

Solid State Transformation of TiO₂ Rutile and its Photocatalytic Activity

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Abstract: Transformation phase TiO₂ Rutile was conducted to improve the photocatalytic activity. This study evaluated the transformation phase of TiO₂ rutile using the solid-state reaction method and tested for glycerol conversion reaction. A semiconductor material can be applied for glycerol conversion. The solid-state reaction using a mixture of TiO₂ Rutile and sodium titanate in mole ratio 1:4 was heated to 750 °C. XRD analysis evaluated the transformation phase of the solid-state

reaction product, while band gap energy was calculated following UV-Vis diffuse reflectance data. The photoactivity of glycerol was exposed by UV-Light at various times (5, 10, 15 h) of the liquid product and was analyzed by gas chromatography. Solid state reaction transformed TiO₂ rutile to polymorph structure (TiO₂ rutile, TiO₂ anatase, and sodium titanate Na₄O₁₂Ti₅). The band gap energy of the product was 3.2 eV. The optimum photocatalytic activity was 62.7% in glycerol concentration 0.25 M for a 15 h time reaction.

Keywords: Solid state reaction; Transformation phase; TiO₂ rutile; photocatalytic reaction; glycerol conversion.

INTRODUCTION

Titanium oxide (TiO₂) was well known as semiconductor materials that proven to be the most suitable for wide environmental and energy applications because of its suitable valence band and conduction band positions, long-term stability, non-toxicity, cost-effectiveness and strong oxidizing power. In nature, TiO₂ has 3 type of crystal structure (Rutile, Anatase, and Brookite). Among these types, Rutile has the most stable structure and the cheapest. Rutile also has smaller band-gap energy (3.0 eV) than anatase (3.2 eV) [1]. However, rutile is less reactive than anatase as material photocatalyst due to anatase has lower charge carrier recombination rates and smaller grain size [2-4]. The lower photocatalytic activity of rutile is also related to its larger grain size, lower specific surface areas, and lower surface adsorption capacity to hydroxyl groups [5].

Various techniques were conducted to improve the photocatalytic activity of rutile such as doping with metal or metal oxide, [6] and phase mixture [7]. However, mixing the different polymorphs was a simpler method to improve the photoactivity and more economic process. Scalon and co. work. Reported that the phase mixture of rutil and anatase has a lower the effective band-gap and an increased photoactivity compared to individual phase [8]. The mixture of anatase and rutile produced staggered alignment of the bands means that migrating holes accumulate in rutile, while electrons in anatase [7]. These case illustrated that the difference coordinating environment and chemical bonding of TiO₂ structure generated the different potential ionization and electron affinity [8].

Transformation structure of TiO₂ rutil can be conducted by solid-state synthesis method, in order to produced multi-polymorphs of the materials. In solid state process, the utilization of mineralizer sodium carbonate plays an important role for decomposing the rutile structure and followed by phase transformation to produce new structure. There are a lot of possibility of phase transformation such as TiO₂ rutile (remained structure), TiO₂ anatase, and also sodium titanate. Zhang et al. (2010) reported that the reaction of TiO₂ with NaOH using hydrothermal method produced high stable phase of sodium

titanate [9]. Sodium titanate demonstrated better photoactivity degradation for 4-chlorophenol [2], chloroform [10], and m-Dinitrobenzene reduction and Sulfosulfuron oxidation [11] comparing P25-TiO₂. To the best of our knowledge, a few references reported the sodium titanate prepared by solid state reaction of TiO₂ rutile and its photocatalytic activity.

As photocatalyst material, TiO₂ was tested on glycerol conversion reaction. Converting glycerol to its derivate was carried out to improve the economic value. Glycerol was a side product of biodiesel production, which amounted to 10% of the product. Recently, glycerol price in the global market is fairly cheap (around \$1.5/kg) regarding its abundance. The activity of TiO₂ was attributed to electronic effects (better separation of photogenerated charge carriers), which selectively activates C–O bonds in glycerol [12]. It was in line with Augugliaro et al. (2010) that glycerol conversion using polymorph TiO₂ (80% anatase, and 20% rutile) was 35% producing 1,3-dihydroxyacetone, glycerinaldehyde, formic acid, and carbon dioxide [13].

This study aims to evaluate the transformation phase of TiO₂ rutile by solid-state reaction. Then, the product materials were tested its photoactivity for glycerol conversion.

METHODS

Chemicals

The chemical precursors used for synthesizing material was commercial unbranded product including Titanium oxide (TiO₂) and Sodium Carbonate (Na₂CO₃). Other chemicals were purchased from Merck Millipore without purification such as HNO₃ 65%, HCl fuming 37%, Na₂SO₄, Oxalic Acid, NaOH, and Glycerol 85%.

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Preparation of Sodium Titanate Photocatalyst

Sodium titanate was prepared by solid-state reaction using a mixture of TiO_2 rutile and Na_2CO_3 in a mole ratio of 1:4. The mixture was homogenized by grinding method and was transferred to a muffle furnace. The precursor material was heated up to $750\text{ }^\circ\text{C}$ for 12 h. The solid product was ground to produce mild powder and washed using a resin ion exchanger to reduce the Na content in the product. Finally, the powder was dried and calcined at $500\text{ }^\circ\text{C}$ for 2 h.

Characterization of Sodium Titanate

Evaluating the crystal transformation during the solid-state process was conducted by X-Ray Diffraction PANalytical X'Pert Pro. The sample was scanned at 2θ range angle $5^\circ - 60^\circ$ using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$). Besides, UV-Vis diffuse reflectance calculated the band-gap energy of the materials.

Photocatalytic Test Activity

Glycerol of 10 mL in every various concentration (0.1, 0.25, and 0.5 M) was placed in a 50 mL reactor. The material photocatalyst Sodium-Titanate of 4 mg was added. The mixture was stirred vigorously and was exposed to UV light for various times 5, 10, and 15 h. Then, the mixture was filtered and the filtrate was analyzed using gas chromatography (GC) (Thermo Scientific Trace 1310, USA) equipped with a flame ion detector

and TR-Wax capillary column. The GC's temperature operation was from $50\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$ at an increasing $5\text{ }^\circ\text{C}/\text{min}$.

RESULT AND DISCUSSION

Characteristic of product material from the solid state reaction

During the solid state reaction, Na_2CO_3 was decomposed to Na_2O and CO_2 which diffused to the structure of TiO_2 rutile. Then, the structure of Ti-O-Ti in TiO_2 rutile can be breakdown and was followed by the rearrangement of the structure to produce a new structure of solid material. The diffractogram x-ray profile in Fig. 1 depicted that TiO_2 rutile was transformed to two types of sodium titanate namely $\text{Na}_{16}\text{Ti}_{10}\text{O}_{28}$ and $\text{Na}_4\text{Ti}_5\text{O}_{12}$, and also the rest of the undecomposed Na_2CO_3 . The crystal structure of $\text{Na}_{16}\text{Ti}_{10}\text{O}_{28}$ can be seen from peaks in $2\theta = 11.00, 12.47, 25.91, 32.22, 38.91, 45.00,$ and 56.85° . Meanwhile, the crystal structure of $\text{Na}_4\text{Ti}_5\text{O}_{12}$ was from peaks in $2\theta = 9, 21, 33-34, 38,$ and 51° . The peaks in $2\theta = 25.91, 30.04, 34.41, 35.15, 37.88, 41.41, 46.45, 48.19,$ and 58.87° showed the structure of Na_2CO_3 . The undecomposed Na_2CO_3 was caused by the heat treatment under its melting point, which the melting was established at $1175 \pm 25\text{ }^\circ\text{C}$ [14].

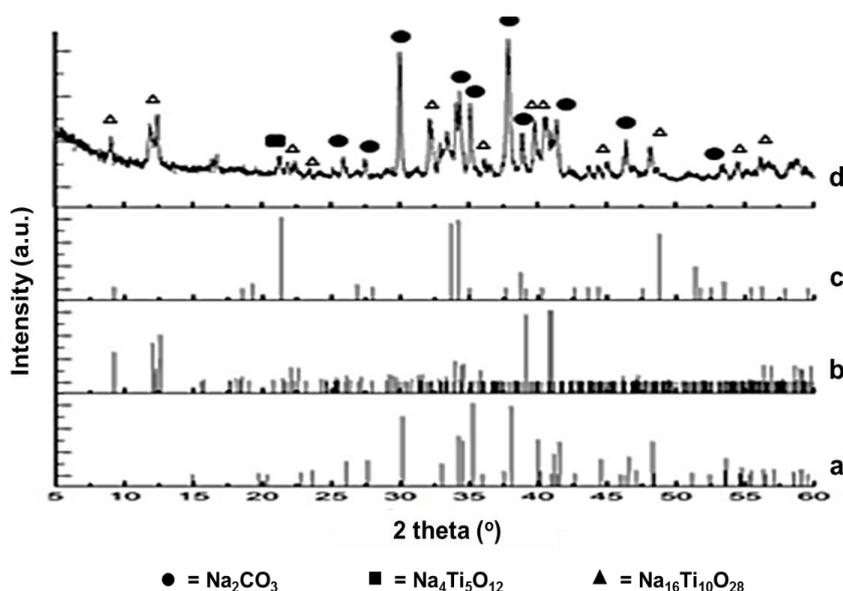


Figure 1. Profile of Difraktogram x-ray: a) Na_2CO_3 ; b). $\text{Na}_{16}\text{Ti}_{10}\text{O}_{28}$; c). $\text{Na}_4\text{Ti}_5\text{O}_{12}$; and d). Product of solid state reaction

The further process was a denatiation using ion exchanger due to decreasing the sodium ion (Na^+) in extra-frameworks of the crystal sodium titanate. However, denatiation process transformed sodium titanate ($\text{Na}_{16}\text{Ti}_{10}\text{O}_{28}$ and $\text{Na}_4\text{Ti}_5\text{O}_{12}$) phase to produce polymorph TiO_2 rutile, TiO_2 anatase, and sodium titanate $\text{Na}_4\text{Ti}_5\text{O}_{12}$ (Fig. 2). TiO_2 anatase can be seen from peaks at $2\theta = 25, 38, 48, 51,$ and 55° , while TiO_2 rutile at $2\theta = 27, 36, 39, 41, 44, 54, 56, 62,$ and 64° . The percentage composition of

the three phase that was calculated by Match programme was 26.9, 19.1, and 54% consecutively for TiO_2 rutile, TiO_2 anatase, and $\text{Na}_4\text{Ti}_5\text{O}_{12}$. It was in line with Xiong and He (2017) that the presence of Na^+ initiated producing multiphase during the calcination process [15]. The absence of sodium titanate $\text{Na}_{16}\text{Ti}_{10}\text{O}_{28}$ was probably transformed to more stable structure $\text{Na}_4\text{Ti}_5\text{O}_{12}$.

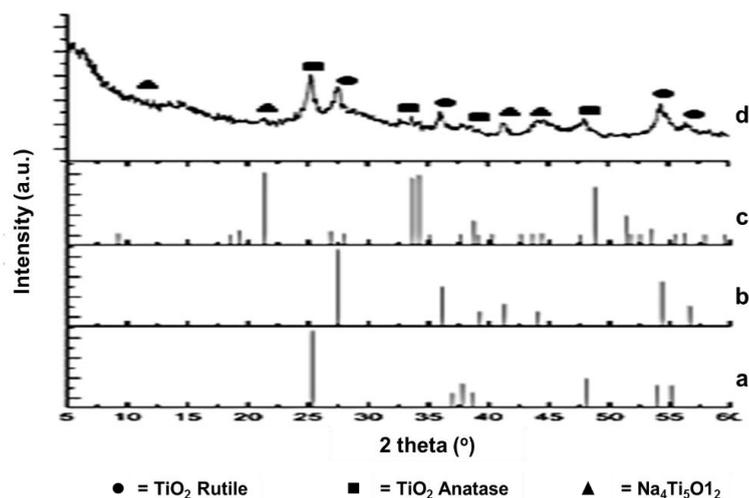


Figure 2. The profile of diffractogram x-ray: a. TiO_2 anatase standard (JCPDS No. 21-1272); b. TiO_2 rutile standard (JCPDS No. 21-1276); c. $\text{Na}_4\text{Ti}_5\text{O}_{12}$ standard; d. Material product of solid-state reaction after denaturation

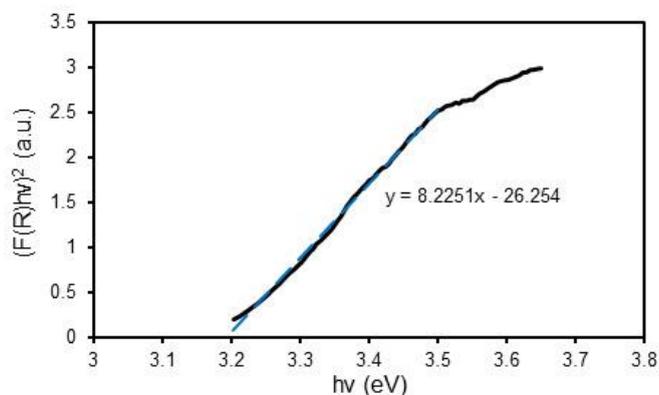


Figure 3. Profile of Tauc plot to calculate the band-gap energy of material product

Other than that, the final product was measured the band-gap energy in order to understand the photoactivity properties. The band-gap energy of the material product was 3.2 eV (Fig. 3). Increasing the band-gap energy comparing the initial (TiO_2 rutile = 3.0 eV) was in line with the presence of polymorph structure of product, which has similar value with TiO_2 anatase (3.2 eV).

Photoactivity of material product for glycerol conversion

Photocatalytic activity of glycerol conversion in the presence of polymorph materials product was carried out in various times reaction and glycerol concentration. Liquid product from the

reaction was analyzed using gas chromatography to identify the chemical composition. The chromatogram in Fig. 4 showed three main peaks at time retention 34.9, 16.5, and 3.15 min that was glycerol, unidentified product conversion (regarding to limitation of standard solution), and short-chain of alcohol, respectively. The photocatalytic reaction was probably occurred by glycerol oxidation. Dodekatos reported that the C_2 and C_1 products of glycerol oxidation was glycolic acid, oxalic acid, acetic acid, and formic acid [16]. However, the most possible unidentified product was acetic acid or formic acid that was assumed by nearly half of glycerol molecular weight.

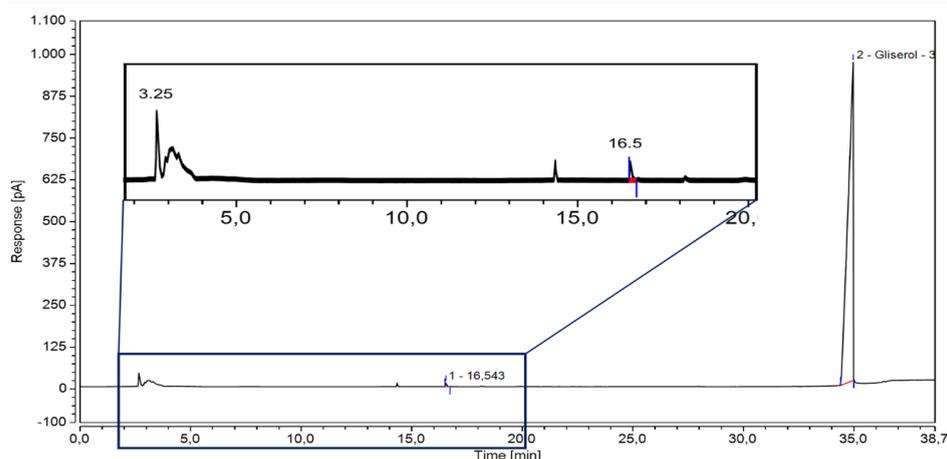


Figure 4. Chromatogram of liquid product from photocatalytic reaction

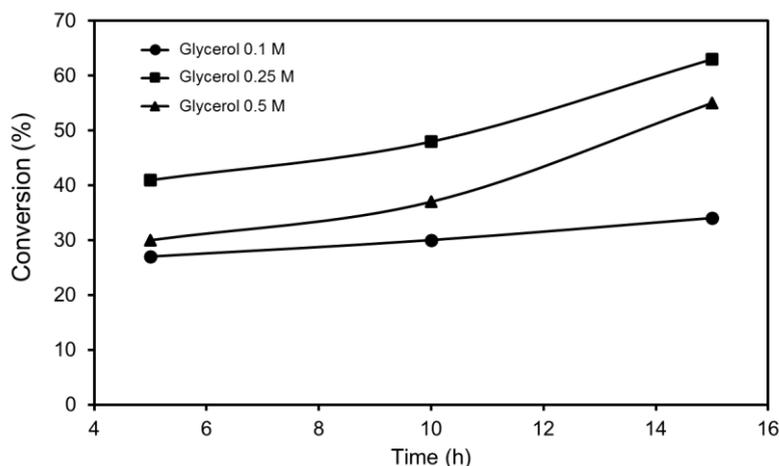


Figure 5. Photocatalytic glycerol conversion using material product synthesis

Moreover, quantitative analysis was conducted to evaluate the percentage conversion of glycerol by photocatalysis reaction. The calculation was determined by comparing the glycerol peak area of liquid reaction product to standard. Increasing the time reaction produced higher glycerol conversion percentage (Fig. 5). Meanwhile, the highest conversion percentage was at 0.25 M of glycerol concentration (62.7%). The higher glycerol concentration caused decreasing the percentage of glycerol conversion (55.5%).

CONCLUSION

The transformation phase of TiO₂ Rutile using the solid-state reaction method was a polymorph structure consisting of rutile, anatase, and sodium titanate Na₄Ti₁₂O₁₅. The presence of the mixture phase increased the band-gap energy to 3.2 eV. The polymorph structure has high photoactivity of glycerol conversion. The highest percentage of glycerol conversion was 62.7% in glycerol concentration 0.25 M for a 15 h time reaction.

REFERENCES

- [1] Y. Mi and Y. Weng, Band alignment and controllable electron migration between Rutile and Anatase TiO₂, *Scientific Reports*, vol. 5, no. 11482, 2015.
- [2] V. Stengl, S. Bakardjieva, J. Subrt, E. Vecernikova, L. Szatmary, M. Klementova, and V. Balek, Sodium titanate nanorods: Preparation, microstructure characterization and photocatalytic activity, *Applied Catalysis B: Environmental*, vol. 63, pp. 20-30, 2006.
- [3] T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter, and M. Batzill, Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO₂ films, *Scientific Reports*, vol. 4, no. 4043, pp. 1-8, 2014.
- [4] J. He, Y. Du, Y. Bai, J. An, X. Cai, Y. Chen, P. Wang, X. Yang, and Q. Feng, Facile formation of anatase/rutile TiO₂ nanocomposites with enhanced photocatalytic activity, *molecules*, vol. 24, no. 2996, 2019.
- [5] J. Zhang, P. Zhou, J. Liu and J. Yu, New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂, *Phys.Chem.Chem.Phys.*, vol. 16, pp. 20382--20386, 2014.
- [6] V. Pfeifer, P. Erhart, S. Li, K. Rachut, J. Morasch, J. Brötz, P. Reckers, T. Mayer, S. Rühle, A. Zaban, I. M. Seró, J. Bisquert, W. Jaegermann, and A. Klein, Energy band alignment between anatase and rutile TiO₂, *J. Phys. Chem. Lett.*, vol. 4, pp. 4182-4187, 2013.
- [7] P. Deak, B. Aradi, and T. Frauenheim. Band lineup and charge carrier separation in mixed rutile-anatase systems, *J. Phys. Chem. C*, vol. 115, pp. 3443-3446, 2011.
- [8] D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh, and A. A. Sokol, Band alignment of rutile and anatase TiO₂, *Nature Materials*, vol. 12, pp. 798-801, 2013.
- [9] D. R. Zhang, C. W. Kim, and Y. S. Kang, A Study on the Crystalline Structure of Sodium Titanate Nanobelts Prepared by the Hydrothermal Method, *J. Phys. Chem. C*, Vol. 114, No. 18, pp. 8294-8301, 2010.
- [10] H. Song, H. Jiang, T. Liu, X. Liu, G. Meng, Preparation and photocatalytic activity of alkali titanate nano materials A₂Ti_nO_{2n+1} (A = Li, Na and K), *Materials Research Bulletin*, vol. 42, pp. 334-344, 2007.
- [11] I. S. Grover, S. Singh, and B. Pal, Enhanced photocatalytic activity of as-prepared sodium titanates for m-dinitrobenzene reduction and sulfosulfuron oxidation, *Nanoscience and Nanotechnology*, vol. 15, pp. 1490-1498, 2015.
- [12] J. Yu, F. Dappozze, J. Martín-Gomez, J. Hidalgo-Carrillo, A. Marinas, P. Vernoux, A. Caravaca, and C. Guillard, Glycerol production by photocatalytic oxidation of glycerol on WO₃-based materials" *Applied Catalysis B: Environmental*, vol. 299, no. 120616, 2021.
- [13] V. Augugliaro, H. A. H. E. Nazer, V. Loddo, A. Mele, G. Palmisano, L. Palmisano, S. Yurdakal, Partial photocatalytic oxidation of glycerol in TiO₂ water suspensions, *Catalysis Today*, vol. 151, pp. 21-28, 2010.
- [14] I. V. Podborodnikov, A. Shatskiya, A. V. Arefiev, A. D. Chanyshev, and K. D. Litasov. "The system Na₂CO₃-MgCO₃ at 3 GPa, *High Pressure Research*, vol. 38, No. 3, pp. 281-292, 2018.
- [15] J. Xiong and L. He, Influence of Na⁺ content on the structure and morphology of TiO₂ nanoparticles prepared by hydrothermal transformation of alkaline titanate

nanotubes, *Journal of Experimental Nanoscience*, vol. 12, no. 1, pp. 384-393, 2017.

- [16] G. Dodekatos, S. Schünemann, and H. Tüysüz, Recent advances in thermo-, photo-, and electrocatalytic glycerol oxidation, *ACS Catal.*, vol. 8, pp. 6301-6333, 2018.