Research Article

Visible-Light-Driven $\text{SO}_4^{2-}/\text{TiO}_2$ Photocatalyst Synthesized from Binh Dinh (Vietnam) Ilmenite Ore for Rhodamine B Degradation

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A low-cost and simplistic approach for the synthesis of nanosized $\text{SO}_4^{2-}/\text{TiO}_2$ photocatalyst was successfully performed using Binh Dinh ilmenite ore and H_2SO_4 as titanium and sulfur sources, respectively. The experimental results indicate that the obtained material exists in the form of particles with a size of about 22 nm and has a specific surface area of about $49 \text{ m}^2 \text{ g}^{-1}$. Compared with the TiO_2 sample, the $\text{SO}_4^{2-}/\text{TiO}_2$ sample shows much higher photocatalytic degradation of rhodamine B (RhB) under the sunlight irradiation. In more details, the nanosized $\text{SO}_4^{2-}/\text{TiO}_2$ sample obtained is capable of completely decomposing RhB after 9 hours of irradiation by a 60 W LED lamp with a corresponding intensity of 9,500 Lux. However, when the $\text{SO}_4^{2-}/\text{TiO}_2$ is irradiated by the sunlight with the intensity of 65,000 Lux, it only takes 2 hours to completely decompose rhodamine B (RhB), facilitating the use of $\text{SO}_4^{2-}/\text{TiO}_2$ as a potential photocatalyst for the RhB photodegradation.

1. Introduction

Coupled with the exploitation of resources to produce a series of different products to serve life, people have been releasing many pollutants into the environment. Among these pollutants, the persistent organic compounds in the water environment are substances that have negative impacts on humans as well as all other living creatures on earth. In order to meet the urgent requirement for wastewater treatment, a variety of water treatment technologies have been proposed such as adsorption [1–3], microwave catalysis [4, 5], and advanced oxidation processes including photocatalysis [6].

In recent years, the interest in the heterogeneous photocatalysis, which allows the use of the sunlight for the photocatalytic degradation of organic pollutants, has noticeably increased due to their potential applications in the water remediation. Compared to other water treatment technologies, this technology has more advantages in terms of envi-

ronmental benefits and operation costs. Thus, photocatalysis is considered one of the most promising technologies to replace the current wastewater treatment technologies in the near future [7–9].

From a practical point of view, a desirable semiconductor for photocatalysis should have the following properties: (i) high photostability, (ii) low toxicity, (iii) suitable band-gap, (iv) resistance to photocorrosion, and (v) affordable fabrication costs [10]. In this respect, among the reported candidates as photocatalysts like ZnO- [11], WO_3 - [12], CdS- [13], MoS_2 - [14], BiVO_4 - [15], and TiO_2 -based materials turn out to be one of the highly promising due to its excellent physical and chemical properties including high photocatalytic activity, nontoxicity, high thermal and chemical stability, and high reproducibility [16, 17].

However, the main reason that limits the use of TiO_2 for the photodegradation in wastewater treatment under solar irradiation is its large bandgap (3.20 eV for anatase, 3.0 eV

FIGURE 1: Process flow for the synthesis of TiO_2 nanoparticles from Binh Dinh ilmenite ore.

for rutile, and about 3.2 eV for brookite). In fact, TiO_2 can only be activated upon irradiation with a photon of light $< 390 \text{ nm}$, which only accounting for 3–5% of the solar spectrum. Hence, it is highly desirable to extend the light response of TiO_2 towards the visible region, enhancing its photocatalytic activity under the visible light irradiation. This can be achieved by (i) metal doping [18–20], (ii) nonmetal doping [19–22], and designing composites based on TiO_2 [23–33].

In this present work, TiO_2 was first successfully synthesized from Binh Dinh (Vietnam) ilmenite ore to reduce the fabrication costs of TiO_2 . After that, the obtained TiO_2 was hydrothermalized with H_2SO_4 to fabricate the $\text{SO}_4^{2-}/\text{TiO}_2$ with the aim to extend the light response of TiO_2 in the visible light region, enhancing its photocatalytic activities under the visible light irradiation. This work is devoted to investigating the effect of the SO_4^{2-} doping on the structural, optical, and photocatalytic activities for the RhB degradation of TiO_2 .

2. Experiments

2.1. Preparation of Nanosized TiO_2 from Binh Dinh Ilmenite Ore. Ilmenite ore, which was taken from Binh Dinh Minerals Joint Stock Company, was used as the starting material for the synthesis of the nanosized TiO_2 . In order to prepare the nanosized $\text{SO}_4^{2-}/\text{TiO}_2$, the nanosized TiO_2 was fabricated by the hydrolysis of ilmenite ore with hydrofluoric acid in three steps which is summarized as in Figure 1:

(Step 1) 10 g of ilmenite ore (titanium accounting for 52% of TiO_2) and 70 mL HF 20% (diluted from HF 48%, Sigma-Aldrich) were put into a plastic beaker and magnetically stirred with a speed of 300 rpm for 5 hours before settling and filtering to remove the solid residue (r_1) and collect the filtrate (I_1)

(Step 2) KCl saturated solution, which was diluted from 99% $\text{KCl}_{(s)}$, Sigma-Aldrich, was slowly added into the filtrate (I_1) under continuously stirring, leading to the formation of a white K_2TiF_6 precipitate. With the aim at eliminating the impurities and purify the K_2TiF_6 precipitate, the precipitate was filtered and dissolved in hot water at 80°C before rapidly cooled down to room temperature to obtain again the K_2TiF_6 precipitate (r_2). The obtained K_2TiF_6 precipitate was dried at 105°C for 2 hours

(Step 3) 5 g of the K_2TiF_6 precipitate was dissolved in 500 mL of distilled water at 80°C before slowly adding 4 M NH_3 solution (prepared from ammonium hydroxide solution 28%, Sigma-Aldrich) until $\text{pH} = 9$. At the end of the hydrolysis process, the suspension was filtrated and washed on a vacuum filter to collect $\text{Ti}(\text{OH})_4$ solid (r_3), which was then dried at 105°C for 2 hours before annealing at 550°C for 3 hours to obtain the nanosized TiO_2 (denoted as TiO_2)

FIGURE 2: XRD patterns for TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$.

2.2. Synthesis of Nanosized $\text{SO}_4^{2-}/\text{TiO}_2$. 1 g aboveobtained TiO_2 was put into a Teflon flask before adding 150 mL of H_2SO_4 0.7 M (diluted from H_2SO_4 99%, Sigma-Aldrich). After that, the mixture was hydrothermalized at 170°C for 24 hours using an autoclave. At the end of the hydrothermal process, the suspension was washed and dried at 105°C for 2 hours, obtaining the nanosized $\text{SO}_4^{2-}/\text{TiO}_2$ material.

2.3. Catalyst Characterization. XRD patterns of obtained samples were recorded at room temperature in the 2θ range of 20 – 70° using a D8 Advance Bruker diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.540 \text{ \AA}$); operated at 40 kV and 0.04 A. The average crystallite size was determined from XRD measurements by applying the Debye–Scherrer equation: $\bar{r} = (0.89 \cdot \lambda) / (\beta \cdot \cos\theta)$ [34], to the highest intensity peak (101), which was fitted with Origin software to identify the full-width-at-half-maximum and the peak position.

FT-IR spectra were collected by means of an IRAffinity-1S spectrometer in the spectra range of 4000 – 400 cm^{-1} . The UV-vis diffuse reflectance spectra were recorded using U4100 UV-Vis-NIR Hitachi.

The specific surface area and porous properties of obtained sample were determined by N_2 adsorption-desorption isotherms methods at 77 K (BET) using Micromeritics ASAP 2000.

XPS measurements were carried out on the ESCALab 250 spectrometer (Thermo VG, UK) using Al $K\alpha$ radiation with the photon energy of 1486.6 eV to identify the element, composition, and oxidation state on the surface of the photocatalyst. A sufficient amount of powder was immobilized on carbon tape before loading into the XPS chamber. Survey scans were acquired using 0.48 eV resolution energy and 0.1 eV/step with charge neutralization. The peaks positions were calibrated according to the C1s peak at 284.6 eV.

Particle size and surface morphology of obtained samples were investigated by SEM and TEM using Nano SEM-450 and JOEL-JEM-1010, respectively. The measurement of photoluminescence (PL) was performed by a spectrometer

Horiba FL3-22 over the wavelength of 400–600 nm with a 450 W Xenon lamp (the excitation wavelength of 380 nm).

2.4. Photocatalytic Measurements for $\text{SO}_4^{2-}/\text{TiO}_2$. Photodegradation of RhB was performed in order to evaluate the photocatalytic activities of the TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ photocatalysts. 60 mg $\text{SO}_4^{2-}/\text{TiO}_2$ photocatalyst was added into a 250 mL containing 100 mL RhB solution (10 mg/L). The suspension was stirred for 60 minutes in the dark to reach the adsorption-desorption equilibrium before irradiating the mixture by the 60 W LED lamp with a corresponding intensity of 9,500 Lux or the sunlight with the intensity of 65,000 Lux. After that, 2 mL of the solution was taken out every 60 minutes and centrifuged (6000 rpm, 20 minutes) for subsequent measurements. The solution obtained after centrifugation was protected in the dark before determining the concentration of RhB with a UV-Vis spectrometer (UV-1800 Shimadzu) by monitoring the absorbance of RhB at 553 nm.

RhB photodegradation efficiency is calculated by the following formula:

$$H = \frac{C_0 - C_t}{C_0} \times 100. \quad (1)$$

In which, C_0 is the initial concentration of RhB before illumination and C_t is the remaining concentration of RhB after each corresponding irradiation time.

3. Results and Discussions

3.1. Determination of Crystal Phase Structure by X-Ray Diffraction. Figure 2 shows the XRD patterns of the TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ samples. As can be seen in Figure 2, the two XRD patterns exhibit the characteristic diffraction peaks of both the anatase and rutile phases. In more details, the diffraction peaks at $2\theta = 25.26, 37.78, 38.56, 48.5$, and 53.90° are characteristic peaks for the anatase-type TiO_2 (JCPDS 21-1272) while the diffraction peaks at $2\theta = 27.50$ and 53.9° are typical peaks for the rutile-type TiO_2 (JCPDS 21-1276) and are indexed as (110) and (101).

The proportion of the anatase and rutile phases in the obtained samples is determined by the following expression [35]:

$$X_{\text{rutile}} = \left(1 + 0.79 \left(\frac{I_A}{I_R} \right) \right)^{-1}, \quad (2)$$

$$X_{\text{anatase}} = 1 - X_{\text{rutile}},$$

where X_{rutile} and X_{anatase} are the percentage (%) of the rutile and anatase phases, I_A is the maximum peak intensity corresponding to the crystal face (101) of the anatase phase, and I_R is the maximum peak intensity corresponding to the crystal face (110) of the rutile phase.

Table 1 shows the average crystallite size, the ratio of the anatase to rutile phase, the crystallinity, the specific surface area, and the RhB photodegradation efficiency for the TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ samples. As can be seen in Table 1, the ratio of the anatase to rutile phase hardly changes while there is a

TABLE 1: Characteristics for TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$.

Sample	Average crystallite size (nm)	Ratio of the anatase to rutile phase	Specific surface area (m^2g^{-1})	RhB photodegradation efficiency (%)	
				After 9 hours of the visible light irradiation	After 2 hours of the sunlight irradiation
TiO_2	19.09	83.16/16.84	89.4135	11.77	26.09
$\text{SO}_4^{2-}/\text{TiO}_2$	22.19	82.95/17.05	49.9120	99.47	99.63

FIGURE 3: SEM images for (a) TiO_2 and (b) $\text{SO}_4^{2-}/\text{TiO}_2$. FIGURE 4: TEM images for (a) TiO_2 and (b) $\text{SO}_4^{2-}/\text{TiO}_2$.

slight decrease in the crystallinity of the obtained sample after the SO_4^{2-} doping. This suggests that the hydrothermal process of the TiO_2 in H_2SO_4 at 170°C for 24 hours enhances the crystallinity of the $\text{SO}_4^{2-}/\text{TiO}_2$ obtained.

3.2. Surface Morphology and Porous Properties. The particle size and surface morphology of the TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ samples were characterized by SEM and TEM. Obtained SEM and TEM images are presented in Figures 3 and 4, respectively.

SEM images shown in Figure 3 indicate that all samples exist in the form of granules and are quite uniform with relatively small particle size.

TEM images shown in Figure 4 indicate that the presence of SO_4^{2-} on the surface of TiO_2 not only increases the particle size but also changes the surface morphology of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample in comparison with the unmodified TiO_2 .

It is well known that the photocatalytic degradation process of organic pollutants is affected by their adsorption on the photocatalyst; thus, the impact of the surface area is

FIGURE 5: The N_2 adsorption-desorption isotherms at 77 K for (a) TiO_2 and (b) SO_4^{2-}/TiO_2 .

FIGURE 6: Pore size distribution of TiO_2 and SO_4^{2-}/TiO_2 .

critical in the entire process. In this present work, the porous properties and specific surface area of the obtained samples were characterized by N_2 adsorption-desorption isotherms methods using Brunauer–Emmett–Teller (BET) surface area analysis and the results are shown in Figure 5.

The adsorption-desorption isotherms of both the TiO_2 and SO_4^{2-}/TiO_2 samples shown in Figure 5 had characteristic features of the type IV isotherm with the type H3 loop according to IUPAC showing structure of the material samples consist by an assemblage of particles joined together. Indeed, the small hysteresis loops occur in the area of relative pressure ($p/p^0 = 0.7-0.98$) higher compared with materials of mesoporous construction (their hysteresis loops usually present at relative pressure zones $p/p^0 = 0.4-0.8$). This suggests that the capillary structure inside the particles of the TiO_2 and SO_4^{2-} materials is not dominant (the material particles

are in the solid form). In other words, the materials have the dominant particle rather than porosity. The adsorption-desorption isothermal hysteresis loops of the two samples shown in Figure 5 are caused by adsorption-desorption in the interparticle space with dimensions in the range of 20–100 nm as determined by the capillary distribution curves in Figure 6. In addition, the peak in the capillary distribution curve of the SO_4^{2-}/TiO_2 material shifts significantly towards the small capillary size compared with the TiO_2 material. This can be explained by the fact that the modification of the TiO_2 materials leads to an increase in surface defects and a decrease in surface bond saturation, and thereby decreasing the strength of free particles and increasing the interaction between particles. As the results, the specific surface area of the particles significantly decreases ($89.4135\text{ m}^2/\text{g}$ and $49.9120\text{ m}^2/\text{g}$ for the TiO_2 and SO_4^{2-}/TiO_2 materials,

FIGURE 7: (a) UV-Vis diffuse reflectance spectra and (b) E_g versus Kubelka–Munk function for TiO₂ and SO₄²⁻/TiO₂.

FIGURE 8: FT-IR spectra for TiO₂ và SO₄²⁻/TiO₂.

respectively) due to the decrease in the spacing between the particles.

3.3. Optical Absorption Capacity. Optical properties of the TiO₂ and SO₄²⁻/TiO₂ samples were investigated by UV-Vis DRS and their UV-Vis DRS spectra are shown in Figure 7(a). It can be seen that the unmodified TiO₂ sample only absorbs photons with the wavelength below 400 nm while the modified SO₄²⁻/TiO₂ sample can absorb photons in the visible light region with the optical absorption edge

spreading to about 550 nm. In other words, compared with the TiO₂ sample, the SO₄²⁻/TiO₂ sample has an absorption band shifting to the lower energy region (higher wavelength), thereby probably utilizing more efficiently the visible light.

Kubelka–Munk function was employed to estimate the bandgap energy of the TiO₂ and SO₄²⁻/TiO₂ samples by plotting $(\alpha h\nu)^{1/2}$ as a function of the photon energy (Figure 7(b)). The bandgap energies of the TiO₂ and SO₄²⁻/TiO₂ samples are 3.17 and 2.75 eV, respectively. Thus, when modification

FIGURE 9: XPS spectra for TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$: (a) XPS survey spectra, (b) O1s spectrum, (c) $\text{Ti}2p_{3/2}$ spectrum, and (d) $\text{S}2p_{3/2}$ spectrum.

of TiO_2 by sulfur in the form of sulfate ions, the bandgap energy of the obtained sample has been significantly reduced. This is in a good agreement with previous reports [36, 37]. The absorption in the visible light region of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample is enhanced compared with the undoped TiO_2 sample may be attributed to the formation of an intermediate energy level below the conduction band of TiO_2 after the SO_4^{2-} doping [38].

3.4. Surface Chemical State of Samples. Bonding characteristics in the obtained samples were characterized by FT-IR and FT-IR spectra are shown in Figure 8.

The FT-IR spectra for both the TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ samples appear modes of oscillation originating from the OH-stretching (around 1634.4 cm^{-1}), the OH-bending of adsorbed water (around 3412.2 cm^{-1}) [39, 40], and tetrahedral/octahedral TiO -stretching (around 692.2 cm^{-1}). How-

ever, coupled with these peaks, the $\text{SO}_4^{2-}/\text{TiO}_2$ sample exhibits two additional peaks at 1391.6 and 1127.7 cm^{-1} which are attributed to the characteristic modes of oscillation of the SO_4^{2-} with bidentate bond [41, 42]. This suggests that there is the chemical adsorption or penetration of SO_4^{2-} ions into the crystal lattice of TiO_2 .

The chemical states of the TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ surfaces were investigated by XPS. Figure 9(a) presents XPS survey spectra of the TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ samples. Compared with the XPS survey spectrum of the TiO_2 sample, that of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample shows an additional peak of S2p, indicating the presence of sulfur in the modified sample. The XPS survey spectra of both samples show a strong peak of C1s at 284.6 eV corresponding to the elemental carbon (graphite) from the substrate. Figure 9(b) shows the XPS O1s core level for the TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ samples. As can be seen, the characteristic peaks are at 529.98 and 531.06 eV of O1s in

FIGURE 10: PL spectra of TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$.

TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$, respectively. The XPS Ti2p core level shown in Figure 9(c) has two characteristic peaks at around 458.2 eV for $\text{Ti}2p_{3/2}$ and 464 eV for $\text{Ti}2p_{1/2}$, confirming that the valence state of titanium exists in Ti^{4+} form. Figure 9(d) shows the S2p doublet core peak locating at 167.06 eV for $\text{S}2p_{1/2}$ and 168.28 eV for $\text{S}2p_{3/2}$, indicating that the valence states of sulfur are S^{4+} (in Ti-O-S bonding) and S^{6+} (in SO_4^{2-}), respectively, [42]. Hence, the presence of SO_4^{2-} ions on the surface of TiO_2 did not significantly affect the peak position at Ti2p but greatly affected the binding energy of O1s and S2p. It is noted that the binding energies of $\text{Ti}2p_{3/2}$ and O1s in pure TiO_2 are 458.5 and 530.28 eV, respectively, and the binding energy of $\text{S}2p_{3/2}$ in pure SO_4^{2-} is 169 eV [43]. The above results show that there is an upward shift in the binding energy of O1s and a downward shift in the binding energy of $\text{S}2p_{3/2}$ (about 0.7 eV) after the SO_4^{2-} doping. This can be explained by the fact that a part of the electron is transferred from oxygen to sulfur [44], resulting in a change in the valence state of a part S^{6+} to S^{4+} and the formation of a new band in energy structure [37].

The XPS spectra demonstrate the formation of bonds among titanium, oxygen, and sulfur atoms. This result is also consistent with the perception of the connection between the elements shown on the FT-IR spectra in Figure 8.

PL measurements were conducted to evaluate the recombination rate of the photoinduced electrons and holes of the obtained samples. As can be seen shown in Figure 10, the luminescent intensity of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample is lower than that of the TiO_2 sample, indicating a different electron-hole recombination path. This may due to the fact that doping SO_4^{2-} on the surface of TiO_2 is suitable for trapping photoinduced electrons and thereby suppressing the recombination of photoinduced electrons and holes [38]. In a nutshell, the SO_4^{2-} doping on TiO_2 improves the charge separation efficiency and consequently promotes the formation of oxidizing agents such as hydroxyl radical, which may increase the photocatalytic activity of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample.

Based on the results obtained from UV-Vis-DRS spectra (Figure 7), XPS spectra (Figure 9), and PL spectra (Figure 10), it can be proposed that the increase in the photocatalytic activity of the $\text{SO}_4^{2-}/\text{TiO}_2$ material is due to the synergistic effect between S^{6+} (SO_4^{2-}) anchored on the surface and S^{4+} doped into the crystalline lattice. Electron shifting from oxygen to sulfur atoms creates extra energy levels which lead to a significant reduction in bandgap energy (Figure 7), facilitating the photon absorption in the visible region for better generation of photoinduced electrons (e^-) and holes (h^+). Consequently, h^+ moves to the surface to continue to produce $\cdot\text{OH}$ while e^- moves to S^{6+} (SO_4^{2-}) on the surface of the material before combining with O_2 and produces $\text{O}_2^{\cdot-}$. This reduces the recombination rate of photoinduced electrons (e^-) and holes (h^+) which is consistent with the PL spectra (Figure 10). The generation processes of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ can be described as

3.5. Photocatalytic Degradation. Evaluation of RhB photodegradation was conducted as mentioned in Section 2.4 and the RhB photocatalytic degradation of the blank sample, TiO_2 , and $\text{SO}_4^{2-}/\text{TiO}_2$ under the irradiation of the 60 W LED lamp and the sunlight is shown in Figure 11. It is noted that the C/C_0 as a function of irradiation time for the blank sample hardly changes under both the visible light and sunlight irradiation, indicating that the presence of TiO_2 and $\text{SO}_4^{2-}/\text{TiO}_2$ plays a major role in the RhB photodegradation.

FIGURE 11: The change in C/C_0 as a function of irradiation time for the blank sample, TiO_2 , and $\text{SO}_4^{2-}/\text{TiO}_2$ under the irradiation of (a) the 60 W LED lamp and (b) the sunlight.

FIGURE 12: The UV-Vis absorption spectra for the photodegradation process of RhB solution for $\text{SO}_4^{2-}/\text{TiO}_2$ under the visible light irradiation.

UV-Vis molecular absorption spectra of RhB solution as a function of irradiation time shown in Figure 12 indicate that RhB was completely decomposed in the visible light region when the $\text{SO}_4^{2-}/\text{TiO}_2$ sample was used as a photocatalyst. Indeed, when continuously irradiating the reaction mixture between 01 and 09 hours by a 60 W LED lamp, the RhB photodegradation efficiency increases from 15.65 to 99.47% (Figure 11(a)). It is worth noting that the improvement of the photocatalytic activities over the $\text{SO}_4^{2-}/\text{TiO}_2$ sample due to electrostatic interaction between negatively charge sul-

phate titania and rhodamine B can be excluded since the C/C_0 in the case of the $\text{SO}_4^{2-}/\text{TiO}_2$ presence hardly change if the LED light was turned off (Figure 11(a)).

The results from Figure 12 show that the absorption peak position of RhB at 553 nm is gradually shifted towards short wavelengths. The shift of absorption peaks during the photodegradation process of RhB solution can be explained by the fact that the RhB decomposition process will form a series of intermediates with a shorter conjugate π . The process of destroying the chromophore cleavage structure of the dye

FIGURE 13: The UV-Vis absorption spectra for the photodegradation process of RhB solution under the sunlight irradiation for (a) $\text{SO}_4^{2-}/\text{TiO}_2$ and (b) TiO_2 .

molecule is quite easy by dividing the conjugate π system into π shorter aromatic, homologous phenol intermediate products, etc. so that RhB will eventually be completely decomposed into CO_2 and H_2O [45].

When using the sunlight as a light source (intensity of 65,000 Lux), the RhB photodegradation efficiency for the $\text{SO}_4^{2-}/\text{TiO}_2$ significantly increases. UV-Vis absorption spectra for the RhB photodegradation process of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample presented in Figure 13(a) reveal that after 2 hours of irradiation by the sunlight, the absorption peaks of RhB in both the visible and ultraviolet regions are almost no longer detected. It is worth noting that the RhB photodegradation efficiency for the $\text{SO}_4^{2-}/\text{TiO}_2$ sample is about 99.63% while that for the TiO_2 -550 sample is only 26.09% (Table 1). Hence, the SO_4^{2-} doping enhances the photocatalytic activities of the obtained sample.

The photocatalytic ability of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample when stimulated by the sunlight is much better than that of the TiO_2 sample may be ascribed to two factors. Firstly, the TiO_2 nondoped sample only adsorbs photons in the ultraviolet light region while the $\text{SO}_4^{2-}/\text{TiO}_2$ sample is capable of absorbing photons of light in both ultraviolet and visible regions. Since the radiation from the sunlight contains only about 5% of UV rays, so the $\text{SO}_4^{2-}/\text{TiO}_2$ sample will have better optical absorption performance and thereby exhibiting higher photocatalytic activity compared with the TiO_2 sample. Secondly, SO_4^{2-} ions doped on the surface of the TiO_2 have a strong electron affinity and thereby hindering the electron-hole recombination by capturing the photoinduced electrons [38]. This is in good agreement with the results of the PL spectra.

It is found that RhB was almost completely decomposed in the presence of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample as a photocatalyst and either the sunlight (Figure 13(a)) or the 60 W LED lamp (Figure 13) was used as an irradiation light source. However, the processing time for the RhB photodegradation of the $\text{SO}_4^{2-}/\text{TiO}_2$ sample shortens when illuminated with the sunlight rather than the 60 W LED lamp (2 and 9 hours, respectively). This is due to the fact that in the experimental conditions, the sunlight has a higher illumination than incandescent light sources. Therefore, under the irradiation of the sunlight, the $\text{SO}_4^{2-}/\text{TiO}_2$ sample absorbs both visible and UV energies to catalyze the reaction.

All things considered, the SO_4^{2-} doping in the TiO_2 narrows the bandgap and reduces the recombination of the photoinduced electrons and holes, thereby making the $\text{SO}_4^{2-}/\text{TiO}_2$ sample such a promising candidate for the photodegradation of RhB solution under the illumination of both the visible light and sunlight.

Reusability plays a pivotal role in choosing a photocatalyst for practical applications. The used $\text{SO}_4^{2-}/\text{TiO}_2$ material was washed with distilled water at least three times before dried at 80°C for 12 hours for regeneration. The photodegradation efficiency of RhB over reused photocatalyst is presented in Figure 14. This result shows a slight decrease in the RhB decomposition efficiency as a function of recycling cycle. However, the RhB photodegradation efficiency still reached over 96.0% after three cycles of recycling. The XRD pattern of the $\text{SO}_4^{2-}/\text{TiO}_2$ material (Figure 15) hardly changes, suggesting that the $\text{SO}_4^{2-}/\text{TiO}_2$ material possesses excellent structural stability after three cycles of recycling.

FIGURE 14: The change in C/C_0 as a function of irradiation time (a) and RhB photodegradation efficiency (b) after three cycles of recycling of the $\text{SO}_4^{2-}/\text{TiO}_2$ material.

FIGURE 15: XRD patterns for the TiO_2 , the initial $\text{SO}_4^{2-}/\text{TiO}_2$ and the reused $\text{SO}_4^{2-}/\text{TiO}_2$ after the third cycle.

4. Conclusions

Nanosized $\text{SO}_4^{2-}/\text{TiO}_2$ nanoparticles have been successfully synthesized from TiO_2 (prepared from Binh Dinh

ilmenite ore) and characterized by modern chemical-physical methods. The experimental results indicate that the formation of Ti-O-S and the chemical adsorption of SO_4^{2-} ions on the TiO_2 surface have shifted the optical absorption band of the obtained sample into the visible light region with the bandgap energy (E_g) of 2.75 eV. With the purpose of manufacturing samples with high photocatalytic activities in the visible light region, the nanosized $\text{SO}_4^{2-}/\text{TiO}_2$ sample is considered as a highly promising candidate for the RhB photodegradation owing to its high photodegradation efficiency under the illumination of both the visible light and sunlight. It is noted that the time treatment is greatly reduced when using the sunlight as an illumination source rather than the 60 W LED lamp.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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