Factors of Controlling the Formation of Titanium Dioxide ($\text{TiO}_2$) Synthesized using Sol-gel Method – A Short Review

K. Abdul Razak$^{1,2}$, D. S. Che Halin$^{1,2}$, M. M. A. Mohamed$^{1,2}$, A. Azani$^{1,2}$, N. Mahmed$^{1,2}$, V. Chobpattana$^3$

$^1$Geopolymer & Green Technology, Centre of Excellence (CEGeoGTech), Universiti Malaysia Perlis (UniMAP), Perlis 02600, Malaysia
$^2$Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis 02600, Malaysia
$^3$Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi (RMUTT), Thailand

Abstract. There have been experiments on TiO$_2$ thin films synthesized utilizing sol-gel techniques. The sol-gel method is a straightforward technology that gives numerous benefits to the researcher, for instance, material’s reliability, reproducibility, and controllability. Following from there, it can be utilized to make high-quality nano-structured thin films. According to previous studies, the TiO$_2$ films’ characteristics occur to be highly dependent on the production parameters and initial materials utilized. Controlling the formation of TiO$_2$ thin films with the sol-gel method was momentarily discussed here.

1 Introduction

For decades, synthesis and modification of titanium dioxide, which is known as titania ($\text{TiO}_2$), has been studied. $\text{TiO}_2$ is an essential inorganic functional material with excellent optical and physical characteristics, making it ideal for a wide range of purposes. Given its intriguing optical, chemical, and electrical characteristics, $\text{TiO}_2$ thin films have recently become one of the most anticipated oxide materials [1-3]. $\text{TiO}_2$ has been investigated because of their numerous applications in industries. $\text{TiO}_2$ high dielectric constant allows its consideration as an alternative silicon dioxide for ultra-thin gate oxide dielectric used in memory and logic devices [4]. Due to its corrosion resistance, outstanding optical transparency and great chemical stability, it has a high refractive index, making it suitable for optical devices [5].

Prior research has found that the TiO$_2$ films characteristics have a significant impact on the process precursors and parameters utilized. Thus, in order to obtain pure TiO$_2$ or better TiO$_2$ properties, researchers applied the sol-gel method to synthesize TiO$_2$ thin films with various controlling parameters, for instance, temperature and time of annealing, number of dipping or spinning, molar ratio of prepared solution, precursor solutions, and the surfactant or dopant used in their research.

2 Factors Controlling the Formation of TiO$_2$ Film via Sol-Gel

2.1 Effect of Temperature and time of annealing

Rutile, anatase, and brookite are the three polymorphic phases of TiO$_2$ nanoparticles. The rutile phase of TiO$_2$ is more durable overall, but the anatase phase is highly intriguing owing to its photocatalytic capabilities. Once heated, anatase and brookite are semi-stable phases that can transition to rutile [6]. The synthesis of TiO$_2$ thin films via the sol-gel method by using various forms of titanium alkoxide as a precursor is a popular approach. Additionally, Nichide et al. [7] discovered that when the synthesis temperature rose, the film changed from anatase to rutile and the refractive index rose. The influence of temperature on the TiO$_2$ thin films’ optical and structural characteristics was investigated by Kim et al. [8]. At 400°C, their thin films crystallize into anatase, which is then converted into anatase-rutile at 1000°C. The refractive index rises as the temperature
rises, but the porosity reduces as the film shrinks and densifies. They reported that choice of materials and selected process conditions affect the TiO₂ films' structural and optical properties. Another group of researchers, Mechikah et al. [9], looked into the TiO₂ thin films' structural and optical features at various annealing temperatures. The anatase crystalline state occurs after 350°C for four layers of TiO₂ film, according to Raman spectroscopy analysis. The crystallinity of the produced anatase particles rose as the annealing temperature rose. Only tetragonal rutile is formed when the sample is annealed at 400°C, but orthorhombic brookite is formed at greater temperatures (400-450°C).

Prominent diffraction peaks at 25° and 48° on XRD patterns indicated TiO₂ in the anatase phase after annealed at 200 to 800°C [10] demonstrates how the strength of the diffraction peak grows as the calcination temperature rises. Their FWHM steadily lowers and narrows, indicating an increase in particle size. The calcined powder sample at 200°C reveals anatase phase with a particle size of approximately 10 nm. According to their findings, rutile peaks arise at 500°C, and as the calcination temperature rises, both the phase coexists and the proportion of rutile phase rises.

The crystallinity of TiO₂ thin films is claimed to be affected by the growing conditions and the number of layers of TiO₂ colloidal coating [11-12]. The anatase phase was produced between 400°C and 700°C, while the rutile phase was produced after 700°C. The TiO₂ thin films' photocatalytic activity is influenced by the anatase phase form. Subsequently, Senain et al. [13] investigated the sol-gel method for producing TiO₂ thin films using titanium (IV) butoxide, acetic acid, hydrochloric acid, triton x-100, ethanol, and deionized water. The materials were mixed together, then heat and aging treatment was applied. TiO₂ thin films in the anatase crystalline phase were effectively placed at 500°C in this experiment.

Furthermore, Senthil et al. [14] investigated the distinct phases of TiO₂ film x-ray diffraction patterns at 350-550°C annealing temperatures. The absence of identifiable peaks reported indicates that the film is amorphous in origin after annealing at 350°C. The peaks of (1 0 1), (1 1 2), and (2 0 0) in the XRD spectras of 450°C and 550°C annealed films matched to the anatase TiO₂ phase. Based on the diffraction peak in the findings, only anatase phase has developed. For the production of TiO₂ thin films for ecological purposes, Elfanaoui et al. [5] discovered that the optimal crystallization settings were 400°C in air.

To mitigate the issue of TiO₂ nanoparticles agglomeration during the crystallization, extended heating time on the as-prepared gel (below 100°C) can be considered. In addition, Chen et al. [15] heated amorphous TiO₂ in air and discovered that substantial amounts of single-phase anatase TiO₂ nanoparticles with average particle sizes ranging from 7 to 50 nm could be produced. The sol-gel method has been extensively investigated in order to get highly crystallized and closely distributed TiO₂ nanoparticles. A semi-continuous reaction technique, a continuous reaction technique, and a two-stage mixed technique have all been adjusted.

### 2.2 Effect of number of dipping/spinning

While employing the sol-gel method to generate thin film coatings, the number of dipping/spinning has an influence. The impact of varying numbers of coatings on the optical characteristics and structure of TiO₂ generated utilizing the sol-gel dip-coating method was examined by Mechikah et al. [16]. Following four dipping coatings and several annealings, they asserted the TiO₂ thin films' X-ray diffraction pattern. The inclusion of anatase from the brookite phase may be seen for a number of coating layers rising from 4 to 7 at greater temperatures, 400°C and 450°C. They also discovered that when the ten layers of coating are annealed at 400°C, the crystalline structure shifts from anatase-brookite to rutile, which isn't observed under 800°C. Apart from that, Senthil et al. [14], for example, utilized sol-gel spin coating to make nanocrystalline TiO₂ thin films. They spin coating, heating, and cooling procedure were replicated five times to get denser films with an influence on crystalline structure and particle size.

The photocatalytic activity was frequently proportionate to the film's thickness. This might be due to a coarser surface that allows for additional photocatalysis reaction sites. The TiO₂ films' photocatalytic performance with a photonic sponge design was inversely proportional to their thickness. They infer from this research that photocatalytic activity is substantially linked with film thickness [17]. Other than that, Kim et al. [18] investigated a TiO₂ film produced from titanium naphthenate employing a three-step coating technique. The TiO₂ film surface demonstrated a high transmittance in the visible range, with reasonably good surface smoothness and no anomalous grain growth.

Meanwhile, Elfanaoui et al. [5] investigated the influence of TiO₂ thin film coating numbers. They applied 1, 3, and 5 layers of coating on a glass substrate and annealed it at 400°C. With any quantity of coating layers, these spectra reveal a peak equivalent to the availability of anatase. They noticed an increase in anatase and the development of rutile crystallizing in the (002) and (112) planes aligned to the surface at annealing temperatures of 400°C and for 1 and 3 coating layers conditions.
They discover that when the quantity of coating layers reduces, the intensity of anatase and rutile increases. According to the calculations, the crystallinity of the resulting anatase particles grew from 2.9 to 8.3 nm as the quantity of coating layers rose, and the size of rutile crystallites rose as well.

2.3 Effect of Dopant

Noble metals, for instance, Ag, Au, Pt, and Pd, when deposited to the TiO$_2$ surface, can improve photocatalytic efficiency. They aid in the holding of electrons, preventing e/h pair recombination and increasing the electron-hole ratio. Noble metals increase visible range light absorption, allowing surface electron activation through plasmon resonances. The characteristics of the photocatalyst surface are also altered by noble metals. The temperature of the anatase-to-rutile phase transition reduced with the incorporation of Ag. They deduce from the X-ray diffraction study that the produced nanostructures crystallize inside an anatase-type structure and that the dopant Ag ions were not completely integrated into the TiO$_2$ host lattice, whereas Ag concentration impacted both the optical band gap and the refractive index [19].

For the transformation process of TiO$_2$ doped with non-metals, there are three primary points of view. Since their energies are so similar, Asashi et al. [20] discovered that the N 2p state hybridizes with the O 2p state in anatase TiO$_2$ doped with nitrogen, narrowing the band gap of N-TiO$_2$ and allowing it to consume visible light. According to Iihara et al. [22], oxygen-deficient sites generated in grain boundaries are crucial for Vis-activity to arise, and nitrogen-doped in part of oxygen-deficient sites is significant as a reoxidation blocker. TiO$_2$ oxygen sites replaced by nitrogen atoms create separate impurity energy levels beyond the valence band, according to Irie et al. [21]. UV light stimulates electrons at both the VB and impurity energy levels, whereas visible light activates electrons solely at the impurity energy level. Also, Zhao et al. [23] investigated the transformation process of anatase doped with non-metals. They explored N-TiO$_2$ and discovered that TiO$_2$ doped with nitrogen possesses shallow receiver levels over the valence state. TiO$_2$ doped with interstitial nitrogen, on the other contrary, exhibits separate impurity forms in the center of the band gap.

A variety of vanadium-doped TiO$_2$ photocatalysts were manufactured using two modified sol-gel methods in a prior work. N-doped TiO$_2$ was documented as having been effectively synthesized and demonstrating increased photoactivity under visible light, supplemented by additional non-metal doped titania photocatalysts, for instance, carbon sulfur, boron, phosphorus, wheat, and iodine. Hydrolysis of titanium precursors in the availability of non-metal atoms, accompanied by calcination, gas-phase thin film deposition technique, oxidative annealing of TiN, TiS$_2$, or TiC powders, and atmospheric pressure plasma-enhanced nanoparticles were all utilized to create titanium dioxide altered with non-metal atoms [24].

Alternatively, Sajid et al. [25] employed the sol-gel method to study silver doped TiO$_2$ (Ag-TiO$_2$) with silver concentration varying from 0.75 % to 3.5 %. They were created in this work by doping 0.75 % silver in TiO$_2$ and producing stable anatase TiO$_2$ phase. On the surface of the Ag-TiO$_2$ sample with 0.75 % silver, there are mostly lightly scattered silver species (Ag$_2$O and AgO). As the silver concentration in the Ag-TiO$_2$ sample rises, so does the fraction of surface agglomerated silver metal (AgO). The influence of silver species and concentration on the structural, textural, and catalytic features of Ag-TiO$_2$ is substantial, as most past investigations have shown.

3 Conclusion

This research focuses on the parameters that influence the creation of TiO$_2$ thin films employing a simple and low-cost sol-gel method. The annealing temperature, the number of dipping/spinning, and the dopants were all reviewed in this review as parameters that influence the formation of TiO$_2$ thin films.

The writer gratefully acknowledges the assistance of the Malaysian Ministry of Education's Fundamental Research Grant Scheme (FRGS) under grant number FRGS/1/2017/TK07/UNIMAP/02/6. The writers appreciate the partial funding provided by the Center of Excellence Geopolymer & Green Technology (CEGeoGTech), Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, UniMAP.

References

1. Norman M T, Ashraf M A and Ali A, Environ Sci Pollut Res. 26, 3291 (2019)
2. Marzec A, Radecka M, Maziarz W, Kusior A and Pedzich Z, J. Eur. Ceram. Soc. 36, 2981 (2016)
3. Lewkowski A, Synak A, Grobelna B, Bojarski P, Bogdanowicz, Karczewski J, Szczodrowski K, and Behrendt M, Opt. Mater. 36, 1739 (2014)
4. Kumar M, Kumar M, Kumar D, Microelectron. Eng. 87, 447 (2010)
5. Elfanaoui A, Elhamri E, Boulkaddat L, Ihla A, Bouabid K, Laanab L, Taleb A and Portier X, Int. J. Hydrog. Energy 36, 4130 (2011)
6. Mechiakh R, Ben Sedrine N, Chtourou R, and Bensahra R, Appl. Surf. Sci. 257, 670 (2010)
7. Nishide T, Sato M, Hara H, J. Mater. Sci. 35, 465 (2000)
8. Kim D J, Hahn S H, Oh S H and Kim E J, Mater. Lett. 57, 355 (2002)
9. Mechiakhc R, Meriche F, Kremer R, Bensahra R, Boudine B and Boudrioua A, Opt. Mater. 30, 645 (2007)
10. Saalinarj S, Ajithprasad K C, Mater. Today: Proc. 4, 4372 (2017)
11. Lewkowicz A, Synak A, Grobelna B, Piotr Bojarski P, Bogdanowicz R, Karczewski J, Karol Szczodrowski K, Behrendt M, Opt. Mater. 36, 1739 (2014)
12. Kumar R, Arora N and Sharma N, Int. J. Pure Appl. Phys. 13, 229 (2017)
13. Senain I, Nayan N and Saim H, Int. J. Integ. Eng. 2, 3 (2010)
14. Senthil T S, Muthukumarasamy N, Agilanb S, Thambidurai M and Balasundaraprabhu R, Mater. Sci. Eng. B 174, 102 (2010)
15. Chen X and Mao S S, Chem. Rev. 107, 2891 (2007)
16. Mechiakh R, Sedrine N B, Chtourou R and Bensahra R, Appl. Surf. Sci. 257, 670 (2010)
17. Wu C Y, Lee Y L, Lob Y S, Lin C J and Wu C H, Appl. Surf. Sci. 280, 737 (2013)
18. Jeong J H, Ahn J H and Kim B H, J. Korean Phys. S. 46, 559 (2005)
19. Bensouici F, Souier T, Dakhel A A, Iratni A, Tala-Ighi R and Bououdina M, Superlattice Microst. 85, 255 (2015)
20. Asahi R, Morikawa T, Ohwak T, Aoki K, Taga Y, Science 293, 5528 (2001)
21. Irie H, Watanabe Y, Hashimoto K, J Phys Chem B 107, 23 (2003)
22. Ihara T, Miyoshi M, Triyama Y, Marsumoto O, Sugihara S, Appl Catal B 42, 403 (2003)
23. Zhao Z, Liu Q, J Phys D Appl Phys. 4, 11 (2008)
24. Zaleska A, Recent Pat. Eng. 2, 157 (2008)
25. Mogal S I, Gandhi V G, Mishra M, Tripathi S, Shripathi T, Joshi P A and Shah D O, Ind. Eng. Chem. Res. 53, 5749 (2014)