

SnO_{2-x}/TiO₂ Photocatalysts for Dye Removal Under Visible Light: Effect of Sn²⁺:Sn⁴⁺ Ratio on Defect Formation

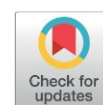
Haroki Madani^{1,2,3}, S. Saepurahman^{2*}, Muhammad Triyogo Adiwibowo¹, Teguh Kurniawan^{1,3}, Marta Pramudita¹, Rusdi Rusdi¹

¹Chemical Engineering Department, Faculty of Engineering, Universitas Sultan Ageng Tirtayasa, Cilegon, 42435, Indonesia.

²Research Center for Environmental and Clean Technologies, National Research and Innovation Agency (BRIN), KST Samaun Samadikun, Bandung 40135, Indonesia.

³Process Integration and Sustainable Systems Research Group, University of Sultan Ageng Tirtayasa, Cilegon 42435, Indonesia.

Received: 15th July 2026; Revised: 24th September 2026; Accepted: 25th September 2026
Available online: 1st October 2026; Published regularly: December 2026



Abstract

Sn²⁺ self-doping of Sn-based photocatalysts is a promising route to visible-light-active photocatalysts, since Sn²⁺ incorporation narrows the band gap and generates oxygen vacancies that extend light absorption beyond the UV region. However, the Sn²⁺:Sn⁴⁺ molar ratio, which directly controls defect formation, has not been systematically varied in this heterostructure system, so its effect on defect density, band structure, and photocatalytic performance remains unclear. This study investigates that effect. SnO_{2-x}/TiO₂ with Sn²⁺:Sn⁴⁺ ratios of 2:1 (ST-2:1) and 1:1 (ST-1:1) were synthesized via a sol-hydrothermal method, characterized by XRD, Raman, XPS, and UV-Vis, and tested for methyl orange (MO) photodegradation under UV-A and visible light. XRD confirmed cassiterite SnO₂ as the dominant phase; Raman detected short-range TiO₂ ordering. XPS detected Sn²⁺, Sn⁴⁺, Ti³⁺, Ti⁴⁺ in both samples, with oxygen vacancies rising from 12.71% to 17.64% and the valence band maximum shifting upward by 0.54 eV as the Sn²⁺:Sn⁴⁺ ratio increased. Tauc plots gave $E_g = 2.21$ eV (ST-2:1) and 2.41 eV (ST-1:1), both narrower than pristine SnO₂ (3.29 eV) and TiO₂ (3.14 eV). ST-2:1 achieved near-complete MO degradation in 10 min under UV-A and 65% in 60 min under visible light, versus only 39% and 10% for ST-1:1, with rate constants 138 and 28 times higher, attributed to its higher defect density and narrower band gap. This study demonstrates that the Sn²⁺:Sn⁴⁺ ratio is an effective, tunable defect-engineering parameter for SnO_{2-x}/TiO₂ heterostructures.

Copyright © 2026 by Authors, Published by BCREC Publishing Group. This is an open access article under the CC BY-SA License (<https://creativecommons.org/licenses/by-sa/4.0>).

Keywords: Photocatalysis; SnO_{2-x}/TiO₂; Sn²⁺:Sn⁴⁺; oxygen vacancy; defect engineering

How to Cite: Madani, H., Saepurahman, S., Adiwibowo, M. T., Kurniawan, T., Pramudita, M., Rusdi, R. (2026). SnO_{2-x}/TiO₂ Photocatalysts for Dye Removal Under Visible Light: Effect of Sn²⁺:Sn⁴⁺ Ratio on Defect Formation. *Bulletin of Chemical Reaction Engineering & Catalysis*, 21 (4), 1007-1017. (DOI: 10.9767/bcrec.20798)

Permalink/DOI: <https://doi.org/10.9767/bcrec.20798>

1. Introduction

Large amounts of colored wastewater from the textile, leather, paper, and printing industries are discharged into water bodies each year. The synthetic dyes in wastewater are chemically stable, difficult to degrade naturally, and toxic [1,2]. Methyl orange (MO) is an anionic azo dye commonly used as a model pollutant in wastewater [3,4]. Conventional treatment of

colored wastewater such as adsorption, filtration, and chemical oxidation generally only remove pollutants without completely mineralizing them, and thus still generate secondary waste [2,5]. Semiconductor photocatalysis offers a better alternative because it can decompose organic pollutants into CO₂ and H₂O without producing secondary waste [1,5]. The mechanism involves the excitation of electrons across the band gap, generating electron-hole pairs that subsequently form reactive oxygen species (ROS), primarily superoxide radicals (O₂^{•-}) and hydroxyl radicals

* Corresponding Authors.

Email: saepurahman@brin.go.id (S. Saepurahman)

($\cdot\text{OH}$), which degrade the pollutants [1,6]. Since visible light constitutes about 43% of the solar spectrum while UV accounts for only about 5%, photocatalysts active under visible light are a primary target in many research [2,6,7].

Titanium dioxide (TiO_2) and tin dioxide (SnO_2) are two widely studied semiconductors for photocatalytic applications. However, their wide band gaps (~ 3.2 eV for TiO_2 and ~ 3.6 eV for SnO_2) restrict their activity in the UV region [1]. The crystal structures of these two materials are quite similar, with both adopting the P42/mnm space group with close lattice parameters, which allows them to readily form stable heterojunctions. These heterojunctions exhibit a type-II band alignment, which helps separate charge carriers and suppress recombination [8]. Several researchers have reported that $\text{TiO}_2/\text{SnO}_2$ heterostructures exhibit better photocatalytic activity than either oxide alone, both under UV and visible light [6,9,10].

To extend their activity into the visible region, a possible approach is by self-doping of SnO_2 by Sn^{2+} to form SnO_{2-x} . The incorporation of Sn^{2+} into the SnO_2 lattice introduces an impurity level that raises the valence band edge and narrows the effective band gap to about 2.2 eV [6,11]. The oxygen vacancies that form as a result of Sn^{2+} introduction contribute to the bandgap narrowing. The Sn_3O_4 phase, which contains both Sn^{2+} and Sn^{4+} , has likewise been reported to have a band gap of about 2.4 eV and active under visible light [3,12]. Our previous work showed that combining Sn^{2+} self-doped SnO_2 with TiO_2 produced a heterostructure with a band gap of 2.35 eV and a photocatalytic performance 3.8 times higher than that of Sn^{2+} - SnO_2 alone under simulated solar light [13].

Despite these advantages, only a few reports have studied Sn^{2+} -doped $\text{SnO}_2/\text{TiO}_2$ heterostructures, and none has systematically varied the $\text{Sn}^{2+}:\text{Sn}^{4+}$ molar ratio within this specific heterostructure. Our own previous work established that a Sn^{2+} - $\text{SnO}_2/\text{TiO}_2$ heterostructure at a single, fixed $\text{Sn}^{2+}:\text{Sn}^{4+}$ ratio of 2:1 outperforms Sn^{2+} - SnO_2 alone [13], but whether or how the ratio itself governs defect density, band structure, and photocatalytic performance in this heterostructure remains unknown. Therefore, this research focuses on systematically varying the $\text{Sn}^{2+}:\text{Sn}^{4+}$ molar ratio to establish this structure-property relationship. The novelty of this work is the direct, ratio-resolved link it establishes between $\text{Sn}^{2+}:\text{Sn}^{4+}$ stoichiometry and the resulting defect chemistry (oxygen vacancy concentration, Ti^{3+} formation, valence band shift) and photocatalytic performance of $\text{SnO}_{2-x}/\text{TiO}_2$, evidenced quantitatively in the XPS and kinetic results. The objectives of this research are to synthesize $\text{SnO}_{2-x}/\text{TiO}_2$ photocatalysts at two $\text{Sn}^{2+}:\text{Sn}^{4+}$ molar ratios (2:1 and 1:1) and to

evaluate the effect of this ratio on defect formation, optical band gap, and photocatalytic degradation of methyl orange under UV-A and visible light.

2. Materials and Methods

2.1 Materials

All reagents were of analytical grade and used without further purification. Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 98%), tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 98%), titanium (IV) butoxide (TBT, 97%), glacial acetic acid (99.8%), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80%), absolute ethanol, and methyl orange (ACS reagent, dye content $\geq 85\%$) were purchased from Merck and Sigma Aldrich. MilliQ water were used as solvent and washing glassware before usage.

2.2. Synthesis of $\text{SnO}_{2-x}/\text{TiO}_2$ Photocatalysts

The synthesis of $\text{SnO}_{2-x}/\text{TiO}_2$ follows a previously reported method [13]. Briefly, 2 mL of titanium(IV) butoxide (TBT) was dissolved in 20 mL of isopropyl alcohol, followed by the addition of 9 mL of glacial acetic acid. 2 molar equivalents of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 1 molar equivalent of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were then added dropwise under continuous stirring until the total $\text{Sn}:\text{Ti}$ molar ratio reached a 1:1 ratio. Hydrazine hydrate (total $\text{Sn}:\text{hydrazine}$ molar ratio of 1:10) was added dropwise and the resulting sol was transferred into a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 150°C for 24 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed repeatedly with deionized water, and dried at 60°C for 24 h. This sample was labelled as ST-2:1. Another sample was prepared in similar fashion, whereby an equimolar $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was used. This sample was labelled as ST-1:1.

2.3. Characterizations of $\text{SnO}_{2-x}/\text{TiO}_2$ Photocatalysts

Phase identification was carried out by X-ray powder diffraction (XRD) analysis using a Rigaku SmartLab diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Patterns were recorded over a 2θ range of $5\text{--}90^\circ$ with a step size of 0.02° . Phase assignment was performed by comparison with the JCPDS reference cards. The average crystallite size (D) was estimated using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where $K = 0.9$ is the dimensionless shape factor, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the diffraction peak in

radians, and θ is the Bragg angle. Analysis was performed at the (110, $2\theta \approx 26.6^\circ$) and (101, $2\theta \approx 33.9^\circ$) reflections.

Raman spectra were acquired using a Horiba iHR320 Raman spectrometer. Spectra were collected over the wavenumber range 50–800 cm^{-1} using a 532 nm excitation laser. UV-Vis absorbance spectra were recorded on a UV-Vis spectrophotometer (UV-Vis spectrophotometer (Genesys 150, Thermo Scientific, USA). The photocatalyst was dispersed in deionized water and placed in a standard cuvette; deionized water was used as the blank reference. Spectra were collected over the wavelength range 200–800 nm. The optical band gap (E_g) was estimated from the Tauc plot using the measured absorbance (A) directly:

$$(ah\nu)^\gamma = B(h\nu - E_g) \quad (2)$$

where $h\nu$ is the photon energy (eV) and B is a proportionality constant.

X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Supra+ spectrometer (Kratos, UK) over a binding energy range of 0–1100 eV. All binding energies were calibrated by referencing the adventitious C 1s peak to 284.8 eV. Peak deconvolution was performed using a mixed Gaussian-Lorentzian function with a Shirley background subtraction.

2.4. Photocatalytic Activity Test

Photocatalytic activity tests were conducted in a batch photoreactor equipped with a magnetic stirrer, as shown in Figure 1. Two irradiation sources were employed: a 15 watt Sankyo Denki Blacklight Blue F15T8BLB lamp ($\lambda_{\text{max}} \approx 352$ nm) and a 15 Watt Phillips TL-D lamp (Visible Daylight). An aqueous MO solution (40 ppm, 50 mL) was used for each test. The photocatalyst loading was 50 mg. Prior to irradiation, the suspension was stirred in darkness for 30 min to reach adsorption-desorption equilibrium. At predetermined time intervals, aliquots were withdrawn, centrifuged to remove the

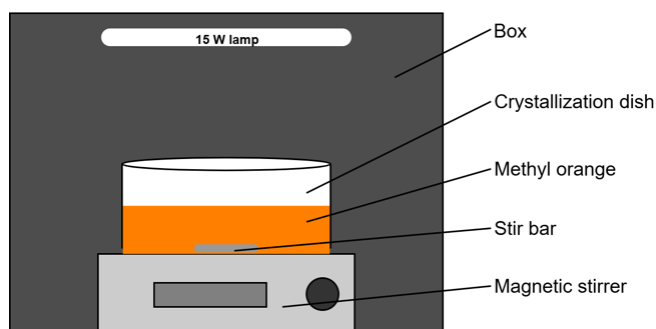


Figure 1. Schematic diagram of the batch photoreactor setup used for photocatalytic activity testing.

photocatalyst, and the residual MO concentration was determined using a Perkin Elmer Cary 60 UV-Vis spectrophotometer. MO concentration at each time point was determined spectrophotometrically from the absorbance of the centrifuged supernatant at MO's characteristic absorption wavelength ($\lambda_{\text{max}} \approx 464$ nm), converted to concentration using a pre-established MO calibration curve. C_0 was taken as the MO concentration immediately after the 30-min dark equilibration (i.e., before irradiation began), and C_t was the concentration of each subsequently withdrawn aliquot at irradiation time t . Photocatalytic degradation kinetics were evaluated using the pseudo-first-order model based on the Langmuir-Hinshelwood model [2,14]:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \quad (3)$$

where C_0 is the initial MO concentration (mg.L^{-1}), C is the concentration at irradiation time t (min), and k is the apparent first-order rate constant (min^{-1}). The value of k was determined from the slope of the linear fit of $\ln(C/C_0)$ versus irradiation time.

3. Results and Discussion

3.1. Crystal Structure and Phase Composition

X-ray diffraction patterns of ST-2:1 and ST-1:1 are presented in Figure 2, which confirmed the cassiterite SnO_2 tetragonal structure (JCPDS 41-1445) as the dominant crystalline phase in both samples. Principal peaks were observed at $2\theta \approx 26.6^\circ$ (110), 33.9° (101), 37.9° (200), 51.8° (211), 54.7° (220), and 65.9° (301), consistent with reported cassiterite lattice parameters [8]. No secondary phases attributable to metallic tin or romarchite SnO were detected.

Despite a fixed Sn:Ti molar ratio of 1:1 in both syntheses, no distinct anatase TiO_2 reflections, including the characteristic (101) peak at $2\theta \approx$

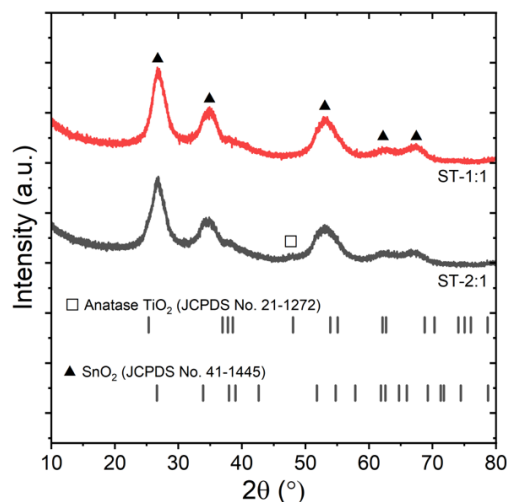


Figure 2. XRD patterns of ST-1:1 and ST-2:1.

25.3°, were detected in either pattern. This absence may be attributed to the suppression of long-range TiO₂ crystallization by the SnO₂ cassiterite phase, which has a faster growth. Thus, it constrains TiO₂ to a short-range ordered state below the XRD detection limit. The broad peak centered near 53.15° in both patterns is likely an overlap of SnO₂ reflections (51.8° and 54.7°) and TiO₂ anatase reflections (53.9° and 55.1°).

Table 1 shows the crystallite sizes estimated from the Scherrer equation using the (110) and (101) SnO₂ reflections. These peaks were selected because they represent single SnO₂ planes with no overlap from other SnO₂ or TiO₂ reflections. ST-2:1 yielded a $D = 3.29$ nm (110) and 3.24 nm (101); whereas ST-1:1 yielded a $D = 3.49$ nm (110) and 3.53 nm (101). ST-2:1 consistently exhibits broader peaks and smaller crystallite sizes. Increasing Sn²⁺ content induces a greater lattice distortion within the cassiterite framework. Since Sn²⁺ ionic radius (≈ 1.18 Å) is substantially larger than the Sn⁴⁺ (≈ 0.69 Å), Sn²⁺ partially replaces Sn⁴⁺. A consistent crystal-growth inhibition effect under ionic size mismatch has been reported for Sn-doped TiO₂ systems [14]. The broader FWHM of ST-2:1 is therefore interpreted as structural evidence of greater lattice disorder.

3.2. Raman Analysis

Figure 3 presents Raman spectra of ST-2:1 and ST-1:1, which reveal complementary structural information between the two samples. ST-2:1 exhibited a well-resolved peak at approximately 145 cm⁻¹, which is assigned to the Eg mode of anatase TiO₂ [15]. This band, however, only forms a shoulder in ST-1:1, likely due to overlap with the tin oxide peak at ~ 140 cm⁻¹. The Raman spectrum directly resolves the apparent contradiction from the XRD pattern. While no anatase diffraction peaks were observed in either pattern, Raman spectroscopy, which is sensitive to short-range crystalline order, can detect the anatase E_g mode in nanocrystalline domains well below the XRD detection limit [16]. TiO₂ is therefore genuinely present, but in a short-range ordered state, as a result of crystallization suppression by the dominant SnO₂ phase during the synthesis.

Both ST-1:1 and ST-2:1 exhibited bands at ~ 237 cm⁻¹, ~ 426 and ~ 614 cm⁻¹. The band at ~ 237 cm⁻¹ is assigned to a sub-bridging oxygen vacancy mode of SnO₂ [17], whereas the band at ~ 614 cm⁻¹ is assigned to a bridging oxygen vacancy mode of SnO₂ [17], corroborating the vacancy assignment at ~ 237 cm⁻¹ and confirming that oxygen vacancies are an intrinsic structural feature of both composites. ST-1:1 also shows a distinct set of peaks at 91, 140, 170, and 237 cm⁻¹. The bands at ~ 140 and ~ 170 cm⁻¹ are consistent with the Raman signature of Sn₃O₄, a mixed-valence tin oxide phase [18]. The Sn₃O₄ bands are, however, less prominent in ST-2:1, suggesting that the higher Sn²⁺:Sn⁴⁺ ratio favors a different distribution of tin oxide phases. Taken together, the Raman data establish that both composites contain TiO₂ in short-range crystalline order, mixed-valence tin oxide phases, and an oxygen-vacancy-rich SnO₂ lattice.

3.3. XPS Analysis

Figure 4 shows the wide and narrow range XPS spectra of ST-1:1 and ST-2:1. The XPS wide range spectra confirmed the presence of Sn, Ti, and O in both samples. The Sn 3d_{5/2} region of ST-1:1 was fitted with two peaks at 486.82 eV (Sn⁴⁺) and 486.30 eV (Sn²⁺), with area fractions of 50.9%

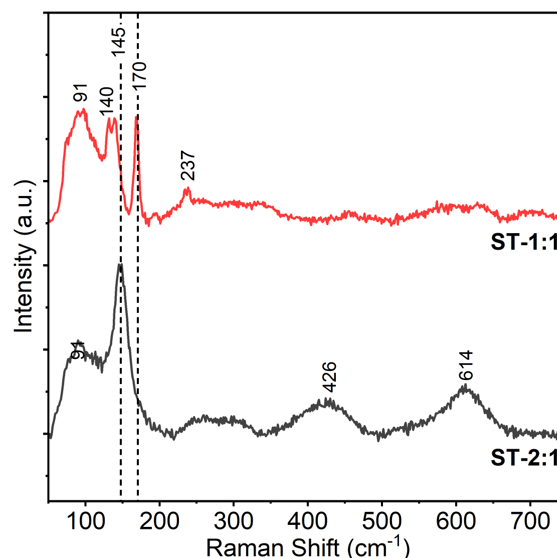


Figure 3. Raman spectra of ST-1:1 and ST-2:1.

Table 1. Crystallite size of ST-1:1 and ST-2:1 photocatalysts as estimated using the Scherrer equation.

Photocatalyst	Plane	2 θ (°)	FWHM (°)	D (nm)
ST-1:1	(110)	26.86	2.34	3.49
	(101)	34.84	2.36	3.53
ST-2:1	(110)	26.80	2.48	3.29
	(101)	34.61	2.57	3.24

and 49.1%, respectively. The Sn^{4+} position agrees well with tin in the SnO_2 lattice [3], while the Sn^{2+} position is consistent with SnO and Sn_3O_4 environments (about 486.20–486.40 eV) [12,19,20]. For ST-2:1, a third peak at 485.43 eV can be attributed to a strongly reduced tin species (SnO or SnO_x), as its position is only about 0.50 eV above the Sn^0 standard (484.90 eV) [3,19]. The area fractions in ST-2:1 were 30.9% (Sn^{4+}), 41.5% (Sn^{2+}), and 27.6% (Sn^0/SnO_x). The absence of the reduced tin species in ST-1:1 may indicate that in ST-2:1, the combination of the higher SnCl_2 loading and hydrazine atmosphere, allowed a fraction of Sn^{4+} to experience a stepwise reduction to Sn^{2+} and metallic Sn^0 [11,21]. However, no corresponding peak of metallic tin was found in XRD, suggesting the minor surface phase is below the detection limit. The broader Sn^{4+} peak in ST-2:1 (FWHM 1.960 vs. 1.116 eV) may also reflect structural disorder from Sn^{2+} incorporation. Table 2 summarizes the fitting parameters and assignment of deconvoluted XPS spectra for both samples.

A similar pattern is observed in the Ti 2p orbital. ST-1:1 showed mainly Ti^{4+} at 458.664 eV, consistent with TiO_2 [22], while ST-2:1 had an additional Ti^{3+} component at 457.601 eV, making up 39.53% of total Ti. When Sn^{2+} replaces Sn^{4+} within the SnO_2 lattice, oxygen vacancies are

formed to compensate for the charge difference [23], and such vacancies can trap electrons and reduce neighboring Ti^{4+} to Ti^{3+} at the $\text{SnO}_2/\text{TiO}_2$ interface [24]. The hydrazine monohydrate used in synthesis also creates a reducing atmosphere in the sealed autoclave that facilitates Ti^{3+} formation under hydrothermal conditions [25,26]. In ST-1:1, the absence of retained Sn^{2+} means very few charge-compensating oxygen vacancies are formed, so even under the same reducing atmosphere there is no localized vacancy environment to stabilize Ti^{3+} .

The O 1s spectra were fitted with four components: Ti-O (530.0 eV), Sn-O (530.9 eV), oxygen vacancies (O_v , 531.9 eV), and surface hydroxyl groups (O_{ad} , 532.8 eV) [19,22]. The O_v fraction increased from 12.71% in ST-1:1 to 17.64% in ST-2:1, confirming that higher Sn^{2+} content leads to more oxygen vacancies. The Sn-O fraction also increased (32.02% to 36.41%) while Ti-O decreased (52.27% to 41.24%), despite the fixed Sn:Ti ratio of 1:1 in both samples. Altogether, the three regions show a consistent picture where Sn^{2+} substitution generates oxygen vacancies, which stabilize Ti^{3+} at the interface.

The valence band spectra showed that the VBM onset shifted from 1.79 eV in ST-1:1 to 1.25 eV in ST-2:1, a 0.54 eV upward shift. In pristine SnO_2 and TiO_2 , the valence band is mainly formed

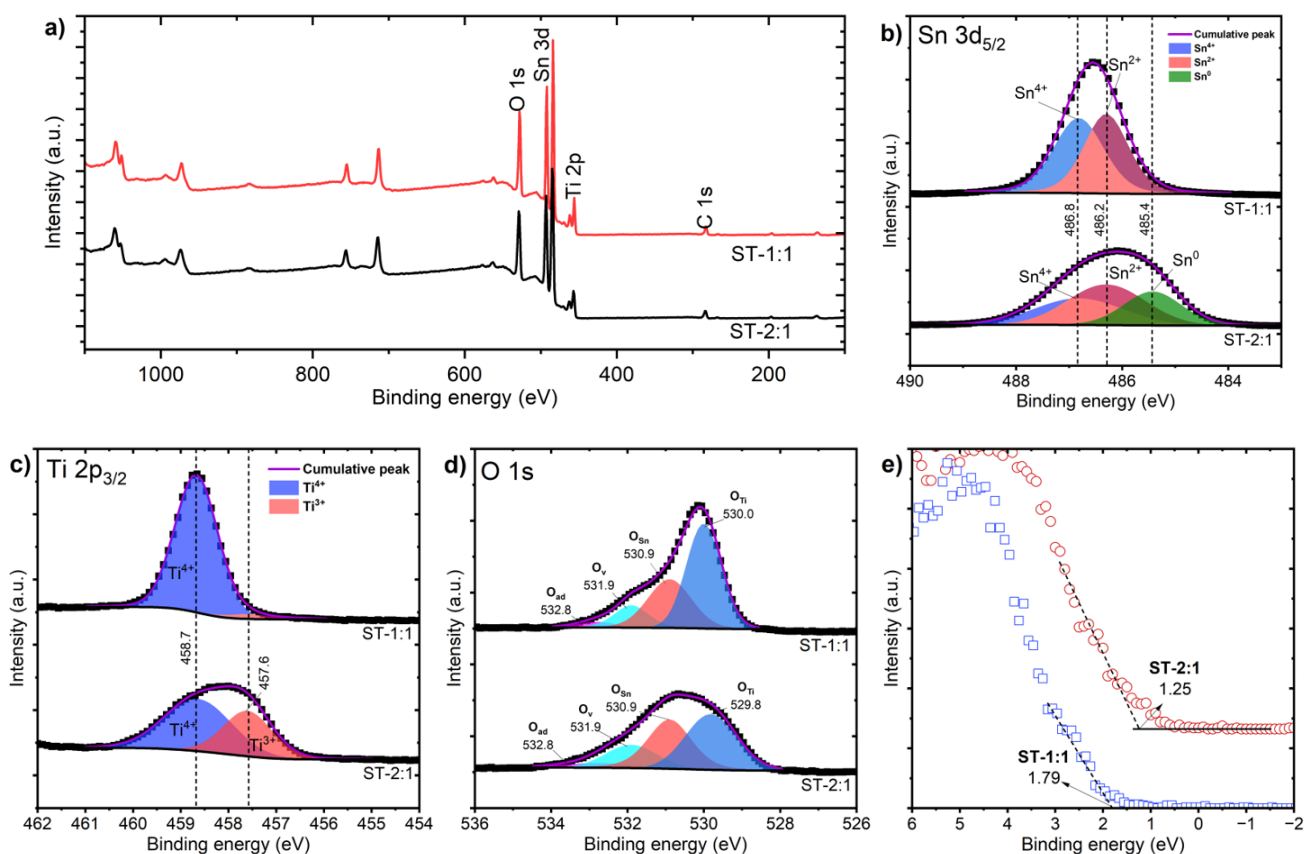


Figure 4. XPS spectra of ST-1:1 and ST-2:1: (a) survey scan, (b) Sn 3d, (c) Ti 2p, (d) O 1s, and (e) valence band (ST-2:1 data adapted from [13]).

by O 2p orbitals, but Sn²⁺ incorporation brings Sn 5s states into the upper part of the valence band, raising the VBM [3,27]. This explains the band gap narrowing from 2.41 eV (ST-1:1) to 2.21 eV (ST-2:1) from UV-Vis. The conduction band minimum, estimated by subtracting the optical band gap from VBM, shifted from -0.62 eV to -0.96 eV. Since both edges moved upward but by different lengths, the VBM upshift was the main driver of band gap narrowing, while the smaller CBM shift partially offset it.

3.4. Optical Band Gap

Figure 5 shows the UV-Vis absorbance spectra of ST-2:1 and ST-1:1. Both samples exhibited a pronounced absorption edge extending well into the visible light region, in marked contrast to pure SnO₂ ($E_g = 3.70$ eV) [28] and pure TiO₂ ($E_g = 3.10$ eV) [13], which absorb primarily in the UV region. The visible-light absorption of both samples is consistent with the structural characteristics mention earlier, oxygen vacancies and Sn²⁺ defect states introduce sub-band gap energy levels that extend the photoresponse of the cassiterite SnO₂ framework well beyond its intrinsic absorption edge [6,11]. Tauc plots analysis estimates the $E_g = 2.21$ eV for ST-2:1 and $E_g = 2.41$ eV for ST-1:1. Both values correspond to absorption threshold wavelengths well within the visible spectrum ($\lambda \approx 561$ nm and 514 nm, respectively), confirming that both composites are suitable for visible-light-driven photocatalysis. Since the samples contain Sn²⁺ defect states

capable of producing sub-band gap absorption, the reported values represent the effective optical band gaps rather than the intrinsic semiconductor band gaps [29].

The lower band gap of ST-2:1 relative to ST-1:1 is consistent with its higher Sn²⁺ proportion. Increasing Sn²⁺ content in SnO₂ introduces a localized impurity level within the band gap

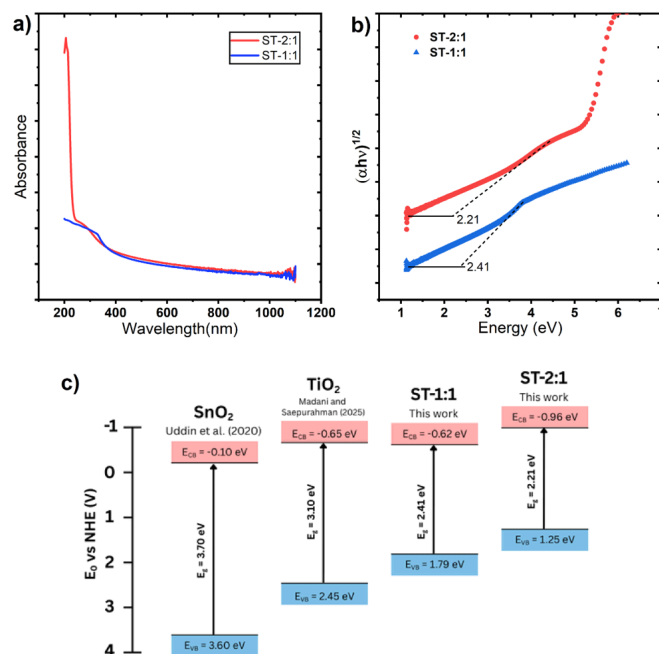


Figure 5. (a) UV-Vis absorbance spectra, (b) Tauc plot of ST-2:1 and ST-1:1, and (c) band structure of ST-2:1 and ST-1:1 compared to SnO₂ and TiO₂.

Table 2. Fitting parameters and assignment of deconvoluted XPS spectra.

Region	Sample	Position (eV)	FWHM (eV)	Area (%)	Assignment
Sn 3d 5/2	ST-1:1	486.822	1.116	50.90	Sn ⁴⁺ (SnO ₂ lattice)
	ST-1:1	486.300	0.990	49.10	Sn ²⁺ (self-doped)
	ST-2:1	486.822	1.960	30.90	Sn ⁴⁺ (SnO ₂ lattice)
	ST-2:1	486.300	1.720	41.50	Sn ²⁺ (self-doped)
	ST-2:1	485.427	1.287	27.60	Sn ⁰ (metallic Sn)
Ti 2p 3/2	ST-1:1	458.673	1.048	95.06	Ti ⁴⁺ (TiO ₂ lattice)
	ST-1:1	457.600	1.042	4.96	Ti ³⁺ (reduced Ti)
	ST-2:1	458.640	1.650	60.47	Ti ⁴⁺ (TiO ₂ lattice)
	ST-2:1	457.601	1.215	39.53	Ti ³⁺ (reduced Ti)
	ST-2:1	457.601	1.215	39.53	Ti ³⁺ (reduced Ti)
O 1s	ST-1:1	530.006	1.077	52.27	Ti-O (lattice oxygen)
	ST-1:1	530.900	1.343	32.02	Sn-O (lattice oxygen)
	ST-1:1	531.900	1.059	12.71	Ov (oxygen vacancies)
	ST-1:1	532.800	1.121	2.99	Oad (adsorbed oxygen)
	ST-2:1	529.820	1.560	41.24	Ti-O (lattice oxygen)
	ST-2:1	530.900	1.349	36.41	Sn-O (lattice oxygen)
	ST-2:1	531.900	1.594	17.64	Ov (oxygen vacancies)
	ST-2:1	532.800	2.028	4.70	Oad (adsorbed oxygen)
Valence band	ST-1:1	1.790	—	—	VBM onset; $E_g = 2.41$ eV; CBM = -0.62 eV
	ST-2:1	1.250	—	—	VBM onset; $E_g = 2.21$ eV; CBM = -0.96 eV

Area (%) = relative peak area within each spectral region. VBM and CBM positions are referenced to the Fermi level. CBM estimated from VBM minus optical band gap. E_g from Tauc plot analysis.

associated with Sn^{2+} 5s states, raising the effective valence band edge and narrowing the optical band gap. This effect is confirmed by both DFT calculations and electrochemical characterization in Sn^{2+} -doped SnO_2 systems [11]. Oxygen vacancies contribute additionally by upshifting the valence band maximum without significantly altering the conduction band position [6], consistent with reports that oxygen-defect engineering in SnO_2 alone similarly extends its visible-light photocatalytic response [30].

The interpretation is further supported by the broader XRD peak widths of ST-2:1, which indicate greater lattice disorder and are consistent with a higher defect density. The band gap of ST-1:1 (2.41 eV) is notably close to the reported value for Sn_3O_4 (~2.4 eV), a mixed-valence tin oxide phase whose Raman signature was more clearly resolved in ST-1:1 than in ST-2:1, suggesting that the phase composition identified by Raman is reflected in the optical properties of the two samples [12].

The electronic band structures of ST-2:1 and ST-1:1, derived from the XPS valence band maximum (VBM) and Tauc-plot band gaps, are presented in Figure 5c alongside literature values

for pure SnO_2 and TiO_2 . The conduction band minimum (CBM) were estimated as $\text{CBM} = \text{VBM} - E_g$, yielding values of -0.96 eV for ST-2:1 and -0.62 eV for ST-1:1. The negative values of both composites indicate sufficient reducing power for superoxide radicals ($\text{O}_2^{\cdot-}$) formation as the reactive oxygen species (ROS) for dye photodegradation [13]. The band gap narrowing observed in both ST composites is likely governed by Sn^{2+} , rather than Sn^{4+} , consistent with the higher Sn^{2+} proportion confirmed by XPS. These results suggest that the $\text{Sn}^{2+}:\text{Sn}^{4+}$ molar ratio is a useful parameter for controlling the optical band gap and band edge positions of $\text{SnO}_2/\text{TiO}_2$ heterostructures.

3.5. Photocatalytic Activity

Figure 6 shows the UV-Vis MO spectrum evolution during the photocatalytic activity testing under UV-A and visible light irradiation. Under UV-A irradiation, ST-2:1 achieved near-complete MO removal within 10 minutes, whereas ST-1:1 reached only 39% of removal within 60 minutes. A similar trend was observed under visible light, where ST-2:1 reached a 65%

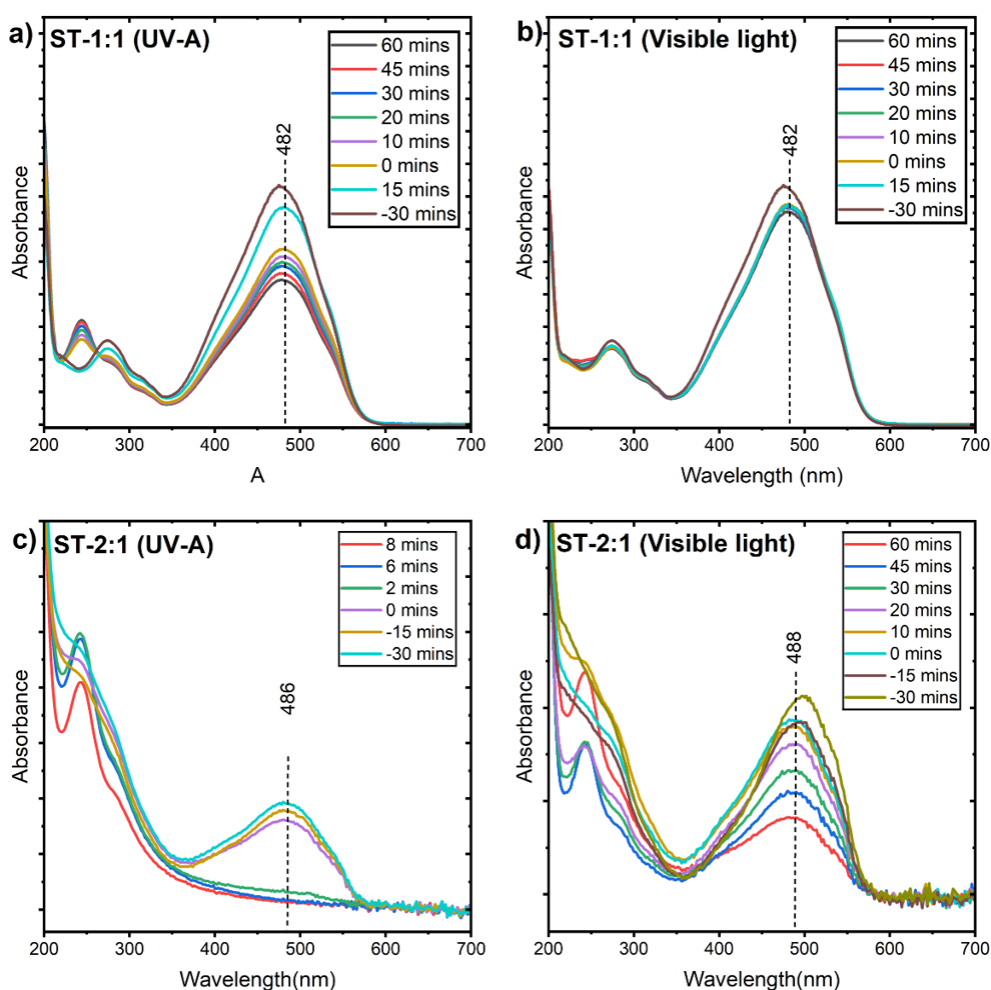


Figure 6. Evolution of UV-Vis MO spectrum during photocatalytic activity testing: a) ST-1:1 (UV-A), b) ST-1:1 (Visible light), c) ST-2:1 (UV-A), and c) ST-2:1 (Visible light).

removal in 60 minutes while ST-1:1 reached only 10%. ST-2:1 therefore outperformed ST-1:1 under both illuminations, consistent with its higher Sn^{2+} proportion, higher oxygen vacancy, and narrower band gap. The data were fitted to a pseudo-first-order kinetic model (Figure 7). ST-2:1 showed rate constants of 0.746 min^{-1} and 0.014 min^{-1} under UV-A and visible light, respectively. ST-1:1 gave lower rate constants of 0.0054 min^{-1} under UV-A and 0.0005 min^{-1} under visible light. The rate constant of ST-2:1 was therefore about 138 times higher than that of ST-1:1 under UV-A and about 28 times higher under visible light.

The magnitude of these differences implies that light absorption alone does not account for the observed activity. The higher oxygen vacancy content of ST-2:1 likely promotes more efficient separation of photogenerated charge carriers, in addition to extending visible-light absorption [6,11]. For both samples, UV-A irradiation produced markedly higher rate constants than visible light, with the UV-A to visible ratio being about 53 for ST-2:1 and about 11 for ST-1:1. Under UV-A irradiation, band-to-band excitation of both the SnO_2 and TiO_2 components occurs, and the

type-II band alignment at the $\text{SnO}_2/\text{TiO}_2$ interface drives electron transfer that suppresses recombination [1,8]. Under visible light, photoexcitation proceeds mainly through sub-band gap transitions involving Sn^{2+} defect states and oxygen vacancies, which enable visible-light absorption but may also act as recombination centers and lower the overall efficiency [6,11].

The visible-light rate constant of $k = 0.014 \text{ min}^{-1}$ at 40 ppm initial MO concentration compares favorably with values reported for related composite systems under comparable conditions. Visible-light rate constants of $0.019\text{--}0.035 \text{ min}^{-1}$ for $\text{TiO}_2/\text{Nb}_2\text{O}_5/\text{SnO}_2$ composites at an initial MO concentration of 20 ppm [2]. A rate constant of $k = 0.045\text{--}0.055 \text{ min}^{-1}$ for Mn-doped SnO_2 quantum dots under simulated sunlight for methylene blue degradation [7]. A comparably direct benchmark comes from a $\text{SnO}_2/\text{TiO}_2$ -coupled photocatalyst tested on Rhodamine B dye, which achieved an average rate constant of 0.0327 min^{-1} , exceeding uncoupled TiO_2 (0.0141 min^{-1}) [31]. The UV-A rate constant of $k = 0.746 \text{ min}^{-1}$ is close with the upper range of values reported for $\text{TiO}_2/\text{SnO}_2$ heterostructures in the

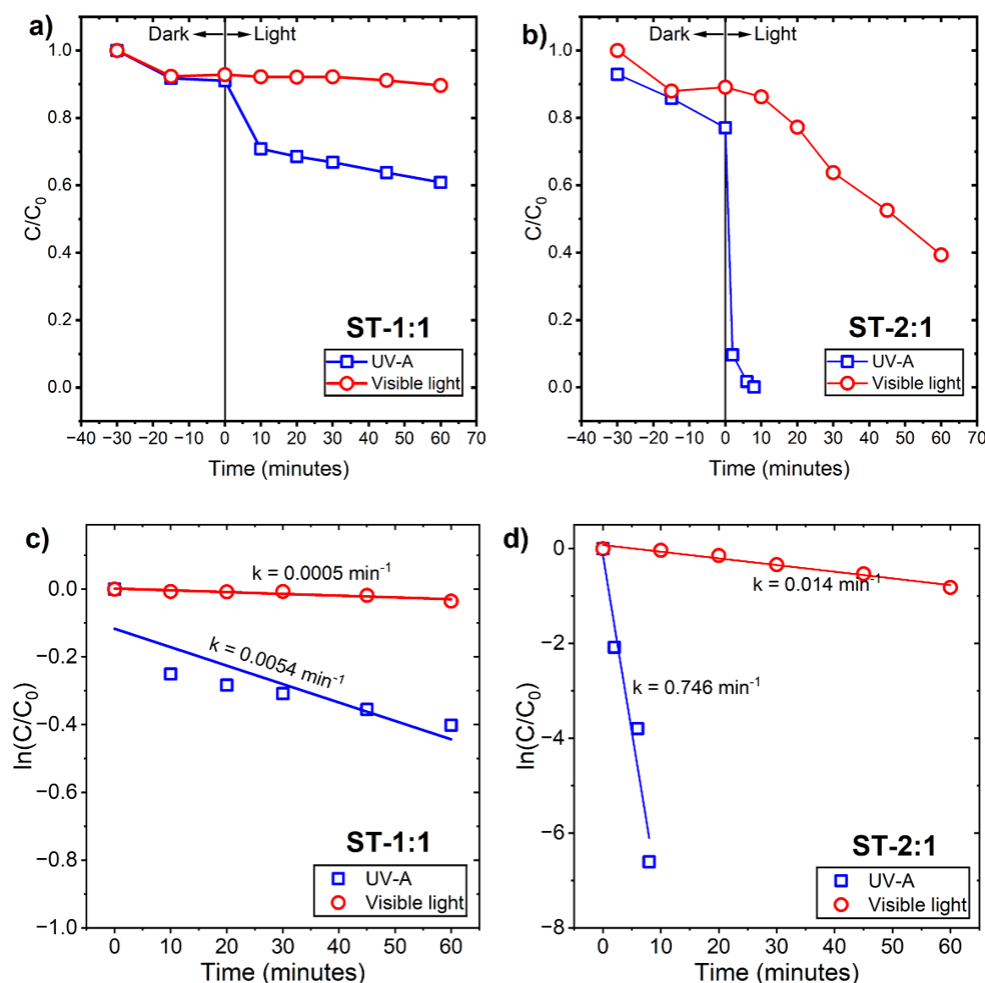


Figure 7. Photocatalytic activity: (a,b) MO degradation by ST-1:1 and ST-2:1 and (c,d) pseudo-first-order kinetic under UV-A and visible light irradiation.

literature, placed broadly between 0.005 and 0.487 min⁻¹ across varying light source intensities, catalyst loadings, and pollutant concentrations [1]. The performance of ST-2:1 also extends the result of our prior work [13], in which a Sn²⁺-SnO₂/TiO₂ heterostructure at a fixed Sn²⁺:Sn⁴⁺ ratio of 2:1 achieved complete MO degradation within 20 minutes under simulated solar light. In contrast, the rate constants of ST-1:1 fell below this reported range, consistent with its lower defect content and weaker visible-light response. This 138-fold (UV-A) and 28-fold (visible light) difference between ST-2:1 and ST-1:1, which is produced solely by changing the Sn²⁺:Sn⁴⁺ molar ratio, quantitatively demonstrates the structure-property relationship induced by Sn²⁺:Sn⁴⁺, as proposed in this work, which affect the defect formation and photocatalytic performance.

4. Conclusion

SnO_{2-x}/TiO₂ photocatalysts with Sn²⁺:Sn⁴⁺ molar ratios of 2:1 (ST-2:1) and 1:1 (ST-1:1) were successfully synthesized via a sol-hydrothermal method. Characterization confirmed cassiterite SnO₂ as the dominant phase in both samples, together with short-range ordered TiO₂ and Sn₃O₄ phases, with the latter being more clearly resolved in ST-1:1. The higher Sn²⁺:Sn⁴⁺ molar ratio yielded a higher Sn²⁺ and Ti³⁺ content, a higher oxygen vacancy concentration, and a narrower band gap (2.21 eV) compared to lower molar ratio. These defect-related features extended the optical response of both composites well into the visible region. ST-2:1 achieved near-complete degradation of 40 ppm methyl orange within 10 minutes under UV-A irradiation and 65% degradation within 60 minutes under visible light, whereas ST-1:1 reached only 39% and 10% removal under the same conditions, respectively. The corresponding pseudo-first-order rate constants of ST-2:1 were about 138 times higher under UV-A and about 28 times higher under visible light than those of ST-1:1, a difference larger than the modest band gap difference alone would suggest and likely associated with more efficient charge carrier separation. These results suggest that, in the Sn²⁺-doped SnO₂/TiO₂ heterostructure system, the Sn²⁺:Sn⁴⁺ molar ratio itself, rather than merely the presence of Sn²⁺, plays an important role in linking defect chemistry to photocatalytic performance. Systematic control of this ratio may therefore offer an effective strategy for tuning the defect structure, optical band gap, and photocatalytic performance of SnO_{2-x}/TiO₂ heterostructures, potentially providing a useful route toward visible-light-active photocatalysts for the removal of organic dye pollutants.

Acknowledgment

The authors gratefully acknowledge the financial support provided by the Ministry of Higher Education, Science, and Technology of the Republic of Indonesia (Kemdiktisaintek) through the Penelitian Dosen Pemula grant scheme under contract number 269/C3/DT.05.00/PL-BARU/2026, and by the National Research and Innovation Agency (BRIN) through the Rumah Program Batch 3, ORHL 2025 under contract number 62/III.5/HK/2025. H. Madani thanks the Directorate of Talent Management of BRIN for providing the postdoctoral fellowship.

CRedit Author Statement

Author Contributions: H. Madani: Conceptualization, Methodology, Investigation, Data Curation, Writing – original draft, Funding Acquisition; S. Saepurahman: Conceptualization, Formal Analysis, Validation, Funding Acquisition, Writing – Review and Editing; T. Kurniawan: Formal Analysis, Validation, Data Curation, Writing – Review and Editing; M.T. Adiwibowo: Writing – Review and Editing, Data Curation, Formal Analysis; M. Pramudita: Formal Analysis, Writing – Review Editing; R. Rusdi: Formal Analysis, Writing – Review Editing. All authors have read and agreed to the published version of the manuscript.

References

- [1] Rajput, R.B., Jamble, S.N., Kale, R.B. (2022). A review on TiO₂/SnO₂ heterostructures as a photocatalyst for the degradation of dyes and organic pollutants. *Journal of Environmental Management*, 307, 114533. DOI: 10.1016/j.jenvman.2022.114533.
- [2] Zarrin, S., Heshmatpour, F. (2020). Facile preparation of new nanohybrids for enhancing photocatalytic activity toward removal of organic dyes under visible light irradiation. *Journal of Physics and Chemistry of Solids*, 140, 109271. DOI: 10.1016/j.jpcs.2019.109271.
- [3] Jorgetto, A.D.O., Boldrin Zanoni, M.V., Orlandi, M.O. (2023). Assessment of the superior photocatalytic properties of Sn²⁺-containing SnO₂ microrods on the photodegradation of methyl orange. *Scientific Reports*, 13(1), 14774. DOI: 10.1038/s41598-023-40659-8.
- [4] Yang, G., Yan, Z., Xiao, T. (2012). Preparation and characterization of SnO₂/ZnO/TiO₂ composite semiconductor with enhanced photocatalytic activity. *Applied Surface Science*, 258(22), 8704–8712. DOI: 10.1016/j.apsusc.2012.05.078.

- [5] Zhao, W., He, M., Chen, F., Jin, X., Duan, H., Long, M., Wu, Z., Cao, B., Yu, Y. (2022). One-pot synthesis of flower-like SnS₂/SnO₂ heterojunction with enhanced visible light photocatalytic performance. *Optical Materials*, 123, 111934. DOI: 10.1016/j.optmat.2021.111934.
- [6] Yang, L., Yang, Y., Liu, T., Ma, X., Lee, S.W., Wang, Y. (2018). Oxygen vacancies confined in SnO₂ nanoparticles for glorious photocatalytic activities from the UV, visible to near-infrared region. *New Journal of Chemistry*, 42(18), 15253–15262. DOI: 10.1039/C8NJ00668G.
- [7] Murugadoss, G., Venkatesh, N., Vijayakumar, B., Panneerselvam, V., Sakthivel, P., Kannappan, T. (2026). Synthesis of Mn(II)-doped SnO₂ quantum dots as high-performance photocatalysts for rapid degradation of textile dyes. *Chemical Physics Impact*, 12, 100998. DOI: 10.1016/j.chphi.2025.100998.
- [8] Rimoldi, L., Meroni, D., Pargoletti, E., Biraghi, I., Cappelletti, G., Ardizzzone, S. (2019). Role of the growth step on the structural, optical and surface features of TiO₂/SnO₂ composites. *Royal Society Open Science*, 6(1), 181662. DOI: 10.1098/rsos.181662.
- [9] Etshindo, L.A., Sousa, C., Tamiasso-Martinhon, P., Colaço, M.V., Camara, A.R., Rocha, A.S. (2025). SnO₂-TiO₂ materials for photocatalytic degradation of cationic dye under UV and visible light and a chitosan composite film investigation. *Catalysis Today*, 444, 114995. DOI: 10.1016/j.cattod.2024.114995.
- [10] Sadik, W., M. El-Demerdash, A., Nashed, A.W., Mostafa, A.A., Lamie, E. (2024). Synthesis and investigation of optical properties and enhancement photocatalytic activity of TiO₂-SnO₂ semiconductor for degradation of organic compounds. *Scientific Reports*, 14(1), 27846. DOI: 10.1038/s41598-024-78755-y.
- [11] Long, J., Xue, W., Xie, X., Gu, Q., Zhou, Y., Chi, Y., Chen, W., Ding, Z., Wang, X. (2011). Sn²⁺ dopant induced visible-light activity of SnO₂ nanoparticles for H₂ production. *Catalysis Communications*, 16(1), 215–219. DOI: 10.1016/j.catcom.2011.10.002.
- [12] Manikandan, M., Tanabe, T., Li, P., Ueda, S., Ramesh, G.V., Kodiyath, R., Wang, J., Hara, T., Dakshanamoorthy, A., Ishihara, S., Ariga, K., Ye, J., Umezawa, N., Abe, H. (2014). Photocatalytic Water Splitting under Visible Light by Mixed-Valence Sn₃O₄. *ACS Applied Materials & Interfaces*, 6(6), 3790–3793. DOI: 10.1021/am500157u.
- [13] Madani, H., Saepurahman (2025). Low-energy light-activated Sn²⁺-SnO₂/TiO₂ photocatalyst for water pollutant removal. *Journal of Water Process Engineering*, 77, 108425. DOI: 10.1016/j.jwpe.2025.108425.
- [14] Zhu, X., Han, S., Feng, W., Kong, Q., Dong, Z., Wang, C., Lei, J., Yi, Q. (2018). The effect of heat treatment on the anatase–rutile phase transformation and photocatalytic activity of Sn-doped TiO₂ nanomaterials. *RSC Advances*, 8(26), 14249–14257. DOI: 10.1039/C8RA00766G.
- [15] Ohsaka, T., Izumi, F., Fujiki, Y. (1978). Raman spectrum of anatase, TiO₂. *Journal of Raman Spectroscopy*, 7(6), 321–324. DOI: 10.1002/jrs.1250070606.
- [16] Kelly, S., Pollak, F.H., Tomkiewicz, M. (1997). Raman Spectroscopy as a Morphological Probe for TiO₂ Aerogels. *The Journal of Physical Chemistry B*, 101(14), 2730–2734. DOI: 10.1021/jp962747a.
- [17] Liu, L.Z., Li, T.H., Wu, X.L., Shen, J.C., Chu, P.K. (2012). Identification of oxygen vacancy types from Raman spectra of SnO₂ nanocrystals. *Journal of Raman Spectroscopy*, 43(10), 1423–1426. DOI: 10.1002/jrs.4078.
- [18] Vázquez-López, A., Maestre, D., Ramírez-Castellanos, J., Cremades, A. (2021). In Situ Local Oxidation of SnO Induced by Laser Irradiation: A Stability Study. *Nanomaterials*, 11(4), 976. DOI: 10.3390/nano11040976.
- [19] Kwoka, M., Ottaviano, L., Passacantando, M., Santucci, S., Czempik, G., Szuber, J. (2005). XPS study of the surface chemistry of L-CVD SnO₂ thin films after oxidation. *Thin Solid Films*, 490(1), 36–42. DOI: 10.1016/j.tsf.2005.04.014.
- [20] Furukawa, M., Iwamoto, D., Inamori, K., Tateishi, I., Katsumata, H., Kaneco, S. (2023). Synthesis of Tungsten-Modified Sn₃O₄ through the Cetyltrimethylammonium Bromide-Assisted Solvothermal Method for Dye Decolorization under Visible Light Irradiation. *Catalysts*, 13(8), 1179. DOI: 10.3390/catal13081179.
- [21] Joy, S., Atapattu, H.R., Sorensen, S., Pruett, H., Olivelli, A.B., Huckaba, A.J., Miller, A.-F., Graham, K.R. (2022). How additives for tin halide perovskites influence the Sn⁴⁺ concentration. *Journal of Materials Chemistry A*, 10(25), 13278–13285. DOI: 10.1039/D2TA01429G.
- [22] Guan, S., Cheng, Y., Hao, L., Yoshida, H., Tarashima, C., Zhan, T., Itoi, T., Qiu, T., Lu, Y. (2023). Oxygen vacancies induced band gap narrowing for efficient visible-light response in carbon-doped TiO₂. *Scientific Reports*, 13(1), 14105. DOI: 10.1038/s41598-023-39523-6.
- [23] Fan, C.-M., Peng, Y., Zhu, Q., Lin, L., Wang, R.-X., Xu, A.-W. (2013). Synproportionation Reaction for the Fabrication of Sn²⁺ Self-Doped SnO₂-x Nanocrystals with Tunable Band Structure and Highly Efficient Visible Light Photocatalytic Activity. *The Journal of Physical Chemistry C*, 117(46), 24157–24166. DOI: 10.1021/jp407296f.
- [24] Carey, J.J., McKenna, K.P. (2019). Screening Doping Strategies To Mitigate Electron Trapping at Anatase TiO₂ Surfaces. *The Journal of Physical Chemistry C*, 123(36), 22358–22367. DOI: 10.1021/acs.jpcc.9b05840.

- [25] Zhao, Y., Zhang, M., Wang, W., Song, W., Jiang, K., Zhang, X. (2021). Preparation of Ti³⁺/N-co-doped TiO₂ by one-step hydrothermal synthesis method with high photocatalytic degradation performance under visible light. *Journal of Materials Science: Materials in Electronics*, 32(18), 22910–22920. DOI: 10.1007/s10854-021-06768-8.
- [26] Mao, C., Zuo, F., Hou, Y., Bu, X., Feng, P. (2014). In Situ Preparation of a Ti³⁺ Self-Doped TiO₂ Film with Enhanced Activity as Photoanode by N₂ H₄ Reduction. *Angewandte Chemie International Edition*, 53(39), 10485–10489. DOI: 10.1002/anie.201406017.
- [27] Luo, Y., Zhou, X., Zhang, J., Qi, Y., Li, Z., Zhang, F., Li, C. (2021). Development of Sn²⁺-based oxyfluoride photocatalyst with visible light response of ca. 650 nm via strengthened hybridization of Sn 5s and O 2p orbitals. *Journal of Energy Chemistry*, 63, 385–390. DOI: 10.1016/j.jechem.2021.07.028.
- [28] Uddin, Md.T., Hoque, Md.E., Chandra Bhoumick, M. (2020). Facile one-pot synthesis of heterostructure SnO₂ /ZnO photocatalyst for enhanced photocatalytic degradation of organic dye. *RSC Advances*, 10(40), 23554–23565. DOI: 10.1039/D0RA03233F.
- [29] Makula, P., Pacia, M., Macyk, W. (2018). How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra. *The Journal of Physical Chemistry Letters*, 9(23), 6814–6817. DOI: 10.1021/acs.jpclett.8b02892.
- [30] Chen, S., Luo, Y., Xu, Y., Chen, Y., Jiang, Y., Li, Z., Tian, L., Wang, F., Liu, Y., Li, J. (2024). Conjugated Polyvinyl Alcohol Modified SnO₂ for Efficient Visible Light Photocatalytic Reduction of Cr(VI). *Bulletin of Chemical Reaction Engineering & Catalysis*, 19(4), 609–621. DOI: 10.9767/bcrec.20226.
- [31] Kadem, A.J., Tan, Z.M., Suntharam, N.M., Pung, S.Y., Ramakrishnan, S. (2023). Synthesis of CuO, ZnO and SnO₂ Coupled TiO₂ Photocatalyst Particles for Enhanced Photodegradation of Rhodamine B Dye. *Bulletin of Chemical Reaction Engineering & Catalysis*, 18(3), 506–520. DOI: 10.9767/bcrec.19532.