

Physico-Chemical Properties of TiO₂ Coatings Derived From Acid Catalyst-Free Precursor via Spin Coating

Alfredo Liboon Jr ^{1,2,*} , Shena Ramyr Cabo ² , Rolando Candidato, Jr ² 

¹ College of Education, Jose Rizal Memorial State University-Tampilisan Campus, alfredoliboonjr@jrmsu.edu.ph (A.L.Jr)

² Department of Physics, College of Science and Mathematics, Mindanao State University-Iligan Institute of Technology, shenaramyr.cabo@g.msuiit.edu.ph (S.R.C.); rolandojr.candidato@g.msuiit.edu.ph (R.C. Jr);

* Correspondence: alfredoliboonjr@jrmsu.edu.ph;

Received: 10.10.2021; Accepted: 1.11.2021; Published: 7.06.2022

Abstract: The present method of producing titania (TiO₂) coatings involves the addition of an acid catalyst to prolong the shelf life of the initial precursor. However, this method has complex chemical routes that favor rutile TiO₂ and result in higher bandgap energy. In this current work, unheated and heated TiO₂ coatings were successfully prepared via spin-coating using an acid catalyst-free titania precursor. The TiO₂ coatings were thoroughly investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman, Fourier transformed infrared (FTIR), and UV-Visible spectroscopic techniques. From XRD and Raman data, the unheated coating is amorphous, while the heated sample consists of anatase polymorph of TiO₂. The FTIR results revealed traces of organic residues for the heated sample due to the organic nature of the precursor used. SEM showed that both samples were not uniform, porous, and consisted of spherical micro/nanostructured particles with some aggregation ascribed to the nature of the precursor. Diffuse reflectance indicated an absorption band edge at the UV region and showed similar absorption spectra to commercial TiO₂ powder. However, a redshift of the UV-Vis reflectance spectra of the heated sample was observed. Using the baseline approach, the indirect optical bandgap of the unheated TiO₂ coating decreased from 3.31 to 3.26 eV (± 0.2 eV) after the heat treatment, which is due to the crystallization of the sample into anatase TiO₂.

Keywords: anatase, TiO₂; spin coating; acid catalyst-free, baseline approach

© 2022 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Semiconductor-mediated photocatalysis has become an effective technique for water and air pollutant degradation, as reported by Paumo *et al.* [1], Imoisili *et al.* [2], and Kotzias *et al.* [3], for water splitting for energy harvesting applications as described in the papers of Garofalo *et al.* [4], Yu *et al.* [5] and Eidsvåg *et al.* [6]. It has also been found to be effective as an anti-reflective coating for solar energy harvesting, as disclosed by Zhang *et al.* [7] and Abu-Shamleh *et al.* [8]. Its central concept generally relies on the light absorption ability of semiconductor material that induces photo-excitation and a series of chemical reactions. Due to its optical, physical, and chemical properties, titanium dioxide (TiO₂) has been extensively studied in semiconductor photocatalysts. This includes non-toxicity, chemical stability, high catalytic activity, and a widely tunable bandgap, suitable for various environmental and energy applications. For practical applications, the properties of TiO₂ strongly depend on the micro-/nano structure and crystallinity of TiO₂, which are dictated by the initial chemistry of the precursor used and the deposition method employed.

Generally, TiO_2 forms in three crystalline structures, namely anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic), as described by Reyes-Coronado *et al.* [9]. Sun *et al.* [10] describe that the composition of these crystalline phases is characterized by periodic arrangements of distorted TiO_6 octahedral units. Due to difficulty in synthesis, brookite is rarely reported as a photocatalyst, making rutile and anatase the more common crystalline TiO_2 phases. At room temperature, the theoretical bandgap energy E_g is 3.0 eV for rutile and 3.2 eV for anatase making TiO_2 primarily active in the ultraviolet light region.

Despite anatase's relatively large bandgap, it exhibits higher photocatalytic activity than rutile due to its higher surface adsorption capacity of hydroxyl groups, as Hanaor *et al.* [12] argued. Anatase also has a lighter effective mass m_0 (where m_0 is the electron mass) than rutile; hence, the photoexcited charge carriers can easily migrate and transfer from the internal structure to its surface to participate in photocatalytic reactions as explained by Hanaor *et al.* [12]. This could result in a slower recombination rate of the photogenerated carriers within anatase as described by TiO_2 Zhang *et al.* [13]. Luttrell *et al.* [14] added that the photocatalytic activity of anatase increases for films up to 5.0 nm thick while the rutile counterpart reaches its maximum activity at 2.5 nm. This indicates that charge carriers excited deeper in bulk contribute to surface reactions in anatase than in rutile. These reports suggest that its phase structure dictates the photocatalytic activity of TiO_2 .

The control of the phase structure and composition of TiO_2 coatings during deposition is crucial as it dictates its photocatalytic properties. Hence, choosing an appropriate yet straightforward preparation and deposition method is essential in obtaining TiO_2 coatings with desirable properties. Sol-gel spin-coating deposition is a relatively simple and easy technique. One can easily control the chemistry of starting precursor solution and spin speed, thereby controlling the coating's phase composition and microstructural features. Sol-gel spin coating of titania usually uses alkoxide precursors where the aid of an acid catalyst controls the hydrolysis and condensation reactions of alkoxide with water, as demonstrated by Zhou *et al.* [14]. However, investigating the characteristics of TiO_2 coatings synthesized from a straightforward route (without acids or base) has not been explored extensively. The acid catalyst is usually incorporated in sol-gel alkoxides precursors to control the hydrolysis (acid-catalyzed hydrolysis), as stated in the paper of Juma *et al.* [15]. It is also used as a stabilizing agent to prolong the shelf life of the solution thus preventing the fast process of gelation obtaining transparent TiO_2 thin films, as expounded by Zhou *et al.* [14] and Juma *et al.* [15].

Nevertheless, the use of different acids affects micro-structural and the optical and photocatalytic properties of a pure or undoped TiO_2 . For instance, the addition of HCl, acetylacetone and/or acetic acid as acid catalysts to titania precursor resulted in larger bandgap energy (between 3.3 eV – 3.7 eV) [17–24] than the reported theoretical bandgap energy (3.0 – 3.2 eV) of undoped or pure TiO_2 as reported by the following literature: Elfanaoui *et al.* [16], Golobostanfard & Abdizadeh [17], Praveen *et al.* [18], Phattepur *et al.* [19], Tahmasebisad *et al.* [20], Nakaruk *et al.* [21] and Rashid *et al.* [22]. Although Zouheir *et al.* [23] had revealed a lower bandgap of TiO_2 with increasing sulfuric acid, this was attributed to the dominance of the rutile phase of the synthesized TiO_2 . Although titania precursor containing strong acids such as HCl and HNO_3 tends to form smaller particle size and cause a redshift in absorption edge in the UV spectra compared to other acids (i.e., HPO_4 , H_3BO_3 , CH_3COOH), they favor the formation of rutile TiO_2 with less porosity as reported by Golobostanfard & Abdizadeh [17] and Eaimsumang *et al.* [24]. These TiO_2 films also contain traces of acids even after calcination Golobostanfard & Abdizadeh [17]. In addition, the recent study of Kilic and Kuru [25] that

involves the addition of acids such as CH_3COOH or NH_4OH to control the pH of TiO_2 solution showed the evolution of the rutile phase. Preparing titania precursors without an acid catalyst may have less solution stability than the precursor with an acid catalyst. However, the stability can be improved when experimental conditions such as type of solvent used, mixing process, humidity, stirring speed, temperature, and deposition technique are controlled. TiO_2 with micro/nanostructures and anatase phase can also be possibly obtained using catalyst-free titania precursor. Obtaining TiO_2 coatings from acid-free precursors and investigating their characteristics will provide a rationale for a more straightforward and more cost-effective method for large production and practical applications of TiO_2 . Pedanekar *et al.* [26] emphasized that production of TiO_2 thin films or coatings photocatalyst has several advantages over TiO_2 powder photocatalyst, including being less expensive due to reduced material usage, avoiding costly recycling and recollection after degradation, carrying less physical impairment, providing comparatively better long-term performance, and allowing for device miniaturization.

In this work, TiO_2 coatings are developed using catalyst-free solution precursors via spin coating deposition. The chemistry of the starting solution precursor is investigated in relation to the chemical, structural and optical characteristics of the TiO_2 coatings. In addition, this study explores a new method called the "baseline approach", described by Makula *et al.* [27], for estimating the bandgap energy. The obtained bandgap energy is compared to the values calculated using the Tauc plot method.

2. Materials and Methods

2.1. Deposition method of TiO_2 coatings.

The TiO_2 coatings were prepared on glass substrates by mixing titanium isopropoxide (TIP) (Sigma-Aldrich, 97%) and absolute ethanol (Scharlau, 99 %, ACS reagent) without further purification through the spin coating technique. Because alkoxides are immiscible in water, alcohol is usually employed as a solvent. Alcoholysis can take place when metal alkoxides are dissolved in different alcohol, not in their parent anhydrous alcohol, as explained by Livage *et al.* [28]. In this case, this results in a decrease in the hydrolysis sensitivity of the starting reagents. In this method, a 1.2 M solution was made by mixing TIP and absolute ethanol (AE) in volumes of 20 mL and 30 mL, respectively, in a closed or covered beaker. Using a pipette, the TIP was slowly dropped into the AE under constant stirring of 100 rpm and was continuously stirred for 3 hours. It was then set aside for 2 hours. The glass substrates with dimensions 1.5 in by 1.5 in were prepared, thoroughly cleaned with acetone and deionized water, and heated prior to spin coating. During the spin coating process, the prepared solution was poured dropwise onto the glass substrate fixed on a target holder and rotated at 3000 rpm for 30 seconds. The as-deposited coating was then subjected to drying at 100°C using a hot plate for 5 minutes. This step was repeated until 5 cycles (limiting the number of spin cycles since going beyond 5 cycles causes the surface coatings to be pulled off the substrate). Finally, the spin-coated sample was post heated at 450°C for 5 hours using an electric furnace and referred to as a heated sample, and cooled naturally.

The parameters such as spin speed, dynamic dispense deposition, pre-heating, post-heating temperature, and solution concentration were selected based on the initial experiments conducted. In particular, the spin speed of 3000 rpm was used because speeds lower or higher than 3000 rpm results in detachment of the coatings from their substrate. The pre-heating

temperature (100 °C) was chosen to remove isopropanol. A modified dynamic dispense step was employed since using static dispense and dropping off the solution while the substrate is spinning slowly resulted in detachment of the coatings from the substrate.

In the modified dispense step, the spin speed and time were set first to 3000 rpm and 30s, respectively. Upon starting the spin and using a dropper, the 1.0 mL solution is slowly dropped onto the substrate (1 s interval per drop, approximately 10 drops for 10s). In addition, the final post-heating temperature (450 °C) was selected due to the use of glass substrate and the limitation of the electric furnace used.

2.2. Characterization of coatings.

The structural and phase composition of the coatings was studied by X-ray diffraction. The morphologies of the samples were observed by scanning electron microscope (SEM). The chemical species present in the sample were studied via Fourier transform infrared spectroscopy (FTIR) in transmittance mode from 400–4000 cm⁻¹, was employed. The optical reflectance spectra of the coatings were obtained in the wavelength range of 200–1100 nm via the UV–Vis spectroscopy. From these reflectance spectra, the band gap energies of the TiO₂ coatings were estimated using the Tauc plot method deduced by the Kubelka-Munk function and the method called baseline approach. The Tauc plot method is based on the assumption that the energy-dependent absorption coefficient α can be expressed by the following relation (1.1):

$$(\alpha h\nu)^\gamma = B(h\nu - E_g) \quad (1.1)$$

where h is the Planck constant, ν is the photon's frequency, E_g is the bandgap energy, and B is a constant. The γ factor depends on the nature of the electron transition and is equal to 1/2 or 2 for the direct and indirect transition band gaps, respectively, as described by Makula *et al.* [27]. The bandgap energy is usually determined from diffuse reflectance spectra. According to Alcaraz de la Osa *et al.* [29], the measured reflectance spectra can be transformed into the corresponding absorption spectra by applying the Kubelka-Munk function ($F(R_\infty)$), eq. 1.2)

$$(F(R_\infty)h\nu)^{\frac{11}{\gamma}} = B(h\nu - E_g) \quad (1.2)$$

where the R_∞ is the reflectance of the sample and K and S are the absorption and scattering coefficients, respectively. Then, replacing α in eq.1.1 with $F(R_\infty)$ in eq 1.2, yields the form

$$(F(R_\infty)) = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \quad (1.3)$$

From these reflectance spectra, the bandgap energy was estimated. The bandgap energy (E_g) is one of the highly significant parameters in discussing photocatalytic properties of TiO₂. An accurate determination of the E_g is crucial in describing or predicting the absorption characteristics of TiO₂. The direct use of the Tauc plot to estimate the bandgap of TiO₂ and other semiconductors may lead to inaccurate results, particularly for defected, doped, bulk, or surface modified samples, as demonstrated by Makula *et al.* [27] since all these modifications may introduce intraband gap states that reflect in the absorption spectrum as an Urbach tail,

(an additional broad absorption band). The presence of the Urbach tail influences the Tauc plot and, therefore, must be taken into account in calculating the E_g . In such cases, a direct application of the Tauc method may result in an inaccurate estimation of E_g (i.e., underestimation). Hence, a new and more accurate baseline approach method is considered. The baseline approach still uses the Tauc method for the linear fit of the fundamental peak (steep curve along the ordinate). Still, a linear fit as an abscissa is added for the slope below the fundamental absorption (see Figure 1). An intersection of the two fitted lines and extrapolation along the x-axis gives the bandgap energy estimation. All the fittings were done at $R_2 = 0.99$.

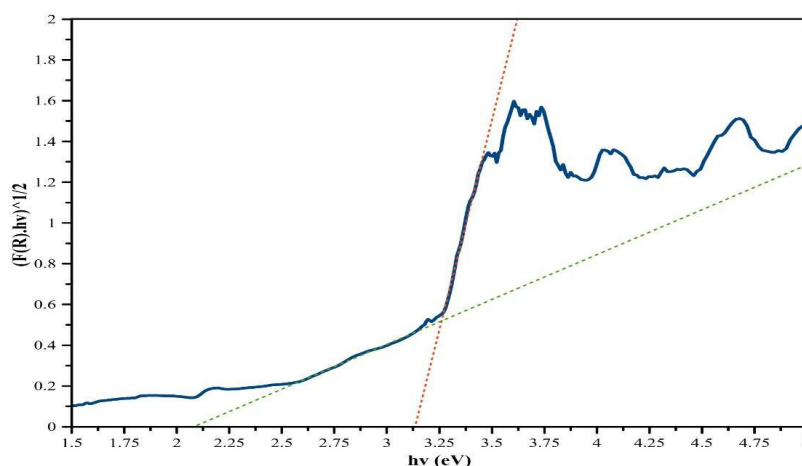


Figure 1. Energy band gap calculation by Tauc and baseline approach.

3. Results and Discussion

3.1. X-ray diffraction.

Primary structural information was given by XRD patterns of the spin-coated TiO_2 coatings, as shown in Figure 2. The unheated TiO_2 coating displays no distinct peaks, indicating that the sample is amorphous. In contrast, the heated sample displays characteristic patterns of TiO_2 in the tetragonal anatase phase. The evolution of the intense peak at about 32° (2θ) for the heated sample is attributed to the glass substrate. The results indicate that heating at 450°C causes crystallization and produces a single anatase phase. This result agrees with previous reports of the stable formation of anatase TiO_2 at 450°C by Sun *et al.* [10] and Sood *et al.* [30], and Khalaghi *et al.* [31].

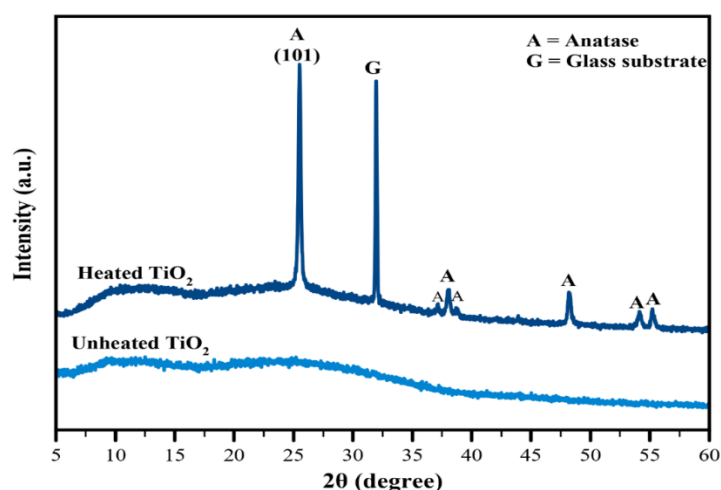


Figure 2. XRD pattern of unheated (light blue) and heated (dark blue) TiO_2 coatings.

3.2. Microstructural characteristics (SEM).

The micrographs of the unheated and heated TiO_2 coatings are shown in Figure 3. It can be observed that both the unheated and heated coatings are not uniform and have cracked surfaces. This uneven distribution of the surface of TiO_2 coatings can be due to the nature of precursor and deposition techniques employed. The lack of acid catalyst as a stabilizing agent in the titania precursor makes it sensitive to humidity. Dropping off the solution precursor to a spinning substrate exposes the solution to a humid environment which causes it to precipitate while the centrifugal force pulls it off from the middle of the substrate across the entire surface quickly. The crack surface might also be attributed to the expansion of the substrate. At lower magnification, it can be observed that both coatings are porous, as depicted in red circles. In addition, the high magnification image revealed that the unheated TiO_2 coating has micrometric particles that appear to be clusters of less fused spherical particles. After the post-heat treatment, the sample consists of strongly fused and interconnected spherical particles of similar sizes with some aggregation, as shown in yellow circles. This formation of micro/nanoparticles can be due to the alcoholysis reaction that occurs when titanium isopropoxide is dissolved with anhydrous alcohol. The alcoholysis reaction reduces the large molecule (bulky) of titanium isopropoxide to small molecule (less bulky) titanium ethoxide, resulting in a less steric hindrance. As a consequence, and with the aid of stirring, fine particles in TIP-ethanol solution are formed.

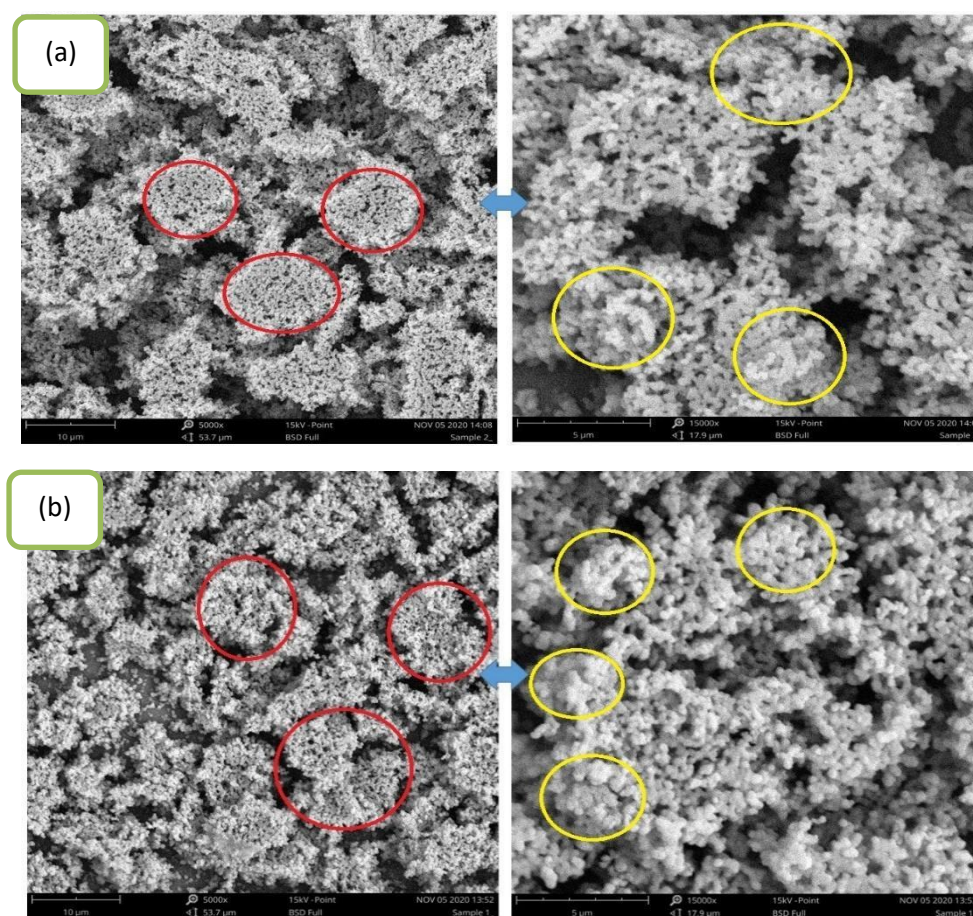


Figure 3.. SEM micrographs of (a) unheated and (b) heated TiO_2 coatings magnified at 500x (left) and 15000x (right).

3.3. FTIR spectroscopy.

Figure 4 shows the FTIR transmittance spectra of the unheated and heated TiO_2 coatings and the anatase TiO_2 commercial powder used as reference. The unheated and heated TiO_2 coatings exhibit a strong, broadband from 400–900 cm^{-1} . This broadband corresponds to the formation of Ti-O and Ti-O-Ti bonds in the spin-coated TiO_2 coatings. The broadband in the unheated sample between 3000 cm^{-1} and 3600 cm^{-1} , and the peak at 1626 cm^{-1} is attributed to the symmetrical and asymmetrical O-H stretching modes of hydroxyl group and H-O-H scissoring vibration, respectively. These vibrations disappeared after the post heat treatment of the sample. In addition, the post-heat treatment caused the peak at 2342 cm^{-1} , which is attributed to the vibrations of C=O bonding as residues, as also observed by Sood *et al.* [30], to become more intense. The heating also caused the evolution of peaks between 1200–1500 cm^{-1} which is associated with $-\text{CH}_3$ stretching. It shifted the shoulder peak of the unheated sample from around 1000 cm^{-1} to a lower wavenumber at 800 cm^{-1} , which shows better agreement with the vibrational modes of anatase TiO_2 commercial powder. The heated sample's residues ($-\text{CH}_3$ and $-\text{CO}$) can be associated with the by-product hydrocarbons due to an organic precursor. Similar findings were also reported in earlier studies by Juma *et al.* [15] and Majeed Khan *et al.* [32] that used organic titania precursors. A higher temperature ($> 450^\circ\text{C}$) is required in order to eliminate these residues and obtain pure TiO_2 . However, it is not advisable to heat the sample at these temperatures because it may promote phase transition (anatase-to-rutile), as explained by Sun *et al.* [10], and could melt the substrate. This means that TiO_2 obtained from the acid-free precursor is not pure, which is also the same as in precursors with added acid catalyst, as reported by Juma *et al.* [15] and Majeed Khan *et al.* [32].

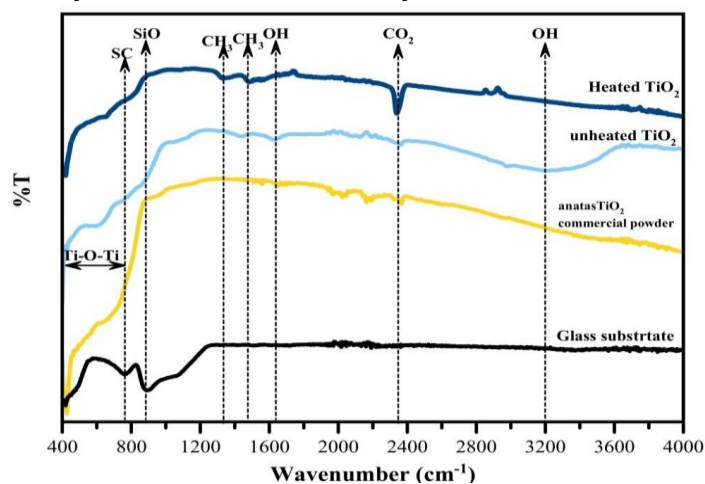


Figure 4. FTIR spectra of the glass substrate anatase TiO_2 commercial powder and the unheated and heated spin-coated TiO_2 coatings.

3.4. Raman spectroscopy.

The Raman spectra of the unheated and heated TiO_2 coatings are shown in Figure 5. There are no significant Raman peaks detected in the unheated sample indicating the low crystalline nature of the sample. After post-heat treatment, five Raman peaks evolved. These peaks are centered at 150 cm^{-1} , 203 cm^{-1} and 636 cm^{-1} , which corresponds to symmetric stretching (E_g) of anatase O-Ti-O , 396 cm^{-1} , which is related to symmetric bending ($B1g$) of anatase O-Ti-O , and peak at 514 cm^{-1} , which is associated to the overlapping, symmetric bending and anti-symmetric bending ($A1g$) of anatase O-Ti-O . These results agree with the

earlier studies of Sun *et al.* [10], Zhang *et al.* [12], Mathews *et al.* [33], and Komaraiah *et al.* [34].

Moreover, Mathews *et al.* [33] described that the strong and sharp Raman peak at 150 cm^{-1} denotes the formation of anatase TiO_2 . No peaks associated with the brookite/rutile phase were detected. This means that the heated TiO_2 coating is in a single anatase phase, as revealed in the XRD.

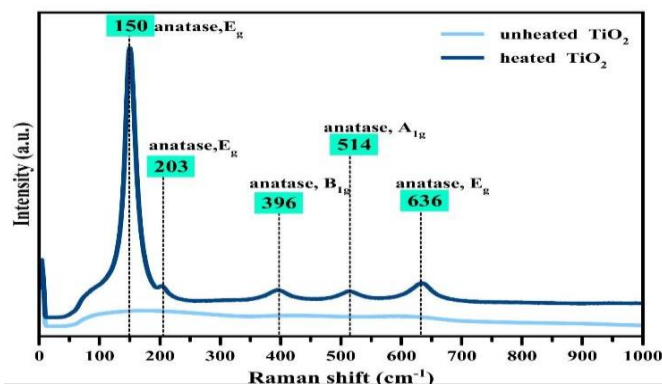


Figure 5. Raman spectra of unheated and heated TiO_2 coatings

3.5. UV-Vis spectroscopy.

Figure 6 shows the UV-Vis reflectance spectra of the spin coated TiO_2 coatings with and without post heat treatment and the anatase TiO_2 commercial powder as reference. Both the unheated and heated TiO_2 coatings showed good agreement with the reflectance spectra of anatase TiO_2 commercial powder. Upon closer inspection, the spectra of the heated sample are slightly red-shifted with respect to the unheated sample, which shows better agreement with that of the spectra of anatase commercial powder. This redshift can be attributed to the crystallization of the amorphous sample into anatase TiO_2 . In addition, all the samples showed a strong absorption edge at the 340–400 nm wavelength range, which corresponds to the UV region of the spectrum. The absorption in this region is a characteristic of TiO_2 due to the electron transition from the valence band to the conduction band.

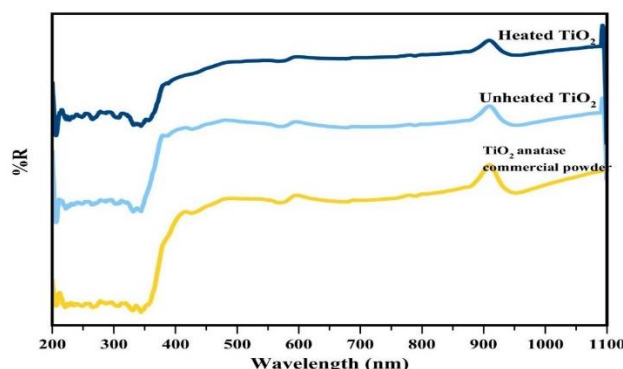


Figure 6. UV-Vis reflectance spectra of the unheated and heated spin-coated TiO_2 coatings and the anatase TiO_2 commercial powder as referenced.

Table 1 displays the calculated bandgap energies by the two methods. Comparing the estimated direct and indirect band gap energies of the spin-coated TiO_2 coatings, both methods revealed greater direct E_g values than indirect E_g . This substantiates the theoretical reports by Zhang *et al.* [12] and Komaraiah *et al.* [34] that TiO_2 is indirect bandgap energy. The calculated values agree with those reported in the literature of Komaraiah *et al.* [34] and Zhu and Gao [35]. In particular, after post-heat treatment of the coating, the indirect bandgap energy reduces

from 3.28 eV to 3.13 eV (± 0.013 eV) by the Tauc method and from 3.31 eV to 3.26 eV using the baseline approach, attributed to the crystallization of amorphous to anatase TiO₂. These values of the heated undoped TiO₂ coating are quite lower than those reported in literature with added acid catalysts by Zhou *et al.* [14], Juma *et al.* [15], Elfanaoui *et al.* [16], Golobostanfard & Abdizadeh [17], Praveen *et al.* [18], Phattepur *et al.* [19], Tahmasebisad *et al.* [20], Nakaruk *et al.* [21], Rashid *et al.* [22], Komaraiah *et al.* [34], Singh and Mehata [36]. Moreover, the 3.26 eV bandgap of anatase TiO₂ coating is very close to that of the reported theoretical bandgap (3.20 eV) of anatase TiO₂.

Meanwhile, comparing the estimated indirect E_g values, the Tauc method underestimates the value to a difference of about ≈ 0.10 eV ± 0.008 eV error, while the E_g obtained by baseline approach overestimates to a lesser difference ≈ 0.02 eV ± 0.0270 eV error in reference to that from anatase commercial powder. This suggests that the baseline approach may be used for a more accurate estimation of the E_g .

Table 1. Calculated band energy of unheated, heated TiO₂ coatings and anatase TiO₂ commercial powder using Tauc plot and baseline approach.

Samples	Tauc Plot		Baseline approach	
	Band gap energy (E_g)		Band gap energy (E_g)	
	Direct	indirect	direct	indirect
unheated TiO ₂	3.51 eV ± 0.0291	3.28 eV ± 0.0017	3.53 eV ± 0.0582	3.31 eV ± 0.0034
heated TiO ₂	3.33 eV ± 0.0044	3.13 eV ± 0.0005	3.33 eV ± 0.0088	3.26 eV ± 0.0105
anatase TiO ₂ com. powder	3.35 eV ± 0.0103	3.23 eV ± 0.0083	3.36 eV ± 0.0206	3.28 eV ± 0.0165

4. Conclusions

TiO₂ coatings were successfully synthesized from acid catalyst-free titania precursors via the spin coating deposition technique. It was confirmed that the unheated TiO₂ coating is amorphous while the heated TiO₂ coating crystallizes in anatase. However, the obtained heated TiO₂ coating was found to contain traces of organic residues, which is attributed to the organic nature of the precursor. Micrographs showed the flat and uneven surface of the amorphous and anatase TiO₂ coatings attributed to the precursor's nature and the deposition technique used. Higher magnification revealed that amorphous TiO₂ coating has a cluster of less fused spherical micro/nanostructures. After the post-heat treatment, fine and connected spherical micro/nanostructural features were observed. The heat treatment resulted in the crystallization of the amorphous TiO₂ into anatase TiO₂, which consequently decreased the bandgap energy from 3.31 eV to 3.26 eV.

Funding

This research was made possible through the Department of Science and Technology (DOST) scholarship under the Accelerated Science and Technology Human Resource Development Program (ASTHRDP).

Acknowledgments

DOST-PCIEERD is acknowledged for partially supporting this work. Ms. Key Simfroso and Dr. Romnick Unabia are also acknowledged for their valuable insights.

Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study, in the collection, analyses, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

References

1. Paumo, H.K.; Dalhatou, S.; Katata-Seru, L.M.; Kamdem, B.P.; Tijani, J.O.; Vishwanathan, V.; Kane, A.; Bahadur, I. TiO₂ assisted photocatalysts for degradation of emerging organic pollutants in water and wastewater. *J. Mol. Liq.* **2021**, *331*, 115458, <https://doi.org/10.1016/j.molliq.2021.115458>.
2. Imoisili, P.E.; Jen, T.-C.; Safaei, B. Microwave-assisted sol–gel synthesis of TiO₂-mixed metal oxide nanocatalyst for degradation of organic pollutant. *Nanotechnol. Rev.* **2021**, *10*, 126–136, <https://doi.org/10.1515/ntrev-2021-0016>.
3. Kotzias, D.; Binas, V.; Kiriakidis, G. Smart Surfaces: Heterogeneous Photo-Catalysis on TiO₂ Based Coatings for De-pollution Purposes in Indoor and Outdoor Environments. *Top. Catal.* **2020**, *63*, 875–881, <https://doi.org/10.1007/s11244-020-01351-7>.
4. Garofalo, E.; Cecchini, L.; Bevione, M.; Chiolerio, A. Triboelectric Characterization of Colloidal TiO₂ for Energy Harvesting Applications. *Nanomater.* **2020**, *10*, 1181, <https://doi.org/10.3390/nano10061181>.
5. Yu, X.; Xing, Q.; Zhang, X.; Jiang, H.; Cao, F. Photoelectrochemical water splitting using TiO₂ nanorod arrays coated with Zn-doped CdS. *J. Mater. Sci.* **2021**, *56*, 11059–11070, <https://doi.org/10.1007/s10853-021-06008-8>.
6. Eidsvåg, H.; Bentouba, S.; Vajeeston, P.; Yohi, S.; Velauthapillai, D. TiO₂ as a Photocatalyst for Water Splitting—An Experimental and Theoretical Review. *Mol.* **2021**, *26*, 1687, <https://doi.org/10.3390/molecules26061687>.
7. Zhang, W.; Hu, K.; Tu, J.; Aierken, A.; Xu, D.; Song, G.; Sun, X.; Li, L.; Chen, K.; Zhang, D.; *et al.* Broadband graded refractive index TiO₂/Al₂O₃/MgF₂ multilayer antireflection coating for high efficiency multi-junction solar cell. *Sol. Energy* **2021**, *217*, 271–279, <https://doi.org/10.1016/j.solener.2021.01.012>.
8. Abu-Shamleh, A.; Alzubi, H.; Alajlouni, A. Optimization of anti-reflective coatings with nanostructured TiO₂ for GaAs solar cells. *Photon- Nanostructures - Fundam. Appl.* **2021**, *43*, 100862, <https://doi.org/10.1016/j.photonics.2020.100862>.
9. Reyescoronado, D.; Gattorno, G.R.; E Espinosa-Pesqueira, M.; Cab, C.; De Coss, R.; Oskam, G. Phase-pure TiO₂nanoparticles: anatase, brookite and rutile. *Nanotechnology* **2008**, *19*, 145605–145615, <https://doi.org/10.1088/0957-4484/19/14/145605>.
10. Sun, S.; Song, P.; Cui, J.; Liang, S. Amorphous TiO₂ nanostructures: synthesis, fundamental properties and photocatalytic applications. *Catal. Sci. Technol.* **2019**, *9*, 4198–4215, <https://doi.org/10.1039/c9cy01020c>.
11. Hanaor, D.A.H.; Sorrell, C.C. Review of the anatase to rutile phase transformation. *J. Mater. Sci.* **2011**, *46*, 855–874, <https://doi.org/10.1007/s10853-010-5113-0>.
12. Zhang, J.; Zhou, P.; Liu, J.; Yu, J. New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂. *Phys. Chem. Chem. Phys.* **2014**, *16*, 20382–20386, <https://doi.org/10.1039/c4cp02201g>.
13. Luttrell, T.; Halpegamage, S.; Tao, J.; Kramer, A.; Sutter, E.A.; Batzill, M. Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO₂ films. *Sci. Rep.* **2014**, *4*, 4043, <https://doi.org/10.1038/srep04043>.
14. Zhou, J.; Song, B.; Zhao, G.; Han, G. Effects of acid on the microstructures and properties of three-dimensional TiO₂ hierarchical structures by solvothermal method. *Nanoscale Res. Lett.* **2012**, *7*, 217, <https://doi.org/10.1186/1556-276x-7-217>.
15. Juma, A.; Acik, I.O.; Mikli, V.; Mere, A.; Krunks, M. Effect of solution composition on anatase to rutile transformation of sprayed TiO₂ thin films. *Thin Solid Films* **2015**, *594*, 287–292, <https://doi.org/10.1016/j.tsf.2015.03.036>.
16. Elfanaoui, A.; Elhamri, E.; Boukaddat, L.; Ihlal, A.; Bouabid, K.; Laanab, L.; Taleb, A.; Portier, X. Optical and structural properties of TiO₂ thin films prepared by sol–gel spin coating. *Int. J. Hydrogen Energy* **2011**, *36*, 4130–4133, <https://doi.org/10.1016/j.ijhydene.2010.07.057>.
17. Golobostanfard, M.R.; Abdizadeh, H. Effects of acid catalyst type on structural, morphological, and optoelectrical properties of spin-coated TiO₂ thin film. *Phys. B: Condens. Matter* **2013**, *413*, 40–46, <https://doi.org/10.1016/j.physb.2012.12.040>.
18. Praveen, P.; Viruthagiri, G.; Mugundan, S.; Shanmugam, N. Structural, optical and morphological analyses of pristine titanium dioxide nanoparticles – Synthesized via sol–gel route. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **2014**, *117*, 622–629, <https://doi.org/10.1016/j.saa.2013.09.037>.
19. Phattepur, H.; Gowrishankar, B.S.; Nagaraju, G. Synthesis of gadolinium-doped TiO₂ thin films by sol–gel spin coating technique and its application in degradation of rhodamine-B. *Indian Chem. Eng.* **2019**, *61*, 167–181, <https://doi.org/10.1080/00194506.2018.1529632>.

20. Tahmasebiazad, N.; Hamedani, M.T.; Ghazani, M.S.; Pazhuhfar, Y. Photocatalytic activity and antibacterial behavior of TiO₂ coatings co-doped with copper and nitrogen via sol–gel method. *J. Sol-Gel Sci. Technol.* **2020**, *93*, 570–578, <https://doi.org/10.1007/s10971-019-05085-1>.
21. Nakaruk, A.; Lin, C.Y.W.; Koshy, P.; Sorrell, C.C. Iron doped titania thin films prepared by spin coating. *Adv. Appl. Ceram.* **2012**, *111*, 129–133, <https://doi.org/10.1179/1743676111y.0000000065>.
22. Rashid, A.R.A.; Tazri, H.K. Optical Properties of ZnO, TiO₂ and ZnO:TiO₂ Composite Films. *Nano Hybrids Compos.* **2021**, *31*, 25–33, <https://doi.org/10.4028/www.scientific.net/nhc.31.25>.
23. Zouheir, M.; Assila, O.; Tanji, K.; El Gaidoumi, A.; Araña, J.; Rodríguez, J.M.D.; Smått, J.-H.; Huynh, T.-P.; Kherbeche, A. Bandgap optimization of sol–gel-derived TiO₂ and its effect on the photodegradation of formic acid. *Nano Futur.* **2021**, *5*, 025004, <https://doi.org/10.1088/2399-1984/abfb7d>.
24. Eaimsumang, S.; Prataksanon, P.; Pongstabodee, S.; Luengnaruemitchai, A. Effect of acid on the crystalline phase of TiO₂ prepared by hydrothermal treatment and its application in the oxidative steam reforming of methanol. *Res. Chem. Intermed.* **2020**, *46*, 1235–1254, <https://doi.org/10.1007/s11164-019-04031-8>.
25. Dokan, F.K.; Kuru, M. A new approach to optimize the synthesis parameters of TiO₂ microsphere and development of photocatalytic performance. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 640–655, <https://doi.org/10.1007/s10854-020-04845-y>.
26. Pedanekar, R.; Shaikh, S.; Rajpure, K. Thin film photocatalysis for environmental remediation: A status review. *Curr. Appl. Phys.* **2020**, *20*, 931–952, <https://doi.org/10.1016/j.cap.2020.04.006>.
27. Makuła, P.; Pacia, M.; Macyk, W. How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra. *J. Phys. Chem. Lett.* **2018**, *9*, 6814–6817, <https://doi.org/10.1021/acs.jpclett.8b02892>.
28. Livage, J.; Henry, M.; Sanchez, C. Sol-gel chemistry of transition metal oxides. *Prog. Solid State Chem.* **1988**, *18*, 259–341, [https://doi.org/10.1016/0079-6786\(88\)90005-2](https://doi.org/10.1016/0079-6786(88)90005-2).
29. De La Osa, R.A.; Iparraguirre, I.; Ortiz, D.; Saiz, J.M. The extended Kubelka–Munk theory and its application to spectroscopy. *ChemTexts* **2019**, *6*, 2, <https://doi.org/10.1007/s40828-019-0097-0>.
30. Sood, S.; Umar, A.; Mehta, S.K.; Kansal, S.K. Highly effective Fe-doped TiO₂ nanoparticles photocatalysts for visible-light driven photocatalytic degradation of toxic organic compounds. *J. Colloid Interface Sci.* **2015**, *450*, 213–223, <https://doi.org/10.1016/j.jcis.2015.03.018>.
31. Khalaghi, M.; Atapour, M.; Momeni, M.M.; Zaeri, M.R.; Ghaffari, G. Photocatalytic activity and photo-electrochemical performance of trimetallic (Cu–Ni–Zn)/TiO₂ coating on AISI 316L stainless steel for water treatment. *Appl. Phys. A* **2020**, *126*, 1–11, <https://doi.org/10.1007/s00339-020-03550-1>.
32. Khan, M.M.; Siwach, R.; Kumar, S.; Alhazaa, A. Role of Fe doping in tuning photocatalytic and photoelectrochemical properties of TiO₂ for photodegradation of methylene blue. *Opt. Laser Technol.* **2019**, *118*, 170–178, <https://doi.org/10.1016/j.optlastec.2019.05.012>.
33. Mathews, N.; Morales, E.R.; Cortés-Jacome, M.; Antonio, J.A.T. TiO₂ thin films – Influence of annealing temperature on structural, optical and photocatalytic properties. *Sol. Energy* **2009**, *83*, 1499–1508, <https://doi.org/10.1016/j.solener.2009.04.008>.
34. Komaraiah, D.; Radha, E.; Sivakumar, J.; Reddy, M.R.; Sayanna, R. Photoluminescence and photocatalytic activity of spin coated Ag⁺ doped anatase TiO₂ thin films. *Opt. Mater.* **2020**, *108*, 110401, <https://doi.org/10.1016/j.optmat.2020.110401>.
35. Zhu, T.; Gao, S.-P. The Stability, Electronic Structure, and Optical Property of TiO₂ Polymorphs. *J. Phys. Chem. C* **2014**, *118*, 11385–11396, <https://doi.org/10.1021/jp412462m>.
36. Singh, M.K.; Mehata, M.S. Enhanced photoinduced catalytic activity of transition metal ions incorporated TiO₂ nanoparticles for degradation of organic dye: Absorption and photoluminescence spectroscopy. *Opt. Mater.* **2020**, *109*, 110309, <https://doi.org/10.1016/j.optmat.2020.110309>.