

Original Research

La₂O₃/BaO Composites With Enhanced Interfacial Charge Transport for High-Performance Photocatalytic Dye Degradation

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Abstract

Background: Reactive dyes are persistent water contaminants that can be difficult to remove by conventional treatment. Herein, we report La₂O₃/BaO composites for the ultraviolet (UV)-assisted degradation of a model dye—Reactive Blue 194 (RB 194)—and examine the influence of the La:Ba precursor ratio on their physicochemical properties. **Methods:** La₂O₃/BaO composites were synthesized by coprecipitation using La:Ba precursor ratios of 1:1, 1:2, and 2:1 (mol/mol) and characterized by X-ray diffraction, Fourier transform infrared spectroscopy, field-emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, thermogravimetric analysis–differential thermal analysis, UV–visible spectroscopy, and photoluminescence (PL) spectroscopy. Based on the results of this characterization, the composite prepared at a La:Ba precursor ratio of 1:2 (La₁/B₂) was selected for RB 194 degradation. We assessed the effects of catalyst dosage, initial dye concentration, pH, and temperature on photocatalytic performance, as well as degradation kinetics, reactive-species scavenging, electrochemical behavior, transformation products, and reusability. **Results:** The composites featured coexisting La- and Ba-containing crystalline phases and composition-dependent optical and PL responses. La₁/B₂ exhibited an apparent indirect band gap of ~4.25 eV and a point of zero charge of 8.92, achieving ~99% apparent decolorization within 120 min under the selected conditions (20 mg L⁻¹ RB 194, 70 mg catalyst per 100 mL, pH 6, 20 °C, and UV irradiation at 450 W). Given that the decolorization extent was calculated from absorbance loss at 600 nm and Total Organic Carbon (TOC)/Chemical Oxygen Demand (COD) analyses were not performed, the value of 99% does not represent complete mineralization. Among the evaluated kinetic models, the pseudo-first-order model provided the best fit (apparent rate constant = 0.04103 min⁻¹ at 20 mg L⁻¹). The charge-transfer resistance decreased from 32.6 Ω for pristine La₂O₃ to 23.2 Ω for La₁/B₂, consistent with improved interfacial electrochemical transport. Scavenging experiments indicated an important contribution from hole-associated surface reactions. **Conclusions:** La₁/B₂ outperformed pristine La₂O₃ in terms of RB 194 decolorization efficiency and electrochemical charge transport, thus holding promise for dye removal. However, direct band-position measurements, mineralization analysis, and long-term stability assessment are required to elucidate the charge transfer mechanism and practical applicability of this composite.

Keywords: La₂O₃/BaO; binary oxide composite; Reactive Blue 194; photocatalytic degradation; interfacial charge transport; UV irradiation

1. Introduction

Population growth, urbanization and industrial expansion have increased the release of dyes, pesticides, solvents and other persistent organic contaminants into aquatic environments [1,2]. Textile dyes are of particular concern because their complex aromatic structures can impart intense colour, reduce light penetration, interfere with aquatic photosynthesis, and resist conventional biodegradation. Reactive dyes are widely used owing to their strong affinity for textile fibers; however, the unfixed fraction may enter industrial effluents and persist in receiving water bodies unless adequately treated [3,4,5,6]. Conventional physical, chemical and biological treatment methods can reduce pollutant concentrations, but their effectiveness may be limited by incomplete removal, secondary-waste production, sensitivity to operating conditions, or treatment cost [7,8]. Advanced oxidation processes, including heterogeneous photocatalysis, offer a complementary treatment approach by

generating reactive species capable of transforming persistent organic molecules under irradiation [9,10,11].

Semiconductor photocatalysts have therefore received considerable attention for wastewater treatment because their composition, surface chemistry, morphology and optical properties can be adjusted through material design [12,13,14,15]. Nevertheless, the performance of an individual semiconductor may be limited by restricted light absorption, rapid recombination of photogenerated electron–hole pairs, slow interfacial charge transport and insufficient availability of reactive surface sites. Several modification strategies, including elemental doping, cocatalyst deposition, surface-defect engineering and heterojunction formation, have been investigated to address these limitations [14,16]. In particular, coupling two semiconductor phases can modify the interfacial electronic environment and provide additional pathways for charge migration. However, improved charge separation cannot be inferred solely from the coexistence of two crystalline phases and should be



supported by complementary optical, electrochemical and mechanistic evidence.

Rare-earth oxides have attracted interest as components of photocatalytic heterostructures because of their distinctive electronic configurations, surface basicity, defect chemistry and interactions with oxygen-containing species. Among them, La_2O_3 is a wide-band-gap rare-earth oxide used in catalysis, adsorption, dielectric materials, optical devices and composite photocatalysts. Reported optical band-gap values vary with crystalline phase, morphology, defect concentration, synthesis conditions and measurement method. For example, band-gap values of 5.18 ± 0.20 eV for La_2O_3 films and approximately 5.8–5.9 eV for La_2O_3 microplates have been reported [17,18]. La^{3+} has an $[\text{Xe}]4f^0$ electronic configuration, which distinguishes La_2O_3 from lanthanide oxides containing occupied 4f states [19]. La-containing surfaces can also interact with oxygenated and anionic species, although their adsorption and catalytic behaviour depend strongly on surface hydroxylation, carbonation, crystallinity and solution conditions [20,21].

Several La_2O_3 -containing heterostructures have been investigated for photocatalytic and photoelectrochemical applications. $\text{La}_2\text{O}_3/\text{g-C}_3\text{N}_4$ and $\text{TiO}_2/\text{La}_2\text{O}_3$ composites have been evaluated for pharmaceutical or dye degradation [21,22], whereas a $\text{La}_2\text{O}_3/(\text{BiO})_2\text{CO}_3/\text{Ag}_3\text{PO}_4$ p–n–p heterojunction has been used for visible-light-assisted doxycycline removal [23]. More recently, $\text{La}_2\text{O}_3/\text{AgCl}$, $\text{Nb}_2\text{O}_5/\text{La}_2\text{O}_3$ and $\text{CdS}/\text{La}_2\text{O}_3$ systems have been described as S-scheme photocatalysts based on the experimental evidence presented in their respective studies [24,25,26]. These reports demonstrate the potential of La_2O_3 as an interfacial component, but most reported systems contain carbon nitride, transition-metal oxides, silver-containing phases, or metal sulfides. The compositions, proposed charge-transfer mechanisms, applications and remaining research gaps of representative La_2O_3 -based heterojunctions are summarized in Table 1 (Ref. [22,23,24,25,26,27]).

Barium oxide is a strongly basic, wide-band-gap alkaline-earth oxide that has been investigated as a heterogeneous catalyst and as a component of electrochemical and photocatalytic composites [28,29,30,31]. BaO-containing materials may provide useful surface and interfacial properties, but these characteristics depend on the coupled phase, precursor composition, morphology and chemical state of the Ba-containing species. Therefore, favorable electrochemical behaviour reported for BaO-based composites should not be attributed to high intrinsic BaO conductivity without direct supporting evidence. BaO is also hygroscopic and can undergo hydration and carbonation during storage, atmospheric exposure, or contact with water. These characteristics require cautious phase assignment and consideration of chemical stability when BaO-containing materials are proposed for aqueous photocatalytic applications [31].

BaO nanoparticles and nanostructures have been studied as base catalysts and for the degradation of model dyes such as malachite green and Rhodamine B [30,31]. In addition, the previously reported ternary system demonstrated that Ba-containing oxide phases can be incorporated into multicomponent photocatalysts [32]. Nevertheless, limited information is available concerning direct coupling of La_2O_3 with a Ba-containing oxide phase for photocatalytic wastewater treatment. In particular, the effects of the La precursor ratio on phase formation, morphology, optical response, surface chemistry, interfacial electrochemical transport and photocatalytic behaviour have not been systematically established for Reactive Blue 194 (RB 194) degradation.

The novelty of the present study therefore lies in the systematic investigation of a comparatively underexplored, silver-free and sulfide-free $\text{La}_2\text{O}_3/\text{BaO}$ binary oxide system rather than merely the preparation of another oxide composite. Unlike previously reported La_2O_3 heterojunctions containing g- C_3N_4 , TiO_2 , AgCl , Ag_3PO_4 , Nb_2O_5 , or CdS [21,22,23,24,25,26], the present system combines a rare-earth oxide with an alkaline-earth oxide and evaluates how changing the La precursor ratio affects the resulting physicochemical and interfacial properties. The binary composition also avoids introducing a third semiconductor phase, thereby allowing the relationship between precursor composition and material behaviour to be examined more directly. However, because BaO-containing materials may undergo surface hydration and carbonation and because direct band-edge and *in situ* charge-migration measurements were not performed, the exact interfacial charge-transfer pathway is treated as a proposed mechanism rather than conclusively assigned as an S-scheme or another specific heterojunction type. The hypothesis of this study was that coupling La_2O_3 with a Ba-containing oxide phase and adjusting the La precursor ratio would modify phase development, optical response, radiative recombination behaviour and interfacial electrochemical transport relative to the corresponding individual oxide phases. These changes were expected to influence the utilization of photogenerated charge carriers and the photocatalytic degradation of RB 194 under ultraviolet (UV) irradiation. Importantly, the potential contribution of the heterointerface was evaluated through the combined interpretation of structural, optical, photoluminescence, electrochemical, scavenging, kinetic and reuse results rather than being inferred from degradation efficiency alone.

This study aims to prepare pristine La_2O_3 , a Ba-containing oxide sample and $\text{La}_2\text{O}_3/\text{BaO}$ composites with La precursor ratios of 1:1, 1:2 and 2:1 using a coprecipitation method; (ii) determine how precursor composition influences their crystalline, morphological, surface-chemical, thermal, optical, and photoluminescence properties. The RB 194 dye degradation under UV irradiation as a function of catalyst dosage, initial dye concen-

Table 1. Recent progress in La₂O₃-based heterojunction photocatalysts.

La ₂ O ₃ -based system	Mechanism reported	Target/application	Major finding	Research gap relevant to the present study	Ref.
La ₂ O ₃ /g-C ₃ N ₄	Semiconductor heterojunction	Tetracycline hydrochloride degradation	Coupling La ₂ O ₃ with g-C ₃ N ₄ improved light utilization and inhibited electron-hole recombination	Uses a metal-free semiconductor; alkaline-earth-oxide coupling was not investigated	[27]
TiO ₂ /La ₂ O ₃	Binary oxide heterojunction	MB and crystal violet degradation under UV and visible light	The composite displayed composition- and irradiation-dependent photocatalytic performance	Relies on TiO ₂ as the principal photocatalytic phase and does not examine BaO–La ₂ O ₃ interfacial behavior	[22]
La ₂ O ₃ /(BiO) ₂ CO ₃ /Ag ₃ PO ₄	p–n–p ternary nanoheterojunction	Visible-light degradation of doxycycline	Multiple interfaces promoted carrier transfer and doxycycline removal; degradation pathways and intermediate toxicity were evaluated	Requires three semiconductor phases, including Ag ₃ PO ₄ ; a simpler rare-earth/alkaline-earth binary oxide was not considered	[23]
La ₂ O ₃ /AgCl	S-scheme heterojunction containing interfacial La–Cl bonding	Bisphenol-A degradation	Interfacial chemical bonding facilitated charge migration and S-scheme photocatalysis	Contains a silver halide and was prepared through high-energy ball milling; it differs compositionally from an all-oxide La ₂ O ₃ /BaO system	[24]
Nb ₂ O ₅ /La ₂ O ₃	S-scheme heterojunction verified using <i>in situ</i> XPS	Photocatalytic H ₂ production	The optimized composite produced 2175 μmol H ₂ g ^{−1} h ^{−1} , substantially exceeding the individual oxides	Focused on solar-fuel production rather than aqueous dye degradation and did not involve an alkaline-earth oxide	[25]
CdS/La ₂ O ₃	S-scheme heterojunction supported by interfacial and photoelectrochemical analyses	H ₂ evolution under simulated sunlight	The optimized material generated 18.50 mmol H ₂ g ^{−1} h ^{−1} , attributed to improved charge separation and preserved redox ability	Incorporates CdS, with potential stability and toxicity concerns; an entirely oxide-based La ₂ O ₃ /BaO interface was not examined	[26]

tration, solution pH, temperature, and irradiation time was evaluated. X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (FE-SEM–EDX), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis–differential thermal analysis (TGA–DTA), UV–visible spectroscopy and photoluminescence analyses were used for material characterization.

2. Materials and Methods

2.1 Chemical and Reagents

Lanthanum(III) nitrate hexahydrate [La(NO₃)₃·6H₂O, ≥99%], barium nitrate [Ba(NO₃)₂, ≥99%], potassium hydroxide pellets (KOH, ≥85%), sodium chloride (NaCl, ≥99%), ethylenediaminetetraacetic acid (EDTA), dimethyl sulfoxide (DMSO, ≥99%), potassium dichromate (K₂Cr₂O₇, ≥99%) and ascorbic acid (AA, ≥99%) were purchased from Sigma-Aldrich. Reactive Blue 194 (RB 194) was obtained from Sandal Dyestuff Industries, Faisalabad, Pakistan. All chemicals were of analytical grade and were used as received without further purification.

Deionized water was used to prepare all solutions and to wash the synthesized precipitates.

2.2 Synthesis of La₂O₃ and BaO and Composites

Pristine La₂O₃, BaO and La₂O₃/BaO composites were prepared by co-precipitation [33]. For the pristine samples, 0.1 M precursor solutions were prepared by dissolving 8.660 g of La(NO₃)₃·6H₂O or 5.227 g of Ba(NO₃)₂ in deionized water and adjusting the final volume to 200 mL. Each solution was stirred for 1 h, followed by the dropwise addition of 0.1 M KOH at approximately 5 mL min^{−1} until pH 12 was attained. The resulting suspensions were stirred separately at 50 rpm and 60 °C for 4 h. For the composites, 0.1 M La(NO₃)₃·6H₂O and Ba(NO₃)₂ stock solutions were prepared using 4.330 and 2.613 g per 100 mL, respectively. La₁/B₁ was prepared by mixing 100 mL of each stock solution, corresponding to 0.010 mol each of La³⁺ and Ba²⁺. La₁/B₂ was prepared using 100 mL of the La solution and 200 mL of the Ba solution, corresponding to 0.010 and 0.020 mol, respectively. La₂/B₁ was prepared using 200 mL of the La solution and 100 mL of the Ba solution, corresponding to 0.020 and 0.010 mol, respectively.

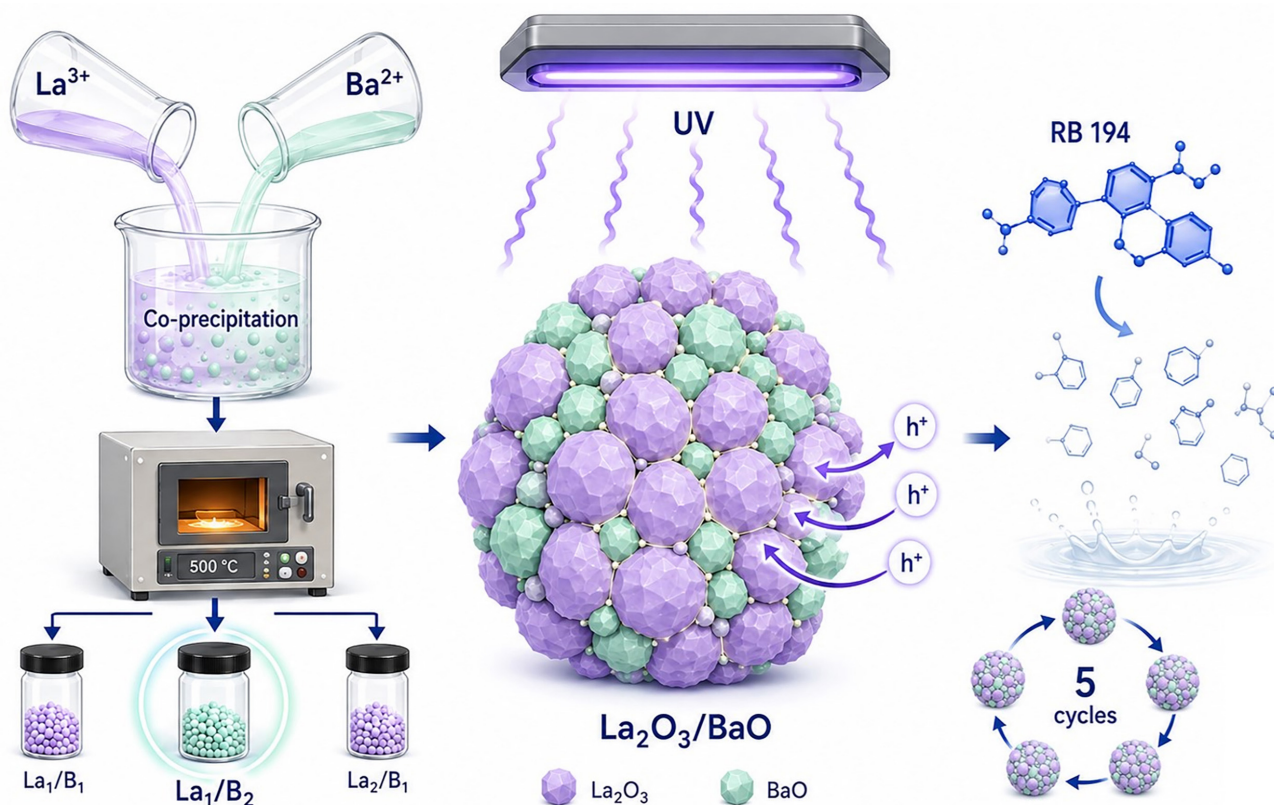


Fig. 1. Synthesis and photocatalytic degradation. Schematic illustration of the synthesis of $\text{La}_2\text{O}_3/\text{BaO}$ composites and UV-assisted degradation of Reactive Blue 194 using the selected La_1/B_2 composition. This figure was created using 3D Max software.

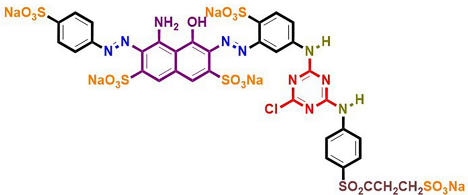
Each mixture was stirred for 1 h, after which 0.1 M KOH was added dropwise at approximately 5 mL min^{-1} until pH 12 was reached. The resulting suspensions were stirred at 50 rpm and $60\text{ }^{\circ}\text{C}$ for 4 h. All precipitates were recovered by filtration, washed repeatedly with deionized water, dried at $60\text{ }^{\circ}\text{C}$ and ground into fine powders. The powders were calcined at $500\text{ }^{\circ}\text{C}$ for 3 h using heating and cooling rates of $5\text{ }^{\circ}\text{C min}^{-1}$ and stored in sealed containers to minimize atmospheric hydration and carbonation [33,34]. The labels La_1/B_1 , La_1/B_2 and La_2/B_1 denote nominal La cationic precursor molar ratios of 1:1, 1:2 and 2:1, respectively; they do not represent the quantitative phase ratios in the final products. The schematic illustration of the synthesis of $\text{La}_2\text{O}_3/\text{BaO}$ composites and UV-assisted degradation of Reactive Blue 194 using the selected La_1/B_2 composition is depicted in Fig. 1.

2.3 Characterization

The crystalline structures and phase compositions of the pristine oxides and $\text{La}_2\text{O}_3/\text{BaO}$ heterojunctions were investigated using powder XRD (Bruker D8 Advance). The diffraction patterns were recorded over a 2θ range of $10\text{--}80^{\circ}$ using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) at an operating voltage of 40 kV and a current of 40 mA and a scanning rate of $2^{\circ}\text{ min}^{-1}$. The crystalline phases were identified by comparison with standard reference diffraction patterns.

The surface functional groups and metal–oxygen bonding environments were examined using FTIR (Thermo Nicolet). The spectra were recorded over $4000\text{--}400\text{ cm}^{-1}$ at a spectral resolution of 4 cm^{-1} using the KBr-pellet mode. The morphology, particle distribution and surface features of the synthesized materials were investigated using field-emission scanning electron microscopy (FE-SEM; Hitachi SU-1500). Elemental composition and spatial elemental distribution were evaluated using an energy-dispersive X-ray detector coupled to the FE-SEM instrument. Before imaging, the powdered samples were mounted on conductive carbon tape and coated with gold. The thermal behaviour of the synthesized materials was investigated using simultaneous thermogravimetric and differential thermal analysis (TGA–DTA; NETZSCH). Approximately 10 mg of each sample was heated from 50 to $800\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an argon atmosphere flowing at $40\text{--}60\text{ mL min}^{-1}$. The optical absorption properties were measured using a UV–Vis spectrophotometer (Shimadzu UV-2450) over the wavelength range of $200\text{--}800\text{ nm}$. The powdered samples were dispersed in ethanol before measurement and ethanol was used as the reference. The optical band-gap energies were estimated from the absorption data using both the photon-energy relationship and Tauc analysis. The photoluminescence spectra of pristine BaO , pristine La_2O_3 and the $\text{La}_2\text{O}_3/\text{BaO}$ heterojunctions were

Table 2. RB 194 dye properties used for photocatalytic activity evaluation.

Molecular formula	C ₃₃ H ₂₂ ClN ₁₀ O ₁₉ S ₆ Na ₅
Chemical Abstracts Service	93050-78-3
Molecular mass (g/mol)	1205.37523
λ_{max}	600 nm
LD50 (oral)	2000 mg/kg
Chemical structure	

recorded using Shimadzu RF-6000 over the emission range of 300–850 nm. The surface elemental composition and chemical states were analysed using X-ray photoelectron spectroscopy (Thermo Fisher Scientific K-Alpha). Survey spectra and high-resolution spectra of the La 3d, Ba 3d, O 1s and C 1s regions were acquired. Electrochemical measurements were performed using an SP-240 potentiostat. Cyclic voltammetry was conducted over the potential range of 0.0–0.8 V at a scan rate of 5 mV s⁻¹.

2.4 Dye Solution Preparation and Properties

Reactive Blue 194 (RB 194), an anionic textile dye, was obtained from Sandal Dyestuff Industries, Faisalabad, Pakistan. Its principal properties and chemical structure are presented in Table 2. A 1000 mg L⁻¹ stock solution was prepared by dissolving 1.0 g of RB 194 in deionized water and adjusting the final volume to 1.0 L. Working solutions with concentrations of 10–50 mg L⁻¹ were prepared by appropriate dilution of the stock solution. The UV–visible absorption spectrum was recorded using a UH5300 spectrophotometer and the principal visible absorption maximum used for quantitative analysis was identified at 600 nm.

Photocatalytic Activity

The photocatalytic performance of the selected La₁/B₂ composite was evaluated using the degradation of Reactive Blue 194 (RB 194) under UV irradiation. In a typical experiment, 25 mg of the photocatalyst was dispersed in 100 mL of a 20 mg L⁻¹ RB 194 solution. Before irradiation, the suspension was stirred in the dark at 250 rpm for 30 min to approach adsorption–desorption equilibrium between the dye and catalyst surface. The reaction vessel was positioned 10 cm below a 450 W UV lamp and the suspension was irradiated for 120 min under continuous stirring. At 10 min intervals, 5 mL aliquots were withdrawn and filtered through 0.22 µm syringe filters to remove suspended catalyst particles. The absorbance of each filtrate was measured at the analytical wavelength of 600 nm using a UV–visible spectrophotometer. After measurement, the filtrate was returned to the reaction vessel to minimize changes in the reaction volume. The apparent RB 194 removal, expressed

as decolourization efficiency, was calculated from the decrease in absorbance at 600 nm using Eqn. 1, where C₀ and C_t represent the corresponding initial and time-dependent absorbance values. This spectrophotometric measurement reflects loss or alteration of the RB 194 chromophore and does not independently demonstrate complete degradation or mineralization.

$$\text{Apparent decolourization efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

3. Results and Discussions

3.1 X-ray Diffraction

The XRD patterns of the pristine La-containing and Ba-containing samples and the La₂O₃/BaO composites prepared using different La precursor ratios are presented in Fig. 2a. The Ba-containing sample exhibited prominent reflections at 2θ values of approximately 19.20°, 23.67°, 28.55°, 34.35°, 39.40°, 44.56°, and 46.52°. These reflections were indexed approximately to the (200), (201), (102), (212), (111), (112), and (103) planes, respectively, based on comparison with PDF/JCPDS No. 26-0178 [29]. Minor reflections observed at approximately 24.2°, 25.70°, 41.82°, and 42.80° could not be assigned unambiguously to this reference pattern and may originate from secondary Ba-containing phases formed through hydration or carbonation. Therefore, these peaks were not indexed as pure BaO without further phase analysis [29]. The La-containing sample displayed reflections at approximately 13.06°, 22.74°, 29.54°, 30.64°, 41.27°, 44.34°, and 46.52° and comparison with JCPDS card No: 05-0602 [35]. However, several of these reflections are consistent with previously reported La-containing oxide patterns [36]. The presence of low-angle reflections and closely spaced peaks indicates that contributions from hydroxide- or carbonate-containing surface phases cannot be excluded.

The composite samples contained reflections associated with both La- and Ba-containing phases, confirming their coexistence in the prepared materials. Changes in peak

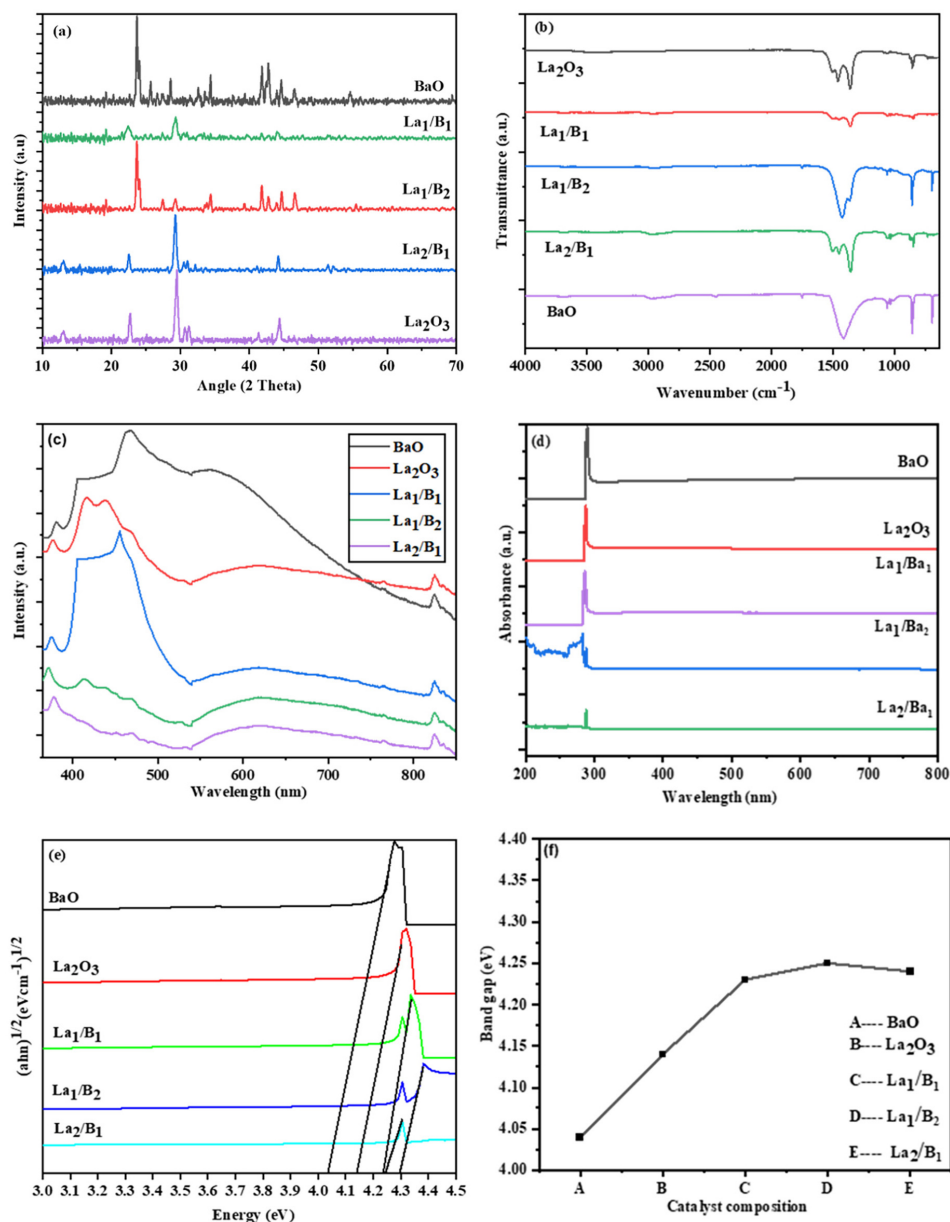


Fig. 2. Structural, vibrational, and optical characterization. (a) X-ray diffraction (XRD) patterns showing the crystalline phases of pristine oxides and La₂O₃/BaO nanocomposites. (b) FTIR spectra identifying the characteristic functional groups and metal–oxygen bonding in pristine oxides and La₂O₃/BaO nanocomposites, (c) Photoluminescence (PL) spectra illustrating charge-carrier recombination behavior in pristine oxides and La₂O₃/BaO nanocomposites, (d) UV–visible absorption spectra and maximum absorption wavelengths (λ_{max}) recorded using a UV–visible spectrophotometer, (e) Tauc plots used to estimate the optical band gap energies of pristine oxides and La₂O₃/BaO nanocomposites, (f) variation in optical band-gap energy for the pristine oxides and La₂O₃/BaO nanocomposites with varying La and Ba composition.

positions, relative intensities and broadening were observed among La₁/Ba₁, La₁/Ba₂ and La₂/Ba₁, indicating that the La precursor ratio influenced the relative phase contribution, crystallinity and crystal-growth behaviour. However, the coexistence of diffraction peaks alone does not conclusively demonstrate electronic heterojunction formation or interfacial charge transfer. These interpretations therefore require

support from the complementary spectroscopic, optical and electrochemical results.

The apparent crystallite size of each sample was estimated from its most intense, sufficiently isolated diffraction peak. After background subtraction, the selected peaks were fitted using a pseudo-Voigt function to determine the peak position and full width at half maximum

(FWHM). The FWHM values of the peaks for La₂O₃, BaO, La₁/B₁, La₁/B₂ and La₂/B₁ were 0.44269, 0.31217, 0.70346, 0.27127, and 0.42269, respectively. Instrumental broadening was corrected according to $\beta_c = (\beta_{obs}^2 - \beta_{inst}^2)^{\frac{1}{2}}$ and the corrected FWHM was converted from degrees to radians before applying the Scherrer equation (Eqn. 2).

$$D = \frac{k \times \lambda}{\beta \cos(\theta)} \quad (2)$$

Where (D) is the apparent crystallite size, (k) is the Scherrer shape factor (0.90), (λ) is the wavelength of the Cu K α radiation (1.5406 Å), (β) is the instrument-corrected full width at half maximum expressed in radians and (θ) is the Bragg diffraction angle. The calculated crystallite sizes of BaO, La₂O₃, La₁/B₁, La₁/B₂ and La₂/B₁ were 25.45, 27.90, 12.54, 31.94 and 20.07 nm, respectively. The composite diffraction patterns contained reflections associated with both La- and Ba-containing crystalline phases, while no additional crystalline phases were detected within the detection capability of the XRD measurements.

The variation in crystallite size among the pristine oxides and composite samples indicates that the La precursor ratio influenced nucleation and crystal growth during precipitation and calcination. La₁/B₁ exhibited the smallest apparent crystallite size, whereas La₁/B₂ showed a larger value than the other composite compositions. These differences may influence the density of crystallite boundaries and the distances over which photogenerated charge carriers migrate to surface reaction sites. Together with the observed changes in peak intensities and broadening, the crystallite-size results demonstrate that precursor composition affected the structural development of the La₂O₃/BaO composites. The possible contribution of these structural changes to photocatalytic performance was interpreted in conjunction with the optical, photoluminescence, morphological and electrochemical results.

3.2 Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was employed to identify the surface functional groups and characteristic bonding environments of pristine La₂O₃, BaO and the La₂O₃/BaO binary heterostructures prepared at La:Ba ratios of 1:1, 1:2 and 2:1, as shown in Fig. 2b. The absence of a broad absorption band within 3500–3000 cm⁻¹ suggests that adsorbed moisture and surface hydroxyl groups were present only in negligible amounts after drying and calcination. The weak bands observed at approximately 2972.6 and 2974.4 cm⁻¹ can be assigned to C–H stretching vibrations, possibly arising from trace surface-bound organic species or adventitious carbon contamination [37]. In the corresponding sample, the weak band at 1751.76 cm⁻¹ is attributed to the stretching vibration of carbonyl (C=O) groups [36]. The feature observed at 2449.97 cm⁻¹ may arise from the asym-

metric stretching of adsorbed CO₂ [28]. Bands appearing within 1407.79–1454.27 cm⁻¹ are associated with the asymmetric and symmetric stretching modes of surface carbonate species, respectively [38]. In addition, the absorption band near 855.4 cm⁻¹ is assigned to the out-of-plane bending vibration of carbonate groups. These carbonate-related features are likely caused by the adsorption of atmospheric CO₂ on the surfaces of the basic metal oxides [28].

The bands appearing within 1359.56–1413.79 cm⁻¹ are attributed to surface carbonate-related C–O vibrations. Additional features at 1032.78, 1053.56 and 1059.22 cm⁻¹ are assigned to C–O stretching modes. In the FTIR spectra of the La₂O₃/BaO heterostructures, the band near 693.3 cm⁻¹ is associated with Ba–O stretching [31]. Whereas the feature at approximately 727.6 cm⁻¹ is attributed to La–O vibrations [37]. The Ba–O-related band becomes less intense in La₂O₃ and the La-rich La₂/B₁ sample because of the lower relative BaO contribution and partial coverage of BaO domains by La₂O₃ [31]. Variations in the relative proportion of the two oxides, together with interfacial interactions, can also produce small shifts in band position and intensity. The simultaneous presence of La–O- and Ba–O-related vibrations, without the appearance of prominent new absorption bands, supports the coexistence of the constituent oxides and the successful formation of La₂O₃/BaO binary heterostructures. However, FTIR evidence alone cannot establish the precise nature of the interfacial chemical bonding.

3.3 Photoluminescence Spectroscopy (PL)

Photoluminescence spectroscopy was used to compare the radiative recombination and trapping behaviour of photogenerated charge carriers in pristine BaO, pristine La₂O₃ and the La₂O₃/BaO composites, as shown in Fig. 2c. Under identical measurement conditions, a lower steady-state PL intensity is generally associated with reduced radiative electron–hole recombination and/or increased carrier trapping. Nevertheless, PL intensity can also be influenced by light absorption, excitation conditions, particle scattering and nonradiative relaxation; therefore, the spectra were interpreted comparatively [27,39].

The PL spectra were recorded over the range of 300–850 nm and displayed emission features in the near-UV, visible and near-infrared regions. The principal near-UV emission maxima of BaO, La₂O₃, La₁/B₁, La₁/B₂ and La₂/B₁ occurred at approximately 381.56, 377.21, 374.97, 371.17 and 377.76 nm, with corresponding intensities of 2577.25, 1374.36, 1634.13, 1618.85 and 1374.36 a.u., respectively. The observed shifts in emission position and intensity indicate that variation in the La precursor ratio modified the local electronic and radiative-transition environments of the materials.

Pristine La₂O₃ exhibited visible-emission bands at approximately 415.97 and 438.32 nm, with intensities of 2311.54 and 2269.10 a.u., respectively. These emissions

occur at photon energies below the measured optical band gap and are therefore attributed to sub-band-gap transitions. Similar visible emissions from La_2O_3 have been associated with deep trap states, structural disorder and oxygen-vacancy-related centres [19,40,41]. Contributions from surface hydroxyl groups, carbonate species and other lattice defects may also influence these broad emission bands.

BaO and the $\text{La}_2\text{O}_3/\text{BaO}$ composites showed composition-dependent visible emissions. The principal visible maxima were observed at approximately 466.13 nm for BaO, 455.74 nm for La_1/B_1 , 413.96 nm for La_1/B_2 and 469.93 nm for La_2/B_1 , with respective intensities of 4669.93, 4016.13, 1403.22 and 622.24 a.u. Compared with pristine BaO and La_1/B_1 , the lower visible-emission intensities of La_1/B_2 and La_2/B_1 are consistent with reduced radiative recombination and/or increased trapping of photogenerated carriers. La_2/B_1 exhibited the lowest visible PL intensity, demonstrating that the effect was dependent on composite composition rather than following a uniform trend with increasing La or Ba content.

Weak near-infrared features were also detected at approximately 824–825 nm, with intensities of 989.81, 564.52, 631.52, 637.52 and 608.66 a.u. for BaO, La_2O_3 , La_1/B_1 , La_1/B_2 and La_2/B_1 , respectively. These weak emissions are provisionally associated with deep defect states and surface-related trapping processes. The formation of the $\text{La}_2\text{O}_3/\text{BaO}$ composites modified the PL response relative to the pristine materials. Although La_2/B_1 showed the lowest visible-emission intensity, selection of La_1/B_2 for detailed photocatalytic testing was based on its combined structural, optical, morphological and electrochemical characteristics rather than PL intensity alone. The reduced PL intensity of La_1/B_2 , together with its lower charge-transfer resistance measured by EIS, is consistent with modified carrier dynamics and improved interfacial electrochemical transport after composite formation.

3.4 UV-Vis Spectroscopy

UV–visible absorption spectroscopy was used to investigate the optical responses of pristine BaO, pristine La_2O_3 , and the $\text{La}_2\text{O}_3/\text{BaO}$ composites prepared using La:Ba precursor ratios of 1:1, 1:2, and 2:1 as presented in Fig. 2d–f. Fig. 2d presents the UV–visible absorption spectra of pristine oxides and the $\text{La}_2\text{O}_3/\text{BaO}$ composites. The absorption spectra and corresponding Tauc plots are presented in Fig. 2e. The samples exhibited their principal absorption responses within approximately 250–450 nm, although the positions and shapes of the absorption edges varied with precursor composition. The apparent optical band-gap energies were estimated using the Tauc relationship shown in Eqn. 3 [42].

$$(\alpha h\nu)^{\frac{1}{2}} = A(h\nu - E_g) \quad (3)$$

where α is the absorption coefficient, $h\nu$ is the incident photon energy, A is a proportionality constant, and E_g is the apparent optical band-gap energy. An indirect allowed-transition model was applied. For each sample, the most linear portion of the principal absorption edge in the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot was fitted and extrapolated to the energy axis. The low-energy absorption-tail and high-energy saturation regions were excluded from the linear fitting.

The apparent Tauc-derived band-gap energies were approximately 4.04, 4.14, 4.23, 4.25, and 4.24 eV for BaO, La_2O_3 , La_1/B_1 , La_1/B_2 , and La_2/B_1 , respectively. Thus, the composite samples exhibited slightly higher apparent band-gap energies than the pristine materials, with La_1/B_2 showing the highest value of approximately 4.25 eV. The relatively small differences among the composites indicate that variation in the La:Ba precursor ratio modified their optical absorption behaviour, although increasing the La precursor fraction did not produce a substantial additional change. La_1/B_1 and La_1/B_2 exhibited more than one optical absorption feature, which may arise from overlapping contributions from the La- and Ba-containing phases. These observations suggest that distinguishable optical responses of the constituent phases were retained following composite formation. However, because the composites contain multiple phases with potentially overlapping absorption contributions, these values are reported as apparent optical band-gap estimates rather than definitive intrinsic band-gap energies. The estimated values also depend on the assumed indirect-transition model and the selection of the linear extrapolation region. Under the applied UV irradiation, the incident photons possessed sufficient energy to excite the pristine and composite materials. Their photocatalytic behaviour was therefore interpreted by considering the optical results together with photoluminescence, interfacial charge transport, surface interactions, and the availability of photogenerated charge carriers for surface redox reactions. Fig. 2f represents the variation in optical band-gap energy for the pristine oxides and $\text{La}_2\text{O}_3/\text{BaO}$ nanocomposites with varying La and Ba composition. The observed changes in E_g with varying La and Ba compositions can be attributed to interactions between the two oxide phases and the formation of an interfacial heterostructure. Such variation may arise due to defect states, interfacial charge transfer interactions, and the electronic environment introduced by both oxides. The overall trend indicates that optical properties of the synthesized heterostructures can be tuned by both oxide phases.

3.5 Thermal Properties

The thermogravimetric and differential thermal profiles of pristine BaO, pristine La_2O_3 and the $\text{La}_2\text{O}_3/\text{BaO}$ composites are presented in Fig. 3a–e. The observed thermal events are attributed mainly to atmospheric hydration and carbonation, removal of adsorbed water, dehydroxylation and decomposition of residual nitrate- and carbonate-

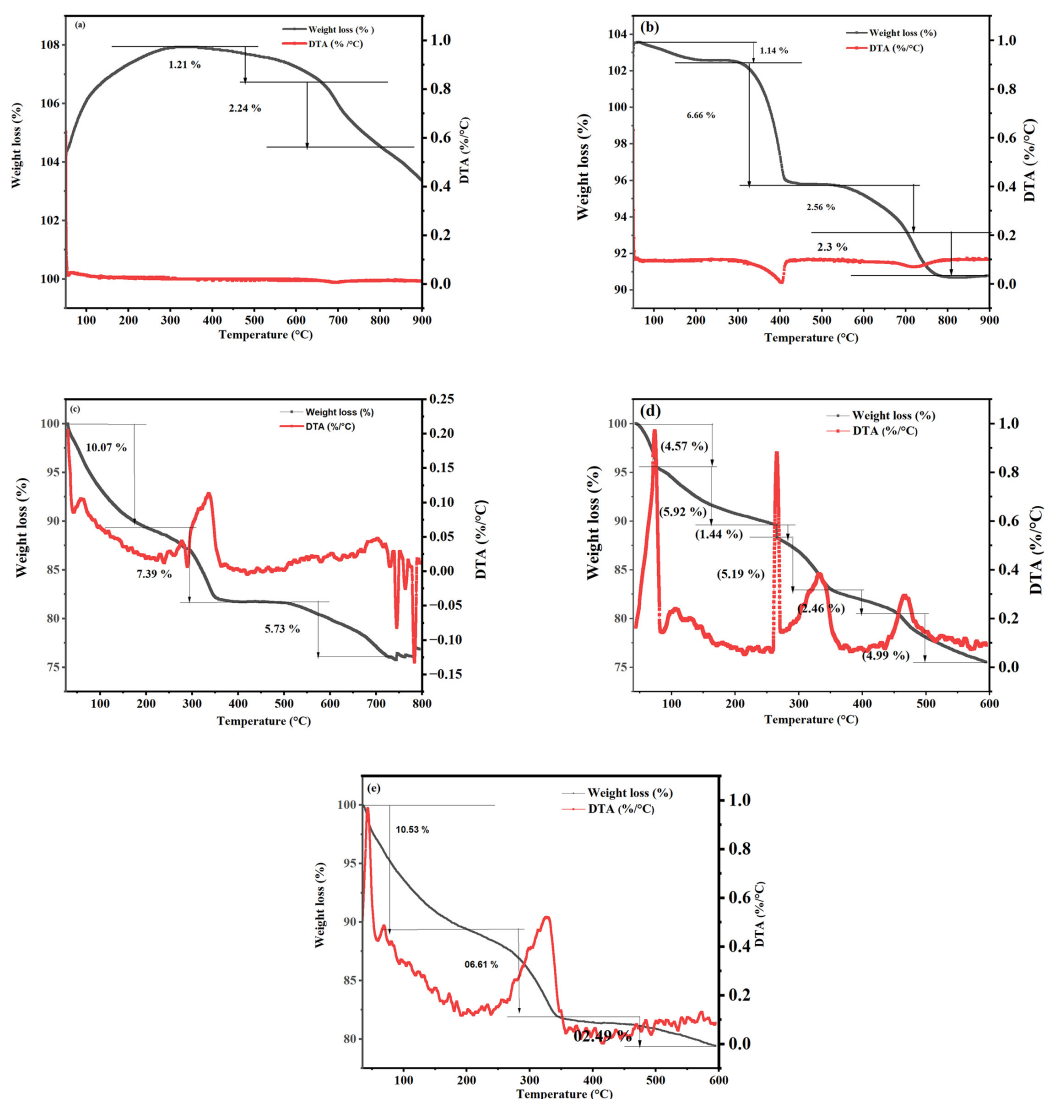


Fig. 3. Thermal analysis of the synthesized samples. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves showing the thermal stability and decomposition behavior of (a) BaO, (b) La_2O_3 , (c) La_1/B_1 , (d) La_1/B_2 , and (e) La_2/B_1 samples.

containing species. The sample exhibited a substantial mass increase upon heating to approximately 300–400 °C, consistent with the strong tendency of BaO to undergo hydration and carbonation during atmospheric exposure and form $\text{Ba}(\text{OH})_2$ and BaCO_3 -related surface species. Two subsequent local mass-loss steps of approximately 1.21% and 2.24% were observed and are attributed to the release or decomposition of adsorbed, hydroxide-containing and carbonate-containing species. Because the final mass remained higher than the initial value, the thermal profile represents an initial mass gain followed by partial mass loss. The comparatively featureless DTA curve indicates the absence of a single dominant, sharply resolved thermal event.

The thermal profile of La_2O_3 is presented in Fig. 3b. An initial mass loss of approximately 1.14% below 285 °C is attributed primarily to the removal of physically adsorbed water and weakly bound surface hydroxyl groups.

A major mass loss of approximately 6.66% occurred between approximately 285 and 450 °C and was accompanied by a thermal feature near 405 °C. This event is associated with the decomposition of residual $\text{La}(\text{OH})_3$ and carbonate-containing species. Further losses of approximately 2.56% and 2.30% at higher temperatures are attributed to continued dehydroxylation and decomposition of residual lanthanum oxycarbonate species. The cumulative labelled mass loss was approximately 12.66%. The La_1/B_1 composite exhibited an initial mass loss of approximately 10.07% below 200 °C, corresponding mainly to the removal of adsorbed water and weakly bound volatile species (Fig. 3c). A second loss of approximately 7.39% between 200 and 350 °C was accompanied by a pronounced thermal feature near 335 °C and is attributed to the decomposition of residual hydroxide-, nitrate- and carbonate-containing species. A further loss of approximately 5.73% occurred between

approximately 500 and 730 °C, indicating continued removal of more strongly bound residual species and thermal stabilization of the composite. The cumulative labelled mass loss was approximately 23.19%.

The TGA-DTA profile of La_1/B_2 is shown in Fig. 3d. Successive mass-loss steps of approximately 4.57%, 5.92%, 1.44%, 5.19%, 2.46% and 4.99% were observed. The initial losses below approximately 250 °C are attributed mainly to the removal of adsorbed moisture, surface hydroxyl groups and weakly bound volatile species. The relatively sharp 1.44% mass change near 265.60 °C, accompanied by a pronounced thermal signal, is associated with decomposition of residual precursor-derived species. Subsequent losses and thermal features near approximately 332 and 465 °C indicate continued decomposition of hydroxide-, nitrate- and carbonate-containing residues and progressive thermal stabilization. The cumulative labelled mass loss was approximately 24.57%. Fig. 3e presents the thermal behaviour of La_2/B_1 . An initial mass loss of approximately 10.53% below 100 °C is assigned primarily to the release of physically adsorbed water and weakly bound volatile species. A second loss of approximately 6.61% occurred between approximately 100 and 350 °C and was accompanied by a strong thermal feature near 326.18 °C. This event is associated with the decomposition of residual hydroxide-, nitrate- and carbonate-containing species. A smaller mass loss of approximately 2.49% was observed between approximately 350 and 500 °C, after which only minor changes were detected. The cumulative labelled mass loss was approximately 19.63%. The principal precursor-decomposition events occurred mainly below approximately 500 °C, although smaller mass changes continued at higher temperatures for some compositions. Accordingly, a calcination temperature of 500 °C for 3 h, with heating and cooling rates of 5 °C min⁻¹, was used to promote precursor decomposition and oxide formation while limiting excessive thermal growth of the particles. The cumulative labelled mass losses were approximately 12.66%, 23.19%, 24.57% and 19.63% for La_2O_3 , La_1/B_1 , La_1/B_2 and La_2/B_1 , respectively. For BaO, the two local mass-loss steps totalled approximately 3.45%, although its overall thermal response was dominated by the initial mass-gain process.

3.6 Surface Morphology and Element Composition

FE-SEM was used to examine the surface morphology of pristine BaO, pristine La_2O_3 and the $\text{La}_2\text{O}_3/\text{BaO}$ composites prepared using different La:Ba precursor ratios. The corresponding micrographs are presented in Fig. 4. Pristine BaO exhibited a heterogeneous, highly agglomerated morphology dominated by elongated rod- and needle-like structures, as shown in Fig. 4a. In contrast, pristine La_2O_3 consisted predominantly of irregular granular and approximately quasi-spherical particles assembled into compact aggregates, as shown in Fig. 4b.

The morphologies of the composite samples differed with precursor composition. La_1/B_1 displayed irregular clusters composed of fine granular particles together with larger agglomerates as shown in Fig. 4c. La_1/B_2 exhibited a more compact, finely aggregated and comparatively uniform granular morphology at the displayed magnification as shown in Fig. 4d. La_2/B_1 showed a more heterogeneous surface containing large irregular aggregates and some elongated or block-like structures as shown in Fig. 4e. These observations indicate that changing the La:Ba precursor ratio influenced particle growth and agglomeration during precipitation and calcination. However, because the images were recorded at different magnifications and scale bars, quantitative comparison of particle size and surface roughness among the samples cannot be made directly from these micrographs. Moreover, FE-SEM images alone cannot confirm an increase in specific surface area or porosity; BET surface-area and pore-size measurements would be required to support such conclusions. The FE-SEM images were interpreted qualitatively because extensive agglomeration, particle overlap, and indistinct boundaries prevented reliable segmentation and measurement of individual particles. In addition, the images were recorded at different magnifications for morphological comparison. Therefore, a defensible particle-size distribution, number of analyzed particles, mean size, and standard deviation could not be obtained from the available micrographs. Higher-resolution imaging of well-dispersed particles, preferably using TEM, would be required for reliable quantitative size analysis.

The EDX spectra of BaO, La_2O_3 , La_1/B_1 , La_1/B_2 and La_2/B_1 are presented in Fig. 5a–e. The spectra of the composite samples show signals attributable to La, Ba and O, confirming the presence of the constituent elements within the regions selected for analysis. The relative intensities and semiquantitative weight percentages of La and Ba varied among the composite samples, which is consistent with the different precursor ratios used during synthesis. The carbon signal is primarily attributed to the conductive carbon tape and/or adventitious surface carbon. EDX confirms elemental presence but does not determine oxidation states, chemical bonding or phase identity. It therefore cannot independently establish that La and Ba are present exclusively as La_2O_3 and BaO, respectively, or conclusively prove formation of an interfacial heterojunction.

The chemical states of La, Ba and O are evaluated more appropriately using XPS, while direct visualization of the interface would require high-resolution TEM, SAED and STEM-EDS or EELS line-profile analysis.

3.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was used to qualitatively examine the surface elemental composition and chemical environments of the pristine Ba-containing sample, pristine La_2O_3 , and the selected La_1/B_2 composite. The survey spectra in Fig. 6a show Ba-, La-, O-, and C-related

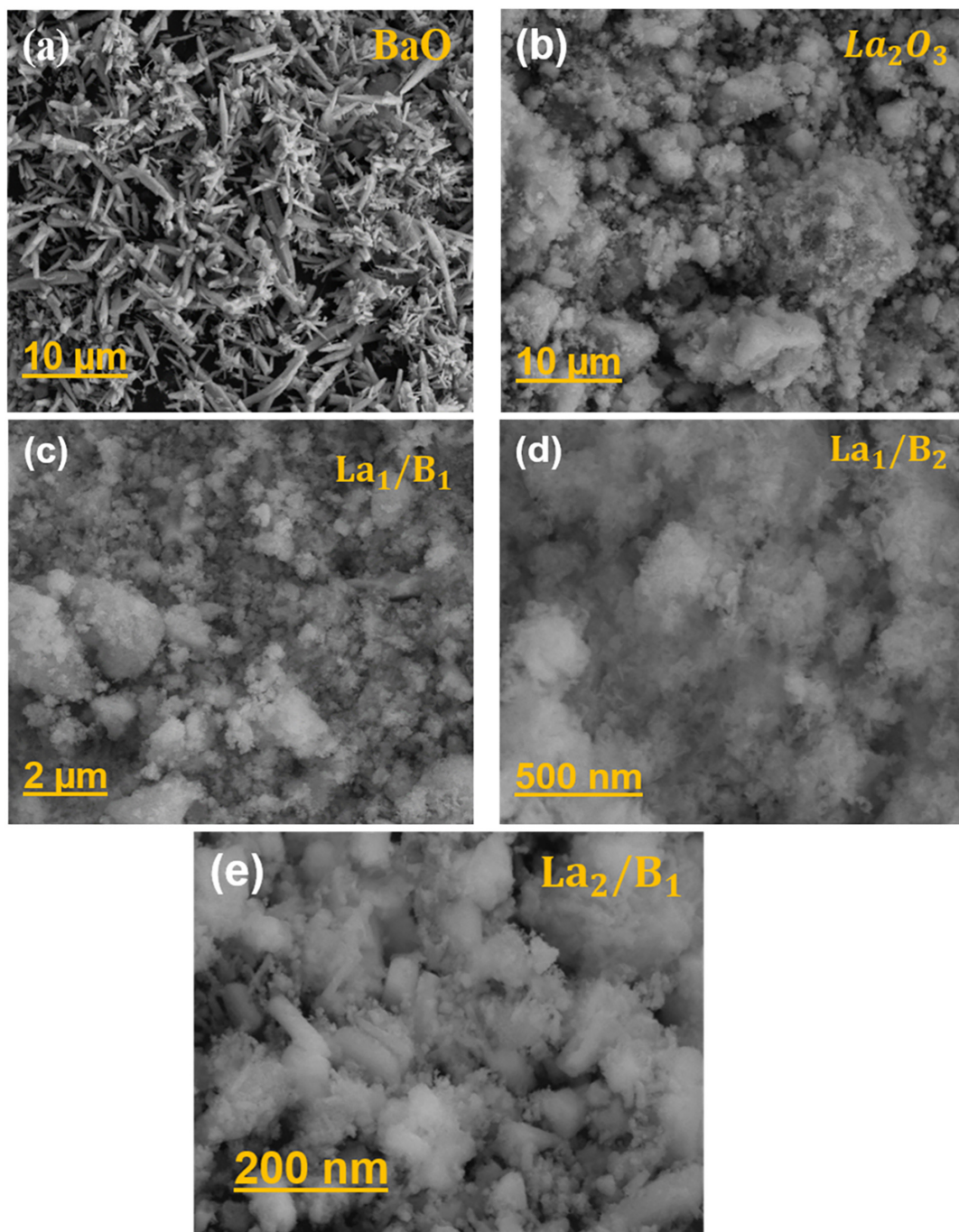


Fig. 4. Morphological characterization by FE-SEM. Energy-dispersive X-ray (EDX) spectra confirming the elemental composition of (a) pristine BaO, (b) pristine La_2O_3 , and the $\text{La}_2\text{O}_3/\text{BaO}$ heterostructures with La:Ba precursor ratios of (c) 1:1 (La_1/B_1), (d) 1:2 (La_1/B_2), and (e) 2:1 (La_2/B_1). 10 μm in (a), 10 μm in (b), 2 μm in (c), 500 nm in (d), and 200 nm in (e).

signals, while the simultaneous detection of La and Ba in La_1/B_2 confirms the presence of both elements within the surface region examined by XPS. The carbon signal is attributed mainly to adventitious surface carbon and possible carbonate-containing species.

The Ba 3d spectrum of the pristine Ba-containing sample exhibited envelope maxima at approximately 778.54 and 793.85 eV, corresponding to the Ba $3d_{5/2}$ and Ba $3d_{3/2}$ regions, respectively (Fig. 6b). In La_1/B_2 , the correspond-

ing maxima occurred at approximately 779.74 and 795.08 eV (Fig. 6d), representing positive shifts of approximately 1.20 and 1.23 eV, respectively. These positions are generally consistent with Ba^{2+} -containing surface species. However, because BaO is hygroscopic and readily reacts with atmospheric moisture and CO_2 , contributions from BaO-, $\text{Ba}(\text{OH})_2$ -, and BaCO_3 -related surface environments cannot be distinguished using the present spectra.

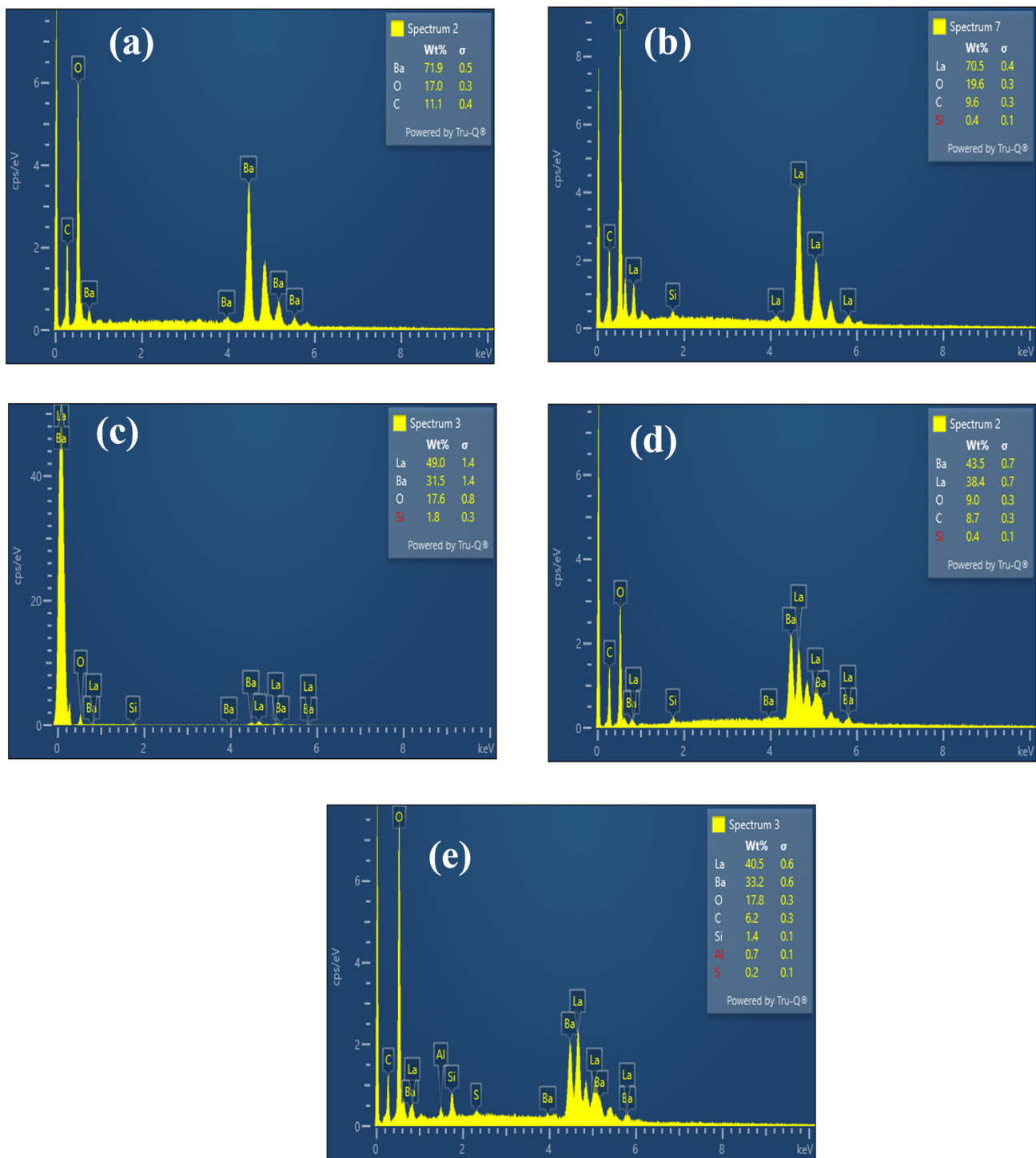


Fig. 5. Elemental composition analysis by EDX. Energy-dispersive X-ray (EDX) spectra of (a) pristine BaO, (b) pristine La₂O₃, and the La₂O₃/BaO heterostructures with La:Ba precursor ratios of (c) 1:1 (La₁/B₁), (d) 1:2 (La₁/B₂), and (e) 2:1 (La₂/B₁).

The La 3d spectrum of pristine La₂O₃ displayed broad envelope maxima at approximately 837.21 and 853.50 eV, associated with the La 3d_{5/2} and La 3d_{3/2} regions, respectively (Fig. 6c). In La₁/B₂, these maxima shifted to approximately 837.96 and 854.78 eV (Fig. 6e), corresponding to positive shifts of approximately 0.75 and 0.98 eV. The overall positions are consistent with predominantly

La³⁺-containing surface species. Nevertheless, La 3d spectra commonly contain overlapping multiplet and ligand-to-metal charge-transfer satellite features; therefore, the broad envelopes cannot be assigned to individual La-containing surface species without appropriately constrained peak fitting.

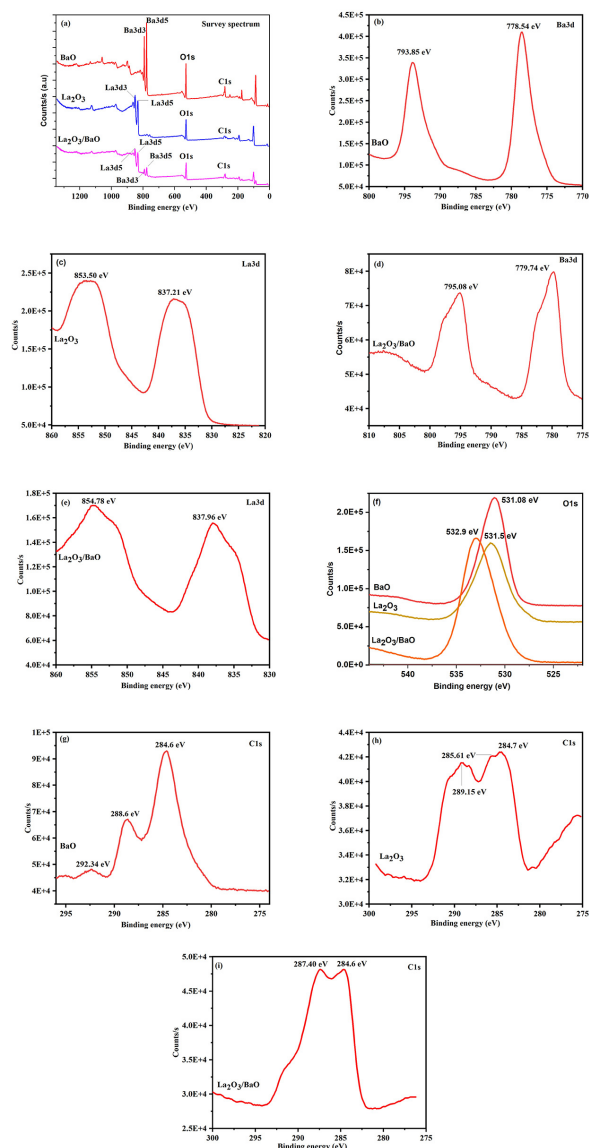


Fig. 6. Surface elemental composition and chemical states by XPS. X-ray photoelectron spectroscopy (XPS) analysis of pristine BaO, La₂O₃, and the La₂O₃/BaO nanocomposites showing (a) survey spectra; high-resolution spectra of (b) Ba 3d in BaO, (c) La 3d in La₂O₃, (d) Ba 3d and (e) La 3d in La₂O₃/BaO; and (f) O 1s and (g–i) C 1s spectra.

The O 1s envelope maxima occurred at approximately 531.08 eV for the Ba-containing sample, 531.5 eV for pristine La₂O₃, and 532.9 eV for La₁/B₂ (Fig. 6f). These broad envelopes may contain overlapping contributions from lattice oxygen, surface hydroxyl groups, adsorbed water, and carbonate-containing species. Consequently, the shift observed for La₁/B₂ is interpreted only as evidence of a modified overall surface oxygen environment relative to the pristine samples; it does not permit quantitative separation of the individual oxygen species.

The principal C 1s signal at approximately 284.6–284.7 eV was assigned to adventitious C–C/C–H species and used as the binding-energy reference. Signals at higher binding energies may arise from oxygenated carbon and carbonate-containing surface species resulting from exposure of the La- and Ba-containing oxides to atmospheric moisture and CO₂. Accordingly, the feature at approximately 287.40 eV in La₁/B₂ is assigned generally to oxygenated carbon species and not specifically to C–N bonding (Fig. 6g–i).

Quantitative peak deconvolution was not performed because the available spectra were acquired and used primarily for qualitative elemental identification and comparison of the overall envelope positions. Their resolution and signal quality were insufficient to support reliable separation of the strongly overlapping multiplet, satellite, hydroxide, oxide, and carbonate contributions using defensible fitting constraints. Consequently, fitted components, FWHM values, component peak areas, and species-specific atomic percentages are not reported. The observed binding-energy shifts should therefore be interpreted qualitatively and do not, by themselves, establish specific chemical bonds, quantify individual surface species, or conclusively demonstrate interfacial charge transfer. The XPS results provide only supporting evidence that composite formation altered the surface chemical environments of the La-, Ba-, and O-containing species and were interpreted together with the structural, optical, photoluminescence, and electrochemical findings.

3.8 Photocatalysis Activity

The maximum absorption wavelength (λ_{max}) of RB 194 was determined, as shown in Fig. 7. For the photocatalytic experiments, 100 mL of a 20 mg L^{−1} RB 194 solution was used. Photolysis in the absence of the catalyst resulted in only minor dye removal compared with the approximately 99% removal achieved in the presence of the catalyst under UV-light irradiation. Therefore, subsequent photocatalytic experiments were performed using the catalyst under UV-light irradiation. Under the selected experimental conditions, the absorbance of RB 194 at 600 nm decreased by approximately 99% after 120 min of UV irradiation. This value is therefore reported as apparent decolourization efficiency rather than mineralization efficiency. Loss of visible absorbance may result from cleavage or modification of the dye chromophore, while colourless or weakly absorbing organic intermediates may remain in solution. Because Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and inorganic-product analyses were not performed, the extent of organic-carbon removal and complete mineralization could not be determined.

3.8.1 Effect of Catalytic Dose

Among the prepared La₂O₃/BaO composites, La₁/B₂ was selected for detailed photocatalytic evaluation based

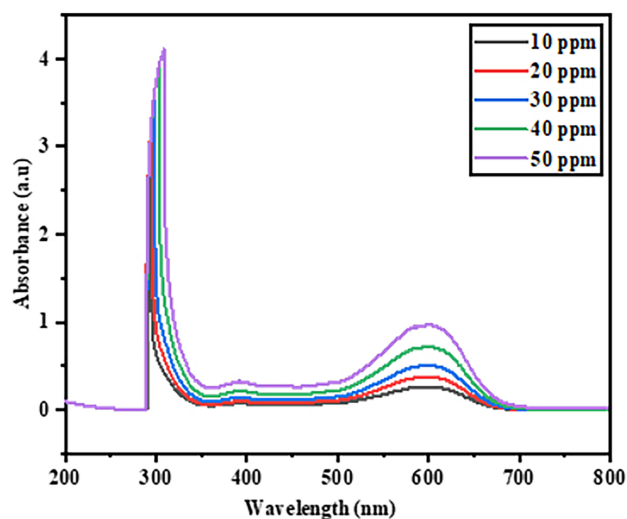


Fig. 7. Maximum wavelength of RB 194 dye determined by UV-vis spectrophotometer.

on its combined structural, morphological, optical, photoluminescence and electrochemical characteristics. The effect of catalyst dosage on RB 194 removal is presented in Fig. 8, with the corresponding data (C_i/C_0) presented in **Supplementary Table 1**. The La_1/B_2 dosage was varied from 7 to 200 mg per 100 mL of a 20 mg L⁻¹ RB 194 solution. Increasing the catalyst loading produced a marked improvement in the initial removal rate. After 10 min of irradiation, 7 mg of the catalyst achieved 34.18% removal, whereas 70 mg achieved 84.85%. This rapid initial removal is attributed to the greater availability of surface-active sites and increased interaction between the incident radiation and the photocatalyst. The comparison of photocatalysis, adsorption and photolysis (catalyst dose 70 mg) is shown in **Supplementary Fig. 1**. The photocatalytic removal was 99% at optimum conditions, including 2.5 and 0.8% contributions from adsorption of dye on the catalyst surface and photolysis.

After 120 min, removal efficiencies of 99.05%, 99.76% and 99.73% were obtained using catalyst dosages of 70, 100 and 200 mg per 100 mL, respectively. Although 100 and 200 mg produced marginally higher numerical efficiencies, the improvement relative to 70 mg was small. Therefore, 70 mg per 100 mL was selected as the practical operating dosage because it achieved approximately 99% removal while using a lower quantity of photocatalyst. The limited improvement above 70 mg per 100 mL may result from the competing effects of increased active-site availability and reduced light penetration at higher solid loadings. Excessive catalyst concentrations can increase particle agglomeration, light scattering and shielding within the suspension, thereby restricting the effective utilization of incident photons. Thus, 70 mg per 100 mL provided an appropriate balance between photocatalytic performance and catalyst consumption under the investigated conditions.

3.8.2 Effect of Dye Concentration

The effect of initial RB 194 concentration on the photocatalytic performance of La_1/B_2 was evaluated over the range of 20–80 ppm using a catalyst dosage of 70 mg per 100 mL and a fixed irradiation time. The results presented in Fig. 9 show that the removal efficiency progressively decreased as the initial dye concentration increased (C_i/C_0) data are given in **Supplementary Table 2**. with the highest removal obtained at 20 mg L⁻¹. At lower concentrations, a greater proportion of the dye molecules can adsorb near accessible surface-active sites and interact with photogenerated charge carriers. As the initial dye concentration increases, the finite number of catalyst surface sites becomes increasingly occupied by dye molecules and transformation products, resulting in greater competition for reactive sites. In addition, the stronger colour and optical absorption of concentrated RB 194 solutions restrict UV-light penetration and reduce the number of photons reaching the photocatalyst surface. Consequently, fewer reactive charge carriers are generated relative to the number of dye molecules present, leading to a lower apparent removal efficiency at higher initial concentrations [43]. Based on these results, an initial RB 194 concentration of 20 mg L⁻¹ was used for the subsequent photocatalytic experiments.

3.8.3 Effect of Temperature

The effect of temperature on RB 194 removal was investigated over the range of 20–70 °C. As shown in Fig. 10, the removal efficiency decreased progressively with increasing temperature and the highest removal was obtained at 20 °C (Fig. 10, **Supplementary Table 4**). Therefore, 20 °C was selected as the preferred operating temperature within the investigated range. Temperature can influence heterogeneous photocatalysis indirectly by modifying dye adsorption, molecular diffusion, desorption, dissolved-oxygen concentration and surface-reaction kinetics. The higher removal observed at 20 °C is consistent with comparatively favourable adsorption of RB 194 near the catalyst's surface-active sites. As the temperature increased, enhanced molecular motion and desorption may have reduced the local concentration of dye molecules near photogenerated holes and other surface-reactive species. Elevated temperatures may also decrease the concentration of dissolved oxygen and alter charge-carrier relaxation and surface-reaction pathways. The observed temperature dependence is therefore attributed primarily to changes in adsorption-desorption equilibrium and interfacial reaction conditions rather than to a direct temperature-induced change in the photocatalyst band gap.

3.8.4 Effect of pH

Fig. 11 illustrates the influence of the initial solution pH on the photocatalytic removal of RB 194 dye. The initial pH was varied from 3 to 11 while maintaining all other experimental conditions constant: catalyst dosage of 70

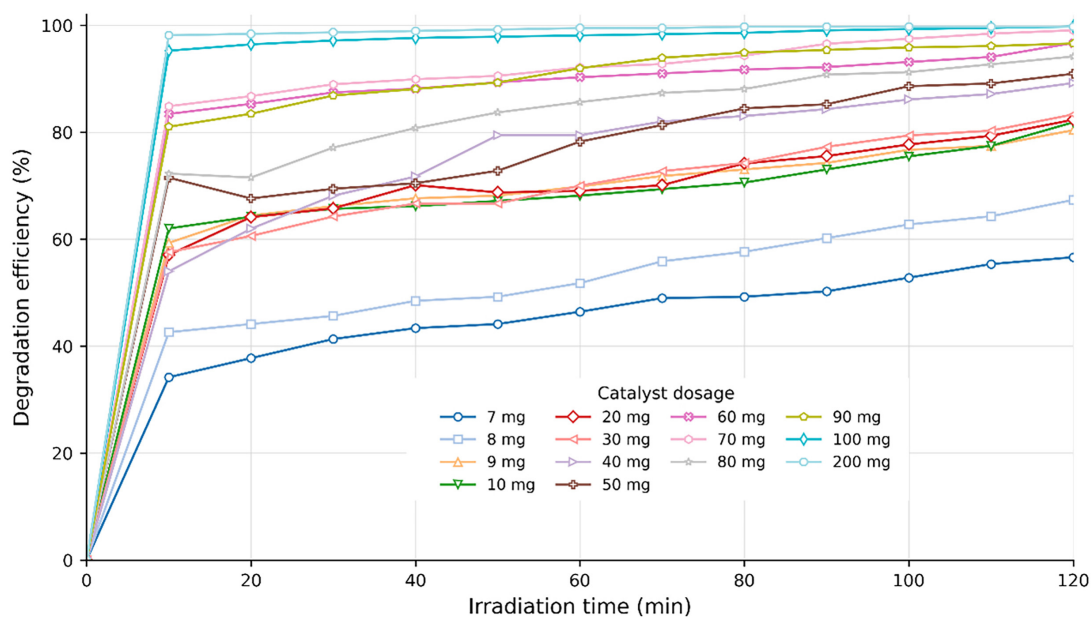


Fig. 8. Effect of catalyst dosage (7–200 mg/100 mL) on the removal efficiency of RB 194 under UV irradiation using the La₁/B₂ photocatalyst.

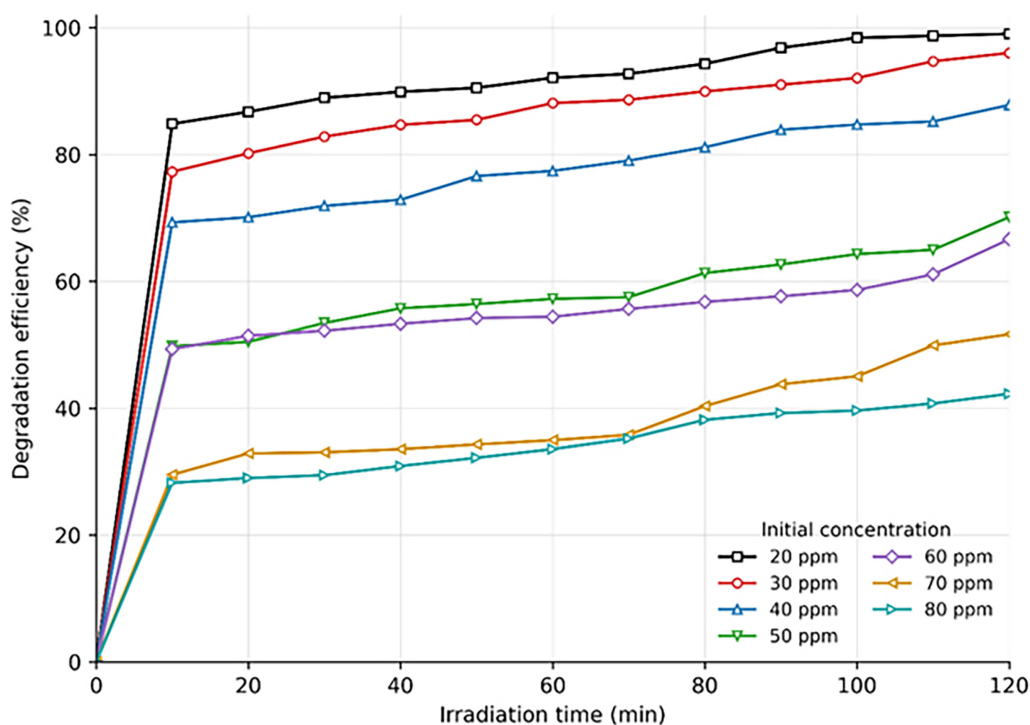


Fig. 9. Effect of initial dye concentration on photocatalytic degradation. Effect of initial RB 194 concentration (20–80 ppm) on removal efficiency over 120 min of UV irradiation using the La₁/B₂ photocatalyst.

mg/100 mL, initial dye concentration of 20 ppm and irradiation time of 120 min (**Supplementary Table 5**). The solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH. Because RB 194 is an anionic dye, its adsorption and photocatalytic removal are strongly influenced by the pH-dependent surface charge of the photocatalyst. The point of zero charge (pHpzc) of the La₁/B₂ heterojunction was deter-

mined using the salt-addition method (Eqn. 4) [44]. The initial pH (pH_i), equilibrium pH (pH_f) and calculated ΔpH values are presented in **Supplementary Table 6**.

$$\Delta pH = pH_f - pH_i \quad (4)$$

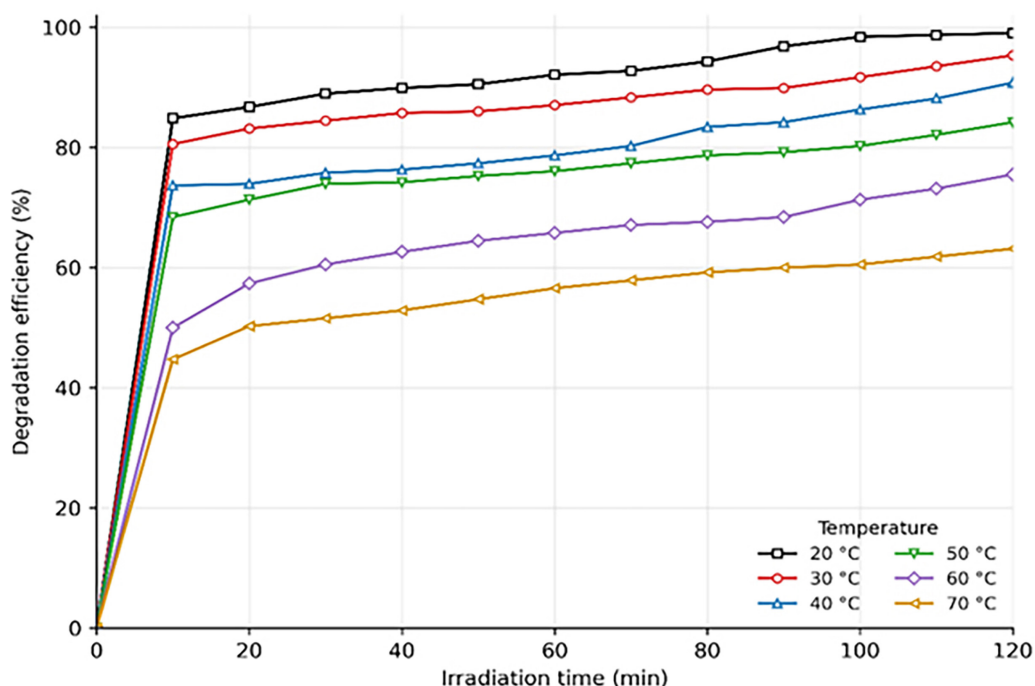


Fig. 10. Effect of temperature concentration on photocatalytic degradation. Effect of reaction temperature (20–70 °C) on RB 194 removal efficiency during 120 min of UV irradiation using the La₁/B₂ photocatalyst.

The pH_{pzc} was obtained from the zero crossing of the ΔpH versus pH_i plot presented in Fig. 12. Linear interpolation between the nearest experimental points, $pH_i = 8.91$ ($\Delta pH = +0.07$) and $pH_i = 8.96$ ($\Delta pH = -0.17$), gave a pH_{pzc} value of 8.92 as represented in Fig. 12. The highest RB 194 removal was obtained at pH 6. At this pH, the positively charged catalyst surface favours electrostatic interaction with the anionic dye, while competition from excess H^+ ions remains comparatively limited. Although the catalyst is also positively charged at pH 3–4, removal was lower under strongly acidic conditions. This behaviour may result from protonation of surface oxygen-containing groups, competition of H^+ ions with dye molecules for accessible surface sites and changes in the surface hydroxylation environment.

At pH values above the (pH_{pzc}), the catalyst surface becomes negatively charged, increasing electrostatic repulsion between La₁/B₂ and anionic RB 194. Competition from OH^- ions and changes in surface-reaction conditions may also contribute to the lower removal observed under alkaline conditions [45]. Therefore, the maximum performance at pH 6 is attributed to a favourable balance among electrostatic attraction, dye adsorption, accessible surface sites and interfacial photocatalytic reactions rather than to surface charge alone. The pH-dependent photocatalytic behaviour is consistent with the combined characterization results. XRD showed the coexistence of La- and Ba-containing crystalline phases; UV–visible analysis demonstrated composition-dependent modification of the optical response and the reduced PL intensity of La₁/B₂ was con-

sistent with lower radiative recombination and/or increased carrier trapping. In addition, EIS showed that the charge-transfer resistance decreased from 32.6 Ω for pristine La₂O₃ to 23.2 Ω for La₁/B₂. Together, these findings indicate that the photocatalytic performance of La₁/B₂ arises from the combined influence of its structural characteristics, optical response, surface-charge behaviour and modified interfacial electrochemical transport.

3.9 Decolourization Kinetics

The photocatalytic decolourization kinetics of RB 194 were evaluated using the pseudo-first-order kinetic model expressed in Eqn. 5. The apparent rate constant, (k), was determined from the slope of the linear plot of $\ln(C_0/C_t)$ versus irradiation time, (t), while the goodness of fit was assessed using the corresponding coefficient of determination (R^2).

$$\ln(C_0/C_t) = kt \quad (5)$$

The kinetic data obtained at different initial RB 194 concentrations were analysed using Eqn. 5. The plots of ($\ln(C_0/C_t)$) versus irradiation time were linear, with the corresponding data provided in Fig. 13. The apparent rate constants calculated from the slopes of the fitted lines are summarized in Table 3. The apparent removal rate decreased as the initial RB 194 concentration increased. The highest (k) value of 0.04103 min^{-1} ($R^2 = 0.95$) was obtained at 20 mg L^{-1} , whereas the lowest value of 0.00565 min^{-1}

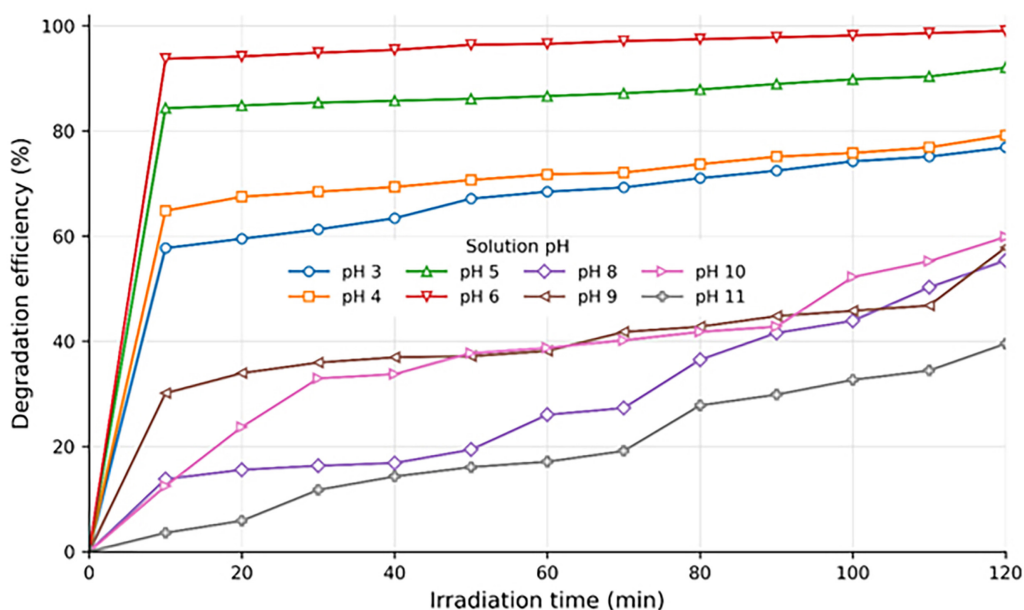


Fig. 11. Effect of solution pH on photocatalytic degradation. Effect of solution pH on the removal efficiency of RB 194 under UV irradiation using the La₁/B₂ photocatalyst.

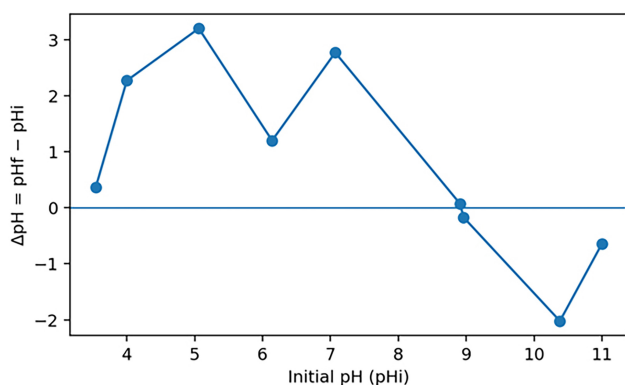


Fig. 12. Point of zero charge determination. Point of zero charge of La₂O₃/BaO (La₁/B₂) nanocomposite determined using the salt addition method.

was recorded at 80 mg L⁻¹ (Fig. 13, Supplementary Table 3). The apparent rate constants calculated from the slopes of the fitted lines are summarized in Table 3. The apparent removal rate decreased as the initial RB 194 concentration increased. The highest (*k*) value of 0.04103 min⁻¹ (*R*² = 0.95) was obtained at 20 mg L⁻¹, whereas the lowest value of 0.00565 min⁻¹ was recorded at 80 mg L⁻¹ (Fig. 13, Supplementary Table 3). This decrease is consistent with the reduced penetration of UV light and increased competition among dye molecules and transformation products for the available surface-active sites at higher initial concentrations. The removal data were also evaluated using zero-order, pseudo-first-order and pseudo-second-order kinetic models. Among the tested models, the pseudo-first-order model provided the highest coefficient of determina-

tion (*R*² = 0.95), compared with the zero-order (*R*² = 0.37) and pseudo-second-order (*R*² = 0.71) models. Thus, the pseudo-first-order expression provided the best representation of the RB 194 removal data among the kinetic models examined under the investigated conditions.

Table 3. The rate constant values determined by analyzing the data using the pseudo-first-order kinetic model at various concentrations of RB 194.

Dye Concentration (ppm)	<i>K</i> (min ⁻¹)	<i>R</i> ²
20	0.04103	0.95
30	0.0295	0.92
40	0.02072	0.90
50	0.01165	0.89
60	0.01055	0.86
70	0.00668	0.92
80	0.00565	0.90

3.10 Scavenging Experiment

Reactive-species scavenging experiments were performed under the same conditions as the photocatalytic removal tests to examine the possible contributions of different charge carriers and reactive species to RB 194 removal. Ascorbic acid (AA), potassium dichromate (K₂Cr₂O₇), dimethyl sulfoxide (DMSO), and ethylenediaminetetraacetic acid (EDTA), each at a concentration of 1 mM, were used as scavengers for superoxide radicals (O₂^{•-}), photogenerated electrons (e⁻), hydroxyl radicals (•OH), and photogenerated holes (h⁺), respectively [46,47]. These scavengers were used as indirect mechanistic probes. Their

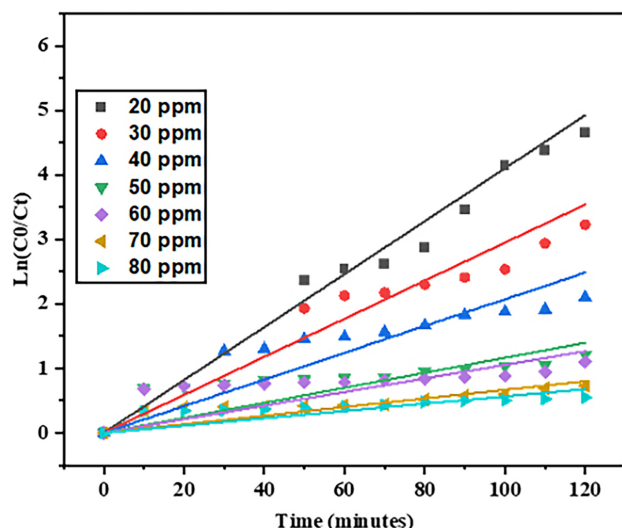


Fig. 13. Pseudo-first-order kinetic analysis. Pseudo-first-order kinetic plots of $\ln(C_0/C_t)$ versus irradiation time for the removal of RB 194 dye at different initial concentrations (20–80 ppm).

effects on dye removal were interpreted qualitatively and were not considered direct evidence for the generation of the corresponding reactive species and are represented in Fig. 14a,b.

In the absence of a scavenger, the apparent RB 194 removal efficiency was approximately 99%, whereas values of 100 %, 97.44 %, and 100% were obtained in the presence of AA, $K_2Cr_2O_7$, and DMSO, respectively (Supplementary Tables 7,8). The values equal to or slightly higher than the scavenger-free control should not be interpreted as evidence that these additives enhanced photocatalytic removal. Several non-mechanistic effects may account for this behaviour. The additives may alter the adsorption–desorption equilibrium of RB 194 on the catalyst surface, solution pH, ionic strength, catalyst surface charge, or interfacial interactions. $K_2Cr_2O_7$ may also participate in secondary photochemical or electron-accepting reactions, whereas DMSO may modify solvent properties or undergo reactions producing secondary species. Moreover, the scavengers or their reaction products may change the UV–visible absorption spectrum, baseline, or absorbance at 600 nm, producing an apparent change in dye concentration that does not necessarily represent additional removal. Because scavenger-only, dye–scavenger, catalyst–scavenger, and spectral-interference controls were not performed, the small differences observed for AA, $K_2Cr_2O_7$, and DMSO cannot be assigned conclusively to specific reactive species. These results are therefore interpreted qualitatively and indicate only that the selected additives did not measurably suppress RB 194 decolorization under the investigated conditions.

EDTA produced a markedly different time-dependent response. The absorbance decreased sharply during the initial stage of irradiation, with a decolorization efficiency of

44.19% achieved within approximately 10 min. Thereafter, the absorbance progressively increased and approached that of the untreated RB 194 solution after 120 min, corresponding to an apparent removal efficiency of only 0.75% as shown in Fig. 14b. The experiment was performed in triplicate, and the same general trend was observed. Nevertheless, because scavenger-only controls were not included and substantial absorbance recovery occurred, this response cannot be attributed exclusively to the trapping of photo-generated holes. It indicates only that hole-associated surface processes may contribute substantially to the observed transformation behaviour of RB 194.

GC–MS analysis was performed on samples collected after 10, 30, and 120 min to investigate the unusual EDTA-associated response represented in Fig. 15. Transformation-related compounds were tentatively detected in the 10-min sample, whereas the 120-min chromatographic profile contained signals corresponding to compounds also observed in the untreated dye sample. A signal tentatively assigned to 5-(2-morpholino-1-thiophen-2-yl-vinyl)-1,2,4-thiadiazole ($MW = 279 \text{ g mol}^{-1}$) was detected in the EDTA-containing samples collected after 10 and 120 min but was not observed in samples treated without EDTA. These findings suggest that EDTA altered the transformation behaviour of RB 194. The recovery of absorbance may reflect a combination of EDTA–dye or EDTA–catalyst interactions, competitive adsorption and desorption, the formation of coloured transformation products with overlapping absorption bands, and reactions involving initially generated intermediates. Therefore, the scavenging results provide only qualitative evidence that hole-mediated surface reactions may represent a major contributing pathway; they do not establish photogenerated holes as the dominant or exclusive reactive species. Definitive identification of the dominant reactive species requires appropriate scavenger-only and interaction controls, together with direct radical-detection techniques such as electron paramagnetic resonance spectroscopy. The GC–MS profiles obtained during the EDTA-containing experiment are presented in Fig. 15. Appropriate control experiments would include: (i) RB 194 plus each scavenger under UV irradiation without catalyst; (ii) RB 194 plus each scavenger in the dark; (iii) catalyst plus each scavenger without RB 194; (iv) complete reaction mixtures maintained in the dark; and (v) UV–visible spectra of each scavenger and its possible reaction products over the analytical wavelength range. Measurements of pH before and after scavenger addition and evaluation of dye adsorption in the presence of each additive would further distinguish genuine photocatalytic effects from changes in solution chemistry, adsorption, and optical response. These controls were not included in the present study and are therefore identified as necessary for future mechanistic verification.

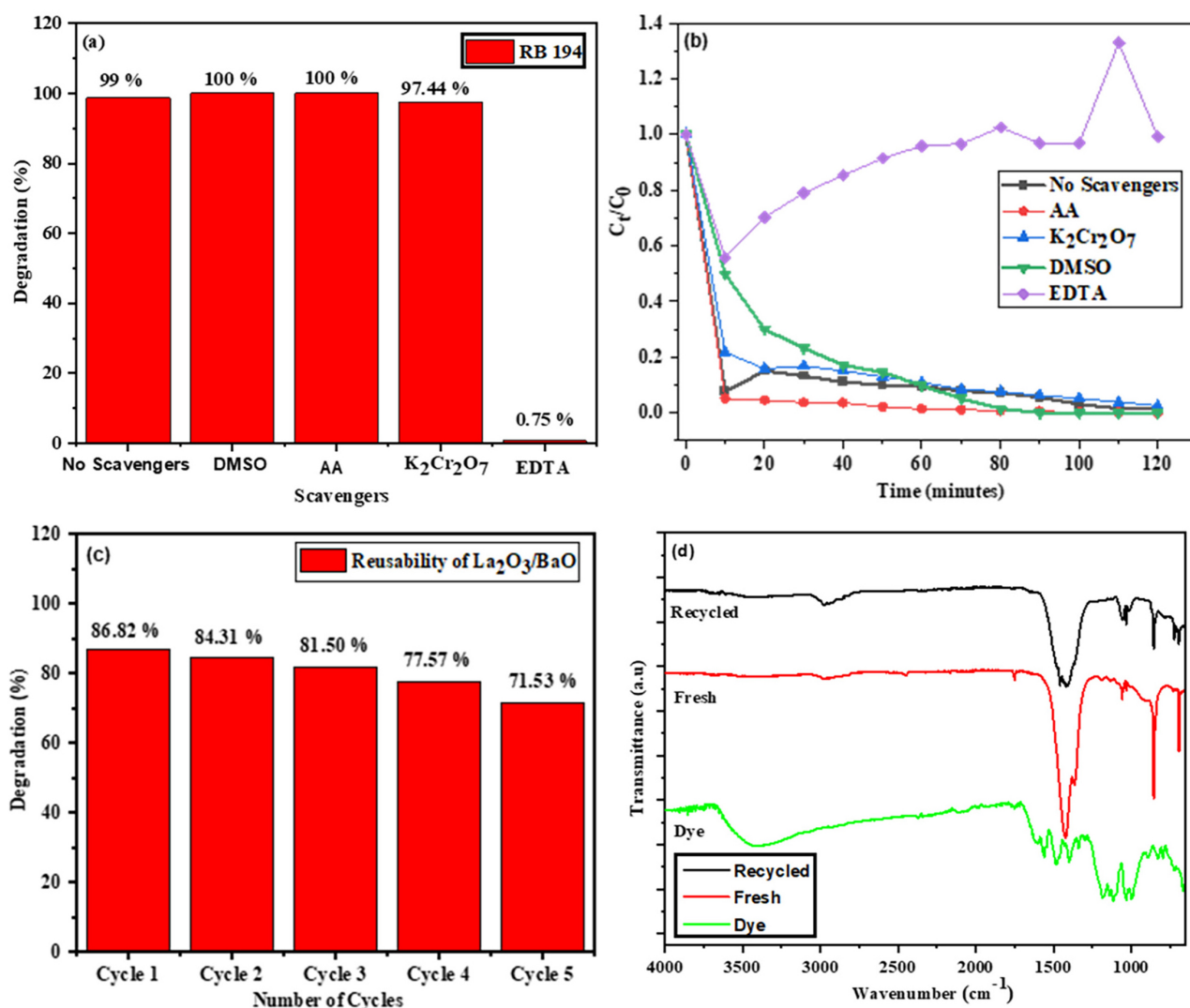


Fig. 14. Scavenger studies, reusability, and FTIR analysis. (a,b) Influence of different scavengers (c) Reusability of the La₁/B₂ photocatalyst over five consecutive cycles and (d) FTIR spectra of RB 194 and the fresh and reused photocatalysts.

3.11 Reusability and Recyclability

The reusability of the La₁/B₂ composite for RB 194 removal was evaluated over five consecutive reuse cycles, as shown in Fig. 14c, with the corresponding data provided in **Supplementary Table 9**. After each experiment, the photocatalyst was separated from the treated solution, washed with deionized water, dried, and reused under the same conditions with a fresh 20 mg L⁻¹ RB 194 solution. Cycle 1 represents the first reuse of the catalyst following its initial photocatalytic application. The removal efficiency decreased from 86.82% in Cycle 1 to 84.31% in Cycle 2 and 71.53% in Cycle 5. Thus, the catalyst retained 82.39% of its Cycle 1 activity after the fifth reuse, corresponding to an absolute decrease of 15.29 percentage points and a relative activity loss of 17.61%. These results experimentally demonstrate continued photocatalytic activity accompanied by progressive partial deactivation; however, they do not establish the mechanism responsible for the observed activity loss.

Several processes may have contributed to the deactivation, including physical catalyst loss during separation and washing, surface fouling by RB 194 or its transformation products, incomplete desorption, blockage of active sites, particle aggregation, and structural or surface-chemical changes. The aqueous behaviour of the Ba-containing phase presents an additional stability concern. BaO is highly reactive toward water and may undergo hydration to form Ba(OH)₂, followed by carbonation through exposure to dissolved or atmospheric CO₂. Consequently, the Ba-containing phase in La₁/B₂ may undergo hydration, carbonation, dissolution, or surface reconstruction during photocatalytic operation and subsequent washing. These processes could alter the catalyst surface and reduce the availability of active sites.

Nevertheless, catalyst-mass recovery, particle-size or surface-area measurements, metal-leaching analysis, and detailed post-reaction phase characterization were not per-

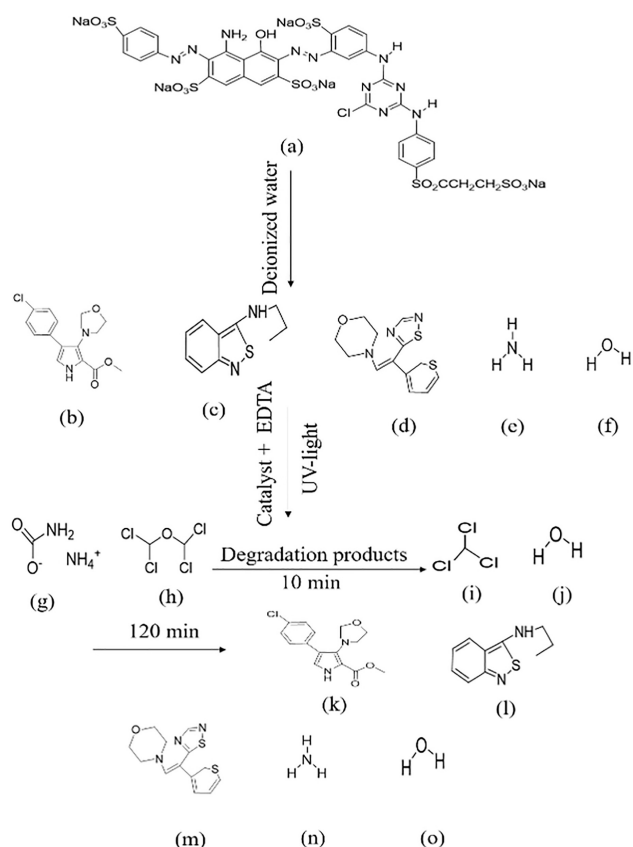


Fig. 15. Proposed photocatalytic degradation pathways based on GC–MS analysis of EDTA-treated samples. (a) Reactive blue 194 (b) Methyl 4-(4-chlorophenyl)-3-(4-morpholinyl)-1H-pyrrole-2-carboxylate (m.w. 320), (c) 3-(n-Propylamino)-2,1-benzisothiazole (m.w. 192) (d) 5-(2-Morpholino-1-thiophen-2-yl-vinyl)-1,2,4-thiadiazole (m.w. 279), (e) ammonia (m.w. 17), (f) Water (m.w. 18) (g) Ammonium carbamate (m.w. 78), (h) Ether, bis(dichloromethyl) (m.w. 182) (i) Trichloromethane (m.w. 118), (j) water (m.w. 18). (k) Methyl 4-(4-chlorophenyl)-3-(4-morpholinyl)-1H-pyrrole-2-carboxylate (m.w. 320), (l) 3-(n-Propylamino)-2,1-benzisothiazole (m.w. 192), (m) 5-(2-Morpholino-1-thiophen-2-yl-vinyl)-1,2,4-thiadiazole (m.w. 279), (n) ammonia (m.w. 17), (o) Water (m.w. 18) Representative GC–MS results for the untreated RB 194 solution and samples collected during treatment in the presence of EDTA are the tentative spectral-library assignments.

formed. Therefore, catalyst loss, surface fouling, aggregation, dissolution, and transformation of the Ba-containing phase remain possible rather than experimentally established deactivation mechanisms, and the observed activity loss cannot be quantitatively assigned to any individual process. Quantitative catalyst-mass recovery would be required to determine physical material loss, while BET and SEM analyses of the recovered material would help evaluate surface fouling and aggregation. ICP–OES or ICP–MS analysis of the treated solutions, together with comparative XRD and XPS characterization of the fresh and reused cata-

lysts, would be required to assess Ba and La leaching, phase transformation, hydration, carbonation, and structural stability.

The FTIR spectra of the fresh and reused catalysts are compared with those of RB 194 in Fig. 14d. After reuse, the Ba–O-associated band shifted slightly from 693.3 to 695.1 cm^{-1} , while the band at 1423.1 cm^{-1} shifted to 1420.1 cm^{-1} . Additional spectral changes included a shift of the 730.6 cm^{-1} band to 723.1 cm^{-1} , displacement of the 756.6 cm^{-1} band to 677.6 cm^{-1} and replacement of the 1360.5 cm^{-1} band by shoulders at approximately 1459.3 and 1420.1 cm^{-1} . These changes are consistent with modification of the catalyst surface after repeated photocatalytic use and may be associated with residual adsorbed species and changes in surface bonding. La₁/B₂ remained photocatalytically active over five reuse cycles; however, the observed activity retention alone does not confirm its structural or chemical stability. The gradual decrease in removal efficiency may reflect catalyst loss, surface fouling, particle aggregation, or chemical changes in the Ba-containing phase. In the absence of metal leaching and detailed post-reaction characterization, the long-term stability and environmental safety of the composite remain unresolved. Dilute HCl washing could be investigated in future studies as a possible regeneration approach for removing strongly adsorbed organic species. However, this procedure was not evaluated in the present study and should not be considered an established regeneration method for the La₁/B₂ composite. Because acid treatment may alter or dissolve the Ba-containing phase, its effects on catalyst composition, metal leaching, structural stability and subsequent photocatalytic activity must be carefully assessed before its suitability can be established.

3.12 Gas Chromatography–Mass Spectrometry (GC–MS)

GC–MS analysis was used to examine changes in the detectable organic composition during the UV-assisted treatment of RB 194 is represented in Fig. 16. Samples collected after 10, 30, and 120 min exhibited different chromatographic profiles, indicating time-dependent changes in the compounds detectable by the applied analytical procedure. The reported compound names were obtained by comparing the acquired electron-ionization mass spectra with reference spectra in the mass-spectral library integrated into the Agilent MassHunter/ChemStation workstation. However, library-match scores, retention indices, diagnostic fragment-ion comparisons, authentic standards, and quantitative calibration data were not available for independent verification of the assignments. Therefore, the reported structures are regarded as tentative library-based assignments rather than conclusively identified products. The observed chromatographic changes support transformation of RB 194 during treatment but do not establish a complete degradation pathway or confirm the origin of every detected signal. Some signals may also originate from solvents, lab-

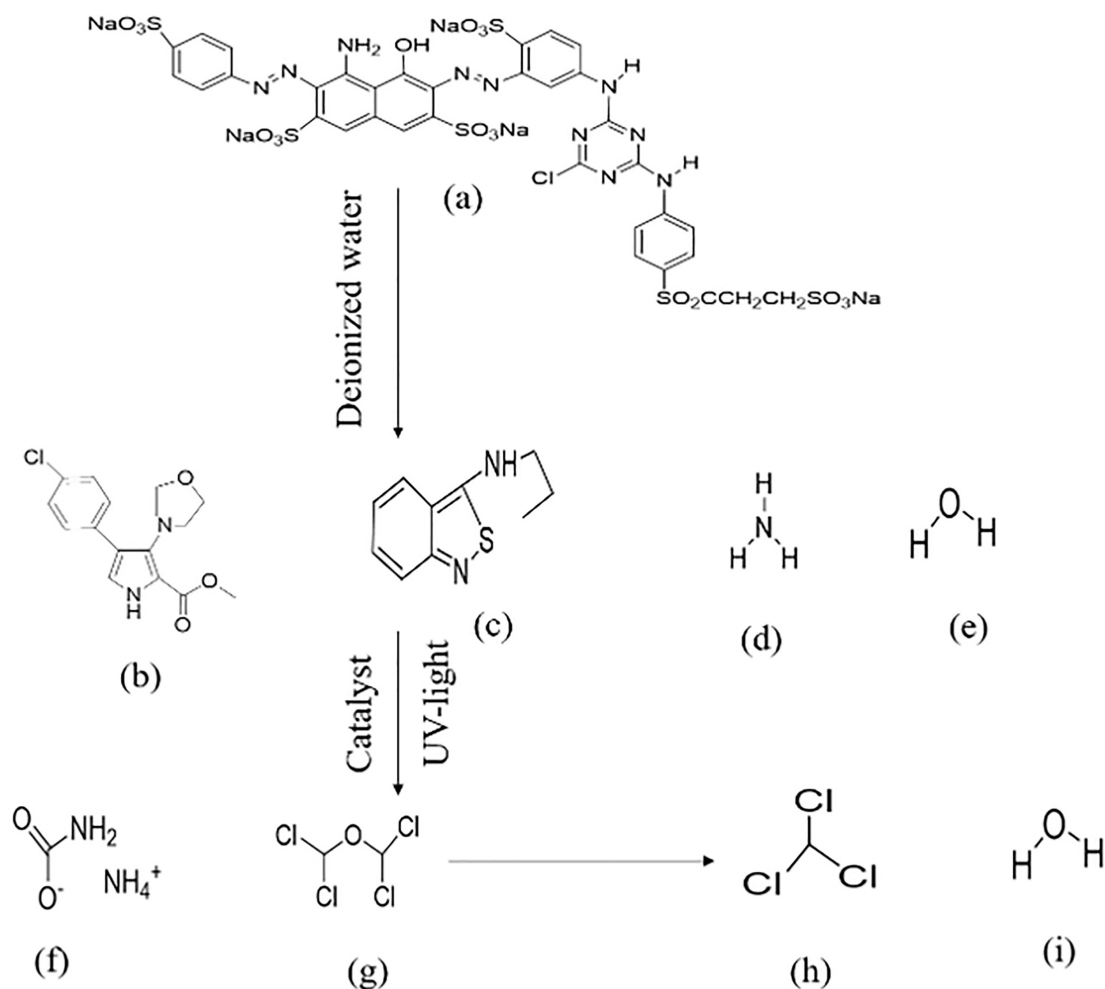


Fig. 16. Proposed photocatalytic degradation pathways of GC–MS analysis of RB 194 degradation products. GCMS results of degradation process (a) Reactive blue 194 (b) Methyl 4-(4-chlorophenyl)-3-(4-morpholinyl)-1H-pyrrole-2-carboxylate (m.w. 320), (c) 3-(n-Propylamino)-2,1-benzisothiazole (m.w. 192) (d) ammonia (m.w. 17), (e) Water (m.w. 18), (f) Ammonium carbamate (m.w. 78), (g) Ether, bis(dichloromethyl) (m.w. 182) (h) Trichloromethane (m.w. 118), (i) water (m.w. 18).

oratory background, column-related contamination, sample preparation, or other matrix components. In particular, the signal assigned by library matching to trichloromethane should be considered provisional and is not identified as a predominant end product (**Supplementary Table 10**). Confirmation of the proposed structures would require reporting the library-match factors and retention information, comparison of major fragment ions with reference spectra, analysis of procedural blanks, and preferably confirmation using authentic standards or high-resolution mass spectrometry.

3.13 Photocatalytic Mechanism

The tentative photocatalytic mechanism of the $\text{La}_2\text{O}_3/\text{BaO}$ composite is illustrated in Fig. 17. Under UV irradiation, photoexcitation may generate electrons (e^-) and holes (h^+) in the constituent oxide phases. The comparatively weak PL response and lower charge-transfer resistance of La_1B_2 relative to pristine La_2O_3

are consistent with modified carrier recombination and interfacial transport; however, these measurements do not establish the direction of charge migration [43,48]. The scavenging experiments showed that EDTA produced the most pronounced effect on the apparent removal of RB 194, suggesting that hole-associated surface reactions may contribute substantially to dye transformation. Nevertheless, this response cannot be attributed exclusively to h^+ because scavenger-only and interaction controls were not performed and the unusual absorbance recovery may have been influenced by adsorption–desorption processes, solution chemistry, coloured intermediates, or spectral interference. The comparatively small effects of AA and DMSO do not confirm either the presence or absence of $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$. These short-lived species were not directly detected because EPR/ESR measurements were not available within the scope of the present study. Therefore, the formation of $\text{O}_2^{\cdot-}$ through the reduction of dissolved O_2 and $\cdot\text{OH}$ through reactions involving h^+ and

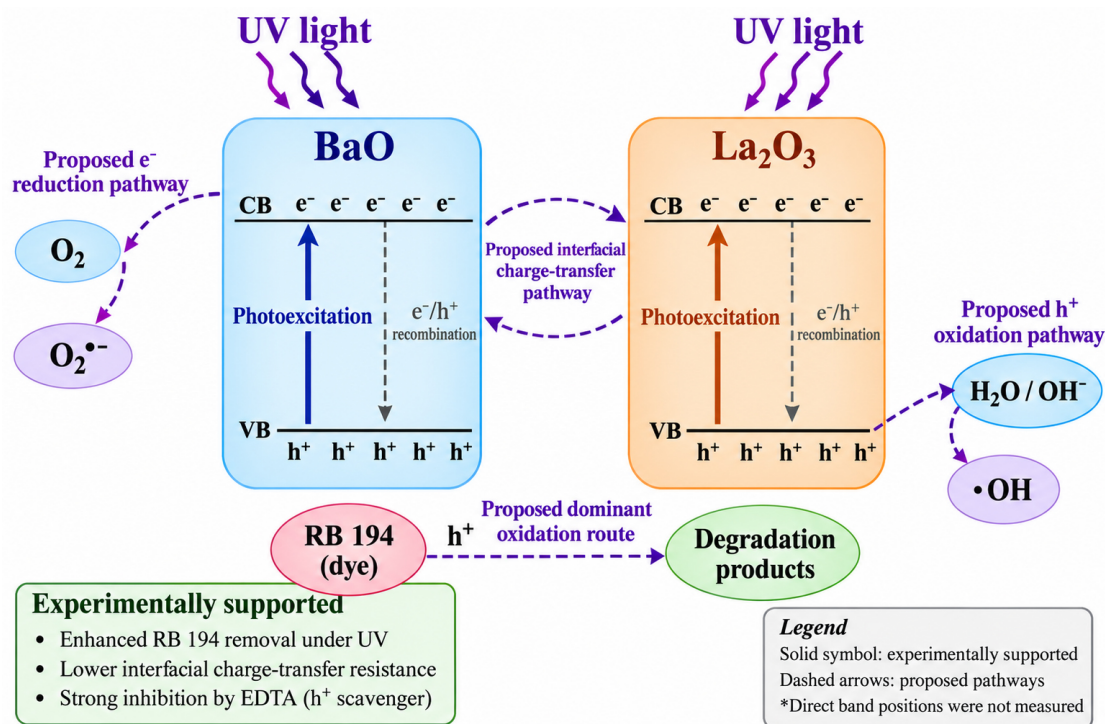
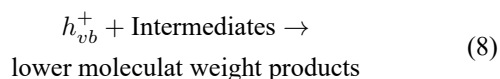
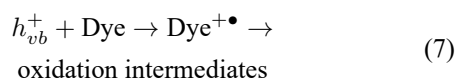
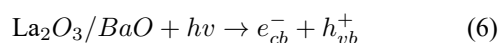


Fig. 17. Experimentally supported observations and tentative interfacial charge-transfer pathways proposed for the BaO/La₂O₃ photocatalyst under UV irradiation. Solid symbols represent experimentally supported observations, whereas dashed arrows indicate proposed carrier-transfer and reactive-species pathways. The formation of $\text{O}_2^{\bullet-}$ and $\cdot\text{OH}$ was not directly confirmed by EPR/ESR, and the absolute band positions and direction of interfacial charge transfer were not experimentally determined. This figure was created using 3D Max software.

$\text{H}_2\text{O}/\text{OH}^-$ is presented only as a possible secondary pathway. Because direct band-position and radical-detection measurements were not performed, Fig. 17 represents a tentative mechanistic interpretation rather than conclusive identification of the charge-transfer direction or reactive species. Further EPR/ESR spin-trapping experiments, together with appropriate scavenger-only controls, are required to verify the proposed reactive-species pathways [49,50].



3.14 Electrochemical Response and Interfacial Charge Transport

Cyclic voltammetry was used to compare the electrochemical responses of pristine La_2O_3 and the selected La_1/B_2 composite. The CV curves were recorded over a potential range of 0.0–0.8 V at a scan rate of 5 mV s^{-1} (Fig. 18a,b). Pristine La_2O_3 exhibited a comparatively low current response and a smaller enclosed CV area. In comparison, La_1/B_2 exhibited higher forward and reverse current responses and a larger enclosed area, demonstrating that composite formation modified its electrochemical behaviour. The increased current response may be associated with changes in electrical transport, the accessibility of electrochemically active surface sites, and the local redox environment following the incorporation of the La- and Ba-containing phases. However, because corresponding CV data for pristine BaO were unavailable, the individual contribution of BaO to the electrochemical response cannot be quantified. Therefore, the CV results demonstrate improved electrochemical performance of La_1/B_2 only relative to the measured pristine La_2O_3 reference and do not independently confirm a synergistic effect between La_2O_3 and BaO.

The logarithmic current–potential curves of pristine La_2O_3 and La_1/B_2 are presented in Fig. 18c,d. La_1/B_2 ex-

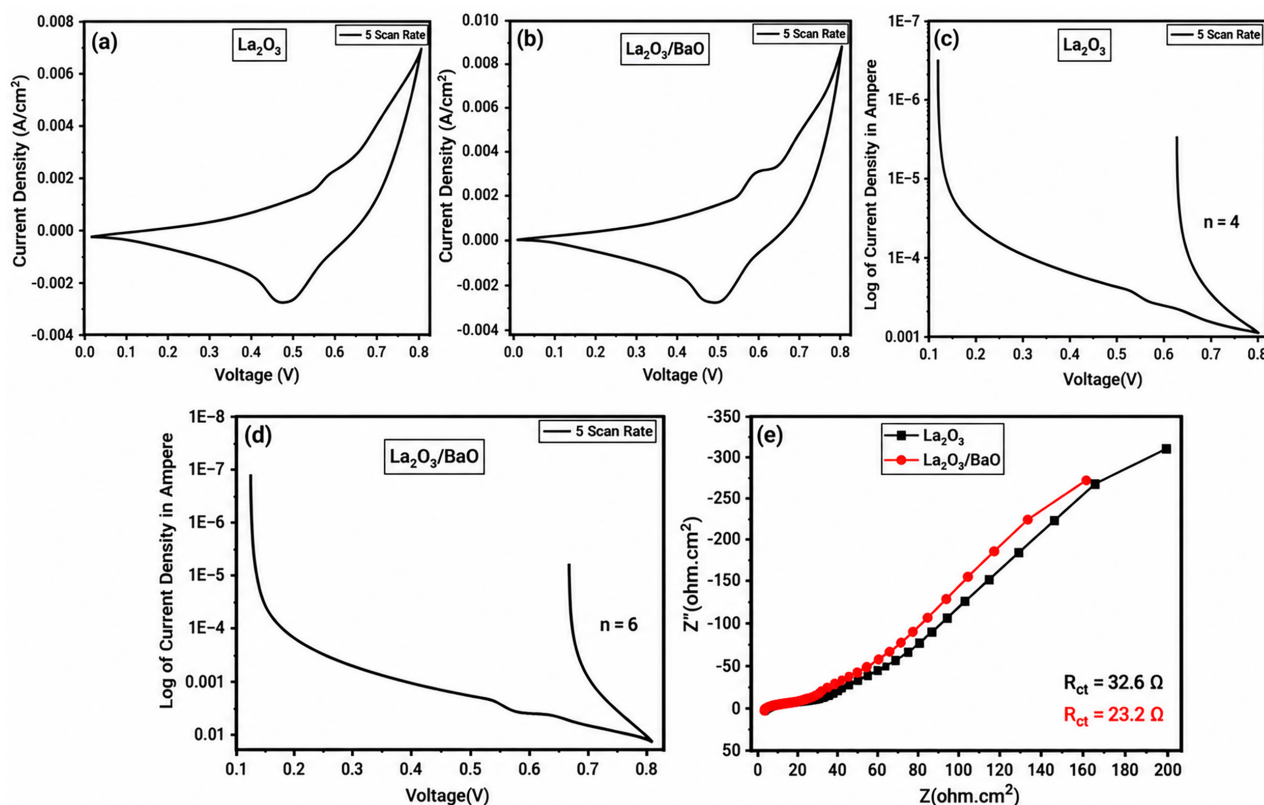


Fig. 18. Electrochemical characterization of La_2O_3 and La_1/B_2 . (a,b) Cyclic voltammograms recorded over 0.0–0.8 V at 5 mV s^{-1} , (c,d) logarithmic current–potential plots of pristine La_2O_3 and La_1/B_2 and (e) EIS Nyquist plots for evaluating electrochemical behavior and charge-transfer resistance.

hibited a higher current response than pristine La_2O_3 , indicating modified interfacial electrochemical kinetics relative to La_2O_3 . The fitted parameters previously expressed as $n = 4$ and $n = 6$ were not treated as conventional Tafel slopes because Tafel slopes must be determined from an appropriately selected linear Tafel region and reported in mV dec^{-1} . Accordingly, these current–potential curves were used only for qualitative comparison of the electrochemical responses of the two measured materials.

The EIS Nyquist plots of pristine La_2O_3 and La_1/B_2 are shown in Fig. 18e. The semicircle diameter in the high-frequency region is associated with the interfacial charge-transfer resistance (R_{ct}) of the electrode material. Pristine La_2O_3 exhibited a larger semicircle and an R_{ct} value of $32.6 \, \Omega$, indicating comparatively slower interfacial charge transport. In contrast, La_1/B_2 displayed a smaller semicircle and a lower R_{ct} value of $23.2 \, \Omega$. This corresponds to an approximately 28.8% reduction in charge-transfer resistance relative to pristine La_2O_3 .

$$\text{Reduction in } R_{ct} = \frac{32.6 - 23.2}{32.6} \times 100 \quad (9)$$

The lower R_{ct} and higher CV current response of La_1/B_2 indicate improved interfacial electrochemical trans-

port relative to pristine La_2O_3 only. Together with the reduced PL intensity, these observations are consistent with altered charge-carrier recombination and transport behaviour following composite formation. Such changes may increase the availability of photogenerated charge carriers for surface reactions and may contribute to the enhanced photocatalytic removal of RB 194 by La_1/B_2 . Nevertheless, electrochemical measurements obtained using an electrode configuration do not directly represent photocatalytic charge-carrier dynamics under UV irradiation. More importantly, because corresponding CV and EIS measurements for pristine BaO were unavailable, the individual electrochemical contribution of BaO cannot be quantified and the improved response of La_1/B_2 cannot be conclusively attributed to heterojunction synergism. These results also do not establish the absolute band-edge positions, direction of photogenerated charge migration, or a specific heterojunction mechanism. Therefore, the electrochemical findings are treated only as supporting evidence of improved interfacial charge transport in La_1/B_2 relative to pristine La_2O_3 , rather than as confirmation of synergistic coupling or a particular charge-transfer pathway.

3.15 Comparison of Photocatalytic Activities

Table 4 (Ref. [31,46,47,51,52]) compares the photocatalytic degradation of dyes using the selected La_1/B_2

composite with previously reported La_2O_3 - and BaO -containing photocatalysts. The principal experimental conditions are included because removal efficiency is influenced by dye identity and concentration, catalyst dosage, light source, irradiation time, solution pH, temperature and reactor configuration. Consequently, the reported values provide a contextual comparison and should not be interpreted as a direct ranking of photocatalyst performance. The reported materials exhibited dye-degradation efficiencies ranging from 86.6% to approximately 100% under UV, visible, or natural sunlight irradiation. $\text{CeO}_2/\text{La}_2\text{O}_3$ binary nanoplates achieved nearly complete degradation of Rhodamine B within 270 min, whereas the $\text{ZnO}/\text{La}_2\text{O}_3/\text{NiO}$ ternary system degraded 98% of methylene blue within 150 min under natural sunlight. For the BaO -based materials, Nd doping increased the reported malachite green degradation from 86.6% for pristine BaO to 96.4% under identical conditions. The $\text{Ag}_2\text{WO}_4/\text{BaO}/\text{NiO}$ heterojunction also achieved approximately 99% Congo red degradation within 30 min under UV irradiation. These findings show that compositional modification, doping and heterojunction formation can substantially influence the photocatalytic response of La_2O_3 - and BaO -containing materials. Under the conditions used in the present study, La_1/B_2 achieved approximately 99% removal of 20 mg L^{-1} RB 194 within 120 min under UV irradiation. Its performance falls within the range reported for the other La_2O_3 - and BaO -containing photocatalysts listed in Table 4. Nevertheless, direct numerical comparison remains inappropriate because the individual studies employed different dyes, initial concentrations, catalyst dosages, light sources, irradiation intensities, pH values, temperatures and reactor configurations. The present study is distinguished by employing a comparatively simple, silver-free and sulfide-free $\text{La}_2\text{O}_3/\text{BaO}$ binary composition prepared by co-precipitation and by examining the relationships among precursor composition, physicochemical characteristics, operating conditions, interfacial electrochemical transport and reuse performance.

The photocatalytic behaviour of La_1/B_2 is consistent with the combined influence of its structural, optical and interfacial properties. XRD indicated the coexistence of La - and Ba -containing crystalline phases, while UV–visible analysis showed modification of the optical absorption response after composite formation. The comparatively weak PL emission of La_1/B_2 was consistent with reduced radiative recombination and/or increased charge-carrier trapping. Moreover, the charge-transfer resistance decreased from 32.6Ω for pristine La_2O_3 to 23.2Ω for La_1/B_2 , corresponding to a reduction of approximately 28.8%. Collectively, these results support improved interfacial electrochemical transport relative to pristine La_2O_3 without requiring assignment of a particular S-scheme, Z-scheme, or type-II charge-transfer pathway.

The La_1/B_2 composite retained approximately 82.39% of its Cycle 1 activity after five reuse cycles, with removal

efficiency decreasing from 86.82% in Cycle 1 to 71.53% in Cycle 5. This result demonstrates continued photocatalytic activity during repeated operation, together with progressive partial deactivation. Radical-scavenging experiments indicated an important contribution from hole-associated surface reactions, while GC–MS analysis revealed time-dependent changes in the detectable organic composition during treatment. Because the GC–MS assignments were based on mass-spectral library matching, they are interpreted as tentative transformation products rather than evidence of a complete degradation pathway or mineralization. The La_1/B_2 represents a potentially useful UV-active oxide photocatalyst for RB 194 removal. Further studies should compare all La precursor compositions under identical photocatalytic conditions, determine total organic carbon removal and metal leaching and characterize structural and surface changes after repeated use. Evaluation under visible and solar irradiation, together with time-resolved spectroscopy, EPR/ESR analysis and direct band-position measurements, would provide further insight into charge-transfer and reactive-species pathways. Testing with real textile effluent and continuous-flow systems would also help establish performance under more representative treatment conditions. Because the studies summarized in Table 4 employed different dyes, catalyst dosages, light sources, pH values and irradiation times, the reported efficiencies are presented only for contextual comparison and should not be interpreted as evidence of superior performance.

4. Discussion

The results collectively indicate that the photocatalytic behaviour of La_1/B_2 cannot be attributed to a single material property. XRD confirmed the coexistence of La - and Ba -containing crystalline phases, while XPS showed changes in their surface chemical environments after composite formation. The composition-dependent optical absorption and PL emission further demonstrate that changing the La precursor ratio modified the electronic and radiative-transition environments of the materials. For La_1/B_2 , the comparatively weak PL emission and reduction in charge-transfer resistance from 32.6 to 23.2Ω are consistent with decreased radiative recombination and improved interfacial electrochemical transport relative to pristine La_2O_3 . Similar improvements in charge utilization following heterojunction formation have been reported for La_2O_3 -containing binary and multicomponent photocatalysts [22,23,24,25,26,27]. However, the present results support interfacial interaction and modified charge transport without requiring assignment of a specific S-scheme, Z-scheme or type-II pathway.

The effects of catalyst dosage, dye concentration, pH and temperature demonstrate the importance of both photophysical and surface-controlled processes. Increasing the catalyst dosage to $70 \text{ mg per } 100 \text{ mL}$ increased the availability of illuminated surface sites, whereas further increases

Table 4. Comparison of reported photocatalytic performance using La₂O₃- and BaO-based photocatalysts under different experimental conditions.

Photocatalyst	Dye	Initial dye concentration	Catalyst dosage	Light source	pH/temperature (°C)	Time (min)	Removal (%)	Ref.
CeO ₂ /La ₂ O ₃ binary nanoplates	Rhodamine B	10 mg L ⁻¹	50 mg	UV/visible light	pH 7	270	100	[46]
ZnO/(3 wt%)La ₂ O ₃ /NiO	Methylene blue	2 mg L ⁻¹	15 mg	Natural sunlight	Optimized conditions	150	98	[47]
BaO nanoparticles	Malachite green	50 mg L ⁻¹	20 mg/100 mL	15 W UV lamp, 254 nm	pH 4; 50	120	86.6	[31]
Nd-doped BaO nanoparticles	Malachite green	50 mg L ⁻¹	20 mg/100 mL	15 W UV lamp, 254 nm	pH 4; 50	120	96.4	[31]
Ag ₂ WO ₄ /BaO/NiO heterojunction	Congo red	NR*	NR	UV irradiation	NR	30	99	[51]
Sn-doped La ₂ O ₃	Safranin/crystal violet	10 mg L ⁻¹	NR	Visible	Ambient	135	93.24/95.28	[52]
La ₁ /B ₂ composite	Reactive Blue 194	20 mg L ⁻¹	70 mg/100 mL	450 W UV lamp; 10 cm distance	pH 6; 20	120	99	Present study

*NR = not reported. The reported dye degradation values are given mainly for contextual comparison because studies are conducted under different experimental conditions.

produced only marginal improvement, probably because of light scattering, shielding and particle aggregation. The decline in removal efficiency and apparent rate constant with increasing RB 194 concentration can be attributed to stronger absorption of incident UV light by the dye solution and increased competition for accessible surface sites. The maximum removal at pH 6 is consistent with the measured pH_{pzc} of approximately 8.92: under these conditions, the positively charged catalyst surface favours interaction with anionic RB 194, while competition from excess H⁺ remains lower than under strongly acidic conditions. Comparable effects of catalyst loading, pollutant concentration and surface charge on heterogeneous photocatalysis have been widely reported [43,44,45]. Thus, the approximately 99% removal obtained under the selected conditions reflects a balance among photon utilization, dye adsorption, surface-site availability and interfacial charge transport.

The scavenging results showed that EDTA produced a markedly different time-dependent response, including an initial decrease followed by substantial absorbance recovery, whereas AA, K₂Cr₂O₇, and DMSO produced comparatively small effects on the apparent removal efficiency. This behaviour suggests that hole-associated surface reactions may represent a major contributing pathway in RB 194 transformation. However, the EDTA response cannot be attributed exclusively to hole scavenging because it may also have been influenced by competitive adsorption and desorption, EDTA–dye or EDTA–catalyst interactions, solution chemistry, the formation of coloured intermediates, and spectral interference. Therefore, these scavenging results are interpreted only qualitatively and do not establish photogenerated holes as the dominant or exclu-

sive reactive species [46,47]. Moreover, EPR/ESR analysis was not performed to directly detect •OH, O₂^{•-}, or other short-lived reactive species. Definitive identification of the dominant reactive species would therefore require appropriate scavenger-only and interaction controls together with direct radical-detection experiments. The time-dependent changes observed by GC–MS support the transformation of RB 194 into other detectable organic species; however, the library-based assignments do not demonstrate complete mineralization. Because TOC and COD analyses were not performed, complete mineralization of RB 194 is not claimed in this study. In addition, the retention of 82.39% of cycle 1 activity after five reuse cycles demonstrates continued photocatalytic function but also reveals progressive deactivation. The underlying reason for deactivation could not be conclusively established because extended stability investigation, post-cycling characterization and metal-leaching experiments were not performed. On the basis of available data, we cannot discriminate among the possible factors such as catalyst surface modifications, active site loss, adsorption of reaction intermediates, or material loss during recovery. However, barium oxide reacts with water to form barium hydroxide and subsequently interacts with carbon dioxide to form barium carbonate (BaCO₃). Therefore, some surface changes of barium oxide cannot be excluded during photocatalytic experiments. Hence, long-term stability issues cannot be claimed without leaching experiments. Compared with the La₂O₃- and BaO-containing systems summarized in Table 4 [30,31,32], the present La₁/B₂ composite offers a comparatively simple, silver-free and sulfide-free binary composition. Its main contribution is therefore the combined

evaluation of precursor composition, operating conditions, interfacial electrochemical transport, reactive-species behaviour and reuse performance for RB 194 removal, rather than a claim of universally superior photocatalytic activity. Recent environmental photocatalysis studies reported for contaminated-water treatment, further demonstrate the potential of composite design for modifying photocatalytic performance [53]. However, direct comparison remains inappropriate because catalyst composition, pollutant identity, irradiation conditions and analytical endpoints differ among studies. Accordingly, the contribution of the present La_1/B_2 system lies in the combined evaluation of precursor composition, operating conditions, electrochemical transport, scavenger response and reuse behaviour rather than a claim of universal superiority or a conclusively established mechanism.

Limitations of the Study

The band positions and interfacial charge-transfer pathway of $\text{La}_2\text{O}_3/\text{BaO}$ were not directly determined because Mott–Schottky, valence-band XPS and ultraviolet photoelectron spectroscopy measurements were unavailable. Although PL, CV and EIS indicated modified carrier recombination and improved interfacial transport, they could not establish the direction of charge migration or confirm a specific heterojunction mechanism. Similarly, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ were not directly detected by EPR/ESR; therefore, the proposed charge-transfer and reactive-species pathways remain tentative. Comparative XRD and XPS analyses of fresh and reused catalysts and metal-leaching measurements were not performed. Consequently, the contributions of surface fouling, catalyst loss, particle aggregation and structural or chemical changes to catalyst deactivation could not be distinguished. Dilute-HCl regeneration also remains a proposed strategy requiring experimental validation. Detailed photocatalytic testing was limited to La_1/B_2 ; therefore, it cannot be identified conclusively as the optimum La precursor ratio. Moreover, RB 194 removal was evaluated primarily from absorbance loss at 600 nm without TOC, COD or inorganic-product analysis. The GC–MS assignments were based on spectral-library matching without authentic standards or quantitative calibration. Thus, the results demonstrate dye transformation and decolourization but do not confirm complete mineralization or a definitive degradation pathway. Metal-leaching analysis was not performed; therefore, the possible release of Ba species during aqueous photocatalysis could not be quantified. Moreover, the tendency of Ba-containing oxides to undergo hydration and carbonation means that the composition and surface state of the catalyst may change during reaction, washing and reuse. Without comparative XRD, XPS and FTIR analyses of the fresh and reused materials, the structural and chemical stability of the Ba-containing phase cannot be confirmed. Dilute-HCl regeneration was not experimentally evaluated in the present study. It is men-

tioned only as a possible direction for future investigation, and its effectiveness and potential effects on the chemical and structural stability of the La_1/B_2 composite remain unknown.

5. Conclusions

$\text{La}_2\text{O}_3/\text{BaO}$ composites with different La precursor ratios were successfully prepared by co-precipitation and their structural, morphological, thermal, optical and surface-chemical characteristics were examined. XRD showed the coexistence of La- and Ba-containing crystalline phases, while the differences in crystallite size, morphology, optical absorption and PL emission demonstrated that precursor composition influenced material development. XPS further supported modification of the surface chemical environments of La and Ba following composite formation. Among the prepared compositions, La_1/B_2 was selected for detailed photocatalytic evaluation based on its combined physicochemical characteristics. Under the selected experimental conditions of 20 mg L^{-1} RB 194, 70 mg catalyst per 100 mL, pH 6 and 20 °C, La_1/B_2 achieved approximately 99% removal after 120 min of UV irradiation. The apparent removal rate decreased with increasing dye concentration and the pseudo-first-order model provided the best fit among the examined kinetic expressions, with ($k = 0.04103$) min^{-1} at 20 mg L^{-1} . The measured pH_{pzc} of approximately 8.92 helped explain the favourable performance at pH 6, where electrostatic interaction with anionic RB 194 was promoted without excessive competition from H^+ ions. The comparatively weak PL response and reduction in charge-transfer resistance from 32.6 Ω for pristine La_2O_3 to 23.2 Ω for La_1/B_2 were consistent with modified carrier-recombination behaviour and improved interfacial electrochemical transport. Scavenging experiments qualitatively suggested the possible involvement of hole-associated surface reactions in RB 194 transformation; however, the responsible reactive species were not conclusively identified. La_1/B_2 remained photocatalytically active over five reuse cycles, retaining approximately 82.39% of its Cycle 1 activity, although the decrease from 86.82% to 71.53% indicated progressive partial deactivation. GC–MS analysis revealed time-dependent changes in the detectable organic composition during treatment, but the library-based assignments represent tentative transformation products rather than confirmation of complete mineralization. Overall, the study demonstrates the potential of a comparatively simple, silver-free and sulfide-free $\text{La}_2\text{O}_3/\text{BaO}$ binary composite for UV-assisted RB 194 removal. Further work should compare all precursor compositions under identical photocatalytic conditions, verify the band alignment and charge-transfer pathway, quantify mineralization and metal leaching and assess long-term performance in real textile effluent and continuous-flow systems.

Availability of Data and Materials

The data presented in the figures and tables of this study are available within the article. The raw datasets generated or analyzed during the current study are available upon reasonable request from the corresponding author.

Author Contributions

HM: Performed the experiments, collected and analyzed the data, and prepared the original manuscript. MAJ: Supervised the research, contributed to data interpretation, and revised the manuscript. MM: Analyzed the data, reviewed and approved the final version of the manuscript. AM: Analyzed the data, and reviewed the computational work. All authors contributed to editorial changes in the manuscript. All authors read and approved the final manuscript. All authors have participated sufficiently in the work and agreed to be accountable for all aspects of the work.

Ethics Approval and Consent to Participate

Not applicable.

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Conflicts of Interest

The authors declare no conflicts of interest.

Supplementary Material

Supplementary material associated with this article can be found, in the online version, at <https://doi.org/10.31083/DJNB56707>.

References

- [1] Lorenzo M, Campo J, Picó Y. Analytical challenges to determine emerging persistent organic pollutants in aquatic ecosystems. *TrAC Trends in Analytical Chemistry*. 2018; 103: 137–155. <https://doi.org/10.1016/j.trac.2018.04.003>
- [2] Dey SR, Devi P, Kumar P. Organic contaminants in aquatic environments: sources and impact assessment. *Metal Organic Frameworks for Wastewater Contaminant Removal*. 2023; 299–317. <https://doi.org/10.1002/9783527841523.ch13>
- [3] Al-Tohamy R, Ali SS, Li F, Okasha KM, Mahmoud YAG, Elsamahy T, et al. A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicology and Environmental Safety*. 2022; 231: 113160. <https://doi.org/10.1016/j.ecoenv.2021.113160>
- [4] Fadzli J, Hamid KHK, Him NRN, Puasa SW. A critical review on the treatment of reactive dye wastewater. *Desalination and Water Treatment*. 2022; 257: 185–203. <https://doi.org/10.5004/dwt.2022.28028>
- [5] Dutta S, Adhikary S, Bhattacharya S, Roy D, Chatterjee S, Chakraborty A, et al. Contamination of textile dyes in aquatic environment: Adverse impacts on aquatic ecosystem and human health, and its management using bioremediation. *Journal of Environmental Management*. 2024; 353: 120103. <https://doi.org/10.1016/j.jenvman.2024.120103>
- [6] Islam MM, Aidid AR, Mohshin JN, Mondal H, Ganguli S, Chakraborty AK. A critical review on textile dye-containing wastewater: Ecotoxicity, health risks, and remediation strategies for environmental safety. *Cleaner Chemical Engineering*. 2025; 11: 100165. <https://doi.org/10.1016/j.clce.2025.100165>
- [7] Periyasamy AP. Recent Advances in the Remediation of Textile-Dye-Containing Wastewater: Prioritizing Human Health and Sustainable Wastewater Treatment. *Sustainability*. 2024; 16: 495. <https://doi.org/10.3390/su16020495>
- [8] Kumari S, Singh R, Jahangeer J, Garg MC. Innovative Strategies for Dye Removal from Textile Wastewater: A Comprehensive Review of Treatment Approaches and Challenges. *Water, Air, & Soil Pollution*. 2024; 235: 720. <https://doi.org/10.1007/s11270-024-07532-4>
- [9] Khan S, Noor T, Iqbal N, Yaqoob L. Photocatalytic Dye Degradation from Textile Wastewater: A Review. *ACS Omega*. 2024; 9: 21751–21767. <https://doi.org/10.1021/acsomega.4c00887>
- [10] Bopape DA, Ntsendwana B, Mabasa FD. Photocatalysis as a pre-discharge treatment to improve the effect of textile dyes on human health: A critical review. *Heliyon*. 2024; 10: e39316. <https://doi.org/10.1016/j.heliyon.2024.e39316>
- [11] Chauhan PS, Singh K, Choudhary A, Brighu U, Singh SK, Bhattacharya S. Combined advanced oxidation dye-wastewater treatment plant: design and development with data-driven predictive performance modeling. *Npj Clean Water*. 2024; 7: 15. <https://doi.org/10.1038/s41545-024-00308-7>
- [12] Tahir MB, Ali S, Rizwan M. A review on remediation of harmful dyes through visible light-driven WO₃ photocatalytic nanomaterials. *International Journal of Environmental Science and Technology*. 2019; 16: 4975–4988. <https://doi.org/10.1007/s13762-019-02385-5>
- [13] Ali HR, Motawea EA. Ternary Photodegradable Nanocomposite (BiOBr/ZnO/WO₃) for the Degradation of Phenol Pollutants: Optimization and Experimental Design. *ACS Omega*. 2021; 6: 22047–22064. <https://doi.org/10.1021/acsomega.1c02644>
- [14] Dostanić J, Lončarević D, Hadnadev-Kostić M, Vulić T. Recent Advances in the Strategies for Developing and Modifying Photocatalytic Materials for Wastewater Treatment. *Processes*. 2024; 12: 1914. <https://doi.org/10.3390/pr12091914>
- [15] Gusain R, Gupta K, Joshi P, Khatri OP. Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. *Advances in Colloid and Interface Science*. 2019; 272: 102009. <https://doi.org/10.1016/j.cis.2019.102009>
- [16] Iqbal M, Bhatti HN, Younis S, Rehmat S, Alwadai N, Almuqrin AH, et al. Graphene oxide nanocomposite with CuSe and photocatalytic removal of methyl green dye under visible light irradiation. *Diamond and Related Materials*. 2021; 113: 108254. <https://doi.org/10.1016/j.diamond.2021.108254>
- [17] Liu QY, Fang ZB, Ji T, Liu SY, Tan YS, Chen JJ, et al. Band Alignment and Band Gap Characterization of La₂O₃ Films on Si Substrates Grown by Radio Frequency Magnetron Sputtering. *Chinese Physics Letters*. 2014; 31: 027702. <https://doi.org/10.1088/0256-307x/31/2/027702>
- [18] Karthikeyan S, Selvapandiyan M, Shanavas S, Anbarasan PM, Acevedo R. A role of annealing temperature on the properties of lanthanum oxide (La₂O₃) microplates by reflux routes. *Materials Today: Proceedings*. 2020; 26: 3576–3578. <https://doi.org/10.1016/j.matpr.2019.07.700>

- [19] Ikram M, Abid N, Haider A, Ul-Hamid A, Haider J, Shahzadi A, et al. Toward efficient dye degradation and the bactericidal behavior of Mo-doped La₂O₃ nanostructures. *Nanoscale Advances*. 2022; 4: 926–942. <https://doi.org/10.1039/d1na00802a>
- [20] Zhou X, Vovk EI, Liu Y, Guan C, Yang Y. An In Situ Temperature-Dependent Study of La₂O₃ Reactivation Process. *Frontiers in Chemistry*. 2021; 9: 694559. <https://doi.org/10.3389/fchem.2021.694559>
- [21] Zhu Z, Xia H, Wu R, Cao Y, Li H. Fabrication of La₂O₃/g-C₃N₄ Heterojunction with Enhanced Photocatalytic Performance of Tetracycline Hydrochloride. *Crystals*. 2021; 11: 1349. <https://doi.org/10.3390/cryst11111349>
- [22] Sudhagar S, Kumar SS, Premkumar IJI, Vijayan V, Venkatesh R, Rajkumar S, et al. UV- and visible-light-driven TiO₂/La₂O₃ and TiO₂/Al₂O₃ nanocatalysts: synthesis and enhanced photocatalytic activity. *Applied Physics A*. 2022; 128: 282. <https://doi.org/10.1007/s00339-022-05293-7>
- [23] Sivarajani PR, Subhiksha V, Okla MK, Janani B, Abdel-Maksoud MA, Al-Amri SS, et al. Construction of p-n-p nano heterojunction through coupling La₂O₃, (BiO)₂CO₃ and Ag₃PO₄ for effective photocatalytic degradation of doxycycline: Insights into mechanism, pathway and intermediate toxicity evaluation. *Environmental Pollution (Barking, Essex: 1987)*. 2024; 345: 123521. <https://doi.org/10.1016/j.envpol.2024.123521>
- [24] Quan Y, Liu M, Wu H, Tian X, Dou L, Ren C, et al. Construction of La₂O₃/AgCl S-scheme heterojunction with interfacial chemical bond for efficient photocatalytic degradation of bisphenol A. *Applied Surface Science*. 2024; 664: 160212. <https://doi.org/10.1016/j.apsusc.2024.160212>
- [25] Ahmad I, AlFaify SA, Alanezi KM, Alfaifi MQ, Abduljawad MM, Liu Y. Improved hydrogen production performance of an S-scheme Nb₂O₅/La₂O₃ photocatalyst. *Dalton Transactions (Cambridge, England: 2003)*. 2025; 54: 1402–1417. <https://doi.org/10.1039/d4dt02913e>
- [26] Ahmad I, Alfaifi MQ, Alassmy YA, Abduljawad MM, Khasawneh MA, Ali MD, et al. Design of S-scheme CdS/La₂O₃ heterojunction for excellent photocatalytic H₂ evolution performance under simulated sunlight irradiation. *International Journal of Hydrogen Energy*. 2025; 98: 1052–1066. <https://doi.org/10.1016/j.ijhydene.2024.12.144>
- [27] Liqiang J, Yichun Q, Baiqi W, Shudan L, Baojiang J, Libin Y, et al. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. *Solar Energy Materials and Solar Cells*. 2006; 90: 1773–1787. <https://doi.org/10.1016/j.solmat.2005.11.007>
- [28] Sundharam E, Jeevaraj AKS, Chinnusamy C. Effect of Ultrasonication on the Synthesis of Barium Oxide Nanoparticles. *Journal of Bionanoscience*. 2017; 11: 310–314. <https://doi.org/10.1166/jbns.2017.1449>
- [29] Bobade RG, Pandit B, Khedulkar AP, Raykar VS, Sarawade PB, Shaikh SF, et al. Electrochemical investigation of crinum asiaticum-like BaO-CeO₂ nanostructure for high-performance asymmetric supercapacitor. *Inorganic Chemistry Communications*. 2025; 177: 114370. <https://doi.org/10.1016/j.inoche.2025.114370>
- [30] Mani Pushpa, Subramanian Mageswari, Arputham Panneerselvam. Unveiling the photocatalytic activities of morphology-controlled ZrO₂, BaO, and Y₂O₃ nanoparticles using Eucalyptus leaf extract. *Materials Science and Engineering: B*. 2025; 320: 118410. <https://doi.org/10.1016/j.mseb.2025.118410>
- [31] Naz F, Saeed K. Synthesis of barium oxide nanoparticles and its novel application as a catalyst for the photodegradation of malachite green dye. *Applied Water Science*. 2022; 12: 121. <https://doi.org/10.1007/s13201-022-01649-9>
- [32] Rawal J, Lee SY, Park SJ. Facile synthesis of a GO-g-C₃N₄/BaTiO₃ ternary nanocomposites for visible-light-driven photocatalytic degradation of rhodamine B. *Chemosphere*. 2023; 345: 140479. <https://doi.org/10.1016/j.chemosphere.2023.140479>
- [33] Kumar M, Rahman A. Innovations in p-n type heterostructure composite materials (La₂O₃/CeO₂) for environmental contamination remediation: synthesis, characterization, and performance assessment. *Biomass Conversion and Biorefinery*. 2024; 14: 23985–24006. <https://doi.org/10.1007/s13399-023-04583-1>
- [34] Basavanagoudra H, Jangannanavar VD, Patil MK, Inamdar SR, Goudar KM. Barium oxide nanorods: Catalyst concentration and surface defects' role in degrading methylene blue organic pollutant. *Chemical Physics Impact*. 2024; 8: 100578. <https://doi.org/10.1016/j.chphi.2024.100578>
- [35] Rashmi B.N., Harlapur SF, Gurushantha K., Ravikumar C.R., Kumar M, Santosh M.S., et al. Facile green synthesis of lanthanum oxide nanoparticles using *Centella Asiatica* and *Tridax* plants: Photocatalytic, electrochemical sensor and antimicrobial studies. *Applied Surface Science Advances*. 2022; 7: 100210. <https://doi.org/10.1016/j.apsadv.2022.100210>
- [36] Karthikeyan S, Dhanakodi K, Shanmugasundaram K, Surendhiran S. Synthesis and characterization of lanthanum oxide nanoparticles: A study on the effects of surfactants. *Materials Today: Proceedings*. 2021; 47: 901–906. <https://doi.org/10.1016/j.matpr.2021.04.473>
- [37] Wang W, Zhang J, Liang D, Li Y, Xie Y, Wang Y, et al. Anodic oxidation growth of lanthanum/manganese-doped TiO₂ nanotube arrays for photocatalytic degradation of various organic dyes. *Journal of Materials Science: Materials in Electronics*. 2020; 31: 8844–8851. <https://doi.org/10.1007/s10854-020-03419-2>
- [38] Kabir H, Nandyala SH, Rahman MM, Kabir MA, Stamboulis A. Influence of calcination on the sol–gel synthesis of lanthanum oxide nanoparticles. *Applied Physics A*. 2018; 124: 820. <https://doi.org/10.1007/s00339-018-2246-5>
- [39] Amjad M, Bibi I, Majid F, Jilani K, Sultan M, Raza Q, et al. NiO/MnFe₂O₄ Nanocomposite Photoluminescence, Structural, Morphological, Magnetic, and Optical Properties: Photocatalytic Removal of Cresol Red under Visible Light Irradiation. *ACS Omega*. 2024; 9: 20876–20890. <https://doi.org/10.1021/acsomega.3c09637>
- [40] Rehman Y, Morlando A, Chaki Borras M, Sluyter R, Wang X, Huang XF, et al. Defect-Rich La₂O₃ Nanoparticles with Antioxidant Activity for Human Keratinocytes. *ACS Applied Nano Materials*. 2021; 4: 6345–6356. <https://doi.org/10.1021/acsanm.1c01177>
- [41] Li B, Metiu H. DFT Studies of Oxygen Vacancies on Undoped and Doped La₂O₃ Surfaces. *The Journal of Physical Chemistry C*. 2010; 114: 12234–12244. <https://doi.org/10.1021/jp103604b>
- [42] Tauc J, Grigorovici R, Vancu A. Optical Properties and Electronic Structure of Amorphous Germanium. *Physica Status Solidi (B)*. 1966; 15: 627–637. <https://doi.org/10.1002/pssb.19660150224>
- [43] Mohamadpour F, Amani AM. Photocatalytic systems: reactions, mechanism, and applications. *RSC Advances*. 2024; 14: 20609–20645. <https://doi.org/10.1039/d4ra03259d>
- [44] Kumaran V, P S, Konga A, Ponniah G. Photocatalytic Degradation of Synthetic Organic Reactive Dye Wastewater Using GO-TiO₂ Nanocomposite. *Polish Journal of Environmental Studies*. 2020; 29: 1683–1690. <https://doi.org/10.15244/pjoes/109027>
- [45] Akıllı A, Özler A, Taymaz BH, Hancı A, Eskizeybek V, Kandaş H. Adsorption-Assisted Photocatalytic Degradation of Anionic Direct Yellow-50 and Cationic Methylene Blue Dyes by Chemically Synthesized Poly(1,5-diaminoanthraquinone). *Journal of Inorganic and Organometallic Polymers and Materials*. 2025; 35: 5509–5530. <https://doi.org/10.1007/s10904-025-03605-x>

- [46] Maria Magdalane C, Kaviyarasu K, Matinise N, Mayedwa N, Mongwaketsi N, Letsholathebe D, et al. Evaluation of La₂O₃-garlanded ceria heterostructured binary metal oxide nanoplates for UV/visible-light-induced removal of organic dye from urban wastewater. *South African Journal of Chemical Engineering*. 2018; 26: 49–60. <https://doi.org/10.1016/j.sajce.2018.09.003>
- [47] Shubha J.P., Sushma N.V., Adil S.F., Khan M, Assal ME, Hatshan MR, et al. ZnO/La₂O₃/NiO based ternary heterostructure nano-photocatalyst: Preparation, characterization and its application for the degradation of methylene blue. *Journal of King Saud University - Science*. 2022; 34: 101738. <https://doi.org/10.1016/j.jksus.2021.101738>
- [48] Aamir M., Bibi I., Ata S., Jilani K., Majid F., Kamal S., et al. Ferroelectric, dielectric, magnetic, structural and photocatalytic properties of Co and Fe doped LaCrO₃ perovskite synthesized via micro-emulsion route. *Ceramics International*. 2021; 47: 16696–16707. <https://doi.org/10.1016/j.ceramint.2021.02.240>
- [49] Haleem A, Ullah M, Rehman SU, Shah A, Farooq M, Saeed T, et al. In-Depth Photocatalytic Degradation Mechanism of the Extensively Used Dyes Malachite Green, Methylene Blue, Congo Red, and Rhodamine B via Covalent Organic Framework-Based Photocatalysts. *Water*. 2024; 16: 1588. <https://doi.org/10.3390/w16111588>
- [50] Dvoranová D, Barbieriková Z, Brezová V. Radical intermediates in photoinduced reactions on TiO₂ (an EPR spin trapping study). *Molecules*. 2014; 19: 17279–17304. <https://doi.org/10.3390/molecules191117279>
- [51] Vai Zoğullar Aİ, Topkara Ç, Uğurlu M. Ternary V-Scheme Ag₂WO₄/BaO/NiO Heterojunction Photocatalysts: Very Fast Degradation Process for Congo Red under UV-Light Irradiation. *ACS Omega*. 2023; 8: 9423–9433. <https://doi.org/10.1021/acsomega.2c08090>
- [52] Karthikeyan S., Dhanakodi K., Surendhiran S., Jagan KSG, Lenin N., Dhatchinamurthy L., et al. Sonochemical synthesis of Sn-doped La₂O₃ nanoparticles and its application for the photocatalytic degradation of hazardous pollutants. *Journal of Materials Science: Materials in Electronics*. 2023; 34: 1157. <https://doi.org/10.1007/s10854-023-10561-0>
- [53] Surendhiran S, Jagan K, Naren Vidaarth TM, Vinoth M, Karthik A, Rajendran V. Photocatalytic prospects of phyto-fabricated CeO₂-rGO nanocomposite as an eco-friendly catalyst for detoxification of contaminated water. *Diamond and Related Materials*. 2026; 162: 113167. <https://doi.org/10.1016/j.diamond.2025.113167>