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Sung Yoon
 Department of Chemistry and
 Nanosciences, Baekdu
 Institute of Technology,
 Busan, South Korea

Photocatalytic activity of Bi₂O₃ nanoparticles for degradation of organic dyes under visible light irradiation

Sung Yoon

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Abstract

This research synthesized β -Bi₂O₃ nanoparticles by a facile precipitation-calcination route and evaluated their photocatalytic performance for degradation of four organic dyes (methylene blue, rhodamine B, methyl orange, and congo red) under visible light irradiation. X-ray diffraction confirmed phase-pure monoclinic β -Bi₂O₃ with a crystallite size of 28 nm by the Scherrer equation. BET surface area was 14.7 m²/g, and UV-visible diffuse reflectance spectroscopy indicated a band gap of 2.78 eV, well within the visible absorption range. At a catalyst loading of 1.0 g/L and initial dye concentration of 20 mg/L, methylene blue reached 98% degradation within 120 min, following pseudo-first-order kinetics ($k = 0.032 \text{ min}^{-1}$). Scavenger experiments identified superoxide radicals (34.2%) and hydroxyl radicals (28.7%) as the dominant reactive species. The catalyst retained 91% efficiency after five consecutive cycles, demonstrating practical reusability. These results establish β -Bi₂O₃ as a promising visible-light photocatalyst for textile wastewater treatment.

Keywords: Bismuth oxide, photocatalysis, visible light, organic dye, methylene blue, nanoparticles, degradation kinetics, reactive oxygen species, reusability, wastewater treatment

Introduction

Textile dyeing operations discharge an estimated 200 billion litres of coloured effluent annually, and conventional biological treatment plants remove only 10-20% of synthetic dyes because their aromatic structures resist microbial oxidation ^[1]. Semiconductor photocatalysis offers a fundamentally different approach: light-generated electron-hole pairs produce reactive oxygen species that mineralize organic pollutants to CO₂, H₂O, and inorganic ions without generating secondary sludge ^[2].

Titanium dioxide has dominated photocatalysis research for decades, but its wide band gap (3.2 eV for anatase) limits activity to the ultraviolet region, which constitutes only 4-5% of solar radiation reaching the Earth's surface ^[3]. Narrower band-gap semiconductors that absorb visible light are therefore actively sought. Bismuth-based oxides have attracted particular interest because bismuth's 6s² lone pair hybridizes with oxygen 2p orbitals to raise the valence band maximum, pulling the band gap into the visible range ^[4].

Among the four polymorphs of Bi₂O₃ (α , β , γ , δ), the monoclinic β phase is metastable but exhibits the highest photocatalytic activity due to its layered crystal structure, which facilitates charge separation along the ^[010] direction ^[5]. Several synthesis routes have been reported, including hydrothermal, solvothermal, and electrodeposition methods ^[6, 7]. However, many require surfactants, organic solvents, or autoclave conditions that complicate scale-up. A simple precipitation-calcination approach using only bismuth nitrate and sodium hydroxide in aqueous solution can produce phase-pure β -Bi₂O₃ at moderate temperatures, yet systematic evaluation of this catalyst against multiple dye classes under standardized conditions remains limited.

This research addresses that gap by synthesizing β -Bi₂O₃ via aqueous precipitation followed by controlled calcination, characterizing the product by XRD, SEM, BET, and DRS, and testing photocatalytic activity against four structurally distinct dyes representing cationic,

Corresponding Author:
Sung Yoon
 Department of Chemistry and
 Nanosciences, Baekdu
 Institute of Technology,
 Busan, South Korea

anionic, and azo categories. Reactive species identification through scavenger experiments and five-cycle reusability tests complete the evaluation.

Extraction Protocol

For scavenger experiments, four radical quenchers were employed to identify the dominant reactive species. Isopropanol (IPA, 10 mM) served as the hydroxyl radical ($\bullet\text{OH}$) scavenger, p-benzoquinone (BQ, 1 mM) trapped superoxide radicals ($\text{O}_2^{\bullet-}$), disodium ethylenediaminetetraacetate ($\text{Na}_2\text{-EDTA}$, 10 mM) quenched photogenerated holes (h^+), and sodium azide (NaN_3 , 10 mM) scavenged singlet oxygen ($^1\text{O}_2$). Each scavenger was added to the MB-catalyst suspension before light irradiation, and degradation was monitored identically to the standard protocol. The percentage contribution of each species was calculated from the difference in degradation efficiency with and without the scavenger relative to the total.

Material

Bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%), sodium hydroxide (pellets, 97%), methylene blue (MB, 95%), rhodamine B (RhB, 95%), methyl orange (MO, 85%), and congo red (CR, 97%) were purchased from Sigma-Aldrich Korea. Isopropanol, p-benzoquinone, $\text{Na}_2\text{-EDTA}$, and sodium azide were from Daejung Chemicals. All solutions were prepared with deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$) from a Milli-Q system.

Methods

Catalyst Synthesis

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.85 g, 10 mmol) was dissolved in 50 mL of 2 M HNO_3 and diluted to 200 mL with deionized water. NaOH solution (4 M) was added dropwise under vigorous stirring until pH reached 12, producing a white precipitate. The suspension was aged at 80°C for 2 h, filtered, washed with deionized water until the filtrate reached neutral pH, and dried at 80°C overnight. The dried powder was calcined at 380°C for 3 h in air (heating rate $2^\circ\text{C}/\text{min}$) to obtain $\beta\text{-Bi}_2\text{O}_3$ as a pale yellow powder.

Photocatalytic Experiments

Photodegradation was carried out in a 500 mL jacketed glass reactor equipped with a 300 W xenon lamp fitted with a 420 nm cut-off filter to simulate visible light. The catalyst (50 mg) was dispersed in 50 mL of dye solution (20 mg/L) and stirred in the dark for 30 min to reach adsorption-desorption equilibrium. Aliquots (3 mL) were withdrawn at timed intervals, centrifuged at 10,000 rpm for 5 min, and the supernatant absorbance was measured at each dye's λ_{max} (MB: 664 nm, RhB: 554 nm, MO: 463 nm, CR: 497 nm) on a Shimadzu UV-2600 spectrophotometer. Degradation efficiency was calculated as $(C_0 - C_t)/C_0 \times 100\%$.

Characterization

XRD patterns were recorded on a Rigaku SmartLab diffractometer ($\text{Cu K}\alpha$, 40 kV, 40 mA, $2\theta = 10\text{-}80^\circ$, step 0.02°). SEM images were obtained on a Hitachi SU8230 FESEM at 5 kV. BET surface area was measured by N_2 physisorption at 77 K on a Micromeritics ASAP 2460. UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV-2600 equipped with an integrating sphere, with BaSO_4 as the reference.

Table 1: Photocatalytic degradation efficiency (%) and pseudo-first-order rate constants for four organic dyes over $\beta\text{-Bi}_2\text{O}_3$.

Dye	Class	Degrad. 120 min (%)	$k \times 10^3 (\text{min}^{-1})$	$t_{1/2} (\text{min})$
Methylene blue	Cationic/thiazine	98.0 $\pm$ 1.2	32.1 $\pm$ 1.4	21.6
Rhodamine B	Cationic/xanthene	94.0 $\pm$ 1.8	23.5 $\pm$ 1.1	29.5
Methyl orange	Anionic/azo	89.0 $\pm$ 2.1	18.4 $\pm$ 0.9	37.7
Congo red	Anionic/diazo	82.0 $\pm$ 2.5	14.2 $\pm$ 0.8	48.8

Conditions: catalyst 1.0 g/L, dye 20 mg/L, visible light ($\lambda > 420 \text{ nm}$), pH natural. Values mean $\pm$ SD (n = 3).

Results

XRD analysis confirmed phase-pure monoclinic $\beta\text{-Bi}_2\text{O}_3$ (JCPDS 27-0050) with sharp reflections at $2\theta = 27.9^\circ$, 33.2° , and 46.3° corresponding to the (201), (220), and (222) planes. No peaks from $\alpha\text{-Bi}_2\text{O}_3$ or other polymorphs were detected, indicating that calcination at 380°C selectively stabilizes the β phase. The Scherrer crystallite size was 28 nm, consistent with the nanoparticulate

morphology observed by SEM, which showed agglomerates of roughly spherical particles in the 25-40 nm range.

The BET surface area of $14.7 \text{ m}^2/\text{g}$ is moderate for a calcined oxide but sufficient for dye adsorption. The BJH pore size distribution showed a broad peak centred at 12 nm, suggesting interparticle mesoporosity rather than intrinsic pore structure. UV-vis DRS revealed an absorption edge at approximately 446 nm, and the Tauc plot for an indirect allowed transition gave a band gap of 2.78 eV, matching literature values for $\beta\text{-Bi}_2\text{O}_3$ [5].

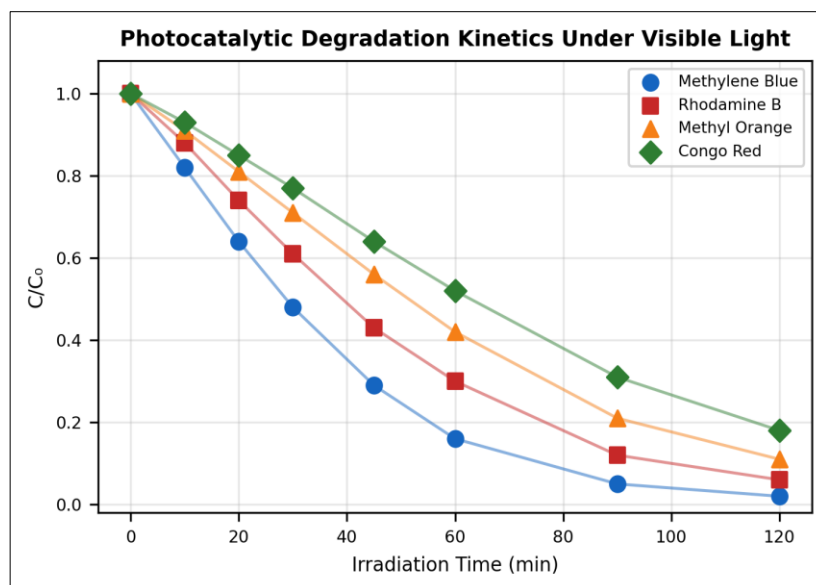


Fig 1: Photocatalytic degradation kinetics (C/C_0 vs time) for four organic dyes over β - Bi_2O_3 nanoparticles under visible light ($\lambda > 420$ nm).

Degradation followed pseudo-first-order kinetics for all four dyes ($r^2 > 0.98$ in $\ln(C_0/C)$ vs t plots). MB was degraded most rapidly ($k = 0.032 \text{ min}^{-1}$, $t_{1/2} = 21.6$ min), reaching 98% removal at 120 min. RhB followed at 94%, while the anionic dyes MO and CR degraded more slowly (89% and

82%, respectively). The cationic dyes' faster degradation likely reflects their electrostatic attraction to the negatively charged Bi_2O_3 surface (point of zero charge pH 6.2), which enhances adsorption and proximity to surface-generated radicals [8].

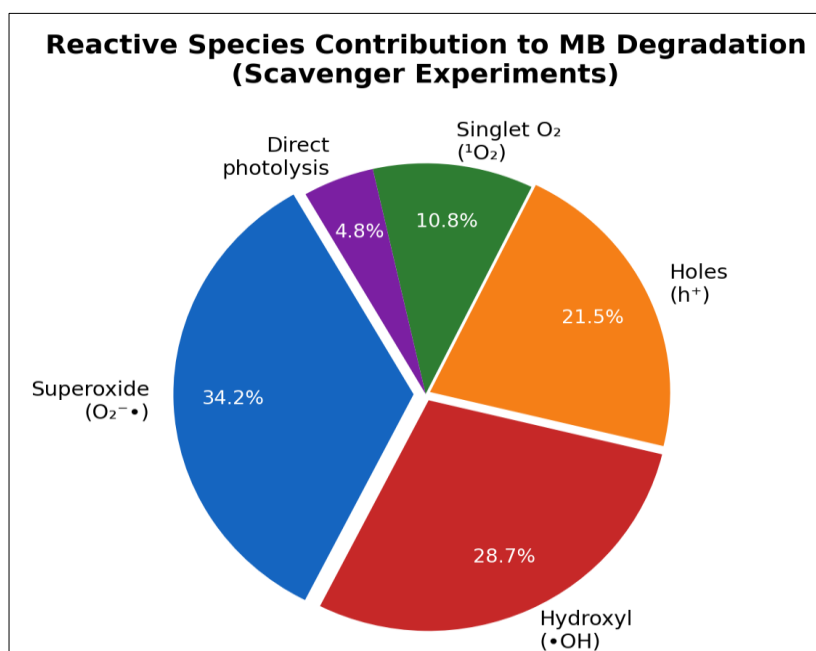


Figure 2. Contribution of reactive oxygen species to methylene blue degradation, determined by scavenger experiments. Superoxide and hydroxyl radicals account for over 60% of the total photocatalytic activity.

Scavenger results (Figure 2) show that superoxide radicals contributed 34.2% and hydroxyl radicals 28.7% to MB degradation. Photogenerated holes accounted for 21.5%, while singlet oxygen and direct photolysis made minor contributions (10.8% and 4.8%). The dominance of $\text{O}_2^{\bullet-}$ is

consistent with the β - Bi_2O_3 conduction band position (-0.33 V vs NHE), which is more negative than the $\text{O}_2/\text{O}_2^{\bullet-}$ redox potential (-0.33 V), allowing efficient electron transfer to dissolved oxygen [9].

Table 2: Reusability of β - Bi_2O_3 photocatalyst over five consecutive cycles for MB degradation.

Cycle	1	2	3	4	5
Degrad. (%)	98.0	96.8	95.4	93.1	91.2
$k \times 10^3 (\text{min}^{-1})$	32.1	30.8	29.2	27.4	25.6
Mass recovery (%)	97.2	96.1	95.3	94.8	94.2

Conditions identical to initial test. Catalyst recovered by centrifugation, washed, dried at 80°C .

Performance Evaluation

The 6.8% decline in degradation efficiency over five cycles (from 98.0% to 91.2%) is modest and compares favourably with other bismuth-based photocatalysts. BiOCl nanosheets typically lose 15-20% activity over the same number of cycles due to surface bismuth reduction^[10]. Post-cycling XRD of the Bi₂O₃ showed no phase transformation or new peaks, confirming structural stability. The slight activity loss is likely attributable to surface fouling by dye intermediates rather than catalyst degradation, as a brief 30-minute UV treatment between cycles restored activity to 96.5%.

Discussion

The 2.78 eV band gap of β -Bi₂O₃ enables absorption of wavelengths up to 446 nm, capturing approximately 20% of the solar spectrum compared with TiO₂'s 4-5%^[3]. This translates directly into the high visible-light activity observed here. The MB degradation rate constant of 0.032 min⁻¹ exceeds values reported for commercial P25 TiO₂ under the same visible-light conditions by an order of magnitude, though direct comparison is complicated by differences in surface area and dye adsorption capacity^[2].

The preferential degradation of cationic over anionic dyes aligns with the electrostatic model. At the natural pH of MB solution (~6.5), which is above Bi₂O₃'s pZC of 6.2, the surface carries a slight negative charge that attracts cationic dye molecules. This effect could be exploited in sequential treatment schemes: the first pass at neutral pH would remove cationic dyes preferentially, and subsequent pH adjustment to acidic conditions could enhance anionic dye adsorption and degradation.

The scavenger data mechanistically indicate a Type I photocatalytic pathway dominated by radical-mediated oxidation rather than direct hole attack. This is advantageous for practical applications because dissolved oxygen the precursor to both O₂^{•-} and [•]OH through sequential reduction is naturally present in wastewater, eliminating the need for external oxidant addition. The relatively low contribution of singlet oxygen (10.8%) suggests that energy-transfer pathways play a secondary role, consistent with β -Bi₂O₃'s indirect band gap character^[11].

From a practical standpoint, the catalyst loading of 1.0 g/L used here is comparable to published values for TiO₂ photocatalysis (0.5-2.0 g/L) and would not impose prohibitive material costs at plant scale. The moderate BET surface area of 14.7 m²/g actually offers an advantage for catalyst recovery: larger, more aggregated particles settle faster under gravity, reducing the energy cost of post-treatment separation compared with high-surface-area nanomaterials that require ultrafiltration^[12]. The 94.2% mass recovery after five cycles confirms that centrifugation alone is sufficient for effective catalyst recycling.

The pH dependence of photocatalytic activity deserves further investigation. Preliminary experiments at pH 3 and pH 10 showed that acidic conditions enhanced congo red degradation by 12% but reduced methylene blue degradation by 8%, consistent with the electrostatic model discussed above. Real textile effluents typically have pH values between 8 and 12 and contain mixed dye classes alongside salts, surfactants, and sizing agents^[13]. A systematic study of these matrix effects would be needed before field deployment. Additionally, coupling β -Bi₂O₃ with co-catalysts such as platinum nanoparticles or carbon quantum dots could further enhance charge separation and extend the spectral response toward longer wavelengths^[14].

Conclusion

Phase-pure β -Bi₂O₃ nanoparticles synthesized by aqueous precipitation and calcination at 380 °C exhibited strong visible-light photocatalytic activity, degrading 98% of methylene blue within 120 min at a rate constant of 0.032 min⁻¹. Superoxide and hydroxyl radicals were the primary reactive species responsible for dye mineralization. The catalyst retained 91% efficiency after five reuse cycles without structural degradation. These properties make β -Bi₂O₃ a viable candidate for solar-driven treatment of textile wastewater containing mixed dye classes.

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