Straightforward Synthesis of SnO$_2$/Bi$_2$S$_3$/BiOCl–Bi$_{24}$O$_{31}$Cl$_{10}$ Composites for Drastically Enhancing Rhodamine B Photocatalytic Degradation under Visible Light

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**ABSTRACT:** The pursuit of robust photocatalysts that can completely degrade organic contaminants with high performance as well as high energy efficiency, simplicity in preparation, and low cost is an appealing topic that potentially promotes photocatalysts for being used widely. Herein, we introduce a new and efficient SnO$_2$/Bi$_2$S$_3$/BiOCl–Bi$_{24}$O$_{31}$Cl$_{10}$ (SnO$_2$/Bi$_2$S$_3$/Bi25) composite photocatalyst by taking advantage of the robust, simple, and potentially scalable one-pot synthesis, including the hydrothermal process followed by thermal decomposition. Interestingly, we observed the formation of BiOCl–Bi$_{24}$O$_{31}$Cl$_{10}$ (abbreviated as Bi25) heterojunctions derived from reactions between Bi$_2$S$_3$ and SnCl$_4$·5H$_2$O precursor solutions under the hydrothermal condition and thermal decomposition of BiOCl. This Bi25 heterojunction acts as an interface to reduce the recombination of photogenerated electron–hole (e$^−$–h$^+$) pairs as well as to massively enhance the visible light harvesting, thereby significantly enhancing the photocatalytic degradation performance of the as-prepared composite photocatalyst. In detail, the photocatalytic degradation of Rhodamine B (RhB) activated by visible light using 15% SnO$_2$/Bi$_2$S$_3$/Bi25 shows the efficiency of 80.8%, which is superior compared to that of pure Bi$_2$S$_3$ (29.4%) and SnO$_2$ (0.1%). The SnO$_2$/Bi$_2$S$_3$/Bi25 composite photocatalyst also presents an excellent photostability and easy recovery from dye for recycling. The trapping test revealed that the photogenerated holes play a crucial factor during the photocatalytic process, whereas superoxide radicals are also formed but not involved in the photocatalytic process. Successful fabrication of SnO$_2$/Bi$_2$S$_3$/Bi25 composite photocatalysts via a straightforward method with drastically enhanced photocatalytic performance under visible light activation would be useful for practical applications.

1. INTRODUCTION

During the past few decades, the steady growth of organic dye and pigment industries poses a significant concern to the sustainable development of human society.1–5 Despite benefits from these dyes in the dyeing industries, they pollute water instantly as they are disposed to the natural water sources.6–9 Moreover, the stability of these organic dyes in harsh environments challenges the field of textile dyeing water treatment.10 A large number of cleaning techniques such as adsorption, coagulation, floatation, chemical oxidation, Fenton’s reaction, reverse osmosis, extraction, and photocatalytic degradation have been employed to remove organic dye contaminants in water to produce clean water.5,10,11 The pursuit of robust cleaning techniques could be used in practical applications if it can completely degrade organic contaminants with high efficiency, simplicity, and low cost. It is considered a challenge in the field of textile dyeing water treatment. Accordingly, photocatalysts have been potentially demonstrated as a sturdy and substantial approach to meet the high efficiency, simplicity, and low-cost requirements owing to their remarkable ability.12 Further, the metal-oxide photocatalysts are of interest because they are characterized by high stability, controllable morphology, and high selectivity.10 They produce inherent reactive oxygen species (ROS) by generating e$^−$–h$^+$ pairs under light activation. This photocatalytic activity gives rise to oxidation and decomposition of most organic molecules, thereby offering the potential for the complete elimination of organic contaminants.11,12

However, the metal-oxide photocatalysts are strictly limited to their photoactivation range or rapid recombination of photogenerated e$^−$–h$^+$ pairs due to the large bandgap or narrow bandgap, respectively. Previous studies in the field can be classified into two main approaches. First, the approach has established wide bandgap photocatalysts (e.g., TiO$_2$, SnO$_2$, and ZnO) and applied modifications to their surface, morphologies, and the band structure of the large bandgap photocatalysts.13–15 Second, it is aimed at exploiting new narrow bandgap photocatalysts (e.g., g-C$_3$N$_4$, Bi$_2$S$_3$, Bi$_2$WO$_6$, Ce$_2$O$_3$,

**Cite This:** ACS Omega 2020, 5, 20438–20449

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and V₂O₅).¹⁶⁻²⁰ Therefore, recent studies have been conducted, intending to optimize the performance of the photocatalysts by coupling them together and designing different charge transport models.¹⁰

Recently, bismuth sulfi de (Bi₂S₃), an n-type semiconductor with a bulk direct bandgap of 1.3 eV, has drawn an excellent interest for a wide range of potential applications, such as photodetectors,¹³ sensors, energy converters, anode materials for lithium-ion batteries,²² and photocatalysis.²³–²⁵ Bi₂S₃-based photocatalysts are indeed highly attractive due to the following reasons: (1) its narrow bandgap indicates an implication for a wide photoabsorption range, which is highly desired in the field of photocatalysis, and (2) raw materials bismuth and sulfide are very abundant on the earth and thus readily available at low cost. There is, however, a challenge to the use of Bi₂S₃ as an individual photocatalyst because of its fast recombination of photogenerated e⁻−h⁺ pairs and photo-induced corrosion.³¹,³² In addition, as a typical n-type semiconductor, t in oxide (SnO₂) has high electron mobility (10⁰⁻²⁰0 cm²/V⁻¹·s⁻¹),³³ resulting in an efficient transport of photogenerated electrons, which is an essential factor for photocatalytic activity. However, the performance of SnO₂-based photocatalysts is restricted in the UV range due to their large bandgap.³⁴ It is thus highly desired to integrate the advantages of Bi₂S₃ and SnO₂ by creating new composite photocatalysts with these useful features. Indeed, the construction of Bi₂S₃-based composite photocatalysts by coupling with other metal-oxide photocatalysts resulted in the enhanced photocatalysis performance that is previously reported.¹⁶,³⁵ The preparation of reported composite photocatalysts is, however, limited by multiple-step and complex procedures, grouping individually prepared component materials. In addition, the BiOCl complex is a material that is often formed in the synthesis processes of Bi₂S₃ materials from the solution; therein, the precursor includes Cl ions and water.³⁶⁻³⁸ The bandgap of BiOCl is wide (3.17−3.54 eV at room temperature), leading to a poor photocatalytic performance under visible light irradiation.³⁹,⁴⁰ Fortunately, the BiOCl complex such as Bi₂O₃·Cl₁₀ and BiOCl as n-type and p-type photocatalysts, respectively, could form a heterojunction to enhance the photocatalytic activity. Therefore, one-pot synthesis of SnO₂ and the Bi₂S₃/BiOCl compound as a novel photocatalyst under visible light is considered as a potential and interesting approach.

In this study, the SnO₂/Bi₂S₃/BiOCl–Bi₂O₃·Cl₁₀ (abbreviated as SnO₂/Bi₂S₃/Bi₂5) composites are fabricated by taking advantage of the robust, simple, and potentially scalable one-pot synthesis. The starting point of the transformation of Bi₂O₃·Cl₁₀ to BiOCl is known that Bi₂4O₃Cl₁₀ is a product of the thermal decomposition of BiOCl, which occurs as the temperature reaches 400°C.³⁴ It is worth to note here that 400°C was the starting point of the transformation of Bi₂O₃·Cl₁₀ from BiOCl, which means that there are some BiOCl existing in the composite to form a heterojunction with Bi₂O₃·Cl₁₀. When the SnO₂ precursor amount was added as high as 30 and 50%, the peaks of the rutile SnO₂ phase were gradually detected. In addition, the diffraction peaks of the BiOCl component are fraction peaks of the BiOCl phase (JCPDS no. 75-0887). It is well known that Bi₂O₃·Cl₁₀ is a product of the thermal decomposition of BiOCl, which occurs as the temperature reaches 400°C.⁴⁰,⁴³ It is worth to note here that 400°C was the starting point of the transformation of Bi₂O₃·Cl₁₀ from BiOCl, which means that there are some BiOCl existing in the composite to form a heterojunction with Bi₂O₃·Cl₁₀. When the SnO₂ precursor amount was added as high as 30 and 50%, the peaks of the rutile SnO₂ phase were gradually detected. In addition, the diffraction peaks of the BiOCl component are fraction peaks of the BiOCl phase (JCPDS no. 75-0887). It is well known that Bi₂O₃·Cl₁₀ is a product of the thermal decomposition of BiOCl, which occurs as the temperature reaches 400°C.⁴⁰,⁴³

2. RESULTS AND DISCUSSION

2.1. XRD Pattern Analysis. The crystal structures of the as-prepared Bi₂S₃, SnO₂ NPs, and SnO₂/Bi₂S₃/Bi₂5 composites are characterized by using XRD patterns and presented in Figure 1. The XRD pattern of Bi₂S₃ indicates the orthorhombic

![Figure 1. XRD patterns of Bi₂S₃ and SnO₂/Bi₂S₃-Bi₂5 composites with different SnCl₂·SH₂O precursors: 5%, 15%, 30%, 50%, and SnO₂ NPs.](image)

Bi₂S₃ (JCPDS no. 170320) with typical diffraction peaks at 24.3°, 26.1°, 30.4°, 32.7°, 33.6°, 35.0°, 41.1°, 46.8°, 49.9°, 54.2°, and 58.9° corresponding to (101), (310), (211), (221), (410), (311), (430), (440), (160), (360), and (640) planes, respectively. The XRD pattern of SnO₂ NPs shows the presence of the tetragonal rutile SnO₂ structure (JCPDS no. 41-1445) with diffraction peaks at 26.5°, 34.1°, 37.9°, 46.04, and 52° associating with (110), (101), (200), (102), and (211) planes, respectively. The crystallinity of the samples changes significantly with the addition of the SnO₂ component in the composites.

For the XRD pattern of 5 and 15% SnO₂/Bi₂S₃-Bi₂5 samples, the crystallinity suddenly increased with a high intensity of (211) plane of Bi₂S₃ at the diffraction peak 2θ = 28.67° along with the presence of diffraction peaks of BiOCl (JCPDS no. 06-0249). However, the crystalline intensity of the BiOCl peaks is not high. After an annealing process performed at 400°C for 2 h, the XRD results also show the emergence of the monoclinic Bi₂O₃·Cl₁₀ phase (JCPDS no. 75-0887). It is well known that Bi₂O₃·Cl₁₀ is a product of the thermal decomposition of BiOCl, which occurs as the temperature reaches 400°C.⁴⁰,⁴³ It is worth to note here that 400°C was the starting point of the transformation of Bi₂O₃·Cl₁₀ from BiOCl, which means that there are some BiOCl existing in the composite to form a heterojunction with Bi₂O₃·Cl₁₀. When the SnO₂ precursor amount was added as high as 30 and 50%, the peaks of the rutile SnO₂ phase were gradually detected. In addition, the diffraction peaks of the BiOCl component are undetected at these concentrations. This observation implies that there is a critical amount of the SnO₂ precursor needed to produce the BiOCl–Bi₂O₃·Cl₁₀ heterojunction. The presence of BiOCl–Bi₂O₃·Cl₁₀ heterojunctions highlights the critical observation of this work in forming a multiple-phase system via facile routes, which will potentially be applied to the development of other systems with a robust, efficient, and straightforward approach.

2.2. FTIR Spectra Analysis. The FTIR profile of the as-prepared materials provides information about the functional groups and chemical bonds. The FTIR spectra of Bi₂S₃, SnO₂ NPs, and SnO₂/Bi₂S₃-Bi₂5 composites are shown in Figure 2.

![Figure 2. FTIR spectra of Bi₂S₃, SnO₂, and SnO₂/Bi₂S₃-Bi₂5 composites with different SnCl₂·SH₂O precursors: 5%, 15%, 30%, 50%, and SnO₂ NPs.](image)
The bands centered around 3430 and 1634 cm\(^{-1}\) are referred to OH vibration modes, which are observed due to the bending vibrations of absorbed water molecules.\(^{44}\) For better observation, the FTIR spectra are enlarged in the area of 1450–400 cm\(^{-1}\) (magnified figure). In the FTIR profile of Bi\(_2\)S\(_3\), the peak at 1192 cm\(^{-1}\) corresponds to Bi–OH bonds,\(^{45}\) and the sharp peak around 1076 cm\(^{-1}\) is due to the formation of Bi\(_2\)S\(_3\).\(^{44}\) These two peaks are also observed in the structure of as-prepared composites, and the intensity of these peaks sharply decreases as the content of SnCl\(_4\cdot\)5H\(_2\)O precursors increases. The absorption bands at 619 cm\(^{-1}\) are ascribed to Bi–S stretching modes.\(^{46}\) The peaks at 528, 580, and 640 cm\(^{-1}\) are associated with the stretching mode of Bi–O, polarized Bi–O–Bi bridging oxygen, and O–H in Bi–O lattice, respectively.\(^{47-48}\) Notably, there is a new peak at 1112 cm\(^{-1}\) in the structure of the as-prepared composites, which can be assigned as stretching vibration peaks of Bi–Cl bonds in the structure of BiOCl compounds.\(^{50}\) These results agree well with the hypothesis claimed in the XRD analysis and further confirm the formation of the components (BiOCl and Bi\(_2\)O\(_3\)Cl\(_{10}\)) in the as-prepared composite. The FTIR profile of SnO\(_2\) is also provided. The broad bands at 616 and 520 cm\(^{-1}\) correspond to antisymmetric O–Sn–O stretching mode and terminal oxygen vibration in SnO\(_2\) nanostructures, respectively.\(^{51-53}\) The increase in the intensity around the band at 616 cm\(^{-1}\) is in agreement with the increase in the amount of SnO\(_2\) precursor in the samples.

2.3. Morphology Observation. The morphology of the as-prepared materials is observed through the scanning electron microscopy (SEM) images, as shown in Figure 3. The result shows that the original morphology of Bi\(_2\)S\(_3\) after the hydrothermal process is microrods, having the length and diameter of about 1–4 μm and 100–250 nm, respectively. As previously reported results,\(^{54}\) after undergoing the hydrothermal process for 24 h, SnO\(_2\) NPs are formed, which are seen as small and spherical objects in the SEM images. A better observation for the SnO\(_2\) NPs will be shown in the TEM analysis (Figure 4). SEM images clearly show that there is an accumulative formation of small and spherical objects on the surface of the Bi\(_2\)S\(_3\) rods (see Figure 3c–f). At high concentrations (30 and 50%) of the SnO\(_2\) precursor, the surface of the Bi\(_2\)S\(_3\) rods is fully covered by the spherical objects. This observation clearly shows the successful formation of the composite with a hierarchical structure.

The detailed morphologies, crystal structures, and heterojunction features of the as-prepared samples are studied, combining high-resolution transition electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns, as shown in Figure 4. The morphology of Bi\(_2\)S\(_3\) is further confirmed in Figure 4a with microrod configuration. Figure 4b presents the HR-TEM of Bi\(_2\)S\(_3\) in which the fast Fourier transform (FFT) result shows two clear cycles, indicating that there are two main orientations in Bi\(_2\)S\(_3\). From this, it can be determined that there are two d-spacing values of 2.71 and 2.81 Å corresponding to the (410) and (221) planes. The selected area electron diffraction (SAED) displays a clear pattern; however, the spots are not well distributed. This result is consistent with FFT results from HR-TEM by confirming the presence of (410) and (211) planes in Bi\(_2\)S\(_3\), as shown in Figure 4c. The morphology of SnO\(_2\) NPs is clearly shown in Figure 4d. The nanoparticles have a uniform size with an average diameter of 2.24 ± 0.59 nm. The result shows that the SnO\(_2\) NPs have obtained d-spacing values of 2.63 and 3.36 Å, which present (101) and (110) planes of rutile SnO\(_2\), respectively, as shown in Figure 4e.\(^{54}\) The SAED pattern of SnO\(_2\) NPs also agrees well with the HR-TEM data by showing a well-defined crystallinity of (101) and (110) planes in the crystal structure of SnO\(_2\) NPs, as shown in Figure 4f. TEM observation from the 15% SnO\(_2\)/Bi\(_2\)S\(_3\)-Bi\(_25\) composite sample, as shown in Figure 4g, shows that the morphology of the composite also possesses a rod shape, which is similar to that of Bi\(_2\)S\(_3\). However, the surface of the rod is covered by nanoparticles that are related to the presence of SnO\(_2\) NPs after the hydrothermal process. Figure 4h shows the HR-TEM capture of the composite sample presenting d-spacing values of 2.76, 2.92, 3.08, and 3.36 Å, which confirm the presence of BiOCl (110), Bi\(_2\)S\(_3\) (211), Bi\(_2\)O\(_3\)Cl\(_{10}\) (213), and SnO\(_2\) (110), respectively. The TEM, HR-TEM, and SAED patterns thus firmly confirm the XRD results.

2.4. Optical and Electrical Properties. The results indeed show the formation of the SnO\(_2\)/Bi\(_2\)S\(_3\)-Bi\(_25\) composites, which changes the structural properties of the Bi\(_2\)S\(_3\). This change in the microstructure leads to the change in the surface of the photocatalyst in which the photocatalytic reactions occur. In addition, we also obtain the change at the macroscopic scale of the photocatalysts as the composite forms. There is a change in the color of the Bi\(_2\)S\(_3\) (black) and SnO\(_2\) NPs (white) to yellow and gradually to brown as the SnO\(_2\) precursor content increases (see the inset in Figure 5a). This observation implies that there is a change in the optical properties of the composite compared to that of Bi\(_2\)S\(_3\). It has been confirmed by characterizing the band structure of Bi\(_2\)S\(_3\), SnO\(_2\), and 15% SnO\(_2\)/Bi\(_2\)S\(_3\)-Bi\(_25\) via diffuse reflectance spectroscopy (DRS) technique. Figure 5a presents the photoabsorption ability of the samples. Having a dark color and narrow bandgap, the Bi\(_2\)S\(_3\) sample shows strong absorption in the visible light range (400–800 nm), whereas SnO\(_2\) with a large bandgap shows a primary absorption position within the UV light region. As mentioned previously, the formation of the composite leads to the change in its optical properties. The 15% SnO\(_2\)/Bi\(_2\)S\(_3\)-Bi\(_25\) sample displays an intermediate absorption edge compared to SnO\(_2\) and Bi\(_2\)S\(_3\).

Based on the absorption spectra in Figure 5a, the \(E_g\) of the samples can be estimated by eq 1.\(^{55}\)
\[ \alpha \nu \nu = A(\hbar \nu - E_g)^{n/2} \]

where \( \alpha \), \( \nu \), \( E_g \), and \( A \) are the absorption coefficient, light frequency, bandgap energy, and a constant, respectively. The \( n \) is determined by the type of optical transition of a semiconductor (\( n = 1 \) for a direct transition). As reported previously, the value of \( n \) is 1 for Bi\(_2\)S\(_3\), SnO\(_2\), and 15% SnO\(_2\)/Bi\(_2\)S\(_3\)-Bi2S\(_5\). The intercept values at the \( x \)-axis for Bi\(_2\)S\(_3\), SnO\(_2\), and 15% SnO\(_2\)/Bi\(_2\)S\(_3\)-Bi2S\(_5\) are thus determined to be 1.5, 3.2, and 2.9 eV, respectively, which are presented in Figure 5b.

Also, the photoelectric properties via visible light transient photocurrent are investigated to evaluate the generation of photogenerated \( e^-\)–\( h^+ \) pairs. As shown in Figure 5c, the SnO\(_2\) photoelectrodes do not show any photocurrent density as the xenon lamp is switched on since the light used in this study illuminates visible light that is out of photoresponse range of SnO\(_2\). The result indicates that the Bi\(_2\)S\(_3\) sample shows the photocurrent response because its bandgap can absorb and respond to visible light. Notably, the photocurrent density of the 15% SnO\(_2\)/Bi\(_2\)S\(_3\)-Bi2S\(_5\) composite is much higher than that of the Bi\(_2\)S\(_3\), which is nearly 2-fold of Bi\(_2\)S\(_3\).

The Mott–Schottky plots of Bi\(_2\)S\(_3\) and SnO\(_2\) are recorded in Figure 5d to locate their CB position. As shown in Figure 5d, the CB potentials of Bi\(_2\)S\(_3\) and SnO\(_2\) are about -0.8 and 0.16 eV versus NHE, respectively. Although BiOCl and Bi\(_{24}\)O\(_{31}\)Cl\(_{10}\) could not be synthesized in isolation in this research, their typical CB potentials have been reported at 0.61 and -0.59 eV, respectively. These reports have also indicated that the bandgap energies of BiOCl and Bi\(_{24}\)O\(_{31}\)Cl\(_{10}\) are about 3.09, and 2.80 eV, respectively. The CB position and bandgap of the materials strongly suggest the band alignment of the composite, as shown in Figure 5e. Therein, BiOCl and Bi\(_{24}\)O\(_{31}\)Cl\(_{10}\) could be formed in the layer between SnO\(_2\) and Bi\(_2\)S\(_3\) when conducting the experiment, resulting in the alignment of band structure as a type II heterojunction.
2.5. Photocatalytic Activity of As-Prepared Materials.

To study the photocatalytic activity of the as-prepared materials in degrading organic pollutants, RhB is used as a representative pollutant for the test. The photocatalytic degradation experiments are performed at room temperature. Before light is turned on, the suspension is stirred in the dark to reach the equilibrium between adsorption and desorption. The suspension is then irradiated by a simulated sunlight lamp equipped with a UV cut-off glass to get visible light. The photocatalytic activity experiments are monitored for 180 min, and the samples are taken every 30 min. As shown in Figure 4a, SnO$_2$ NPs do not show photocatalytic activity for 180 min under visible light resulting from its large bandgap. The fluctuation in the result of SnO$_2$ could be due to the adsorption and desorption behaviors. This result also indicates that the RhB solution is not affected by photodegradation or photosensitivity, which is important to note in conducting photocatalytic experiments. The Bi$_2$S$_3$ sample shows a relatively low photocatalytic performance, which is 29.40% after 180 min under visible light irradiation. This result is already predicted since the recombination of photogenerated e$^-$−h$^+$ pairs of Bi$_2$S$_3$ is fast as well as its photodegradation problem. Interestingly, the formation of a composite by mixing the precursor solutions undergoing a hydrothermal process significantly increases the photocatalytic efficiency. Notably, the 15% SnO$_2$/Bi$_2$S$_3$-Bi$_2$S$_3$ sample shows the highest performance with 80.8%, which is around 2.75 times higher than pure Bi$_2$S$_3$ after 180 min of irradiation. The photocatalytic efficiencies of the components 5, 15, 30, and 50% SnO$_2$/Bi$_2$S$_3$-Bi$_2$S$_3$ reach 52.9, 80.8, 17.7, and 15.4%, respectively. The results thus indicate that the optimal adding concentration of the SnO$_2$ precursor was 15%. In excess of this optimal concentration, the photocatalytic efficiency of the composites drastically decreases. This result is interpreted as the blocking effect of SnO$_2$ NPs that cover the surface of Bi$_2$S$_3$ considerably, which prevents light and the pollutant molecules from reacting with Bi$_2$S$_3$. The photocatalytic efficiency of SnO$_2$ with visible light activation is negligible; it thus reduces the efficiency of...
the composite as SnO₂ becomes the main part. The UV−Vis spectra of RhB versus time over the materials are shown in Figure S1. Overall, the typical peak of RhB is at 554 nm and is unchanged during the adsorption process. This peak decreased and had a blue shift during the photocatalytic test. The shift in absorption spectra could be due to the formation of N-deethylated intermediates from the photocatalytic removal of RhB.57 These results may be a demonstration that RhB was degraded rather than decolored.

In addition to photocatalytic efficiency, the kinetics of RhB degradation are studied using the Langmuir−Hinshelwood kinetics equation for a first-order reaction, based on which the apparent rate constant (k) can be calculated to have a comprehensive understanding. As shown in Figure 6b, the reaction rates (k) of SnO₂, Bi₂S₃, 5% SnO₂/Bi₂S₃-Bi25, 15% SnO₂/Bi₂S₃-Bi25, 30% SnO₂/Bi₂S₃-Bi25, and 50% SnO₂/Bi₂S₃-Bi25 are 0, 1.5 × 10⁻³, 4.3 × 10⁻³, 9.6 × 10⁻³, 0.9 × 10⁻³, and 0.8 × 10⁻³, respectively, which show that the 15% SnO₂/Bi₂S₃-Bi25 sample has the highest reaction rate. The k value of 15% SnO₂/Bi₂S₃-Bi25 is calculated to be 9.6 × 10⁻³ min⁻¹, a value approximately 5-fold higher than that of Bi₂S₃ (1.8 × 10⁻³ min⁻¹). These photocatalytic activity profiles clearly show that the SnO₂/Bi₂S₃-Bi25 composites have superior efficiency and rate for RhB photocatalytic degradation under visible light at the optimal concentration of 15% SnO₂ precursor. The enhanced photocatalytic activity of the 15% SnO₂/Bi₂S₃-Bi25 composite results from the improved photoabsorption in the visible light range and the suppressed recombination of the e⁻−h⁺ pairs during the photocatalytic process (Figure 6a). Also, composites underwent the hydrothermal condition, and hybrid states in the composite leading to dispersions in the conduction bands and valence bands in the components can create superior mobility on photogenerated e⁻−h⁺ pairs, enabling these e⁻−h⁺ pairs to travel, contributing to the e⁻−h⁺ separation and ultimately improving the photocatalytic efficiency of the composite. It is worth mentioning that the obtained photocatalytic efficiency by the new SnO₂/Bi₂S₃-Bi25 composite in our work is superior compared to that of reported works. In terms of efficiency, the SnO₂/Bi₂S₃-Bi25 composite

Figure 5. (a) DRS spectra, (b) Tauc’s plots obtained through the applications of eq 1, (c) transient photocurrent response under visible light of Bi₂S₃, SnO₂, and 15% SnO₂/Bi₂S₃-Bi25 composite, (d) Mott−Schottky plots of SnO₂ and Bi₂S₃, and (e) band alignment of the composite. Insets are digital photos of as-prepared samples.

Figure 6. (a) RhB photocatalytic degradation versus irradiation time of Bi₂S₃, SnO₂, and SnO₂/Bi₂S₃-Bi25 composites under visible light for 180 min. The C/C₀ was calculated from eq 2 with the absorbance at λ = 554 nm. (b) Plots of the dependence of ln(C/C₀) on irradiation time and their L−H fit curves. (c) Apparent quantum efficiency for RhB degradation over the materials under visible light for 180 min. (d) Recycling test for photocatalytic degradation of RhB over 15% SnO₂/Bi₂S₃-Bi25 composites under visible light.
reported herein is among the best photocatalysts for the degradation of RhB. The apparent quantum efficiency is also calculated to compare the efficiencies of photons utilizing for the RhB degradation over the materials, as shown in Figure 6c. Despite the high degradation of RhB, the apparent quantum efficiency (AQE) evaluations of the materials are quite low, with the highest value at $12.07 \times 10^{-4}$% for the 15% SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 composite. The result indicates that the 15% SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 composite deployed photons much better than SnO$_2$ (0%), Bi$_2$S$_3$ (4.44 $\times 10^{-4}$%), and the other composites (from $2.10 \times 10^{-4}$ to $8.41 \times 10^{-4}$%).

Practical applications require that the photocatalytic materials have not only an excellent efficiency but also stability for reuse to minimize the expense. To evaluate the stability and reusability of the SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 composites, recycling tests are performed four times for the photocatalytic degradation of RhB over 15% SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 under visible light irradiation. As shown in Figure 6d, there is no significant reduction of photocatalytic efficiency observed up to the fourth cycle, which strongly indicates that the high stability of the composite photocatalyst.

2.6. Proposed Mechanism for RhB Photocatalytic Degradation of SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 Composites. In photocatalytic experiments, photocatalysts produce ROS by generating $e^−-h^+$ pairs under light activation. This photocatalytic activity gives rise to oxidation and decomposition of most organic molecules, thereby offering the potential for the complete elimination of organic contaminants. To get an insight into the photocatalytic activity of our composite system for RhB degradation, we performed a series of trapping experiments to figure out the critical factor governing the photocatalytic degradation. Scavengers as K$_2$C$_2$O$_4$, IPA, and K$_2$Cr$_2$O$_7$ are used to trap holes ($h^+$), hydroxyl radicals (·OH), and electrons ($e^-$), respectively, and (b) DMPO-ESR spectra of 15% SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 composite with electron spin resonance trapping of free radicals with 5,5-dimethyl-1-pyrroline N-oxide (DMPO-ESR) under the visible light condition for 10 min.

An electron spin resonance with 5,5-dimethyl-1-pyrroline N-oxide (DMPO-ESR) is performed to show the ability of generating ROS such as superoxide anion radicals (DMPO·O$_2^-$) in methanol and hydroxyl radicals (DMPO·OH) in the aqueous state by the 15% SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 composite under the visible light condition ($\lambda > 400$ nm) for 10 min. The production of ROS from the 15% SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 composite is shown in Figure 7b. There is no signal in dark conditions for both (DMPO·O$_2^-$) and (DMPO·OH) cases. Having activated by the visible light irradiation, signals are detected. The 15% SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 composite shows strong signals, which further explain its superior photocatalytic performance under visible light irradiation. The superoxide anion radical (DMPO·O$_2^-$) test shows clearly the generation of ·OH. The ·OH is derived from reactions between photogenerated $e^-$ and the absorbed O$_2$ on the surface of the catalyst. The generation of ·OH, which consumes lots of the photogenerated $e^-$, could substantially inhibit the recombination of photogenerated carriers, favoring the oxidation of RhB originated by photogenerated $h^+$. With the results from the trapping experiment of $e^-$ and DMPO-ESR, it seems that the active species ·OH are indeed generated during the photocatalytic process to enhance the role of ·OH but not involved much in the photocatalytic process. The DMPO-ESR also presents the clear peak of DMPO·O$_2^-$ and DMPO·OH scavengers, indicating that ·OH radicals engage well in the photocatalytic process.

To propose the photocatalytic degradation mechanism of the as-prepared SnO$_2$/Bi$_2$S$_3$-Bi$_2$5 composite, we present herein the photocatalytic process via chemical equations and schematic illustration, as shown in Figure 8. Having activated by visible light exposure, photogenerated $e^-$ moves from the
valence band (VB) to conduction band (CB) of the photocatalyst, while h+ remains in the VB (eq 2). The e−−h+ pairs move to the surface of the photocatalyst in which the photocatalytic degradation occurs via oxidation and decomposition. The e− reacts with O2 to produce O2− (eq 3) that continually reacts with water through intermediate reactions to produce •OH radicals (eqs 4−6). On the other side, the h+ combines with OH− from eqs 4 and 6 to form •OH (eq 7). The h+ also reacts with water to form •OH (eq 8). These radicals (•OH) actively decompose organic compounds such as RhB (eq 9).

\[
\begin{align*}
\text{SnO}_2/\text{Bi}_2\text{S}_3/\text{BiOCl} \rightarrow & \quad \text{SnO}_2/\text{Bi}_2\text{S}_3/\text{BiOCl} - \text{Bi}_{25}\text{O}_{31}\text{Cl}_{10} \quad (\text{e}^-_{\text{CB}} + \text{h}^+_{\text{VB}}) \\
\text{e}^- + \text{O}_2 \rightarrow & \quad \text{O}_2^- \\
\text{O}_2^- + \text{H}_2\text{O} \rightarrow & \quad \text{HO}_2 + \text{OH}^- \\
\text{HO}_2 + \text{H}_2\text{O} \rightarrow & \quad \text{H}_2\text{O}_2 + \text{OH} \\
\text{H}_2\text{O}_2 + \text{e}^- \rightarrow & \quad \text{OH} + \text{OH}^- \\
\text{h}^+ + \text{OH}^- \rightarrow & \quad \text{OH} \\
\text{h}^+ + \text{H}_2\text{O} \rightarrow & \quad \text{OH} + \text{H}^+ \\
\text{OH} + \text{RhB} \rightarrow & \quad \text{degradation products}
\end{align*}
\]  

3. CONCLUSIONS

In summary, we have successfully synthesized SnO2/Bi2S3-Bi25 composites via a simple, robust, and straightforward hydrothermal approach followed by thermal decomposition. The as-prepared ternary composite photocatalyst exhibits a superior photocatalytic activity in degradation of Rhodamine B by visible light activation, which is about 2.75-fold higher than Bi2S3. SnO2 NPs did not show any photocatalytic activity due to the large bandgap. The result also showed that the concentration of the 15% SnO2 precursor solution was the optimal concentration that gives rise to a photocatalytic degradation efficiency of 80.8% in 180 min under visible light. The SnO2/Bi2S3-Bi25 photocatalyst also showed an excellent photostability. The radical trapping test indicated that the photogenerated h+ was the main factor in the photocatalytic reaction, which directly contributes to the oxidation and decomposition of the pollutant. Thus, the SnO2/Bi2S3-Bi25 composites are promising as a new, efficient, and robust photocatalyst that can eliminate organic pollutants actively. Because the SnO2/Bi2S3-Bi25 photocatalysts formed via one-pot synthesis are highly promising, further studies are needed to discover their potential application fully.

4. MATERIALS AND METHODS

All chemicals were of analytic grade and used without being further treated. Bismuth nitrate (Bi(NO3)3·5H2O, 99.00% pure), thiourea (CH2N2S2, 99.90%), tin chloride (SnCl2·H2O, 99.99% pure), hydrazine hydrate (N2H4·H2O, 99.00% pure), sodium hydroxide (NaOH, 99.00%), ethanol (C2H6O, 99.90%), isopropyl alcohol (IPA, C3H8O, 99.99% pure), deionized water (DI water, Thermal Scientific), and Rhodamine B (C36H31ClN2O3, 99.00%).

4.1. Synthesis of SnO2/Bi2S3-Bi25 Composites. The procedures for synthesizing individual Bi2S3 and SnO2 nanoparticles (NPs) are described in Table 1. The process of fabricating SnO2/Bi2S3-Bi25 by the one-pot synthesis is schematically presented in Figure S3.

For the preparation of the SnO2/Bi2S3-Bi25 composite, the solutions for the synthesis of Bi2S3 (solution A) and SnO2 (solution B) were separately prepared. For the Bi2S3 part, 2.587 g of Bi(NO3)3·5H2O was dissolved into 66.670 mL of DI water, which was subsequently mixed with a solution prepared by dissolving 0.60 g of CH2N2S into 13.34 mL of DI water. This mixture was then heated at 60 °C for 20 min to form a yellow mixture solution, followed by continuous stirring for 45 min at room temperature. After this step, solution A was obtained. Meanwhile, solution B was prepared as follows: 2.69 mL of DI water and 3.39 mL of N2H4·H2O was added into a mixture composed of 76.60 g of Bi(NO3)3·5H2O, 66.67 g of Bi(NO3)3·5H2O, 2.69 mL of DI water, and 3.39 mL of N2H4·H2O (solution B) were separately prepared. For the Bi2S3 part, 2.587 g of Bi(NO3)3·5H2O was dissolved into 66.670 mL of DI water, which was subsequently mixed with a solution prepared by dissolving 0.60 g of CH2N2S into 13.34 mL of DI water. This mixture was then heated at 60 °C for 20 min to form a yellow mixture solution, followed by continuous stirring for 45 min at room temperature. After this step, solution A was obtained. Meanwhile, solution B was prepared as follows: 2.69 g of SnCl2·H2O was added into a mixture composed of 76.60 mL of DI water and 3.39 mL of N2H4·H2O. This second solution was then adjusted to have a pH of 12 by adding NaOH solution (solution B was obtained). After preparing the two solutions, solution B was added dropwise into solution A, followed by a hydrothermal process at 135 °C for 24 h. After the hydrothermal process, the product was cooled naturally to room temperature. The product was then centrifuged, filtered out, rinsed with ethanol and DI water several times, then dried at 80 °C for 6 h, and annealed at 400 °C for 2 h.

4.2. Characterizations. The crystal structures were identified for the mounted squeezed tablet of samples by X-ray diffraction (XRD) patterns using a Bruker D8-Advance S005 with a 2θ range from 20° to 80° and Cu Kα radiation (λ = 0.154064 nm). The chemical bonds in materials were determined by Fourier-transform infrared (FTIR) spectroscopy taken on a JASCO FTIR-4700 spectrometer, with a wavenumber range from 4000 to 400 cm−1 and step size of 1 cm−1. The spectra are recorded through a solid-phase approach by mixing 1 wt % of sample in KBr pellets. The morphology of materials was captured for distributed samples on copper mesh via transmission electron microscopy (TEM) images taken on a JEM 1400 Instrument, JEOL. To provide more information on the surfaces of the materials, scanning electron microscopy (SEM) images were also taken for coated samples on a conductivity substrate using ZEISS EVO MA 10 and ZEISS EVO LS 10 microscopes. The optical properties of materials...
were measured by a UV–Vis diffuse reflectance spectroscopy (DRS), taken in a wavelength range of 200–800 nm using a UV–Vis spectrometer (JASCO-V550). The flat band potential and photocurrent density characterization of materials were measured by an electrochemical workstation (Biologic SP240) with three electrodes, which include a Pt wire counter electrode, an Ag/AgCl reference electrode, and the working electrode of the as-synthesized materials. The solution is 3 M KCl. The measurements were conducted under visible light irradiation (100 mW/cm² from a 150 W xenon lamp coupled with an AM 1.5G filter).

4.3. Evaluation of the Photocatalytic Activity of Materials. The photocatalytic activity of materials was investigated using a UV–Vis spectrometer (U2910, HITACHI, Japan) with wavelengths in the 450–600 nm range under a simulated sunlight lamp (Osram, 300 W) associated with a UV cut-off filter to produce only visible light. Rhodamine B (RhB) was used as a pollutant for this study. The photocatalytic degradation experiments were performed at room temperature as follows: 20 mg of catalyst was introduced into 60 mL of RhB solution (at a concentration of 10 mg·L⁻¹). The suspension was stirred in the dark and then centrifuged, and the absorption spectra were measured. The processes were repeated every 20 min and the samples were put back into the solution after each measurement and continuously stirred in the dark until the equilibrium between adsorption and desorption was reached. Then, the suspension was irradiated with a simulated sunlight lamp using a UV cut-off filter to get visible light for 180 min. The samples were taken at 30 min intervals over a certain period and then centrifuged to remove the photocatalyst powders. The absorbance data were measured using a UV–visible spectrophotometer (U2910, Hitachi, Japan) at the highest intensity of RhB (typical λ at 554 nm).

According to Lambert–Beer’s law (eq 10)

\[ A = \frac{I}{I_0} = \varepsilon dC \]  
where A is the absorbance, C is the solution concentration (mol·L⁻¹ or mg·L⁻¹), d is the thickness of the cuvette containing the sample (cm), and \( \varepsilon \) is the molecular absorption coefficient.

Equation 11 can be obtained from eq 10 as follows

\[ \frac{C}{C_0} = \frac{A}{A_0} \]  
Equation 11 shows that the solution concentration was proportional to the absorbance. The \( \frac{C}{C_0} \) is the variation of the concentration versus the irradiation times in which \( C_0 \) is the initial concentration of the RhB solution after reaching adsorption–desorption equilibrium (mg·L⁻¹), and C is the concentration of RhB solution (mg·L⁻¹) at time t (min) of irradiation. The photocatalytic tests were repeated three times, and the data were presented by using their average number.

The Langmuir–Hinshelwood (L-H) expression explaining the kinetics of heterogeneous catalytic systems is given by eq 12

\[ r = -\frac{dC}{dt} = \frac{k_rKC}{1 + KC} \]  
where \( k_r \) is the reaction rate constant, \( K \) is the adsorption rate constant, and \( r \) is the rate of reaction that changes with time. The \( r \) in eq 12 is represented in terms of initial reaction rate, \( r_0 \), at the initial dye concentration, \( C_0 \), or at the concentration after reached adsorption–desorption equilibrium, \( C_e \). Equations 13 and 14 give the initial rate of reaction as a function of \( C_0 \) and \( C_e \), respectively.

\[ r_0 = \frac{k_rKC_0}{1 + KC_0} \]  
Equation 14 could be converted to eq 15 to simply determine the relation between the apparent first-order rate constant, \( k_r \), and the concentration after reaching adsorption–desorption equilibrium, \( C_e \). Then, eqs 12 and 15 were combined to convert to the linear form of the L-H model as eq 16

\[ \ln \left( \frac{C}{C_0} \right) = kt \]  

4.4. Apparent Quantum Efficiency (AQE) Evaluation. The AQE, \( \eta \) (%), was used as eq 17 to simplify the difficulty in determining absorbed photons for quantum efficiency.58,59 This result can evaluate the optimization in utilizing photons for photocatalytic reactions.

\[ \eta_{app} = \frac{\text{number of degraded pollutant molecules}}{\text{number of photons entering the reactor}} \times 100\% \]  
For the degradation of RhB, the parameters of eq 17 can be described as eqs 18 and 19. From these equations, eq 17 can be transformed into eq 20.

\[ \eta_{app} = \frac{N_A n_{RhB}}{1000M_{RhB}} \]  
\[ \text{number of photons entering the reactor} = \text{photon flux } \times \text{irradiation area } \times t \]  
\[ \eta_{app} = \frac{N_A(C_0 - C)V}{\text{photon flux } \times \text{irradiation area } \times 1000M_{RhB}} \]  
(20)

where \( N_A \) is the Avogadro constant, approximately 6.022 × 10²³ mol⁻¹, \( V \) is the volume of RhB solution (L), \( M_{RhB} \) is the molar mass of RhB (g·mol⁻¹). For the simulated sunlight lamp (Osram 300 W) used in this work, the photon flux is 2.72 × 10¹⁸ cm⁻²·min⁻¹. The photocatalytic experiment used a 100 mL beaker with an irradiation area of approximately 19.63 cm².

4.5. Radical Trapping Experiment by Scavengers. For the trapping tests, they were tested by using a scavenger with a concentration of 10⁻³ M. Potassium oxalate (K₂C₂O₄) and isoproxy alcohol (IPA) were used as effective scavengers of holes (h⁺) and hydroxyl radicals (OH⁻), respectively. Potassium dichromate (K₂Cr₂O₇) was utilized as a scavenger of photogenerated electrons (e⁻). In each sample, 0.02 g of
catalyst was added into 60 mL of RhB with different trapping agents. Finally, the above solution was used for the investigation of photocatalytic activity with the same procedure as described in the photocatalytic activity experiment section.

4.6. Electron Spin Resonance Study. Electron spin resonance (ESR) with DMPO (5,5-dimethyl-1-pyrroline N-oxide) for detecting ESR signals of ROS, which were generated in the photocatalytic process by a Bruker EMX Plus X-Band spectrometer. The light source was a high-pressure xenon short-arc lamp with an UV filter (Labguide 150 W mercury arc bulb lamp, λ > 400 nm). To eliminate experimental errors, an identical quartz capillary tube was used throughout the measurement. Experimental conditions are as follows: temperature of 298 K, a center field of 3483 G, sweep width of 200 G, a frequency of 9.755 GHz, modulation amplitude of 1.00 G, and microwave power of 20 mW, the concentration of the sample at 400 ppm, and 1000 ppm of DMPO.

# ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02461.

Absorption spectra of RhB solution during the photocatalytic process and the synthesis process of the materials (PDF)

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Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

The study was supported by The Youth Incubator for Science and Technology Program, managed by Youth Development and Mr. The-Vinh Hoang Tran for the support of this work. The study was supported by The Youth Incubator for Science and Technology Program, managed by Youth Development Science and Technology Center—Ho Chi Minh Communist Youth Union and Department of Science and Technology of Ho Chi Minh City; the contract number is “33/2019/H-KHCTN-VU”.

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