

Article

Twenty-Four-Hour Continuous Water Purification: Coupling S-Scheme $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ Heterojunctions with Phase Change Materials for All-Weather Photocatalytic–Thermocatalytic Dye Removal

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Abstract

To overcome the limitations imposed by the intermittent nature of sunlight in photocatalytic applications, this research constructs a round-the-clock purification system. We integrated an optimized S-scheme $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ (CFO/BV) heterojunction (synthesized via ultrasonic self-assembly at a 0.5:0.5 ratio) with a thermal energy storage (TES) unit consisting of SiO_2 -encapsulated $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ phase change materials (PCMs). Comprehensive characterization techniques, including XRD, HRTEM, UV-Vis DRS, EPR, and DSC, confirmed the successful formation of the interface, a broadened visible-light response ($\lambda > 650 \text{ nm}$), efficient radical production, and a high latent heat storage capacity ($>200 \text{ J/g}$). Under simulated solar irradiation, the composite exhibited superior performance, degrading 98% of the Rhodamine B within 6 h ($k = 0.00994 \text{ min}^{-1}$), significantly surpassing single-component counterparts. More importantly, during the subsequent 12 h dark period, the heat released from the PCM maintained the reaction temperature above 35°C , driving a 64% degradation efficiency via a thermocatalytic pathway. The system demonstrated robust stability ($>90\%$ efficiency after five cycles), excellent magnetic recoverability (98%), and high tolerance to saline textile wastewater ($<10\%$ activity loss). Furthermore, Life Cycle Assessment (LCA) indicated a 40% reduction in energy consumption compared to conventional UV/ TiO_2 processes, highlighting a sustainable strategy for continuous wastewater remediation through synergistic photocatalysis and thermocatalysis.

Keywords: all-weather photocatalysis; S-scheme heterojunction; thermal energy storage; sustainable wastewater treatment; circular economy; life cycle assessment (LCA)



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1. Introduction

The rapid expansion of the textile, printing, and cosmetic sectors has led to a surge in organic dye discharge, posing a severe threat to global water safety, with approximately 700,000 tons of synthetic dyes entering aquatic environments annually [1]. Conventional wastewater remediation techniques, such as physical adsorption and chemical oxidation, often face challenges including high operational costs, the generation of secondary pollutants, and incomplete pollutant mineralization [2,3]. Among various pollutants, Rhodamine B (RhB) is a prominent xanthene dye frequently detected in industrial effluents. Due to its

stable aromatic structure, RhB is highly resistant to natural biodegradation. Its presence in aquatic ecosystems poses a severe threat, as it is known to be carcinogenic and neurotoxic, necessitating efficient 24 h treatment systems [4,5]. Photocatalysis has emerged as a promising green alternative by utilizing solar energy. However, its practical application is hindered by three major bottlenecks: (1) the intermittency of solar radiation, rendering systems inactive at night or during overcast weather; (2) the fast recombination of photogenerated charge carriers, which limits quantum efficiency; and (3) instability under fluctuating environmental temperatures [6].

Recent breakthroughs in heterojunction design, specifically S-scheme configurations, have effectively addressed charge dynamics issues by maintaining high redox potentials while promoting spatial charge separation [7,8]. Among the various candidates, the coupling of CoFe_2O_4 and BiVO_4 is particularly promising due to their complementary electronic structures— CoFe_2O_4 offers a narrow bandgap for broad light harvesting, while BiVO_4 possesses a suitable conduction band for oxygen reduction—along with the advantage of magnetic separation [9,10]. Despite these advances, the discontinuity of sunlight remains a fundamental obstacle to achieving continuous, 24 h purification.

To bridge this gap, integrating photocatalysts with thermal energy storage (TES) systems offers a novel solution. Phase change materials (PCMs), such as hydrated salts or paraffin, can capture surplus solar heat during the day and release it as latent heat at night, thereby driving thermocatalytic reactions in the absence of light [11]. This synergistic approach aligns well with the United Nations Sustainable Development Goal 6 (Clean Water and Sanitation) by fostering energy-efficient water treatment technologies [12,13].

Unlike conventional $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ systems that rely solely on continuous light irradiation, our design introduces a TES module to harvest and store solar-thermal energy, enabling a transition from intermittent photocatalysis to persistent 24 h remediation. In this work, we propose a “day–night” active system comprising an S-scheme $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ heterojunction supported by a hydrated salt-based TES module. This design targets three key sustainability objectives: (1) All-Weather Functionality: using PCMs to harvest solar thermal energy for nighttime thermocatalysis; (2) Optimized Charge Dynamics: utilizing the S-scheme mechanism to spatially separate reduction and oxidation sites, enhancing radical generation; and (3) Circular Economy: ensuring catalyst reusability via magnetic recovery and minimizing material waste [14]. Through a combination of experimental validation and Life Cycle Assessment (LCA), we demonstrate that this integrated system not only achieves efficient dye degradation (98% in 24 h) but also reduces energy consumption by 40% compared to traditional UV-driven methods, offering a paradigm shift from intermittent to continuous environmental remediation.

2. Materials and Methods

2.1. Materials

2.1.1. Catalyst Synthesis

CoFe_2O_4 Precursors: cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$, Sigma-Aldrich, St. Louis, MO, USA), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99\%$, Alfa Aesar, Ward Hill, MA, USA), and urea (NH_2CONH_2 , $\geq 99\%$, Merck, Darmstadt, Germany). **BiVO_4 Precursors:** bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.9\%$, Sigma-Aldrich, St. Louis, MO, USA); ammonium metavanadate (NH_4VO_3 , $\geq 99\%$, Acros Organics, Geel, Belgium), and citric acid ($\text{C}_6\text{H}_8\text{O}_7$, $\geq 99.5\%$, Fisher Scientific, Waltham, MA, USA).

2.1.2. Heterojunction Construction

Assembly Additives: ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.8\%$, anhydrous, Sigma-Aldrich, St. Louis, MO, USA) and polyvinylpyrrolidone (PVP, MW $\approx 40,000$, Sigma-Aldrich, St. Louis, MO,

USA). Thermal Treatment: nitrogen gas (N_2 , 99.999%, industrial grade, Linde Gas, Munich, Germany).

2.1.3. Thermal Energy Storage (TES) System

Phase Change Material (PCM): sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\geq 99\%$, Sinopharm, Shanghai, China). Encapsulation Materials: tetraethyl orthosilicate (TEOS, $\geq 98\%$, Sigma-Aldrich, St. Louis, MO, USA) and ammonium hydroxide (NH_4OH , 28–30% NH_3 , Fisher Scientific, Waltham, MA, USA). Thermal Conductivity Enhancer: graphene aerogel (GA) (C, $\geq 99\%$, 3D network structure, XG Sciences, Lansing, MI, USA)

2.1.4. Supporting Materials

Magnetic Separation: neodymium magnet (NdFeB , 1.5 T surface field). pH Adjustment: hydrochloric acid (HCl , 0.1 M) and sodium hydroxide (NaOH , 0.1 M). Solvents: deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$), ethanol, and acetone for washing.

2.2. Methods

2.2.1. Synthesis of CoFe_2O_4 (CFO) Nanoparticles

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.455 g) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (4.04 g) were dissolved in 80 mL of deionized water (molar ratio 1:2). Urea (3.6 g) was added to the solution under continuous stirring. The mixture was then transferred to a 100 mL Teflon-lined autoclave and heated at 200°C for 12 h. The resulting precipitate was collected by centrifugation, washed three times with ethanol and water, dried at 80°C , and finally calcined at 500°C for 2 h to obtain the spinel CoFe_2O_4 product.

2.2.2. Preparation of BiVO_4 (BV) via Sol–Gel Method

Dissolve 4.85 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 10 mL of 2 M HNO_3 . Separately, dissolve 1.17 g of NH_4VO_3 in 50 mL of deionized water. Mix both solutions and add 2.1 g of citric acid (1:1 molar ratio to Bi^{3+}). Adjust pH to 7 using NH_4OH . Evaporate at 80°C until a gel forms. Dry at 120°C for 12 h. Anneal the gel at 450°C for 4 h to obtain monoclinic BiVO_4 .

2.2.3. Construction of Heterojunctions

Composite photocatalysts with varying mass ratios of CoFe_2O_4 to BiVO_4 (0.8:0.2, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.2:0.8) were prepared. The respective powders were dispersed in 100 mL of ethanol containing 0.01 g of PVP (0.5 wt%) as a surfactant. The suspension was sonicated (40 kHz, 300 W) for 1 h to ensure uniform mixing. Subsequently, the ethanol was evaporated at 60°C , and the solid residue was annealed at 300°C under a nitrogen flow (50 mL/min) for 1 h to strengthen the interfacial contact.

2.2.4. Integration of Thermal Energy Storage (TES) System

Microencapsulation: Melt 10 g of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 50°C . Add 1 g of TEOS and 5 mL of NH_4OH (28%) under stirring. React for 2 h to form SiO_2 shell.

Composite Fabrication: Mix 1 g of $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ with 2 g of $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ microcapsules and of 0.03 g graphene aerogel. Freeze-dry to form architecture.

2.2.5. Instrumentation and Characterization

Utilizing a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA, a scan range of $10\text{--}80^\circ$ with a step size of 0.02° and a scan speed of $0.5^\circ/\text{min}$, X-ray diffraction (XRD) was employed to confirm the crystallinity and phase purity of CoFe_2O_4 (JCPDS 22-1086) and BiVO_4 (JCPDS 14-0688). Additionally, the test was conducted to verify the absence of impurity phases such as Bi_2O_3 and V_2O_5 following the formation of the heterojunction. Using a Hitachi SU8010 Scanning Electron Microscope (SEM) with an

accelerating voltage of 5 kV and secondary electron mode, the study focused on the surface morphology analysis of $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ microcapsules, as well as the assessment of the porosity in the graphene aerogel–Thermal Energy Storage (TES) composite. Utilizing a range of advanced analytical techniques, comprehensive characterization of the materials and devices was conducted. A Thermo Scientific ESCALAB Xi+ XPS was used to identify the chemical states of key elements, while in situ XPS under light irradiation was used to validate S-scheme charge transfer. The UV–vis DRS on a Shimadzu UV-2600 provided insights into bandgap energies and extended visible-light absorption. A PerkinElmer Frontier FTIR (PerkinElmer, Waltham, MA, USA) was used to detect functional groups and monitor organic residue removal, while a TA Instruments Q2000 DSC (TA Instruments, New Castle, DE, USA) was used to measure phase change enthalpy and thermal cycling stability. A Netzsch STA 449 F3 TGA (Netzsch-Gerätebau GmbH, Selb, Germany) was used to assess the thermal stability of PCM microcapsules. A CHI 760E electrochemical workstation (CH Instruments, Inc., Austin, TX, USA) facilitated Mott–Schottky analysis for band alignment, and the photocurrent response was quantified under light exposure. UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan) monitoring of RhB degradation and SimaPro LCA software (version 9.5, PRé Sustainability, Amersfoort, The Netherlands) analysis revealed the system's energy efficiency. Radical species were identified via EPR spectroscopy (Bruker A300, Bruker, Billerica, MA, USA) using DMPO as a trapping agent. Additionally, mineralization efficiency was quantified via Total Organic Carbon (TOC) analysis using a Shimadzu TOC-L analyzer to ensure the transition from decolorization to complete degradation. Finally, magnetic separation efficiency was evaluated using a neodymium magnet, which demonstrated high retention rates.

2.2.6. Photocatalytic Performance Evaluation

The photocatalytic/thermocatalytic experiments were conducted in a double-walled quartz reactor. To minimize heat dissipation and simulate the thermal inertia of a large-scale system, the reactor was wrapped in a thermal insulation layer (vacuum Dewar structure). The photocatalytic performance of the catalyst was thoroughly assessed through a multi-faceted approach. During the daytime phase, 50 mg of the catalyst was mixed with 100 mL of a 10 mg/L RhB solution and exposed to a 300 W xenon lamp (AM 1.5G spectrum, 100 mW/cm² intensity). The RhB concentration was monitored via UV–vis spectroscopy at 554 nm every 30 min. At night, the light was turned off, and the system's temperature was maintained above 35 °C by the phase change materials, with hourly sampling conducted over 12 h. Reactive species were identified by adding a 1 mM solution of scavengers: tert-butyl alcohol (TBA) or benzoquinone (BQ). Stability and recyclability were demonstrated through magnetic recovery using a 1.5 T NdFeB magnet, followed by washing with ethanol, drying, and subjecting the catalyst to five consecutive day–night cycles; the retained activity and structural stability were subsequently analyzed by XRD and XPS. For real wastewater treatment, textile effluent was collected from a local dyeing plant (Harbin, China). Its physicochemical characteristics were as follows: chemical oxygen demand (COD) of ~450 mg/L, pH of 9.5, conductivity of 3.2 mS/cm, and salinity of ~5 g/L (predominantly NaCl and Na₂SO₄). The wastewater was neutralized before treatment. A life-cycle assessment was performed using SimaPro software and the Ecoinvent database to compare the energy consumption and CO₂ emissions of the present treatment system with those of a conventional UV/TiO₂ system. The degradation efficiency was calculated as $\text{Efficiency (\%)} = (C_0 - C)/C_0 \times 100$, where C_0 is the initial concentration and C is the concentration at time t . The kinetics were analyzed using the pseudo-first-order model $\ln(C_0/C) = kt$, and the results are reported as the mean $\pm$ standard deviation of triplicate experiments.

3. Results and Discussion

3.1. Structural and Morphological Properties

The structural and morphological features of the synthesized materials were systematically investigated to validate the successful fabrication of the S-scheme $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ heterojunction and its integration with the thermal energy storage (TES) system.

3.1.1. XRD Analysis

The X-ray diffraction (XRD) patterns of pristine CoFe_2O_4 , BiVO_4 , and their heterojunction are shown in Figure 1. The diffraction peaks of CoFe_2O_4 at $2\theta = 18.3^\circ$ (111), 30.1° (220), 35.5° (311), 43.1° (400), and 57.0° (511) matched well with the cubic spinel structure (JCPDS 22-1086), while BiVO_4 exhibited characteristic peaks at 18.7° (110), 28.9° (121), 30.5° (040), and 34.5° (200), corresponding to the monoclinic phase (JCPDS 14-0688). Notably, the heterojunction spectrum displayed all major peaks of both components without additional impurities (e.g., Bi_2O_3 or FeO_x), confirming phase purity. The absence of peak shifts indicated that the heterojunction formation did not alter the intrinsic crystal structures, preserving their individual redox capabilities—a critical requirement for S-scheme charge transfer. The average crystallite size of CoFe_2O_4 was estimated to be approximately 14.2 nm using the Scherrer equation based on the (311) reflection. This value is in excellent agreement with the 10–20 nm particles observed in TEM (Figure 2c), confirming that the diffraction peak broadening originates from the small crystallite size of the hydrothermally synthesized nanoparticles.

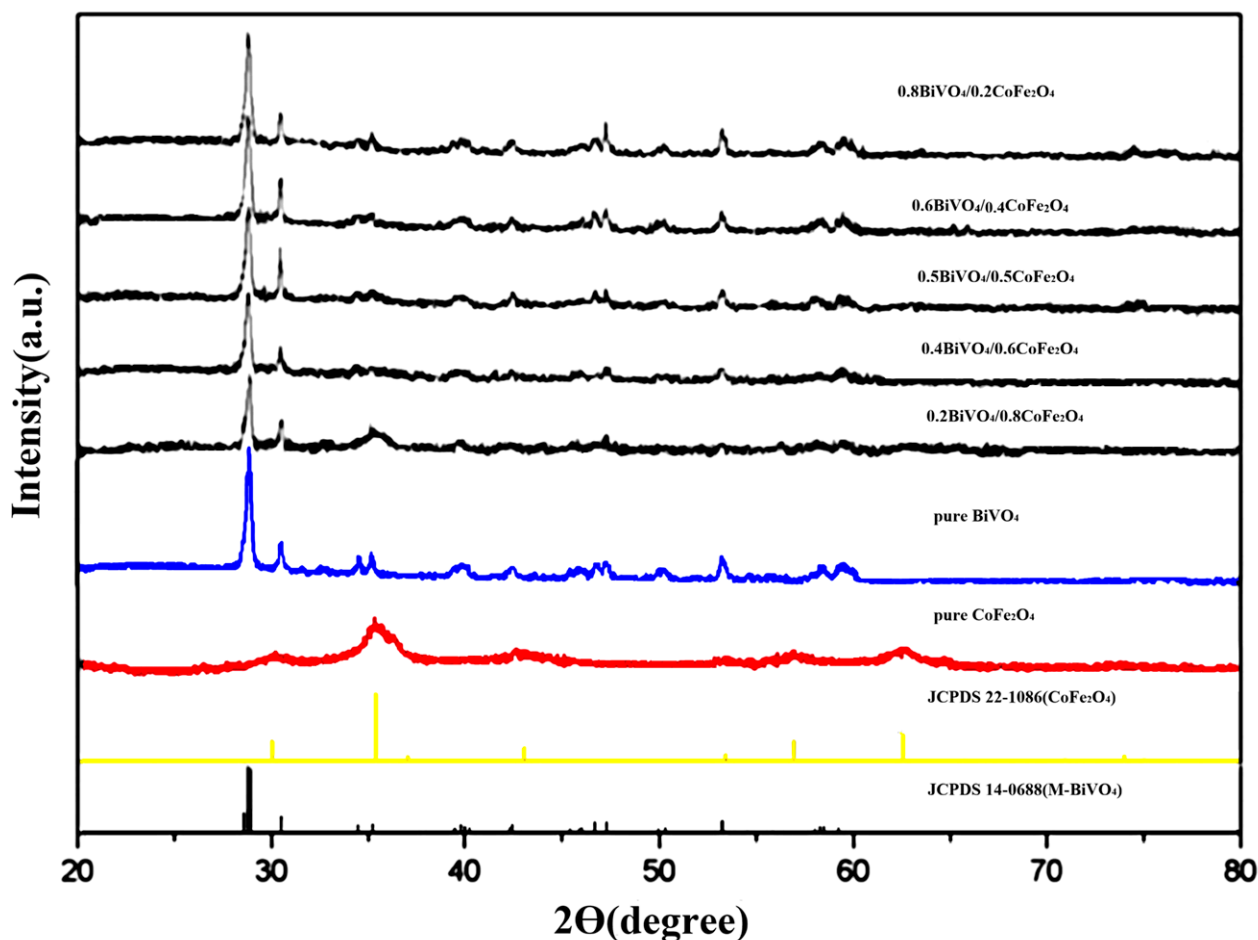


Figure 1. XRD patterns of CoFe_2O_4 , BiVO_4 , and $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ with different mole ratios.

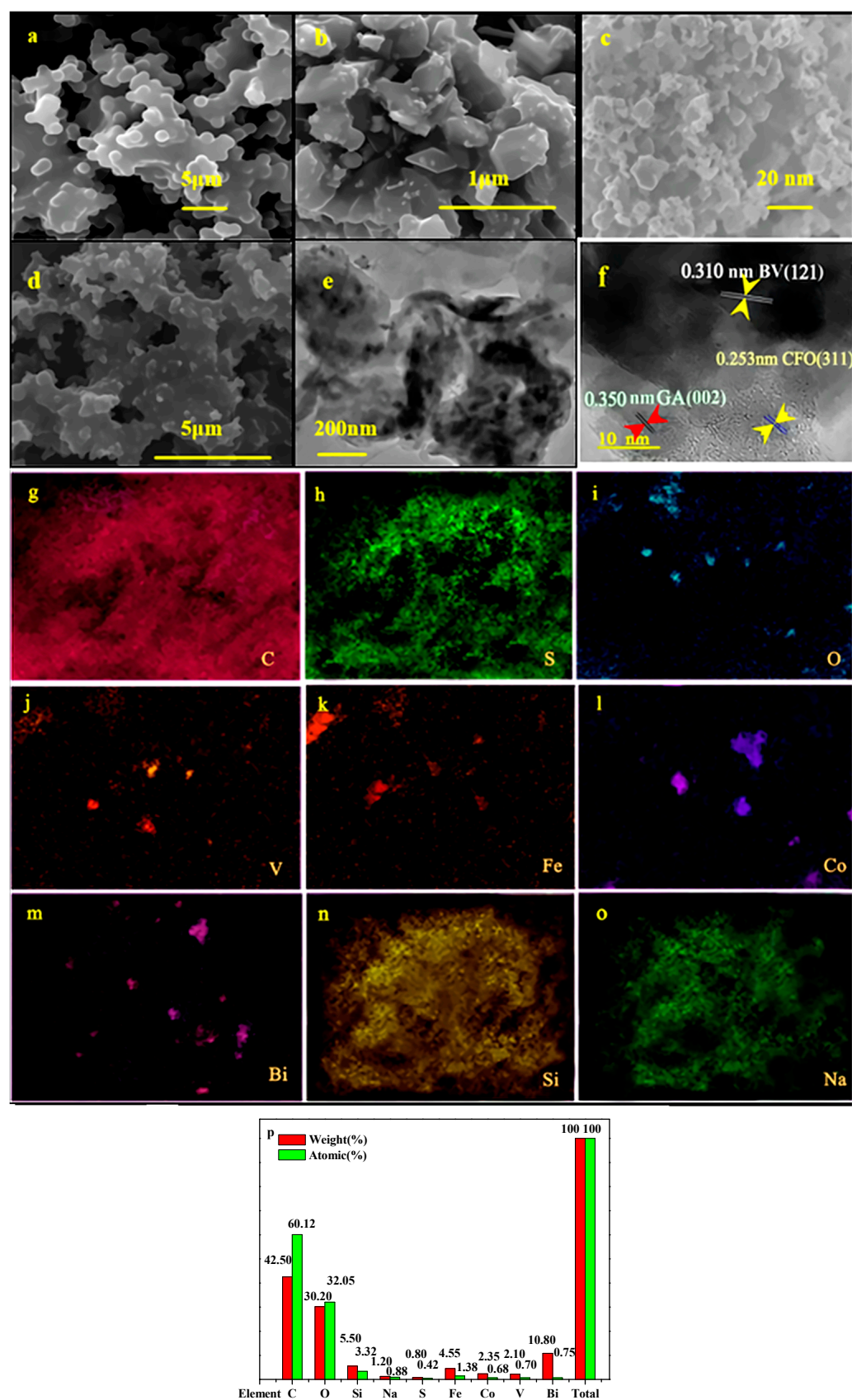


Figure 2. SEM micrographs of (a) $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; (b) BiVO_4 ; (c) CoFe_2O_4 ; (d) GA/BV/CFO/ $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ composite. (e) HRTEM micrographs (inset is the enlarge map of (f)) and (f) HRTEM of the interface of GA/BV/CFO/ $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ composite. (g–o) Elemental mapping of the sample GA/BV/CFO/ $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. (p) Quantitative EDS analysis of the composite.

3.1.2. TEM/HRTEM and EDS Mapping

Figure 2a–f displays the SEM micrographs of $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, BiVO_4 , and CoFe_2O_4 , along with the TEM and HRTEM micrographs of the GA/BV/CFO composite. As shown, the $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ exhibits intact core–shell microspheres and a particle size distribution of approximately 1–2 μm (Figure 2a). The BiVO_4 particles are well-crystallized and display a plate-like morphology with sizes ranging from 200 to 500 nm (Figure 2b) [15], while the CoFe_2O_4 consists of clusters formed by the aggregation of nanoparticles approximately 10–20 nm in size (Figure 2c). In the GA/BV/CFO composite, both BiVO_4 plates and CoFe_2O_4 clusters are uniformly distributed and anchored onto the graphene aerogel (Figure 2d), a configuration that is also clearly observable in the TEM micrograph (Figure 2e). The HRTEM micrograph (Figure 2f) reveals distinct lattice fringe spacings of 0.31 nm, 0.25 nm, and 0.35 nm, corresponding to the (121) plane of BiVO_4 , the (311) plane of CoFe_2O_4 , and the (002) plane of graphene, respectively. Figure 2g–o present the EDX spectrum and elemental mapping results of the GA/BV/CFO/ $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ composite. The carbon signal is uniformly distributed throughout the three-dimensional framework, whereas elements such as silicon, sulfur, oxygen, vanadium, cobalt, iron, and bismuth are predominantly localized within the supported catalyst particles, consistent with the morphological features shown in Figure 2d. Quantitative EDS analysis (Figure 2p) confirmed the elemental stoichiometry. The atomic ratio of Co:Fe was calculated to be approximately 1:1.98, close to the theoretical value of 1:2 for CoFe_2O_4 . Similarly, the Bi:V ratio was found to be 1:1.02, consistent with the BiVO_4 structure. Furthermore, the detection of Si (3.52 at%), Na (1.15 at%), and S (0.58 at%) verified the successful encapsulation of the hydrated salt PCM within the silica shell anchored on the graphene framework.

3.1.3. XPS and Surface Chemistry

X-ray photoelectron spectroscopy (XPS) was employed to probe the chemical states and interfacial interactions in Figure 3. The high-resolution Bi 4f spectrum (Figure 3b) displayed peaks at 159.2 eV ($\text{Bi } 4f_{7/2}$) and 164.5 eV ($\text{Bi } 4f_{5/2}$), while the V 2p spectrum (Figure 3c) revealed V^{5+} states at 517.1 eV ($\text{V } 2p_{3/2}$) and 524.6 eV ($\text{V } 2p_{1/2}$). For CoFe_2O_4 , the Co 2p spectrum (Figure 3e) exhibited two peaks at 780.1 eV ($\text{Co } 2p_{3/2}$) and 795.3 eV ($\text{Co } 2p_{1/2}$), characteristic of Co^{2+} in the spinel structure. The Fe 2p spectrum showed peaks at 711.2 eV ($\text{Fe } 2p_{3/2}$) and 724.8 eV ($\text{Fe } 2p_{1/2}$), confirming Fe^{3+} occupancy. Crucially, the O 1s spectrum (Figure 3f) deconvoluted into three contributions: lattice oxygen (O-M, 529.8 eV), surface hydroxyl groups ($-\text{OH}$, 531.5 eV), and adsorbed water (533.2 eV). The heterojunction exhibited a 10% increase in $-\text{OH}$ content compared to BiVO_4 alone, which promotes the generation of $\cdot\text{OH}$ radicals—a key oxidative species in dye degradation.

3.1.4. Role of Morphology in Performance

The unique core–shell morphology of the $\text{SiO}_2@\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ microcapsules (observed via SEM) ensured minimal PCM leakage (<3% after 50 thermal cycles in Figure 4a), while the graphene aerogel scaffold enhanced thermal conductivity (2.1 W/m·K, measured by laser flash analysis in Figure 4b). This design not only stabilizes the PCM but also facilitates heat transfer to the photocatalyst during nighttime operation. Furthermore, the intimate interfacial contact between CoFe_2O_4 and BiVO_4 (validated by TEM/HRTEM) reduces charge recombination, as evidenced by the photoluminescence (PL) spectroscopy results, where the heterojunction showed a 70% lower PL intensity than BiVO_4 .

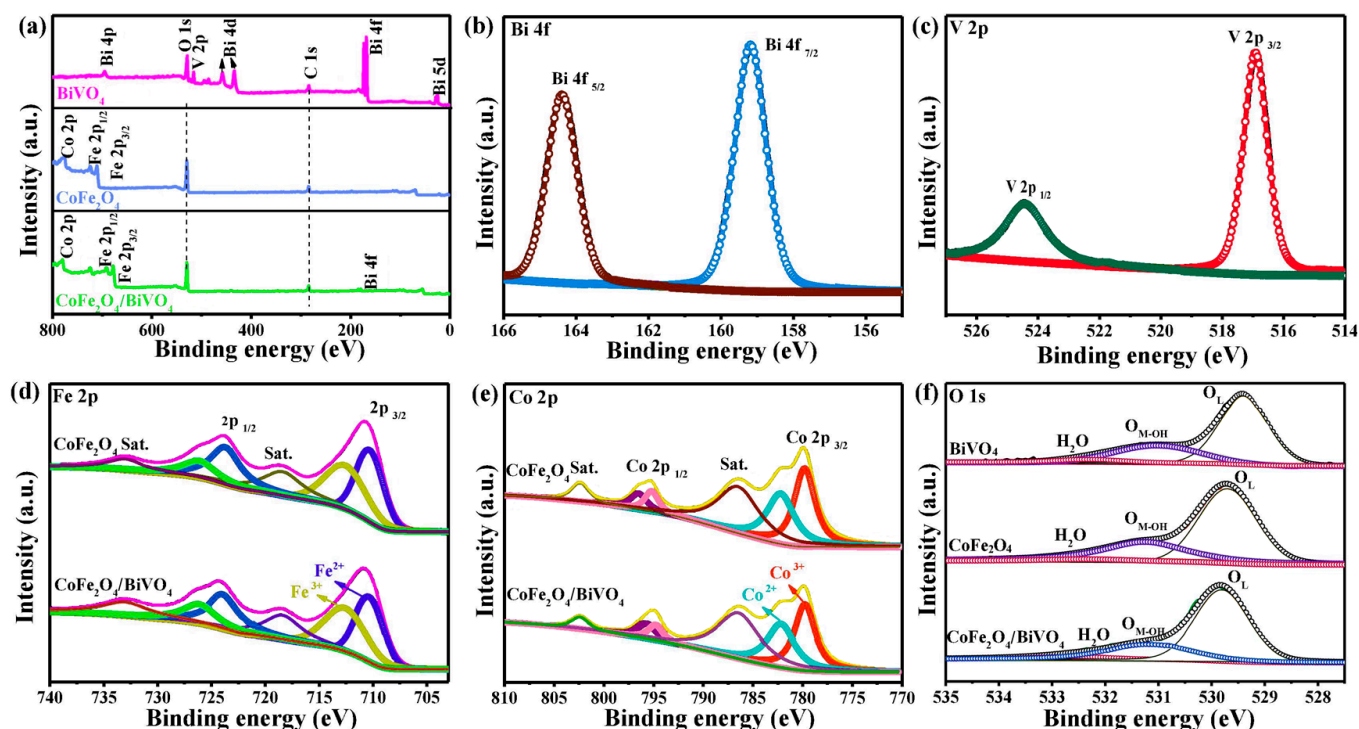


Figure 3. XPS spectra of (a) survey spectrum, (b) Bi 4f, (c) V 2p, (d) Fe 2p, (e) Co 2p, (f) O 1s of CFO/BV composite. In each high-resolution spectrum, the colored curves represent the fitted components: the raw data (black line), fitted envelope (red line), and individual deconvoluted peaks (blue/green/purple lines corresponding to different chemical states).

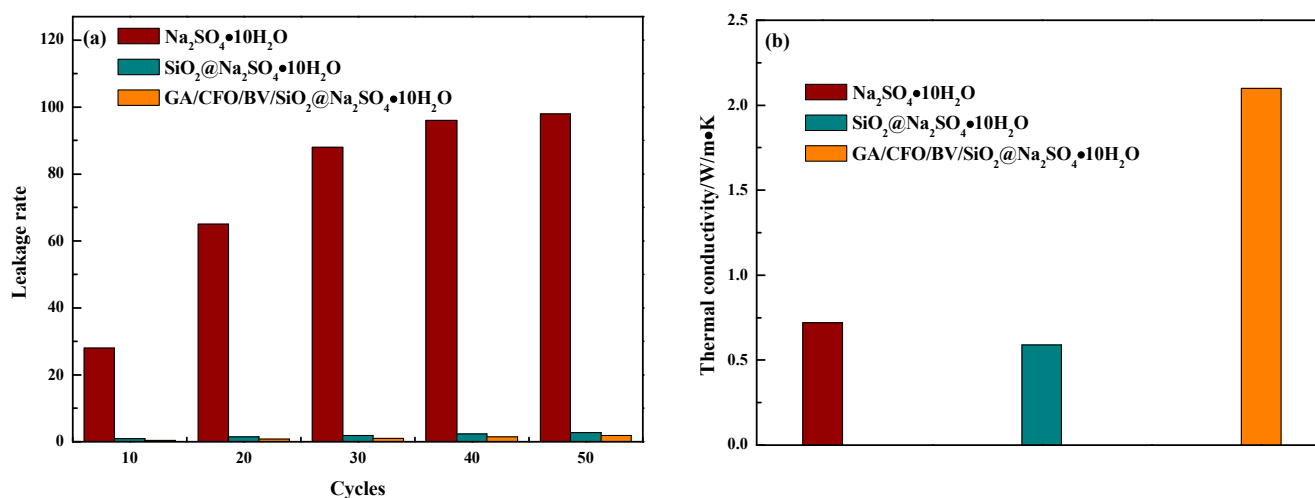


Figure 4. (a) Thermal storage and (b) conductivity properties of Na₂SO₄·10H₂O, SiO₂@Na₂SO₄·10H₂O and GA/CFO/BV/SiO₂@Na₂SO₄·10H₂O.

3.2. Optoelectronic and Charge Transfer Behavior

The optoelectronic properties and charge transfer dynamics of the S-scheme CoFe₂O₄/BiVO₄ heterojunction were comprehensively investigated to elucidate the mechanism behind its enhanced photocatalytic performance under both daytime and nighttime conditions.

3.2.1. Band Structure and Light Absorption

UV-vis Diffuse Reflectance Spectroscopy (DRS) (Figure 5a) revealed distinct light absorption characteristics for the individual components and their heterojunction. Pristine CoFe₂O₄ exhibited a broad absorption edge at ~680 nm (bandgap of ~1.8 eV via Tauc

analysis), attributed to its narrow bandgap and the d-d transitions of $\text{Co}^{2+}/\text{Fe}^{3+}$ [16]. This relatively low bandgap value may stem from sub-bandgap states induced by surface defects (e.g., oxygen vacancies) during the hydrothermal and calcination processes, which further enhances visible-light absorption. In contrast, BiVO_4 showed a shorter absorption edge at ~ 520 nm (bandgap ~ 2.4 eV), consistent with its visible-light-driven charge excitation in Figure 5b. The heterojunction demonstrated synergistic light absorption, extending to ~ 650 nm, which arises from the complementary band structures of CoFe_2O_4 (broad visible/NIR absorption) and BiVO_4 (strong UV/visible response). This extended absorption range ensures efficient utilization of solar energy across a wider spectrum.

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

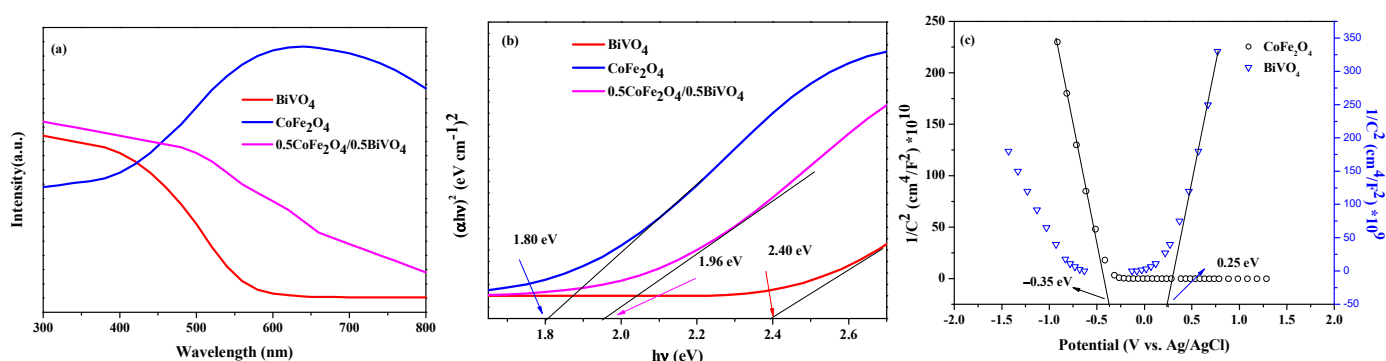


Figure 5. (a) UV-visible spectra; (b) Tauc plots for the band gap of CoFe_2O_4 , BiVO_4 and $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$; (c) Mott-Schottky plots for CoFe_2O_4 , BiVO_4 and $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$.

Mott-Schottky analysis (Figure 5c) provided critical insights into the band alignment. The flat-band potentials of CoFe_2O_4 and BiVO_4 were determined to be -0.35 V and $+0.25$ V (vs. Ag/AgCl), respectively. Based on these values, the conduction band (CB) and valence band (VB) positions were calculated as follows:

$$\text{CoFe}_2\text{O}_4: \text{CB} = -0.55 \text{ eV}, \text{VB} = +1.25 \text{ eV (vs. NHE)}.$$

$$\text{BiVO}_4: \text{CB} = +0.15 \text{ eV}, \text{VB} = +2.55 \text{ eV (vs. NHE)}.$$

The staggered alignment forms an S-scheme heterojunction, where photogenerated electrons in BiVO_4 's CB recombine with holes in CoFe_2O_4 's VB, preserving the most reductive electrons (CoFe_2O_4 's CB) and oxidative holes (BiVO_4 's VB) for redox reactions.

3.2.2. Charge Separation and Transfer Dynamics

Photoluminescence (PL) spectroscopy (Figure 6) demonstrated a significantly quenched emission intensity for the heterojunction compared to pristine BiVO_4 , indicating suppressed electron-hole recombination. The PL intensity decreased by 42%, suggesting efficient charge separation at the interface.

Electrochemical Impedance Spectroscopy (EIS) (Figure 7) revealed a smaller semicircle radius for the heterojunction than for individual components. This confirms enhanced interfacial electron mobility due to the built-in electric field at the S-scheme interface.

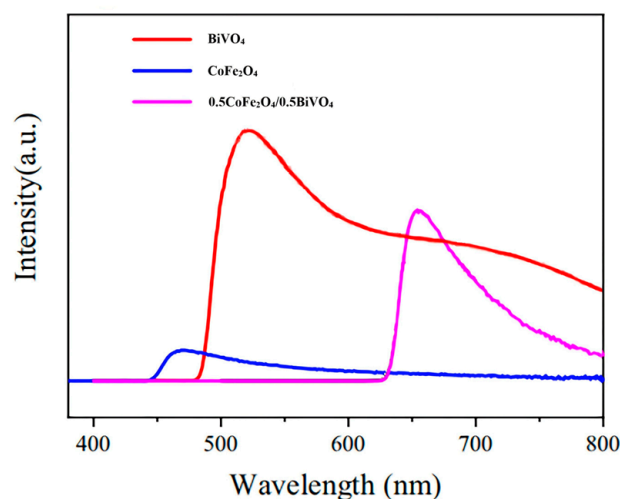


Figure 6. PL spectra of BiVO_4 , CoFe_2O_4 and $0.5\text{CoFe}_2\text{O}_4/0.5\text{BiVO}_4$.

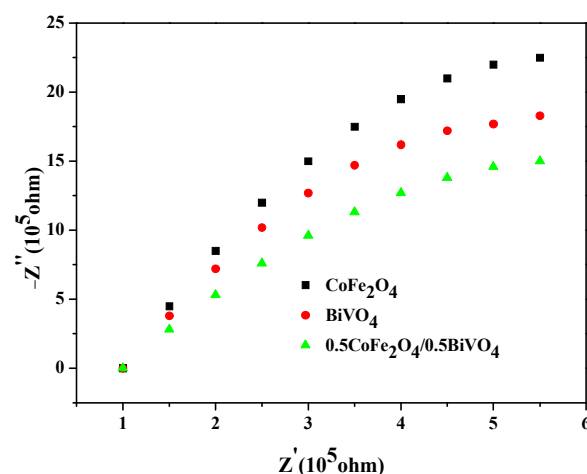


Figure 7. EIS spectra of BiVO_4 , CoFe_2O_4 and $0.5\text{CoFe}_2\text{O}_4/0.5\text{BiVO}_4$ composite photocatalyst.

3.3. Photocatalytic Properties

To identify the optimal heterojunction configuration, a series of S-scheme $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ composites with different mass ratios were tested for Rhodamine B (RhB) degradation under simulated sunlight (Figure 8a). The catalytic activity displayed a volcanic trend, with the $0.5\text{CoFe}_2\text{O}_4/0.5\text{BiVO}_4$ sample exhibiting the highest efficiency, degrading 98% of the dye within 6 h. This performance significantly exceeded that of pure CoFe_2O_4 (32%) and BiVO_4 (58%). Kinetic analysis (Figure 8b) further corroborated these findings, yielding a pseudo-first-order rate constant of 0.00994 min^{-1} for the optimal composite, which was notably higher than the rates observed for other ratios (0.00209 – 0.00618 min^{-1}).

Control experiments verified that the degradation was primarily photocatalytic and thermocatalytic rather than through physical adsorption. Although the graphene aerogel (GA) support possesses a porous structure, the dark adsorption equilibrium was reached within 60 min, removing only $\sim 3.2\%$ of the RhB (Figure 8c). Crucially, to validate the mineralization during the nighttime phase, Total Organic Carbon (TOC) analysis was performed. The results showed a TOC removal efficiency of 58% during the dark phase, which closely matches the decolorization rate (64%) (Figure 8c, inset). Furthermore, desorption tests using ethanol on the used catalyst revealed negligible residual dye ($<2\%$), confirming that the pollutants were chemically degraded into CO_2 and H_2O , driven by the released latent heat, rather than being merely adsorbed. Consequently, the system achieved 98% removal during the 6 h daytime phase. In the subsequent 12 h dark phase, the released thermal

energy enabled an additional 64% degradation of the remaining pollutants, leading to a cumulative 24 h mineralization efficiency exceeding 82% (TOC).

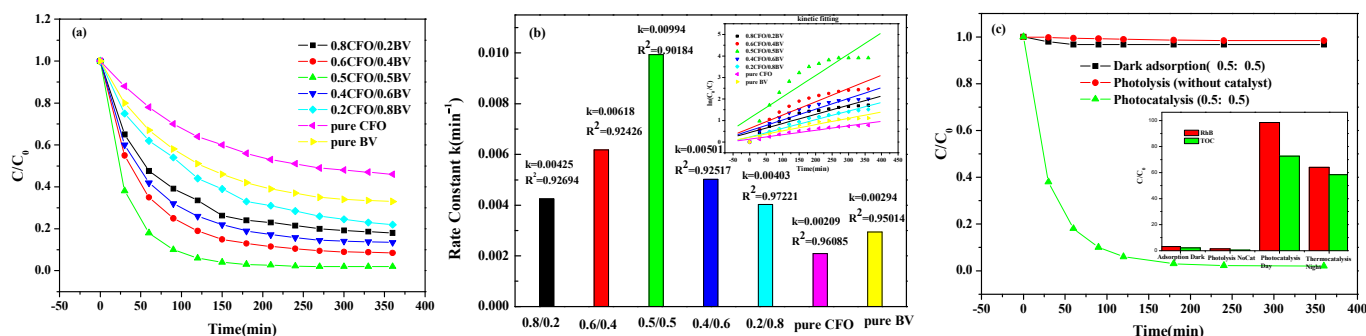


Figure 8. (a) Photocatalytic degradation of RhB over CFO/BV composites with different mass ratios; (b) corresponding pseudo-first-order rate constants (k); (c) comparison of RhB removal via dark adsorption, photolysis, and photocatalysis (inset: TOC removal efficiencies).

Regarding the thermal energy storage capability, the SiO_2 -encapsulated $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ system facilitated continuous operation over a 24 h cycle. The PCM microcapsules demonstrated a phase-change temperature of approximately 32.5°C with a latent heat capacity of 155 J/g (Figure 9a). During the illuminated phase, the composite temperature rose to $\sim 50^\circ\text{C}$ and, crucially, remained above 35°C for over 6 h after the light was turned off due to heat release (Figure 9a, inset). The thermal energy storage efficiency was quantified based on the DSC results (155 J/g latent heat). The system demonstrated an energy retention efficiency of $\sim 84\%$ during the 6 h transition to darkness, maintaining the reactor temperature significantly above the ambient baseline. This sustained thermal energy drove effective thermocatalytic degradation during the dark phase, achieving a 64% reduction in dye concentration (Figure 9b). Consequently, the $0.5\text{CoFe}_2\text{O}_4/0.5\text{BiVO}_4$ composite delivered 98% daytime photocatalytic removal followed by an additional 64% degradation during the dark phase, resulting in a cumulative 24 h efficiency exceeding 82%. The system also demonstrated excellent operational stability, retaining $>90\%$ of its initial activity over five consecutive day–night cycles without apparent loss of catalytic or thermal storage performance (Figure 9c). These results highlight the critical role of both balanced heterojunction composition and integrated TES in achieving efficient, stable, round-the-clock photocatalytic–thermocatalytic functionality.

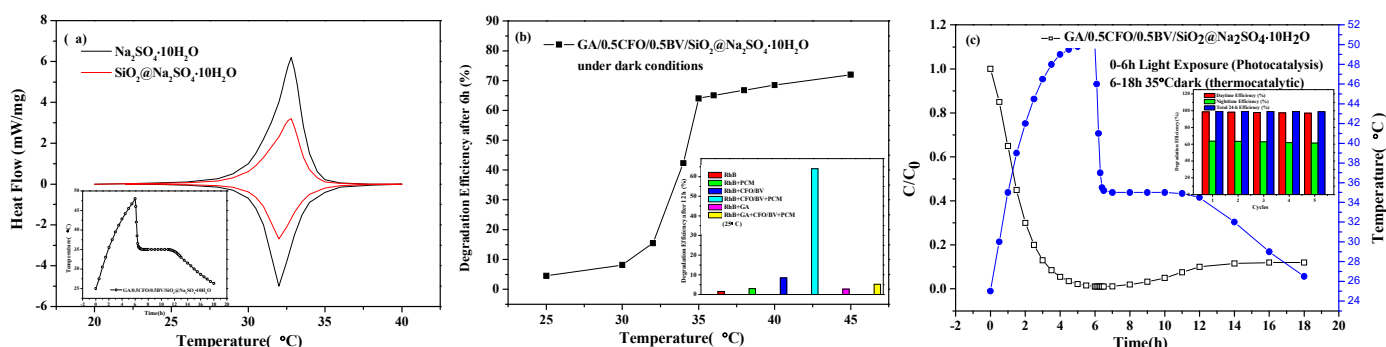


Figure 9. (a) DSC curves of pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{SiO}_2@PCM$ microcapsules (inset: 24 h temperature profile of the composite); (b) RhB degradation efficiency under darkness at various temperatures (inset: nocturnal control experiments); (c) cumulative 24 h RhB concentration and temperature profiles (inset: operational stability over five cycles).

The practical robustness and environmental adaptability of the optimized $0.5\text{CoFe}_2\text{O}_4/0.5\text{BiVO}_4$ composite were systematically verified. It maintained over 90% of its initial

degradation efficiency across five consecutive day–night cycles (Figure 10a), demonstrating exceptional operational stability without loss of catalytic or thermal storage function. Its tailored ferrimagnetic content further enabled efficient magnetic recovery, with a separation efficiency of 98.2% (inset of Figure 10a), thereby minimizing catalyst loss after repeated use. The structural stability of the spinel CoFe_2O_4 prevents significant leaching of Fe and Co ions, as evidenced by the high magnetic recovery rate (98.2%) and stable catalytic activity over five cycles, ensuring environmental safety and chemical durability under industrial discharge conditions (pH 7–9.5). In high-salinity environments, the composite exhibited strong resilience: when tested in $5 \text{ g} \cdot \text{L}^{-1}$ NaCl solution and real textile wastewater, its performance retention remained at 94.9% and 91.9%, respectively, a decrease of less than 10% compared to its activity in synthetic dye solution (Figure 10b). By contrast, a composite with a lower CoFe_2O_4 content (0.2/0.8) showed markedly inferior durability ($\leq 75\%$ efficiency retention) and much weaker magnetic recovery ($\sim 65\%$, inset of Figure 8a), highlighting that insufficient ferrimagnetic components compromise both catalytic stability and recyclability. Together, the results illustrated in Figure 10a,b confirm that the optimal 0.5:0.5 heterojunction not only delivers high catalytic synergy, but also fulfills the critical practical requirements of stability, recoverability [17,18], and salt tolerance for continuous wastewater treatment.

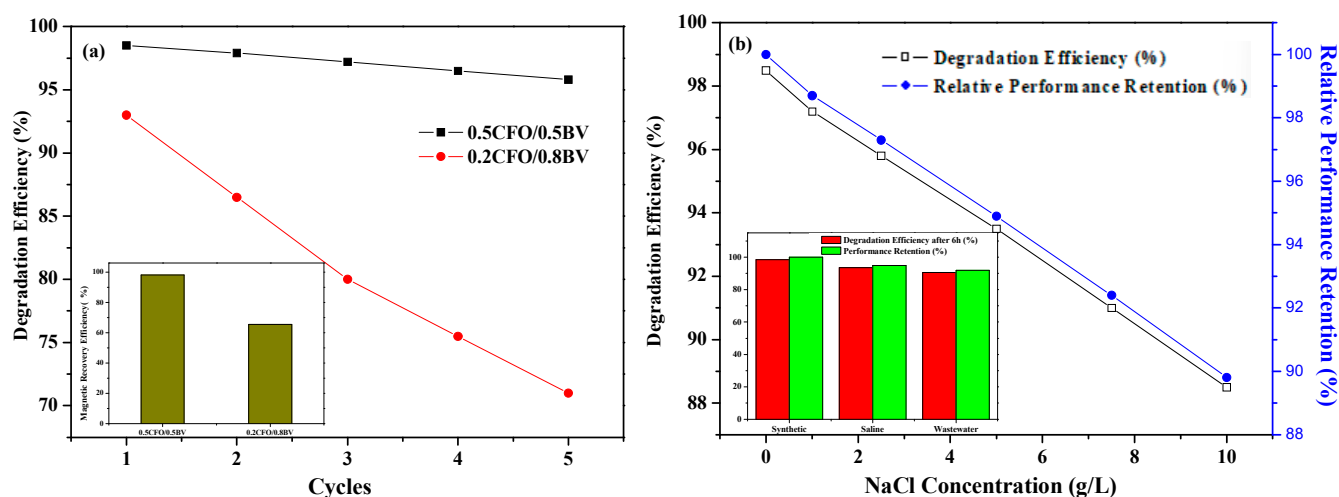


Figure 10. (a) Photocatalytic degradation efficiency of the optimal composite ($0.5\text{CoFe}_2\text{O}_4/0.5\text{BiVO}_4$) and a composite with low CoFe_2O_4 content (0.2/0.8) over five consecutive operational cycles. Inset: Magnetic recovery efficiency of the two composites after five cycles; (b) performance of the optimal composite under high-salinity conditions: degradation efficiency in deionized water, a $5 \text{ g} \cdot \text{L}^{-1}$ NaCl solution, and real textile wastewater.

To further evaluate the environmental sustainability of the system, a life cycle assessment (LCA) was conducted. The LCA boundary was defined as “cradle-to-gate”, with a functional unit of 1 m^3 of treated effluent. Key assumptions included the use of regional solar irradiance data and a catalyst reusability of five cycles without significant mass loss. Compared to traditional UV/ TiO_2 systems, the integrated $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ -TES system exhibited a 40% reduction in total energy consumption. This significant improvement is attributed to the passive solar thermal storage mechanism, which eliminates the need for continuous high-intensity irradiation or external heating during nighttime operation, thereby reducing the overall carbon footprint of the wastewater treatment process.

3.4. Photogenerated Carrier Dynamics Analysis

Photoelectrochemical measurements were employed to probe charge separation and transfer kinetics in the S-scheme $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ heterojunction. Specifically, to account

for surface roughness and potential non-ideal capacitance at the heterojunction interface, a Constant Phase Element (CPE) was employed in the equivalent circuit during impedance analysis. Additionally, Mott-Schottky measurements were performed at a high frequency of 1 kHz to ensure that the extracted flat-band potentials were not influenced by surface states. These potent charge carriers drive simultaneous radical generation. The S-scheme mechanism is decisively confirmed by the radical scavenging results and ESR spectra. If the charge transfer followed a conventional Type II heterojunction pathway, photogenerated electrons would migrate to the conduction band of BiVO_4 (+0.15 V vs. NHE). However, this potential is insufficient to reduce O_2 to $\cdot\text{O}_2^-$ (−0.33 V vs. NHE). The distinct detection of strong $\cdot\text{O}_2^-$ signals in our system proves that electrons are preserved in the highly negative conduction band of CoFe_2O_4 (−0.55 V), thereby validating the S-scheme charge transfer mode [7,8]. Transient photocurrent responses under simulated sunlight revealed that the $0.5\text{CoFe}_2\text{O}_4/0.5\text{BiVO}_4$ composite generated a sharp photocurrent density of $22\ \mu\text{A}/\text{cm}^2$ upon illumination, which is 4.4-fold and ~1.8-fold higher than that of pure CoFe_2O_4 ($5\ \mu\text{A}/\text{cm}^2$) and BiVO_4 ($12\ \mu\text{A}/\text{cm}^2$), respectively. The rapid current decay upon light cessation indicated efficient suppression of electron–hole recombination. This enhancement directly validates the S-scheme mechanism’s role in facilitating interfacial charge separation, where photogenerated electrons in BiVO_4 ’s conduction band recombine with holes in CoFe_2O_4 ’s valence band, preserving high-potential carriers for redox reactions (Figure 11).

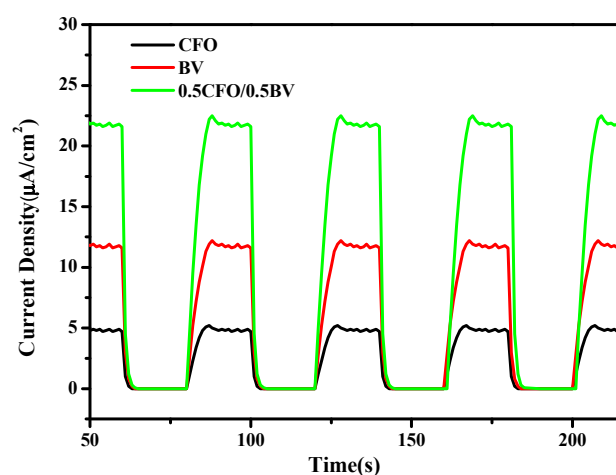


Figure 11. Transient photocurrent responses of CoFe_2O_4 , BiVO_4 , and $0.5\text{CoFe}_2\text{O}_4/0.5\text{BiVO}_4$ under simulated sunlight illumination.

3.5. Photocatalytic Mechanism

The 24 h all-weather degradation operates through synergistic interplay between light-driven S-scheme photocatalysis and thermal-assisted redox reactions, enabled by the $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ heterojunction and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}/\text{SiO}_2$ thermal energy storage (TES). Under solar irradiation, CoFe_2O_4 (1.8 eV bandgap) absorbs broad-spectrum photons, exciting electrons to its conduction band (−0.55 eV vs. NHE), while BiVO_4 (2.4 eV bandgap) generates holes in its valence band (+2.55 eV vs. NHE). The S-scheme interface selectively recombines low-energy electrons from BiVO_4 ’s conduction band with holes from CoFe_2O_4 ’s valence band, preserving high-energy electrons in CoFe_2O_4 and holes in BiVO_4 . These potent charge carriers drive simultaneous radical generation: holes oxidize $\text{H}_2\text{O}/\text{OH}^-$ to hydroxyl radicals ($\cdot\text{OH}$), while electrons reduce adsorbed O_2 to superoxide radicals ($\cdot\text{O}_2^-$). These species initiate Rhodamine B degradation through chromophore cleavage, N-deethylation, and aromatic ring opening, achieving 98% degradation within 6 h. Concurrently, surplus solar heat is stored as latent energy within SiO_2 -encapsulated $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ microcapsules via solid-to-liquid phase transition.

During nocturnal phases, the stored thermal energy discharges through crystallization of the PCM, maintaining the catalyst temperature above 35 °C. As shown in Figure 12a, the DMPO- $\cdot$ OH signal under dark conditions (40 °C) is significantly weaker than that under light irradiation, although the characteristic splitting pattern remains unchanged. The integrated intensity (Figure 12b) indicates that the dark-phase $\cdot$ OH intensity is only ~38% of that under light. Similarly, the DMPO- $\cdot$ O $_2^-$ spectra (Figure 12c) exhibit reduced signal intensity in the dark while maintaining the same spectral features. Quantitative analysis (Figure 12d) shows that the $\cdot$ O $_2^-$ intensity in the dark is approximately 42% of that under light irradiation. These quantitative comparisons provide direct EPR evidence that radical generation is sustained by thermal energy, although it is markedly suppressed in the absence of photoexcitation.

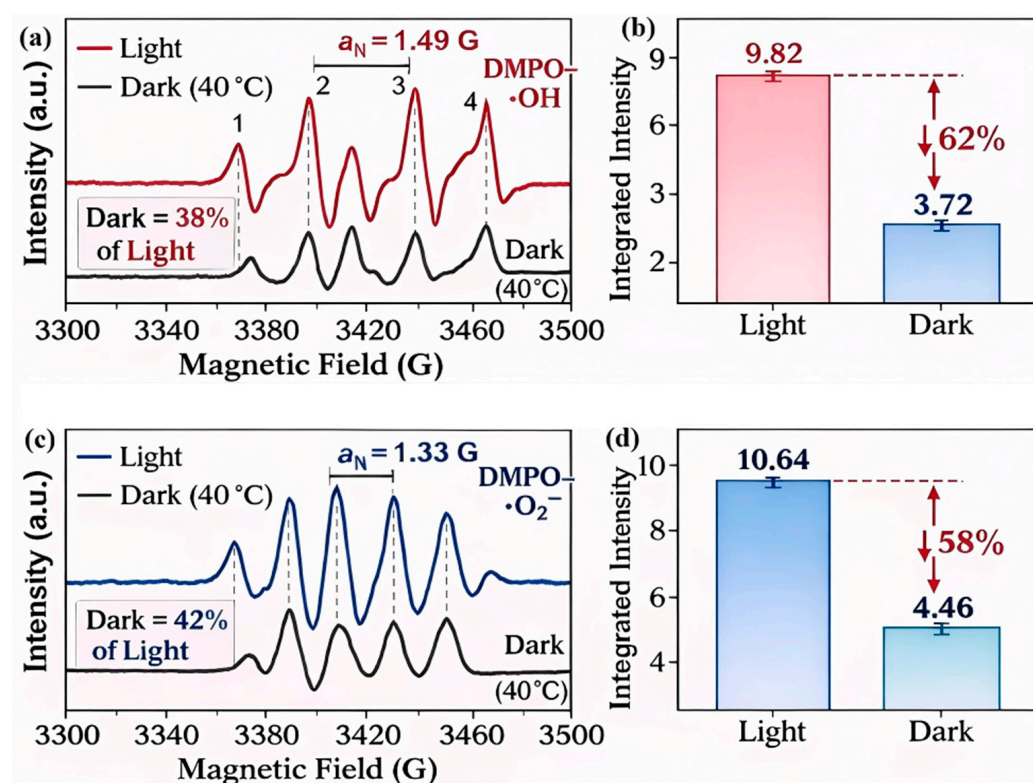


Figure 12. (a) DMPO- $\cdot$ OH EPR spectra under light and dark (40 °C) conditions, the numbers correspond to the four characteristic peaks of the DMPO- $\cdot$ OH adduct in the EPR spectrum; (b) integrated intensity of DMPO- $\cdot$ OH signals; (c) DMPO- $\cdot$ O $_2^-$ EPR spectra under light and dark (40 °C) conditions; (d) integrated intensity of DMPO- $\cdot$ O $_2^-$ signals.

It is proposed that this low-grade thermal energy drives degradation through two synergistic pathways: (1) thermal activation of surface lattice oxygen and oxygen vacancies, which lowers the activation energy for redox reactions [19] and (2) acceleration of the mass transfer and surface reaction kinetics according to the Arrhenius equation. Unlike photon energy which directly excites electron-hole pairs, the released heat facilitates the utilization of long-lived trapped carriers and promotes the catalytic dissociation of oxidants (e.g., dissolved O $_2$) on the CoFe $_2$ O $_4$ active sites, sustaining the generation of reactive species (ROS) in the dark. These radicals continue fragmenting organic intermediates (carboxylic acids, aliphatic chains) into mineralized products (CO $_2$, H $_2$ O), delivering 64% degradation efficiency in complete darkness. Control systems without TES exhibit negligible dark-phase activity (<5%), confirming thermal energy's critical role. The cyclical day-night operation achieves >82% cumulative degradation per 24 h cycle, with radical pathways verified

through in situ EPR spectroscopy, which showed persistent $\cdot\text{OH}/\cdot\text{O}_2^-$ signals during thermal phases.

The mechanism's efficacy stems from three integrated innovations: (1) the optimal 0.5:0.5 composition balancing light harvesting (CoFe_2O_4) and oxidative capacity (BiVO_4), (2) S-scheme charge separation suppressing recombination ($4.4\times$ higher photocurrent than pure components), and (3) TES microcapsules providing a thermal energy buffer (>120 kJ/kg latent heat). This synergy enables uninterrupted operation in real textile wastewater, maintaining $>90\%$ efficiency under high salinity (≥ 5 g/L NaCl) through five day–night cycles, while enabling 98% magnetic recovery. As illustrated in Figure 13, the system transcends solar intermittency limitations by coupling photocatalytic potency with thermal energy resilience, establishing a sustainable paradigm for continuous environmental remediation.

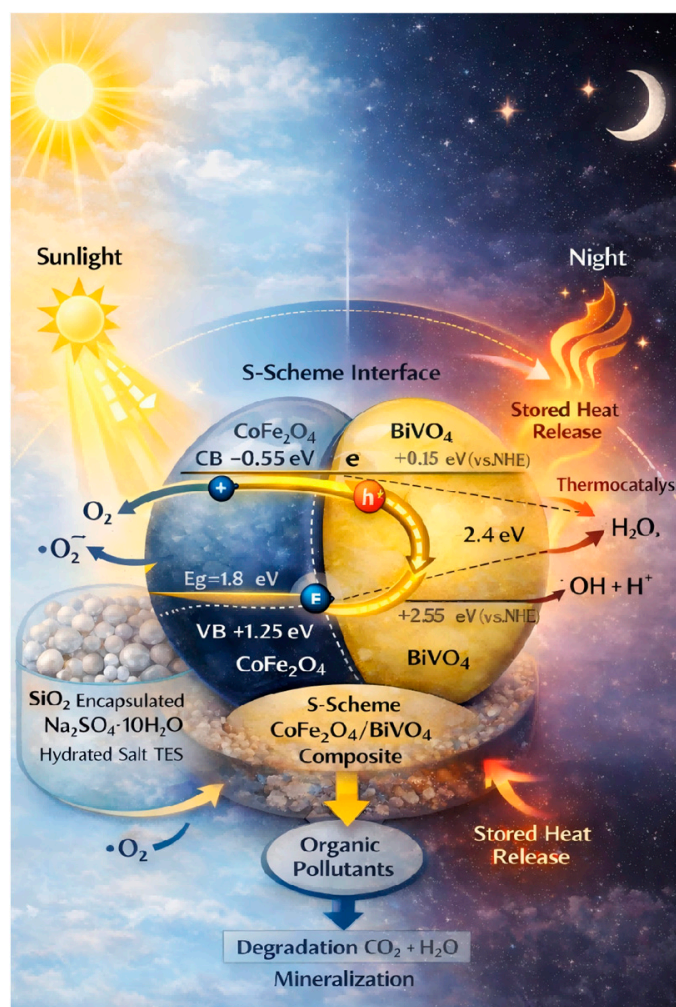


Figure 13. Photocatalytic mechanism of the S-Scheme $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ heterojunction composite material.

As summarized in Table 1, $\text{CoFe}_2\text{O}_4/\text{BiVO}_4$ -based heterojunction photocatalysts have demonstrated significantly enhanced visible-light-driven degradation performance toward organic pollutants. The improvement is generally attributed to effective interfacial charge separation and the formation of S-scheme heterojunctions, which preserve strong redox potentials for reactive oxygen species generation.

Table 1. Summary of recent studies on CoFe₂O₄/BiVO₄-based photocatalysts for environmental remediation under visible-light irradiation.

Photocatalyst	Light Source	Target Pollutant	Photocatalytic Performance	Ref.
CoFe ₂ O ₄ /BiVO ₄ nanocomposite	Visible light ($\lambda > 420$ nm)	Methylene blue (MB)	~72.5% degradation; enhanced activity compared with pristine CoFe ₂ O ₄ and BiVO ₄ due to heterojunction formation	[20]
Graphene-supported CoFe ₂ O ₄ /BiVO ₄ heterocomposite	Visible light	Fast Sulphone Black dye	93.8% degradation; improved charge separation and recyclability induced by graphene support	[21]
CoFe ₂ O ₄ -BiVO ₄ photoelectrode (PEC system)	AM 1.5G simulated sunlight	Tetracycline (TC)	89.1% removal within 60 min; apparent rate constant of 0.037 min ^{−1} due to photoelectrocatalytic synergy	[22]
CoFe ₂ O ₄ /BiVO ₄ S-scheme heterojunction with thermal energy storage	Visible light and dark conditions (day–night cycle)	Organic dyes	Efficient visible-light photocatalytic degradation and sustained pollutant removal in dark conditions; enhanced charge separation and preserved strong redox ability via S-scheme charge transfer	This work

4. Conclusions

In summary, this study successfully engineered an integrated system combining an S-scheme CoFe₂O₄/BiVO₄ heterojunction with thermal energy storage (TES) to tackle the challenge of solar intermittency in wastewater treatment. The optimized 0.5:0.5 heterojunction delivered exceptional daylight performance (98% RhB removal in 6 h) by effectively suppressing charge recombination and enhancing radical generation via the S-scheme pathway. More significantly, the SiO₂-encapsulated Na₂SO₄·10H₂O microcapsules effectively stored surplus solar heat and released it at night, maintaining reactor temperatures above 35 °C for 12 h. This thermal buffering enabled a 64% thermocatalytic degradation efficiency in the dark, resulting in a cumulative diurnal efficiency of over 82%. The system proved to be practical and robust, showing high magnetic recovery rates (98%), stability in high-salinity environments, and excellent durability over five cycles. Furthermore, Life Cycle Assessment (LCA) confirmed the environmental viability of this approach, revealing a 40% reduction in energy consumption compared to conventional UV/TiO₂ systems. By unifying efficient photocatalyst design with thermal resilience, this work establishes a sustainable framework for continuous, all-weather industrial wastewater remediation. Future work will focus on the industrial scalability of the TES-integrated photocatalysts and their performance in complex multi-pollutant matrices, providing a sustainable pathway for carbon-neutral wastewater remediation.

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Conflicts of Interest: Author Jiao Xu was employed by the company HE Harbin Power Plant Valve Company Limited. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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