase of all samples, the citric acid and lactic acid samples were heated by rapid heating, while DEA was heated by slow heating rate (15^{o}C/min). This coating cycle was repeated 5 times.

2.2 Characterization of the TiO_2 Thin Films

The morphologies of the TiO_2 thin films with the use of different stabilizing agents were examined by scanning electron microscopy (Hitachi S-4800) instrument at low acceleration voltage of 5 kV and 9.4-9.6 mm working distance. SEM images were captured after coating the samples with an osmium layer. The crystalline phase was determined using X-Ray Diffractometer (Rigaku Ultima IV) with CuKα (λ = 1.54Å) radiation. XRD patterns were obtained at a can rate of 2^{o} min^{-1} in the 2θ range from 2 to 70^{o}. The crystallite sizes of the samples were estimated from the XRD peak widths using the Scherrer equation. Optical absorption spectra of the films were recorded

from 200 to 1100 nm on a spectrometer (Hitachi U-4100). The refractive index and thickness of the film were estimated from the interference patterns observed in the UV-Vis spectra [17].

2.3 Photocatalytic Activity Test

The photocatalytic activity of the films was evaluated through degradation of methylene blue. A 500 W ultrahigh pressure mercury lamp was used as the UV light source. The films, with a surface 2.7 cm^2, were immersed in quartz cells containing 3 mL of a 10 ppm methylene blue (MB) aqueous solution. The UV lamp was placed at a distance of 43 cm from the films. First, an adsorption test was conducted in the dark for 30. After MB was totally adsorbed on the surface of the test material, reaching equilibrium, a photocatalytic test was carried out under UV irradiation. The change in methylene blue content was determined from the change in the area under the curve of the absorption spectra. The optical absorption spectra of the aqueous solutions were collected within the time range 0-120 min at regular interval 30 min. During the irradiation, bubbling oxygen was conducted through to the MB solution in order to enhance the photocatalytic activity [19]. The absorbance of the solution was measured using a UV-Vis spectrophotometer (Ocean Optics) at λ=663 nm.

3. RESULTS AND DISCUSSION

The UV-Vis spectra of the thin films deposited on a sapphire substrate prepared with different stabilizing agents precursors are presented in Fig. 1. From the spectra, it was observed that the films were transparent in the visible region, showing characteristic absorption in the UV region at shorter wavelengths. In addition, the transparent films suggest that the addition of the three additives successfully act as stabilizer to prevent precipitation of TTIP. The 2-propanol seems to be better solvent to prepare TiO_2 thin films rather than water solvent [18]. The changes in transmittance spectra and absorption edge wavelength of TiO_2 films prepared with different stabilizing agents might be attributed to the differences in film thickness, surface microstructure, and absorption of light. The thickness and refractive index of the thin films can be obtained from their spectra. The thicknesses of TiO_2 thin films with DEA, lactic, citric additive are 153 nm, 163 nm, and 156 nm, respectively. The difference in the thickness of the thin films is not significant. Meanwhile, the refractive index of them are 2.46, 2.53, and 2.12 for DEA, lactic, and citric stabilizing agents, respectively.

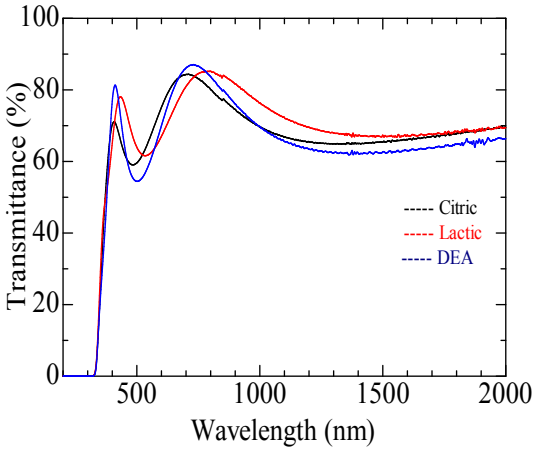

Fig. 1. Transmittance spectra of the TiO_2 thin films synthesized by different stabilizing agents

Fig. 2 shows the XRD patterns of TiO_2 thin films with different stabilizing agents. XRD patterns of DEA by rapid heating exhibited peak assigned to rutile (110) and (101), while DEA by slow heating rate exhibited peak assigned to anatase (101) and rutile (110). TiO_2 films that were formed with DEA by rapid heating had a tendency to crystallized as rutile, while the slow heating had a tendency to crystallized as anatase [20]. The diffraction pattern of citric acid and lactic acid samples exhibit peaks in 2θ of around 25.3° which attributed to the reflections of the anatase TiO_2 only. These results indicate that the chemical species in the precursor solutions control the crystal form, and consequently the properties of the resultant TiO_2 films. Organic chelates are well known to control the hydrolysis but tend to reside in the films until higher temperatures [18]. The rutile formation seems to be accelerated by property of amine species rather than carboxylic acid species. The average crystallite size was calculated using Scherrer's equation based on the broadening of the (101) anatase reflection and found to be 40, 49, and 48 nm for the addition of DEA, lactic acid, and citric acid, respectively. XRD analysis confirms the existence of anatase phase for all samples, which is considered as most suitable for the photocatalyst [15].

The observed SEM micrographs are shown in Fig. 3. The films were found to be crack free, uniform in size, and homogeneous owing to the

crystalline nature, where they are closely packed and featured by their highly dense structure. The particle size of all samples was around 40-50 nm.

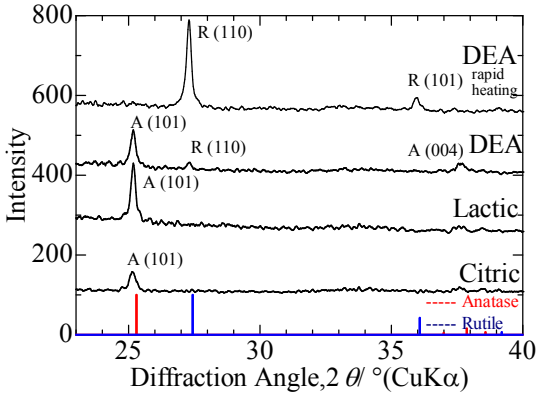

Fig. 2. XRD patterns of the TiO_2 thin films synthesized by different stabilizing agents

The photocatalytic degradation of MB in the samples is shown in Fig. 4(a). *Co* is the concentration at 0 min, *Co'* is the concentration after 30 min absorption, and *Ct* is the concentration at *t* min. At the first 30 minutes, degradation of only a small amount of MB was observed in the samples. After 30 min in the dark, the UV light source was applied. The apparent rate constants were evaluated from their slopes starting after 30 min of absorption (ln (*Co'*/*Ct*) = *k*. *t*) (Fig. 4(b)).

The apparent rate constant and photodegradation of the MB are shown in Table 1. It is observed that the TiO_2 thin films fabricated with different stabilizing agents have excellent photocatalytic performance. All of the samples show the degradation of MB more than 90% after 2 h of irradiation. However, the TiO_2 thin film fabricated with the addition of lactic acid showed a slightly better photocatalytic performance compared two other samples. This might be related to the higher crystallinity of TiO_2 based on XRD analysis results and the thicker films based on UV-Vis analysis results using lactic acid. Increased crystallinity of TiO_2 leads to a lower band gap, resulting in the better photocatalytic performance [21]. The degradation rate constant increases with increasing the thickness films, which can be attributable to the increase amount of TiO_2 providing more reaction sites for photocatalyst [16]. It is inferred that although the TiO_2 samples were synthesized by different stabilizing agents, when the thin films have almost the same crystallinity, thickness of the films, and uniformity of microstructure, the photocatalytic performance doesn't show much difference.

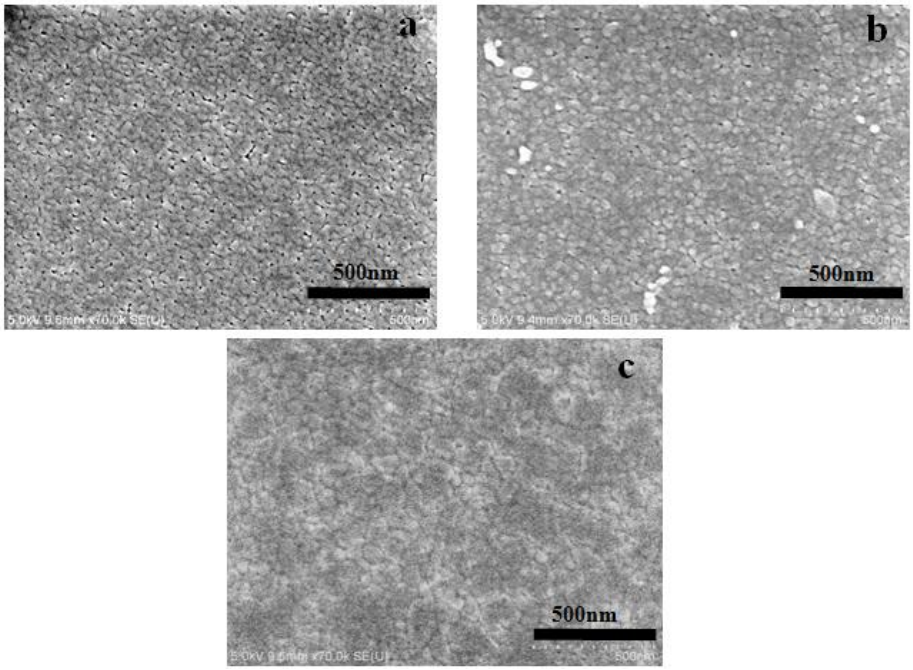

Fig. 3. SEM micrographs of the TiO_2 thin films synthesized by different stabilizing agents (a) DEA (b) Citric acid (c) Lactic acid

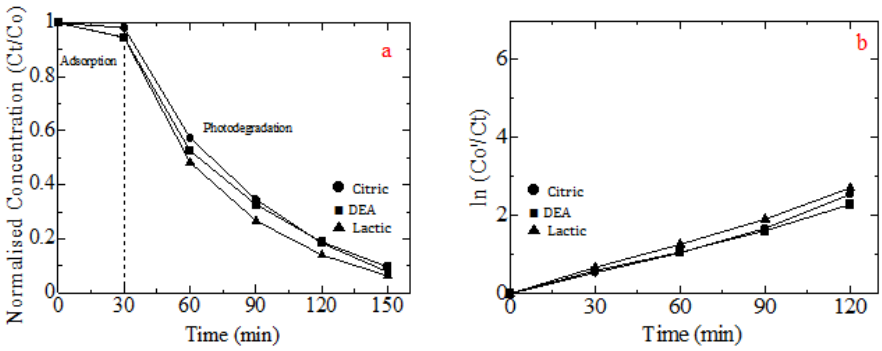

Fig. 4. (a) Photocatalytic degradation of MB under UV irradiation (b) Logarithm plots of the concentration ln (Co'/Ct) with reaction time for MB by the samples

Table 1. The apparent rate constant and photodegradation of MB by the samples

Sample	% of MB degradation	Rate constant for MB degradation (/min)
Citric	92.3%	0.0188
Lactic	93.7%	0.0218
DEA	90.4%	0.0186

4. CONCLUSION

Sol–gel process derived TiO_2 thin films were fabricated from 2-propanol solution of titanium isopropoxide, in the presence of three kinds stabilizing agents such as diethanolamine (DEA), citric acid and lactic acid. A transparent crack free films with good adherence and quality were obtained from all the routes. All of the thin films have anatase phase. The photocatalytic performance of all the samples doesn't show significant difference, due to the same crystallinity, thickness of the films, and uniformity of the microstructure.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

ACKNOWLEDGEMENTS

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Patel N, Jaiswal R, Warang T, Scarduelli G, Dashora A, Ahuja BL, Kothari DC, Miotello A. Efficient photocatalytic degradation of organic water pollutants using V-N-codoped TiO_2 thin films. App. Catal. B: Environ. 2014;150:74-81.
2. Kabra K, Chaudhary R, Sawhney RL. Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: A review. Ind. Eng. Chem. Res. 2004;43:7683-7696.
3. Binas V, Venieri D, Kotzias D, Kiriakidis GJ. Modified TiO_2 based photocatalysts for improves air and health quality. J. Materiomics. 2017;3(1):3-16.
4. Meher SR, Balakrishnan L. Sol-gel derived nanocrystalline TiO_2 thin films: A promising candidate for self-cleaning smart window applications. Mater. Sci. Semicond. Process. 2014;26:251-258.
5. Vicente GS, Morales A, Gutierrez MT. Preparation and characterization of sol-gel TiO_2 antireflective coatings for silicon. Thin Solid Films. 2001;391:133-137.
6. Phillips RW, Dodds JW. Optical interference coatings prepared from solution. App. Opt. 1981;20(1):40-47.

7. Sun J, Yang X, Zhao L, Dong B, Wang S. Ag-decorated TiO_2 nanofibers for highly efficient dye sensitized solar cell. Mater. Lett. 2020;260:126882.
8. Tryk DA, Fujishima A, Honda K. Recent topics in photoelectrochemistry: Achievements and future prospects. Electrochim. Acta. 2000;45:2363-2376.
9. Verma A, Samantha SB, Bakhshi AK, Agnihotry SA. Effect of stabilizer on structural, optical and electrochemical properties of sol-gel derived spin coated TiO_2 films. Sol. Energ. Mat. Sol. C. 2005;88:47-64.
10. Keerthana BGT, Solaiyammal T, Muniyappan S, Murugakoothan P. Hydrothermal synthesis and characterization of TiO_2 nanostructures prepared using different solvents. Mater. Lett. 2018;220:20-23.
11. Poddar NP, Mukherjee SK, Gupta M. Anatase phase evolution and its stabilization in ion beam sputtered TiO_2 thin films. Thin Solid Films. 2018;666:113-120.
12. Wang W, Ma J, Wang M, Li Z, Du X, Feng X, Zhao W, Xu H, Luan C. Characterization of anatase TiO_2 epitaxial films deposited on YSZ (100) substrates by metal-organic chemical vapor deposition. Mater. Lett. 2015;161:9-12.
13. Mergel D, Buschendorf D, Eggert S, Grammes R, Samset B. Density and refractive index of TiO_2 films prepared by reactive evaporation. Thin Solid Films. 2000;371:218.
14. Haimi E, Lipsonen H, Larismaa J, Kapulainen M, Krzak-Ros J, Hannula SP. Optical and structural properties of nanocrystalline anatase (TiO_2) thin films prepared by non-aqueous sol-gel dip-coating. Thin Solid Films. 2011;519(18): 5882-5886.
15. Yadav HM, Kim JS. Fabrication of SiO_2/TiO_2 double layer thin films with self-cleaning and photocatalytic properties. J. Mater. Sci: Mater. Electron. 2016;27: 10082.
16. Dulian P, Nachit W, Jaglarz J, Zieba P, Kanak J, Zukowski W. Photocatalytic methylene blue degradation on multilayer transparent TiO_2 coatings. Opt. Mater. 2019;90:264.
17. Ohya Y, Saiki H, Tanaka T, Takahashi Y. Microstructure of TiO_2 and ZnO films fabricated by the sol-gel method. J. Am. Ceram. Soc. 1996;79:825.
18. Ohya T, Nakayama A, Shibata Y, Ban T, Ohya Y, Takahashi Y. Preparation and characterization of titania thin films from aqueous solutions. J. Sol-Gel Sci. Technol. 2003;26:799-802.
19. Away RDY, Fujii S, Ban T, Ohya Y. Preparation of mesoporous titania thin films and their photocatalytic activity. Trans. Mat. Res. Soc. Japan. 2018;43:223.
20. Ohya Y, Mishina J, Matsuda T, Ban T, Takahashi Y. Crystallization and microstructure development of sol-gel derived titanium dioxide thin films with single and multiple layer. J. Am. Ceram. Soc. 1999;10:2601-2606.
21. Paola AD, Bellardita M, Palmisano L, Barbierikova Z, Brezova V. Influence of crystallinity and OH surface density on the photocatalytic activity of TiO_2 powders. J. Photochem. Photobio. A Chem. 2014;273: 59-67.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle4.com/review-history/59863