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Research Paper

Bismuth Silicate/Silica-Titania Synthesis from In Situ Decomposition of Oil Palm Leaves as Silica Source

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Abstract
In this work, bismuth silicate-titania has been synthesized in two stages by utilizing bismuth oxynitrate as an elemental source of bismuth, oil palm leaves (OPL) as a source of silica and titanium tetraisopropoxide (TTIP) as source of titania (TiO_2). In the first stage, bismuth silicate/silica ($Bi_4Si_3O_{12}/SiO_2$) was formed, which occurs due to the in-situ decomposition of palm leaves and reacts directly with the bismuth precursor at high temperatures (900°C). The reaction could possibly occur through a solid-state reaction mechanism between bismuth oxide and silica or through a more complex mechanism within the reaction mixture. The resulting product then reacts with TTIP, which is added and heated at the same temperature to form $Bi_4Si_3O_{12}/SiO_2$-TiO_2 (bismuth silicate/silica-titania). Characterization of the as-prepared product using X-ray diffraction showed the dominance of bismuth silicate and small amount of titania (TiO_2). As a result, TiO_2 could not be detected in the diffractogram. Nevertheless, an analysis using energy-dispersive X-rays showed the presence of titanium elements in the resulting composite. The results of this study can be used to develop ternary metal oxides based on natural resources and agricultural wastes, such as oil palm leaves.

Keywords
Bismuth Silicate, Titania, Oil Palm Leaves, Bismuth Oxynitrate, Agricultural Waste

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1. INTRODUCTION

Binary and ternary metal oxide structures have vast technological uses, e.g., transistors and computing, devices and are of basic scientific interest because of their electrical, optical, and catalytic properties. Extensive research has been conducted in the past few years to create novel synthetic techniques for these materials (Mao et al., 2005; Bilecka et al., 2008; Wang and Wu, 2017). For instance, to form multilayered thin films demonstrating superhydrophilicity, antifogging ability in the dark environment, and self-cleaning ability toward stearic acid under photocatalytic conditions, a mesoporous $SiO_2/Bi_2O_3/TiO_2$ compound was synthesized using a sol-gel method (Bai et al., 2017). Another $SiO_2/Bi_2O_3/TiO_2$ compound, which was prepared using $Bi(NO_3)_3$, SiO_2, and $TiOSO_4$ under mild conditions, exhibited good photocatalytic performance toward benzene degradation (Ren et al., 2015). To afford an effective electrode material with a discharging capacity of 298 mAh g^{-1}, TiO_2/SiO_2 hybrid material with a TiO_2:SiO_2 molar ratio of 8:20 was doped with Bi_2O_3 (2% mass) and calcined at 800°C (Kurc et al., 2018). $Bi_2O_3/TiO_2/SiO_2$ with various ratios was synthesized from their single metal oxide components at high temperatures, with glass formation occurring depending on the composition ratio (Slavov and Dimitriev, 2016). Moreover, at high temperatures, a mixture of Bi_2O_3 and TiO_2 was reported to furnish bismuth-titanate ceramic materials (Thiruramanathan et al., 2016; Khodadoost et al., 2017; Gadea et al., 2018; Marela et al., 2021), whose insertion into mesoporous SiO_2 produced a material with specific characteristics for application in the catalytic degradation of methyl orange (Zaccariello et al., 2017) and as a UV protection substance in the cosmetic formulation (Zaccariello et al., 2019).

Some preparation methods to produce combined materials of bismuth oxide and silica were also reported, including their characterization and applications. For example, melting (Lu et al., 2013; Back et al., 2020), mechanical (Belik et al., 2020), hydrothermal (Jia et al., 2017), and sintering (Bai et al., 2007) processes were developed for the purposes of reactions. Another synthetic method developed for bismuth silicate is using the hydro-/solvothermal form $Bi(NO_3)_2$ and commercial silica sources (Shabalina et al., 2022). As can be extracted from the literature on bismuth silicate compounds synthesis, the pres-

ence of SiO_2 is very important. Generally, the silica source used in various reactions for the synthesis of bismuth silicate is a commercial precursor. The development of bismuth silicate synthesis using silica from several biomasses is still rarely reported. One recent example that has been reported is the synthesis of bismuth silicate (Bi_2SiO_5) using silica from rice husk (Arefieva et al., 2023). The development of alternative bismuth silicate synthesis, both in terms of finding new precursors and developing methods, is an important part of chemical science. This also means that it will affect the applications that may be developed in advanced research. Therefore, the discovery of silica sources that are more sustainable and available in nature in large quantities is highly desirable. To provide information regarding the experimental utilization of abundant natural resources, especially in tropical countries, this paper describes the use of oil palm leaves (OPL) as a source of SiO_2 in the context of chemical and environmental research.

2. EXPERIMENTAL SECTION

2.1 Materials

Bismuth oxynitrate (BON) and isopropanol (IPA) were provided by Merck, titanium tetraisopropoxide (TTIP) was purchased from Sigma-Aldrich, while HNO_3 and HCl were purchased from Smart Lab Ltd. OPL used in this experiment was obtained from oil palm plantation around Bengkulu city (Indonesia). The OPL powder was treated with HCl 10% under heating to remove any other minerals that may be present in the samples.

2.2 Methods

The first investigation is to know the possible products formed from one pot reaction of TTIP–BON and OPL powder. TTIP (0.285 g, ~0.3 mL) was diluted in 50.0 mL of IPA in a crucible. Dried OPL powder (4.0 g) was added to the TTIP solution in IPA and stirred for 30 min. Conversely, bismuth oxynitrate (BON; 1.462 g) was dissolved in HNO_3 65% (10 mL) in an Erlenmeyer flask, and then, the BON solution was poured into the mixture of OPL and TTIP. The Erlenmeyer was washed with HNO_3 65% twice (each with 2.5 mL) and poured again into the reaction mixture under stirring using magnetic stirring. The stirring was continued for 1 h while heating at 85°C until the solvents evaporated and a red-brown residue was observed. The obtained residue was kept at room temperature (27°C) for 20 h and then taken to a muffle furnace (Nabertherm, Germany). The furnace temperature was increased from room temperature to 900°C for 2 h, and further annealing was conducted at 900°C for 5 h. The procedure is modified from previously reported procedures (Batool et al., 2020; Chandrawanshi et al., 2020). The sample was cooled down to room temperature without any cooling rate control.

Based on the results using one pot reaction between OPL-TTIP and BON, a two-step reaction was performed as follows: First, 0.731 g of BON was reacted with 4.0 g of OPL as explained above but without TTIP. Then, the as-obtained

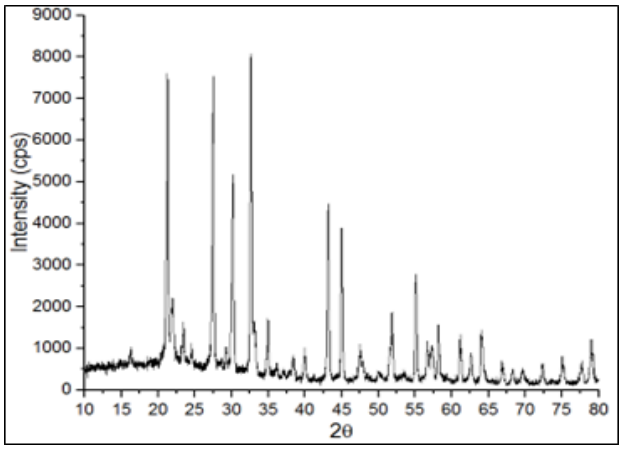

Figure 1. XRD Patern of Existing Compounds in the Reaction Product of Bismuth Oxynitrate, TTIP and Oil Palm Leaves

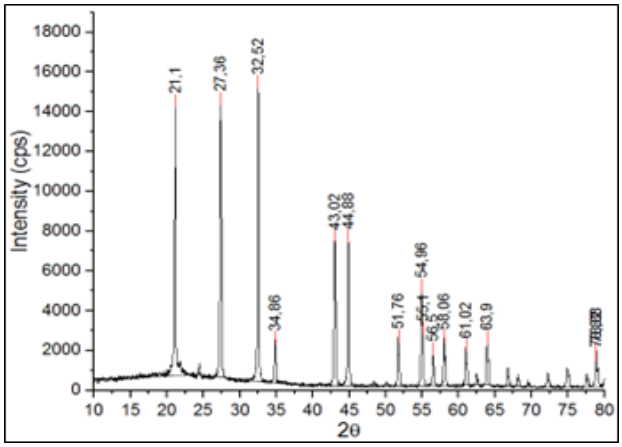

Figure 2. XRD Pattern of the Synthesis of Bismuth Silicate from Bismuth Oxynitrate and Oil Palm Leaves at 900°C for 5 h

product was mixed with TTIP in IPA, followed by solvent evaporation and calcination at 900°C for 5 h. The microstructure and structural properties of the synthesized powder were evaluated via X-ray diffraction (Benchtoph Powder XRD Rigaku-Miniflex 600) and scanning electron microscopy (SEM). To determine the chemical composition of the nanopowder, energy-dispersive X-ray spectroscopy (EDX) (JEOL JSM 6510 LA) was used. The functional groups of bismuth silicate/silica were determined via Fourier transform infrared spectroscopy (FTIR, Bruker-Compact FT-IR Alpha II) in a wave number range of 500-4000 cm^{-1}. Moreover, bismuth silicate/silica powder that has been obtained from the previous procedure, which weighed as much as 0.75 g, was then put into a crucible followed by the addition of $CHCl_3$ as much as 20 mL. The mixture was stirred using a magnetic stirrer while adding liquid TTIP in amounts up to 1 mmol (0.284 g; 0.296 mL). Stirring was continued until the $CHCl_3$ evaporated and left a white solid residue. The crucible containing the residue was transferred into a furnace

Table 1. The Remark of Existing Compounds in the Reaction Product

	Bi_2O_3	TiO_2	$Bi_4Ti_3O_{12}$	$Bi_4Si_3O_{12}$
Crystalinity (%)	59.4%	39.9	70.3	70.0
Crystal Size (nm)	254	161	150	309
ICDD Card	00-041-1449	00-016-0617	00-072-1019	00-076-1729
Weight Ratio (%)	13	4	30	53

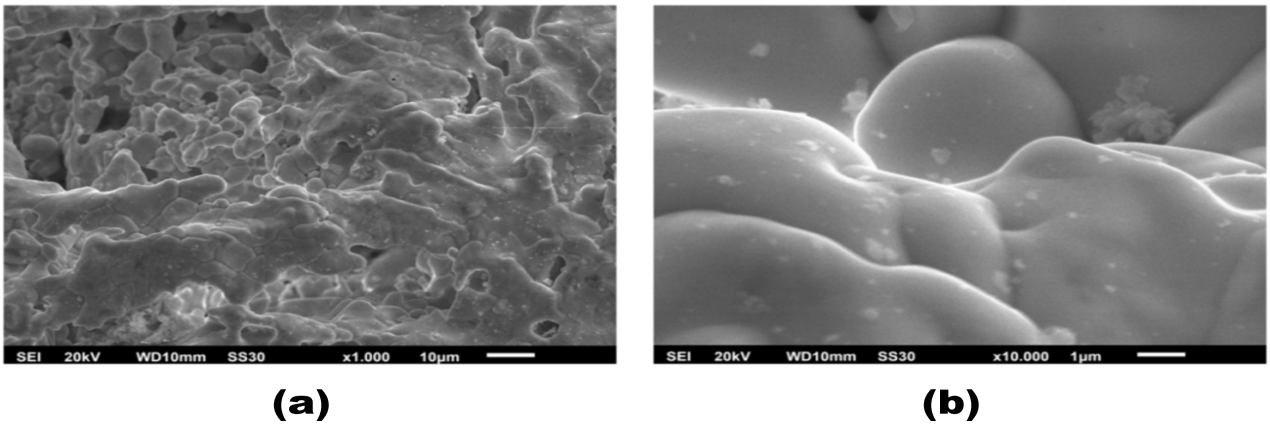

Figure 3. Morphology of the Binary Metal-Oxide Compound $Bi_4Si_3O_{12}/SiO_2$ Resulting from Analysis using Scanning Electron Microscopy (SEM); (a) 1000× Magnification; (b) 10000×

and heated at 500°C for 3 h. The final solid obtained was analyzed via XRD and SEM-EDX.

3. RESULTS AND DISCUSSION

XRD data are obtained based on the initial efforts that have been made by conducting in situ reactions, as shown in Figure 1. The diffractogram shows the presence of several crystalline phases that have been identified as Bi_2O_3, TiO_2, $Bi_4Ti_3O_{12}$, and $Bi_4Si_3O_{12}$. Based on quantitative analysis using the existing XRD data bank, each of these oxide compounds has a weight ratio, as shown in Table 1.

Table 1 shows that bismuth precursors react more effectively with silica derived from OPL. This fact encourages researchers to first create bismuth silicate compounds before combining them with TiO_2 derived from TTIP. The amount of bismuth oxynitrate used was reduced in half compared to that used in the previous procedure, and the OPL was constant at 4 g. Except for the addition of TTIP, the entire procedure was the same. Figure 2 depicts the XRD results.

Figure 2 shows that several peaks (2θ) are found: 21.10°, 27.36°, 32.52°, 34.86°, 43.02°, 44.88°, 51.76°, 54.96°, 55.10°, 56.50°, 58.06°, 61.02°, 63.90°, and 78.88°. The peak at 21.10 is the peak for $Bi_4Si_3O_{12}$, which may overlap with cristobalite silica. It is supported by other peaks that are typical peaks for $Bi_4Si_3O_{12}$, and no peaks for Bi_2O_3 or Bi_2SiO_5 are detected (Tian et al., 2009; Karthik et al., 2019b; Karthik et al., 2019a). This result indicates that there is excess silica in the reaction between bismuth oxynitrate and silica. Therefore, the resulting composite can be called a $Bi_4Si_3O_{12}/SiO_2$ composite (Chandrawanshi et al., 2020).

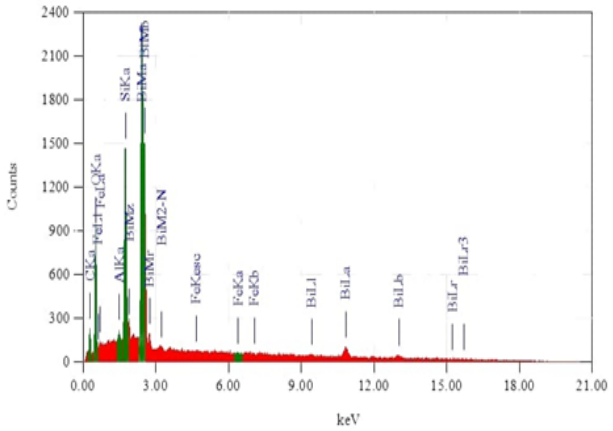

Figure 4. Elemental Analysis of Binary Metal-Oxide Compounds $Bi_4Si_3O_{12}/SiO_2$ Resulting from Analysis using Energy Dispersive X-Ray (EDX)

The reaction mechanism that may occur in the synthesis of bismuth silicate is a complexing reaction between a complex compound of silicon in powdered OPL and bismuth ions in the compound bismuth nitrate. Moreover, by heating at high temperatures, the degradation reaction of the complex compound occurred as well as the reaction process for the formation of

Table 2. Elemental Composition of $Bi_4Si_3O_{12}/SiO_2$ Resulting from Analysis using Energy Dispersive X-Ray (EDX)

Element	K(eV)	%Mass
C	0.277	13.68
O	0.525	19.05
Al	1.486	0.22
Si	1.739	8.37
Bi	2.419	58.00
Fe	6.398	0.07

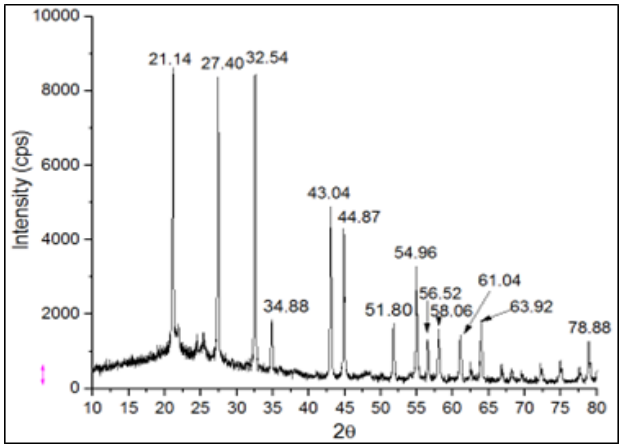

Figure 5. X-Ray Diffraction Pattern of the Ternary Metal-Oxide $Bi_4Si_3O_{12}/SiO_2$-TiO_2

bismuth silicate. Another possibility is that the silicon complex compound in palm leaf powder first degrades into SiO_2, as well as bismuth oxynitrate, which turns into Bi_2O_3. These two compounds then interact through a solid-state reaction and produce bismuth silicate. To investigate the morphology and elemental content of the resulting $Bi_4Si_3O_{12}/SiO_2$ materials, SEM-EDX analysis was conducted. Figure 3 shows the results of the SEM analysis, and Figure 4 and Table 2 show the results of the EDX analysis.

Figure 3 shows that the morphology of the resulting $Bi_4Si_3O_{12}/SiO_2$ material is in the form of an uneven solid that is also interspersed with several detectable pores. As shown in Figure 4 and Table 2, further analysis using SEM-EDX gives the morphology and element content.

Figure 4 and Table 2 show that the bismuth content is very large, as is the accompanying silica. This indicates that the main composition contained in the sample actually contains bismuth and silica compounds. The research was continued by synthesizing the ternary metal oxide $Bi_4Si_3O_{12}/SiO_2$-TiO_2 by carrying out the reaction between TiO_2 precursors by adding TTIP. Figure 5 presents the results of the XRD analysis of the synthesized products using TTIP.

Figure 5 shows that the peaks detected mainly indicate the presence of the $Bi_4Si_3O_{12}$ compound. The TiO_2 compound, which is expected to be visible in the XRD diffraction, cannot

Table 3. Elemental Composition of $Bi_4Si_3O_{12}/SiO_2$-TiO_2 Resulting from Analysis using Energy Dispersive X-Ray (EDX)

Element	K(eV)	% Mass
C	0.277	10.55
O	0.525	35.68
Si	1.739	18.25
Bi	2.419	32.49
Ti	4.508	0.85
Cu	8.040	1.25
Zn	8.630	0.94

be clearly detected. This is mainly because the precursor added to synthesize TiO_2 is very small compared to the content of $Bi_4Si_3O_{12}$. Figure 6, Table 3, and Figure 7 show the titanium content in the sample and the morphology of the resulting compound.

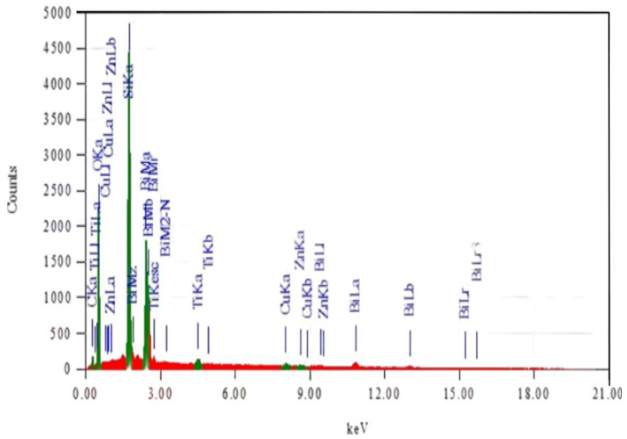

Figure 6. Elemental Analysis of Binary Metal-Oxide Compounds $Bi_4Si_3O_{12}/SiO_2$-TiO_2 Resulting from Analysis using Energy Dispersive X-Ray (EDX)

In Figure 6 and Table 3, elemental titanium is detected in the product resulting from the heating of $Bi_4Si_3O_{12}/SiO_2$ and TTIP. The presence of this titanium indicates that TTIP has been degraded and further oxidized to TiO_2 at high temperatures.

Figure 7(a) shows that the ternary metal oxide compound $Bi_4Si_3O_{12}/TiO_2$-SiO_2 undergoes surface changes compared to $Bi_4Si_3O_{12}/SiO_2$ itself. This surface change can be caused due to the presence of TiO_2, which has been attached to the $Bi_4Si_3O_{12}/SiO_2$ solid. As shown in Figure 7(b), the pores of the resulting solid material are more clearly visible compared to the $Bi_4Si_3O_{12}/SiO_2$ solid.

Figure 8 shows the presence of several typical peaks that emerge from the $Bi_4Si_3O_{12}/TiO_2$-SiO_2 solid. These peaks are 3457, 1632, 1098, 795, 615, and 549 cm^{-1}. The peaks at 3457 and 1632 cm^{-1} show the presence of water molecules adsorbed in the solid. The presence of TiO_2 causes the typical

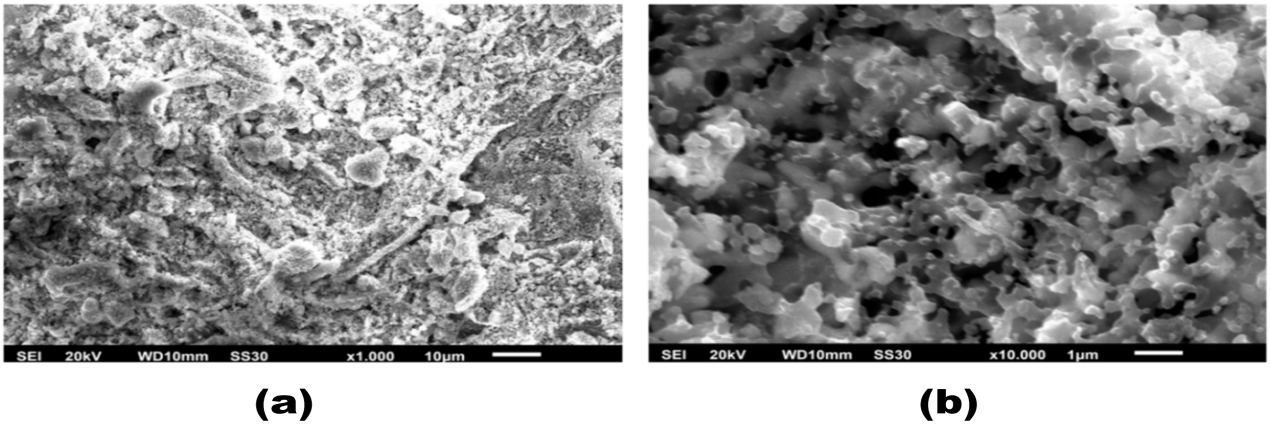

Figure 7. SEM Pattern of the as-Prepared $Bi_4Si_3O_{12}/SiO_2$-TiO_2 (a) 1000× Magnification; (b) 10000× Magnification

peaks for this ternary metal oxide, namely, 1098, 795, 615, and 549 cm^{-1}.

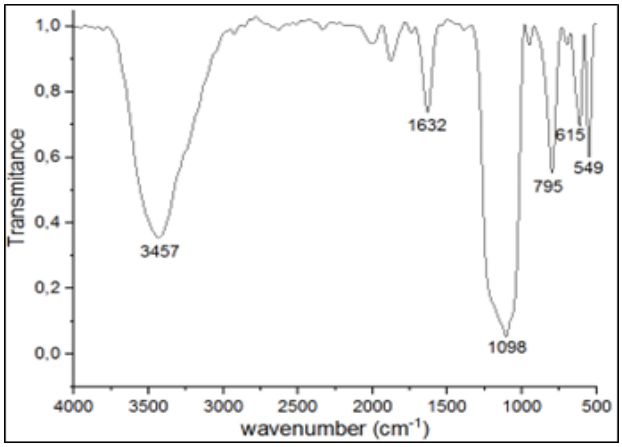

Figure 8. FTIR Pattern of the as-Prepared $Bi_4Si_3O_{12}/SiO_2$-TiO_2

4. CONCLUSIONS

The synthesis of bismuth silicate has been successfully carried out by utilizing the in situ reaction between bismuth oxynitrate and powdered OPLs as a source of silica. The reaction product in the form of a solid powder that has been produced can be used to form ternary metal oxide ($Bi_4Si_3O_{12}/SiO_2$-TiO_2) by reaction with TTIP as a precursor. The resulting composite has the potential to act as antibacterial and/or catalyst, especially in photocatalytic reactions.

5. ACKNOWLEDGMENT

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