Original Article

Effect of titanium (IV) isopropoxide molarity on the crystallinity and photocatalytic activity of titanium dioxide thin film deposited via green sol–gel route

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ABSTRACT

In this paper, the effect of titanium (IV) isopropoxide TTIP molarity on the crystallinity and TiO\textsubscript{2} thin film properties deposited via green sol–gel route was reported. The green sol–gel route is a pioneering approach for eco-friendly coating where solvent is not utilized in the sol formulation. This is in contrast to the common TiO\textsubscript{2} sol formulation where solvent is used despite the long term harmful the environment. TiO\textsubscript{2} solution with different TTIP molarity of 0.2 M, 0.3 M, 0.4 M and 0.5 M were utilized during coating deposition. Deposition were conducted for ten times using dip coating and treated at 500 °C (1-h). The crystalline phases and phase content were characterized using X-ray diffraction (XRD) and reference intensity ratio (RIR) equation. Crystallites size was obtained by Scherrer’s equation while coating morphologies was analyzed using scanning electron microscope (SEM). The photocatalytic activity was conducted by the degradation of methylene blue (MB) towards UV-light and visible light. At higher TTIP molarity (0.5 M), higher crystallinity of mixed anatase (∼17 nm) and rutile (∼29 nm) phases were obtained along with homogeneous coating (cracking and visible pore). Also, higher MB degradation were obtained at UV-light (95%) and visible-light (86%) irradiation. In conclusion, higher TTIP molarity produced TiO\textsubscript{2} film with higher crystallinity, small crystallite size, cracking morphology thus contribute good performance in photocatalytic activity. Findings in this work shown that TiO\textsubscript{2} thin film deposition is possible conducted without the use of solvent through optimized formulation of only precursor, acid and water. This is beneficial for the environment sustainability.

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1. Introduction

Water crisis or water pollution have become a most frightening threat to health and environment. Nowadays, increased in water contaminant and colouring in residual waters from...
industries have been reported [1–3]. Many approaches have been used to eliminate the contaminant and colourants in water like adsorption, flocculation, ozonation and photocatalysis [4]. Photocatalysis promising an efficient and economic method to decompose water contaminant by transform them to benign substances [5].

Introducing titanium dioxide (TiO₂) as a photocatalyst, befitted fascinated attention due to non-toxicity, low cost, simple synthesis, high catalytic activity and high photo-thermal stability [6–8]. Crystallinity, morphology, crystallite size and surface area of the TiO₂ thin film have a substantial influence in determining the photocatalytic performance [9,10]. For example, high crystallinity of TiO₂ polymorphs and small crystallite size with large surface area exhibit good photocatalytic [11]. Lorena [12] claimed that, rapid degradation of methyl orange with the fastest degradation rate observed at the cracking surface deposited with glass substrate. The cracking structure is expected to reduce the surface area exposed to light and photocatalytic activity [13]. It is also reported that the film consists of anatase crystal with small size of ∼19 nm [12].

TiO₂ exist with three different polymorphs: anatase, rutile and brookite. These three polymorphs promise a photocatalytic reaction based on its properties. Hanoar [14] reported that mixed TiO₂ polymorphs give a good sign in photodegradation of methylene blue compared to single polymorphs. Similar finding is affirmed by Fischer [15], where anatase mixed rutile reduced the photo-generated electrons holes and increased light absorption. A mixture of rutile and brookite as well as anatase and brookite also reported to generate fast degradation rate in organic molecules [14–16]. About 70:30 phases content of anatase to rutile, 91:9 phases content of anatase to brookite and 61:27:12 phase content of anatase to rutile to brookite had generated high photocatalytic performance by >39% degradation of methylene blue at 1-h irradiation by UV-light [15]. Few researchers had also reported that 70:30 content ratio of anatase to rutile exhibit >65% of photodegradation above 1-h irradiation at UV-light [9,10], while pure brookite was reported exhibit 92% degradation of methylene blue under 4-h irradiation at visible light [6]. Thus, it can be observed that all three polymorphs do act as a reaction agent however the photodegradation activity is dependent on the TiO₂ phase’s content.

TiO₂ thin film deposited by sol–gel dipping is the most conventional method that offers low temperature processing, provides high surface homogeneity, easy coating in large surface area and low cost [3]. Manasi [13] had found that the TiO₂ nanoparticles prepared via sol–gel route is highly crystalline and have smaller crystallite size compared to the one prepared by hydrothermal method. In sol gel, precursor, solvent, water and catalyst are the known basic parameters which can control the TiO₂ properties for photocatalytic activity such as phase content, phase transfer kinetics, particle size distribution, surface area, morphology, and crystallinity of the TiO₂ thin film. Precursor were used to derive the TiO₂ polymorphs and its crystallinity reported by Hafizah [11]. There are many types of precursor that have been used such as titanium(IV) isopropoxide (TTIP), titanium tetrachloride, titanium tetrabutoxide and titanium alkoxides. TTIP promising a good precursor in producing stable solution at low hydrolysis ratio [17]. In addition, solvent [18] catalyst [7] and water [14] are also functioning in hydrolysis and influencing the condensation rate in forming a stable TiO₂ solution.

Solvent have been reported to slow down the rate of hydrolysis and condensation due to the single phase deposited and low specific surface area of the produced TiO₂. Ethanol promotes anatase crystalline at low temperature (∼350 °C and 400 °C) compare to isopropyl alcohol and 2-ethoxycethanol. It is also favours the growth of rutile with lower growth rate compare to methanol. 100% of ethanol produced anatase crystalline while 100% of methanol produced 100% of rutile [19]. However, it is also reported that the used of ethanol can hinder the anatase formation and produce larger nucleus formation and critical particle size of anatase and form amorphous structure. Using ethanol and methanol exhibit >80% methylene blue degradation at 3-h irradiation in pure anatase due to UV light [8]. Nevertheless, it should be noted that organic solvents are volatile organic compounds (VOCs) that can harmful the environment. Based on Babu and Redy [20], solvents from different chemical groups can differ markedly in their characteristics and show varied physiological and toxicological properties, which all too often are neglected in daily life. For example; Plotka [18] stated that organic solvents act as modifier (co-solvent) for carbon dioxide extraction to achieve greenness but due to the high percentage of solvent used to increase the solubility of the target compound had lead towards high toxicity. This is unhealthy and harmful to human and environment. Consequently, it is vital to practice green chemistry approach in work related to TiO₂ deposition. In this pioneering work, first green chemistry principle which is prevention (it is to better to prevent waste than to treat or clean up waste after it has been created) is applied where the use of solvent is avoided during the sol formulation. This is in contrast to the common formulation sol utilized in most work related to TiO₂ thin film deposition where solvent is almost a compulsory ingredient.

At present, few researchers had reported an alternative method in replacing solvent by utilizing additives, dopants and stabilizers in favours to growth mixed polymorphs with different band gap for photocatalytic performance in UV-light and visible light [4,21,22]. Yu [22] reported that TiO₂ doped with Au will exhibit strong absorption of the visible light and thus increased photocatalytic performance under the visible light illumination. 95% and 97% of Rhodamine B was degrade at UV and visible light with the Au decoration. Next, stabilizer was used to replace the solvents on promoting the anatase and rutile phase precipitation on TiO₂ coating films [22]. It can be concluded that, phase content and photocatalytic performance can be acquired without the use of solvent, but critical or complex formulation was derived.

Therefore, 5th principle of green chemistry (waste prevention, design of safer, non-persistent, biodegradable chemicals and inherently safer chemistry for accident prevention) was introduced in this research to minimize the solvent utilization during TiO₂ coating [18]. Deposited TiO₂ thin film with solvent free (without solvent) would be ideal to green coating technology. Moreover, this work employs simple formulation in developing less chemical consumption based on this principle. Basic parameters such as precursors, catalyst and water are required to produce green TiO₂ thin film.
In the basic parameters, concentration of precursors paid a critical effect in TiO₂ properties. Concentration of precursor helps in determining TiO₂ structure, crystallite size and crystallinity that can have enhanced photocatalytic performance. Hafizah [11] reported that crystallite size depends on the concentration of TTIP precursor. Decreased in TTIP concentration will decrease the crystallite size. In contrast, Fagnern [3] claimed that increased the TTIP concentration from 2 mol to 3 mol had increase the anatase content with an average crystallite size of ~20 nm. These resulted producing high photodegradation on Reactive Blue19 solution at 88% after 5 h irradiation by UV-light [3]. Moreover, TTIP concentration also influenced the surface morphology of the TiO₂ thin film. 1 mol of TTIP produced no surface cracking while 2 mol and 3 mol of TTIP shown cracking due to internal stress and film shrinkage [3]. It is found that most of the works on the effect of TTIP concentrations were conducted during deposition of TiO₂ thin film with solvent in the formulation.

Therefore, in this work, effect of TTIP molarity on the crystallinity and photocatalytic activity of TiO₂ thin film deposited without solvent were studied. This is in line with an effort to attain green TiO₂ coating for photocatalytic activity via UV-light and visible light applications.

2. Methodology

2.1. TiO₂ thin film preparation

TiO₂ solutions were prepared by sol–gel method. Titanium (IV) isopropoxide (TTIP) (Sigma–Aldrich Co.), hydrochloric acid (37% HCl) and deionized water (DI) are used as titanium precursor, catalyst and hydrolysis medium respectively. In general, TiO₂ solutions were prepared by dissolving TTIP to DI water under constant stirring for 30 min at 25 °C followed by 0.4 ml of HCl. The solutions were keep on continuous stirring for 3 h before they kept in room condition for 48 h ageing process. Varied molarity of TTIP was prepared by using different ratio of deionized water to TTIP volume shown in Table 1. Next, TiO₂ solution with different TTIP molarity of 0.2 M, 0.3 M, 0.4 M and 0.5 M are deposited on the glass slides, 25.4 mm × 10 mm × 10 mm in size to examine influence of TTIP molarity on the crystallinity, crystallite size, morphology and photocatalytic activity of TiO₂ thin film. The dip coating procedure was carried out by using a mechanical dip coater machine employing 30 mm/min dipping speed and 5 s dwelling time. The coated substrates were then allowed to dry for 24 h followed by oven dry at 110 °C for 30 min. The coating procedures are repeated for ten times to produce TiO₂ thin film coating. Heat treatment process was carried out at 500 °C for 1 h with a heating rate of 5 °C/min.

2.2. Characterization of TiO₂ thin film

Analysis of the crystalline structures was performed by XRD diffractometer (PANalytical X’PERT PRO MPD Model PW 3060/60) with wavelength of Cu Kα (~1.54060 Å at 30 mA and 40 kV) radiation in 2θ range from 10° to 80°. Further analysis on crystalline structures was affirmed by Raman Spectrometer (UniRAM-3500) with 532 nm to match the resulted obtained from XRD diffractometer. Next, phase content of TiO₂ thin film were calculated from the integrated intensities of the anatase (101), rutile (110) and brookite (121) diffraction peaks by reference intensity ratio (RIR) method shown in Eqs. (1)–(3):

\[
W_R = \frac{A_R}{0.884A_A + A_R} \quad (1)
\]

\[
W_A = \frac{0.886A_A}{0.886A_A + A_R} \quad (2)
\]

\[
W_B = \frac{2.721A_B}{0.886A_A + A_R + 2.721A_B} \quad (3)
\]

where \(W_B, W_A, W_R, A_R, A_A, A_B\) were representing the mass fraction and integrated intensity for the rutile, anatase and brookite respectively. The average of crystallites size, \(L\) were calculated at strongest XRD line [(101) at 25°], [(110) at 27°] and [(121 at 30°)] by Scherrer’s equation (4):

\[
L = \frac{K\lambda}{\beta\cos \theta} \quad (4)
\]

where \(L\) is the mean size of the crystalline with \(K\) denoted as a constant with a value of 0.94 and \(\lambda\) is the wavelength of X-rays. \(\theta\) is the Bragg angle while \(\beta\) is the line broadening at half the maximum intensity (FWHM). Morphologies of the TiO₂ thin film structured was studied by scanning electron microscopic (SEM) Carl Zeiss EVO 50 at an accelerating voltage of 10 kV.

2.3. Photocatalytic activity

Photocatalytic activity was evaluated by degrading the methylene blue (MB) solutions under UV-light (Philips, 58 W) and visible light (OSRAM, 200 W) conditions at 5-h irradiation. The degradation of MB obtained by residual absorbance was analyzed by SHIMADZU UV-1700 UV-Vis spectrometer at 664 nm. The decrease in absorbance indicate the degradation of MB. The percentage of MB degradation was calculated by Eq. (5):

\[
\%MB\ dep = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100 \quad (5)
\]

where \(C_0\) represents the initial concentration after the equilibrium adsorption, \(C\) represents the reaction concentration of MB solution, \(A_0\) represents the initial absorbance, and \(A\) represents the changed absorbance of the MB solution.

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<th>Table 1 – Varied molarity of TTIP prepared by different ratio of DI and TTIP volume.</th>
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3. Results and discussion

3.1. Crystallinity of TiO$_2$ thin film

Fig. 1 shows the XRD pattern and Raman spectrum of TiO$_2$ thin film with different TTIP molarity heat treated at 500 °C (A: anatase, R: rutile, B: brookite). Increased in TTIP molarity had increased the crystallinity of TiO$_2$ phases defined by the number of crystalline peaks shown in Fig. 1(a). For 0.2 M, mixed anatase and rutile are observed where anatase are detected at peak 25°, 48°, 54° and rutile at peak 27°. The present of rutile is confirmed by Raman spectrum detected at 448 cm$^{-1}$ shown in Fig. 1(b). For 0.3 M, mixed of three polymorphs are observed which are anatase, rutile and brookite. Brookite presence is identified at peak 31°. This is confirmed by Raman spectrum detected at 248 cm$^{-1}$ and 321 cm$^{-1}$. For 0.4 M and 0.5 M, mixed anatase and rutile (without brookite) are observed. Where anatase were seen at peak 25°, 48°, 54°, 56°, 59°, 63°, 68°, 73° while rutile was seen at 27°, 35°, 37°, 41°, and 44°. Number of crystalline peaks identified represent the crystallinity of TiO$_2$ thin film [11]. Hafizah [11] claimed that, increased of TTIP concentration would increase the viscosity of the TiO$_2$ solution hence produced more crystalline peak of the TiO$_2$ thin film. This is also in agreement with Fagnern [3] findings where increased in the concentration of TTIP precursors by 1 mol until 3 mol had increased the crystallinity of anatase. Thus, it is believed that higher of TTIP molarity produced more crystalline peak during deposition of TiO$_2$ without solvent.

Fig. 2(a) shows the phases content of anatase, rutile and brookite calculated from XRD lines located at peak 25° for anatase, 27° for rutile and 31° for brookite. For 0.2 M, 76:24 percent of the phases content was observed and identified as anatase and rutile. For 0.3 M, 53:39:8 percent of the phases content was observed and assigned as anatase, rutile and brookite. Decreased in anatase content was caused by transformation of rutile to brookite phase as had been also reported by Han [14]. For 0.4 M, 59:41 percent of the phases content was observed and identified as anatase and rutile. For 0.5 M, 63:37 percent of the phases content was observed and identified as

![Fig. 2 - Phases content and crystallite size of TiO$_2$ thin film with different TTIP molarity.](image-url)
anatase and rutile. Increased in anatase content from 0.4 M to 0.5 M of TTIP was due to higher anatase crystallinity observed at XRD pattern. This agrees with Wong [23] findings where increased in the concentration of precursors had increased the anatase crystallinity with reduced rutile phases content.

Fig. 2(b) shows the crystallite size of TiO₂ thin film with different TTIP molarity located at peak 25° for anatase, 27° for rutile and 31° for brookite. For 0.2 M, crystallite size of anatase and rutile were identified at 21 nm and 34 nm. The crystallite size of anatase and rutile decreased in size (~14 nm for anatase and ~11 nm for rutile) at 0.3 M due to the presence of brookite. At higher molarity at 0.5 M crystallite size of anatase and rutile reduced to ~17 nm and ~29 nm. This observation agrees with Hafizah and Fagnern findings where increased in precursor molarity had decreased the TiO₂ crystallite size.

3.2. Photocatalytic activity

Fig. 3 shows the percentage of MB degradation for UV-light spectrum and SEM images of TiO₂ thin film at different TTIP molarity. At 0.2 M, 81% of MB solution was degraded, while at higher molarity of TTIP 0.4 M and 0.5 M, the degradation of MB solution increased to above 90% (Fig. 3(a)). 0.5 M of TTIP shows the highest MB degradation of 97%. The higher degradation of MB solutions is due to the higher crystallinity presence at higher TTIP molarity. Moreover, it is also due to the small crystallite size obtained during the TiO₂ deposition (~17 nm for anatase and ~29 nm for rutile). The surface morphology of the TiO₂ thin film revealed that at 0.2 M, the surface of TiO₂ thin film shown cracking with no pores observed (Fig. 3(b)). In contrast, 0.3 M less cracking was identified. At higher molarity of TTIP (0.4 M and 0.5 M), severe cracking and visible pores were observed. Large pore produced was due to internal stress exerted caused by high viscosity of TTIP content [11]. It has been suggested by Lorena [12] that, rapid degradation of methyl orange obtained when high cracking and large pore deposited on the glass substrate due small surface area exerted lead to high absorption during photocatalytic activity. Thus, this agrees with microstructure observed and high MB degradation at 0.5 M by UV-light.

Fig. 4 shows percentage of MB degradation for visible light spectrum of TiO₂ thin film at 0.3 M and 0.5 M TTIP. These two formulations were selected for visible light analysis due to the presence of brookite at 0.3 M and highest MB degradation obtained at 0.5 M during UV-light irradiation. For 0.3 M, 65% of MB solution was degraded for visible light while 0.5 M show 86% of MB degradation. Higher in MB degradation presented at 0.5 M of TTIP molarity was caused by the higher crystallinity peaks obtained during this formulation [14]. Thus, it is shown that TiO₂ thin film deposited with higher TTIP molarity using formulation without solvent, dopants or stabilizers had been able to produce good photocatalytic activity in visible light.

4. Conclusion

TiO₂ film with different TTIP molarity (without solvent) have been successfully deposited on glass substrate via sol–gel dip-coating technique. The higher TTIP molarity had increased the crystallinity of mixed phases TiO₂ (anatase and rutile) produced. Small crystallite size (~17 nm of anatase and 29 nm of rutile) and cracking surface of TiO₂ thin films were also observed with higher TTIP molarity. For photocatalytic activity, TiO₂ thin films with higher TTIP molarity had increased MB degradation ≥97% in UV-light. Further works will be directed on optimizing other process parameter (for example increase in soaking time with 0.3 M of TTIP formulation) to achieve high MB degradation (>95%) in visible light application. In conclusion, this work had also shown that TiO₂ thin film deposition is possible to be conducted without the use of solvent.
through optimized formulation of only precursor, acid and water (despite the common formulation which utilize solvent and less eco-friendly method). This green sol–gel route applies the prevention method of green chemistry principle, thus is beneficial for environment sustainability. Therefore, this green sol–gel route is recommended to be utilized for related work in TiO₂ thin film deposition.

**Conflicts of interest**

The authors declare no conflicts of interest.

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