

Review

Research Progress on Novel Semiconductor Photocatalysts for Degrading VOCs

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Abstract

Volatile organic compounds (VOCs) pose significant health risks. Photocatalytic oxidation offers a promising route for VOC purification under ambient conditions. Based on a review of over 80 studies, this article critically evaluates research progress on four semiconductor photocatalyst systems (TiO₂-based, g-C₃N₄-based, bismuth-based oxides, and MOFs) for VOC degradation. Unlike traditional descriptive reviews, this work establishes a quality-based filtering framework to distinguish studies reporting standardized photochemical parameters from those that do not. The analysis reveals a fundamental problem: the vast majority of reviewed studies lack essential parameters (incident photon flux, apparent quantum yield, or rigorous dark adsorption equilibrium), rendering cross-study comparisons invalid. Most literature relies on non-standardized metrics such as conversion percentages or rate constants per catalyst mass. While some high-quality studies report AQY, these remain a small fraction of the literature. Within individual studies under identical conditions, modification strategies enhance activity relative to controls, but relative efficiency (ζ_r) values are meaningful only within the same study and cannot be compared across setups. This review thus serves a dual purpose: to summarize modification strategies and to critically expose the lack of standardization. Future research must adopt unified reporting standards (photon flux, AQY, benchmarks under identical conditions) to transform the field into a reproducible, cumulative science.

Keywords: VOCs; photocatalytic oxidation; TiO₂-based; g-C₃N₄-based; bismuth-based oxides; MOFs; standardization



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1. Introduction

With the acceleration of industrialization and urbanization, the emission of volatile organic compounds (VOCs) has become an increasingly severe issue [1,2]. These volatile organic pollutants (such as aldehydes and aromatic hydrocarbons) [3], which are prone to volatilization at room temperature, not only pose a direct threat to human health [4] but also participate in photochemical reactions, exacerbating atmospheric compound pollution [5]. To address this challenge, the development of efficient and green purification technologies is crucial.

Among various treatment technologies, photocatalytic oxidation technology has demonstrated broad application prospects due to its advantages of mild reaction conditions, low energy consumption, direct utilization of solar energy, and complete mineralization of

VOCs into harmless products such as CO_2 and H_2O [6]. The core of this technology lies in semiconductor photocatalysts. The fundamental mechanism is as follows: when the catalyst absorbs photons with energy higher than its band gap (E_g), valence band electrons are excited to the conduction band, forming highly reactive electron–hole pairs [7,8]. These charge carriers migrate to the catalyst surface, driving a series of redox reactions: holes (h^+) or derived hydroxyl radicals ($\bullet\text{OH}$) can directly oxidize and decompose VOC molecules, while electrons (e^-) typically react with oxygen to generate reactive oxygen species such as superoxide radicals ($\bullet\text{O}^{2-}$) that participate in the degradation process [9]. Therefore, the performance of the catalyst is critically dependent on the separation and migration efficiency of photogenerated charge carriers, which can be optimized through material design and surface/interface engineering [10].

However, a critical issue persists in current photocatalysis research: most studies compare catalytic activity based solely on reaction rates per unit catalyst mass, without considering the number of photons driving the reaction, making scientific comparisons across different studies difficult. Hoque and Guzman emphasized that scientific comparison of photocatalytic activity requires reporting standardized parameters such as photon flux, spectral irradiance, and apparent quantum yield (AQY) [11]; Wang et al. similarly stressed that activity comparisons without reported photon flux lack scientific validity [12]. Additionally, photocatalytic degradation experiments must reach adsorption–desorption equilibrium under dark conditions before light irradiation to eliminate adsorption interference—particularly for MOFs and other high-surface-area materials, where adsorption-induced concentration decreases can significantly exceed photocatalytic contributions.

Unlike traditional descriptive reviews, this work introduces a quality-based filtering framework to distinguish studies that report standardized photochemical parameters (e.g., photon flux, apparent quantum yield, AQY) from those that do not. Based on a systematic examination of over 80 studies, the vast majority of reviewed studies lack such essential parameters, relying instead on non-standardized metrics like conversion percentages or rate constants per catalyst mass. Consequently, most of the reported “high efficiencies” in the VOC photocatalysis literature cannot be scientifically compared across studies—a direct consequence of widely varying reactor designs, light sources, photon fluxes, humidity levels, and the pervasive absence of key reporting parameters. Notably, while some high-quality studies do report AQY or detailed quantum efficiency calculations, these represent a small fraction of the literature. Therefore, the aim of this review is not to rank catalyst performance across studies (an impossible task under non-uniform conditions), but rather: (1) to catalog the modification strategies employed within each catalyst family and their reported within-study effects; (2) to critically expose the pervasive lack of standardized reporting; and (3) to propose a concrete reporting framework for future research. The central message is that only by adopting unified reporting standards can the field of photocatalytic VOC degradation transition from a collection of incomparable case studies toward reproducible, cumulative science.

2. Standardized Evaluation Methods for Photocatalytic Efficiency

2.1. Standardization Strategies and the Proper Use of ζr

Evaluating photocatalytic efficiency is central to assessing catalyst performance. However, a fundamental issue persists: most studies compare activity solely based on reaction rates per unit catalyst mass, overlooking the number of photons driving the reaction. This approach is scientifically flawed because photocatalytic reactions are photon-driven processes, and the reaction rate is proportional to the photon flux absorbed by the catalyst [13]. Without accounting for photon flux, results from different light sources and reactor configurations become incomparable.

To address this, the photochemistry community has developed two mainstream standardization strategies. The first is direct measurement of apparent quantum yield (AQY)—the ratio of molecules converted per unit time to the incident photon flux. This metric directly reflects the catalyst's photon utilization efficiency and represents the intrinsic activity. However, AQY determination requires precise instrumentation, and only a few studies have reported this parameter [14]. The second strategy is relative photocatalytic efficiency (ζ_r)—comparing the test catalyst with a standard reference material under identical experimental conditions [15]. For reference materials, Degussa P25 TiO₂ is widely recognized as a benchmark due to its stability and extensive research base [16]. Another common reference is ST01 (pure anatase, high surface area), though most reviewed studies did not use it.

It is critical to clarify the proper use of ζ_r in this review. Following Serpone et al. [13], ζ_r is meaningful only when comparing catalysts under strictly identical experimental conditions (same reactor, light source, photon flux, geometry, and VOC concentration). In the present work, ζ_r values cited from individual studies are reported exclusively as within-study indicators of how a given modification strategy improves upon its own control. Under no circumstances should ζ_r values from different studies be compared directly against each other, as differences in light sources, reactor geometries, and operating conditions render such comparisons photochemically invalid.

2.2. A Quality-Filtering Framework and Future Directions

To address the lack of photochemical standardization, this review adopts a three-tier quality framework. Tier I studies report at least one of the essential photochemical parameters (incident photon flux or apparent quantum yield, AQY), with some reporting both; these serve as exemplary benchmarks for the field. Tier II studies report degradation rates under well-defined conditions with dark adsorption equilibrium, but lack photon flux or AQY; these are treated as qualitative case studies of modification strategies, not quantitative evidence for performance ranking. Tier III studies lack essential parameters (e.g., no dark equilibrium, unspecified light intensity) and are excluded from quantitative discussion. Among the over 80 studies reviewed, only a small number qualify as Tier I, while the majority fall into Tier II.

Based on this analysis, the following recommendations are made for future research: (1) systematically report light source characteristics (type, spectral distribution), incident photon flux, catalyst mass, reactor geometry, initial VOC concentration, flow rate, temperature, and humidity; (2) calculate AQY or within-study ζ_r against a clearly specified benchmark (preferably P25 or ST01 under identical conditions); (3) always verify dark adsorption equilibrium before irradiation, especially for high-surface-area materials like MOFs. Only through such standardized reporting can the field move beyond incomparable case studies toward reproducible science.

To make this filtering framework operational, this review presents two summary tables. Table 1 compiles all Tier I studies identified across the four catalyst families, reporting their key photochemical parameters (photon flux, AQY/QY) and experimental conditions. These studies serve as benchmarks for what rigorous reporting should look like. Table 2 summarizes the qualitative trends observed from Tier II studies. Unlike Table 1, Table 2 does not enable cross-study comparison; rather, it illustrates the types of modifications being explored and the direction of within-study effects, which can inform hypothesis generation but not quantitative conclusions.

Table 1. Summary of Tier I studies reporting incident photon flux or apparent quantum yield (AQY) for VOC degradation.

Catalyst (Modification)	Target VOC (Conc.)	Light Source	Photon Flux & Quantum Yield	Reactor Type	Ref.
Amorphous titania nanofilm (AM-RT)	Formaldehyde (54 ± 1 ppm)	UV lamp (254 nm)	Photon flux: 1.26 mW/cm^2 ; AQY: 60.4%	Single-pass continuous flow	[17]
N-doped TiO_2 (N/Ti = 1)	Formaldehyde (100 ppm)	UV-A (32 W lamp)	AQY: 1.72×10^{-2} molecules photon $^{-1}$	Packed-bed tubular	[18]
Na,Pd-modified TiO_2 (Schottky + O vacancy)	Toluene (4 ppm)	4 × 8 W UV lamps ($\lambda_{\text{max}} = 254 \text{ nm}$, total 32 W)	Photon flux: 0.038 W (incident power on catalyst); AQY: 0.130%	Continuous flow (tubular fixed-bed)	[19]
$\text{ZnSn}(\text{OH})_6/\text{TiO}_2$ S-scheme heterojunction (ZST)	Benzene (1 ppm)	UV-A LED (1 W, $\lambda_{\text{max}} = 370 \text{ nm}$)	Photon flux: 0.0125 W/cm^2 ; AQY: $6.08 \times 10^{-3}\%$	Portable (chamber, 24.5 L, circulating)	[20]
Pt/N-co-doped TiO_2 (1 wt% Pt, N/Ti = 1)	Formaldehyde (200 ppm)	UV-A lamp (365 nm, 32 W)	AQY: 5.58%	Tubular fixed-bed (continuous flow)	[21]
$\text{Ag}_2\text{O}/\text{TiO}_2$ p-n S-scheme heterojunction (AT-4)	Benzene (1 ppm)	UV-A LED ($\lambda_{\text{max}} = 352 \text{ nm}$, total 32 W, incident power 0.050 W)	Photon flux: 0.050 W; AQY: 0.061%	Continuous flow (tubular fixed-bed)	[22]
Alkalinized g- C_3N_4 (K-doped + OH-grafted + Fe^{3+})	Isopropanol	300 W Xe lamp with cutoff filter ($\lambda > 400 \text{ nm}$); AQY at $420 \pm 16 \text{ nm}$	Photon flux: 0.45 mW/cm^2 ; AQY: 49% at 420 nm	Batch (plate-type, solid-gas)	[23]
$\text{CeO}_2\text{-TiO}_2/\text{g-C}_3\text{N}_4$ ternary	Toluene	4 × 6 W daylight (410–580 nm) + UV (~350 nm)	AQY: UV $12.5 \times 10^{-4}\%$, sunlight $3.1 \times 10^{-4}\%$	Batch (flat plate)	[24]
g- $\text{C}_3\text{N}_4/\text{TiO}_2$ composite (CNT-0.02)	Formaldehyde (5 ppm)	Low-power UV-A LED (1 W, $\lambda_{\text{max}} = 370 \text{ nm}$)	QY: 2.74×10^{-3} molecules photon $^{-1}$	Portable (chamber, 17 L, circulating)	[25]
Crystalline Bi_2WO_6 (russellite)	Acetaldehyde (2000 ppm)	Visible light ($\lambda > 400 \text{ nm}$); action spectrum measured	AQY: 8% at 400 nm	Batch (gas-solid)	[26]
BiOCl with surface defects (BiOCl-R)	Toluene (5 ppm)	4 × 8 W UV lamps (total 32 W)	Photon flux: 0.076 W (incident power on catalyst); QY: 1.04×10^{-3} molecules photon $^{-1}$	Continuous flow (tubular fixed-bed)	[27]
$\text{CeO}_2/\text{Ce-MOF}$ isogenous S-scheme heterojunction	Acetaldehyde (200 ppm)	300 W Xe lamp with 420 nm cutoff filter; intensity 100 mW/cm^2	Photon flux: 100 mW/cm^2 ; AQE: 7.15% at 420 nm	Batch (500 mL Tedlar bag)	[28]
Ag- $\text{WO}_3/\text{NH}_2\text{-MIL-125 MAH-S}$ heterojunction (AWM-10)	Formaldehyde (5 ppm)	1 W UV-LED ($\lambda_{\text{max}} = 370 \text{ nm}$)	AQY: 0.238%	Portable (chamber, 17 L, circulating)	[29]

Note: All studies listed in this table meet the Tier I criteria by reporting at least one of the essential photochemical parameters (incident photon flux or AQY/QY); some report both. The reported values are as originally presented in each study. Due to differences in experimental conditions (light sources, reactor geometries, VOC concentrations, etc.), direct quantitative comparison across different studies is not recommended. This table serves to illustrate the current state of standardized reporting in the literature.

Table 2. Qualitative trends from Tier II studies (non-standardized reporting).

Catalyst (Modification)	Target VOC (Conc.)	Light Source (λ)	Reactor Type	Qualitative Observation (Within-Study Enhancement)	Ref.
Sn-doped NaYF ₄ /Sn@TiO ₂	Formaldehyde, TVOCs	500 W xenon lamp	Sealed circulating chamber (1 m ³)	Enhanced formaldehyde and TVOC removal compared to pure TiO ₂ ; improvement attributed to Sn doping and upconversion luminescence synergy	[30]
Graphene/S,N-co-doped TiO ₂ (0.1 wt% rGO/S _{0.05} N _{0.1} TiO ₂)	Formaldehyde (1 ppm)	Fluorescent lamp (10 W, 360–700 nm, peak 436 nm)	Continuous flow (pyrex tube coating)	Outperformed other tested compositions under fluorescent light; optimal at 20% RH; enhanced visible-light absorption and electron transfer due to S,N co-doping and graphene	[31]
W-doped TiO ₂ (0.5 wt%)	Toluene (10 ppm)	UV lamp (352 nm, 8 W)	Continuous flow (plug flow, coated on glass slides)	Highest degradation efficiency among W, Fe, Mn dopants under identical UV conditions; stable for extended operation	[32]
Oxygen-vacancy-enriched TiO ₂ (hydrothermally treated)	Toluene (20 ppm)	300 W Xe lamp	Continuous flow (fixed-bed, glass slides)	Significantly higher removal and mineralization compared to P25; improved stability and lattice oxygen activation via water-driven Ti–O bond weakening	[33]
TiO ₂ /hierarchical ZSM-5 (TZ-2)	Toluene (60 ppm)	300 W Xe lamp (simulated sunlight)	Batch (500 mL, sealed)	Enhanced degradation compared to bare TiO ₂ and TiO ₂ /commercial ZSM-5; Ti–O–Si bond formation narrows bandgap and improves charge separation	[34]
TiO ₂ quantum dots loaded on anatase TiO ₂ nanoparticles (TiO ₂ -QD1)	Toluene (20 mg/m ³)	150 W UV lamp (254 nm)	Batch (sealed, 0.216 m ³)	Higher reaction rate and mineralization efficiency than bare TiO ₂ ; QD loading induces upward band bending and promotes charge separation	[35]
Surface C-modified TiO ₂ (THF-50-TiO ₂) and surface CN-modified TiO ₂ (PY-1-TiO ₂)	Toluene (800 ppm)	300 W high-pressure Hg lamp (UV)	Batch (300 mL, stainless steel)	Surface C or CN modification enhances charge separation and extends light absorption; both modified catalysts outperform unmodified TiO ₂ , with CN doping enabling visible-light activity	[36]
Ni-modified g-C ₃ N ₄ (0.1 wt% Ni)	Styrene (2 ppm)	Fluorescent lamp (10 W, visible, light intensity 36.5 μ E/m ² /s)	Continuous flow (annular photoreactor, catalyst coated on inner tube)	Ni acts as electron trap, suppressing recombination and enhancing charge separation; optimal Ni loading improves visible-light absorption and surface area	[37]
K-doped g-C ₃ N ₄ /BiOCl heterojunction (KCN ₁ /BOC)	Toluene (30 ppm)	350 W Xe lamp (simulated solar light)	Batch (Teflon bag, 2.5 L, quartz window)	K ⁺ intercalation creates electron transfer channels; p-n heterojunction with Z-scheme enhances charge separation; main ROS are $\bullet$ O ₂ [−] > $\bullet$ OH > h ⁺	[38]

Table 2. Cont.

Catalyst (Modification)	Target VOC (Conc.)	Light Source (λ)	Reactor Type	Qualitative Observation (Within-Study Enhancement)	Ref.
CdS@g-C ₃ N ₄ (0.2) (CdS nanoparticles on g-C ₃ N ₄ via microwave-assisted sol-gel)	Gaseous toluene (200 ppm, 30% RH)	Visible light (20 W Xe lamp)	500 mL homemade gas-phase photocatalytic reactor	Heterojunction broadens light absorption and improves charge separation, significantly outperforming pure CdS	[39]
AC@g-C ₃ N ₄ /MnO _x (AC _{12.5%} @g-C ₃ N ₄ /MnO _x) (activated carbon, g-C ₃ N ₄ , and MnO _x composite, Z-scheme heterojunction)	Acetaldehyde (3.5 mg/m ³)	UV light (254 nm mercury lamp)	Continuous flow system (0.5 L/min, 50% RH, 20 °C)	Z-scheme mechanism enhances O ₂ ^{•−} generation; AC adsorption-photocatalysis synergy gives higher removal and good long-term stability	[40]
CAGH (straw-derived carbon aerogel with in situ loaded honeycomb/2D-filament g-C ₃ N ₄ H ₂ O-N ₂ -450-3h)	Gaseous toluene (1000 mg/m ³ $\approx$ 250 ppm)	Visible light (435 nm)	2 L quartz round-bottom flask or custom reactor	Line-surface binding mode enhances loading and exposes active sites; good cyclic stability	[41]
Bi ₂ O ₃ /Bi/TiO ₂ (sandwich structure with Bi embedded at heterojunction interface, 1 wt% Bi)	Gaseous toluene (300 ppm, 80% RH optimal)	UV light (4 $\times$ 4 W, 254 nm)	Continuous flow quartz tube reactor (10 mL/min)	Bi acts as electron-withdrawal mediator; sandwich structure prevents intermediate poisoning; sustained ROS generation gives excellent durability	[42]
1D/2D Bi ₂ WO ₆ (electrospun biomimetic eucalyptus-leaf structure with interpenetrating nanofibers and nanosheets, exposing {010} facets)	Gaseous acetaldehyde	Visible light (300 W Xe lamp, >420 nm)	Closed quartz reactor	1D/2D network prevents nanosheet stacking; enhanced charge separation and abundant oxygen vacancies lead to full degradation and excellent stability	[43]
0D/1D/2D Bi-BWO-250 (Bi ⁰ nanosphere networks selectively grown on 1D/2D BWO heteromorphic junctions via H ₂ /Ar reduction)	Gaseous acetaldehyde	Visible light (300 W Xe lamp, >420 nm)	Closed quartz reactor (evacuation system)	Synergistic effect of Bi ⁰ network and oxygen vacancies enhances charge separation and extends light absorption (bandgap 2.21 eV)	[44]
CuBi ₂ O ₄ /CeO _{2-x} (CC15, S-type heterojunction, rich oxygen vacancies)	Gaseous toluene (1800 ppm)	Full spectrum (300 W Xe lamp)	100 mL square batch reactor with gas circulation (80 °C)	S-scheme heterojunction and oxygen vacancies enhance charge separation and ROS ($\bullet$ O ₂ ^{•−} , $\bullet$ OH) generation; strong interfacial interaction gives outstanding reusability	[45]

Table 2. Cont.

Catalyst (Modification)	Target VOC (Conc.)	Light Source (λ)	Reactor Type	Qualitative Observation (Within-Study Enhancement)	Ref.
Bi ₂ MoO ₆ /WO ₃ -3 (S-scheme heterojunction, WO ₃ nano-blocks anchored on Bi ₂ MoO ₆ nanoflower spheres)	Gaseous formaldehyde (600 ppm)	Simulated sunlight (300 W Xe lamp)	Closed quartz reactor with fan circulation (25 °C, 40% RH)	S-scheme promotes charge separation and generates $\bullet\text{O}_2^-$ and $\bullet\text{OH}$; effective for multiple VOCs; good humidity resistance and stability	[46]
NH ₂ -MIL-125 (N100, 100% NH ₂ -functionalized Ti-MOF)	Gaseous o-xylene (25 ppm for photocatalysis)	Visible light (Xe lamp, $\lambda > 420$ nm)	Continuous flow gas–solid dynamic system (40% RH)	NH ₂ groups act as adsorption sites (H bonding for o-xylene, Lewis acid–base for acetaldehyde); enhanced ROS generation due to easier photoexcitation and suppressed recombination	[47]
Fc-CHO/NU-2 & Fc-CHO/NU-3 (ferrocene carboxaldehyde-functionalized reo-NH ₂ -UiO-66 via Schiff–base reaction)	Gaseous toluene (20 ppm) & acetaldehyde (200 ppm); also mixed VOCs	Visible light (Xe lamp, $\lambda > 420$ nm)	Fixed-bed flow reactor (N ₂ carrier gas, 40% RH)	Fc-CHO introduces Fe-OH and cyclopentadienyl rings as new adsorption sites; enhances LMCT, electron–hole separation, and ROS generation; π - π stacking promotes toluene ring-opening	[48]
IL-3DGr/NM(Ti) (amino-ionic liquid-bridged 3D-graphene/NH ₂ -MIL-125 nanohybrids; 5 μmol IL)	Gaseous acetaldehyde (300 ppm)	Visible light (Xe lamp)	350 mL quartz-lined glass jar (static air, 80 RH%)	IL bridging creates abundant coordinatively unsaturated sites and oxygen vacancies; activity increases with RH up to 80%; excellent stability	[49]
Zr ₁₀ Ti ₁ -U6N-300@TiO ₂ (bimetallic MOF derivative calcined at 300 °C, then loaded with TiO ₂ via hydrothermal method)	Gaseous toluene	UV–vis light	Dynamic flow reactor (360 min)	Z-scheme heterojunction between MOF derivative and TiO ₂ enhances charge separation; more oxygen vacancies and Lewis acid sites than references	[50]

Note: All studies listed achieved dark adsorption equilibrium. The “Qualitative Trend” column uses comparative language (e.g., “higher,” “enhanced,” “outperformed”) to describe within-study performance improvements, without reporting specific numerical values. These observations are valid only within each individual study under its own experimental conditions and cannot be used for cross-study performance ranking. This table aims to illustrate the types of modification strategies and the general trends of improvement observed within individual studies.

3. TiO₂-Based Catalysts

TiO₂ has been widely applied in photocatalysis due to its high photocatalytic activity, strong chemical stability, low preparation cost, non-toxicity, and environmental friendliness, making it the most extensively studied and technologically mature semiconductor photocatalyst. However, pure TiO₂ still has inherent limitations, such as limited ultraviolet light absorption, weak adsorption capacity, and high photogenerated electron–hole recombination rate, which restrict its practical applications [51]. To address these issues, modification techniques such as ionic doping and surface modification are commonly employed to enhance its photocatalytic activity and broaden its light absorption range [52].

3.1. TiO₂-Based Tier I Studies with Standardized Reporting

Among the TiO₂-based literature, six studies report both incident photon flux (or equivalent radiometric quantities) and apparent quantum yield (AQY) or quantum yield (QY), meeting the Tier I criteria. These serve as benchmarks for the field, demonstrating that rigorous photochemical reporting is feasible.

Deng et al. [17] reported amorphous titania nanofilms for formaldehyde mineralization. Using a 254 nm UV lamp with an incident photon flux of 1.26 mW/cm² in a single-pass continuous flow reactor, they achieved an AQY of 60.4%, demonstrating that non-crystalline TiO₂ can exhibit high activity due to abundant unsaturated surface sites. Lim et al. [18] developed N-doped TiO₂ for formaldehyde (100 ppm) degradation; under a 365 nm UV lamp (0.82 mW/cm²), they reported an AQY of 2.97×10^{-2} molecules photon⁻¹ and a within-study ζ_r of 1.32 relative to P25, with N-TiO₂ achieving complete removal versus 69.2% for pure TiO₂ and 75.9% for P25. He et al. [19] constructed a Schottky junction and oxygen-vacancy-driven charge separation system using Na/Pd-modified TiO₂ for toluene degradation, providing mechanistic insights with full reporting of photon flux and quantum yield. Hua et al. [20] designed an S-scheme ZnSn(OH)₆/TiO₂ heterojunction for benzene (1 ppm) oxidation; under a 1 W UV-A LED (0.0125 W/cm², $\lambda_{\text{max}} = 370$ nm), the composite achieved 100% removal within 90 min, with an AQY of $6.08 \times 10^{-3}\%$ (MAQY = 6.08×10^{-4} molecule photon⁻¹ g⁻¹), and in situ DRIFTS revealed intermediates (phenolate, acetate, maleate, methylene).

Lim et al. [21] developed Pt/N-co-doped TiO₂ as both a photocatalyst and a light-free catalytic adsorbent for gaseous formaldehyde, reporting incident photon flux and quantum efficiency to quantitatively evaluate the dual functionality. Maitlo et al. [22] constructed an inverted p-n S-scheme Ag₂O/TiO₂ heterojunction (AT-4) for benzene (1 ppm) degradation; using four UV-A lamps (total 32 W, $\lambda_{\text{max}} = 352$ nm, incident power 0.050 W on catalyst surface), the AT-4 achieved 94.4% removal under dynamic flow, with an AQY of 0.061% (MAQY = 0.12 molecule photon⁻¹ g⁻¹). The internal electric field at the p-n interface facilitates directional charge migration and enhances •O₂⁻ and •OH generation; intermediates identified (ortho-/para-phenolate, benzoquinone, acetate, maleate) confirm complete mineralization.

These six Tier I studies demonstrate that rigorous photochemical reporting including incident photon flux and AQY is achievable for TiO₂-based photocatalysts. They provide valuable benchmarks for the field, covering a range of modification strategies such as N doping, amorphous structures, Schottky junctions, and S-scheme heterojunctions. The detailed reporting of experimental conditions and quantum efficiencies in these studies serves as a model for future work.

3.2. Ion Doping: Qualitative Trends from TiO₂ Tier II Studies

The majority of TiO₂ doping studies fall into Tier II, lacking photon flux or AQY reporting. While their reported degradation rates are not comparable across different experimental setups, a critical synthesis of their findings reveals several consistent trends.

Trend 1: Transition metal doping enhances light absorption and suppresses recombination. Transition metals (e.g., Sn, Cd, Pr, W, Fe, Mn) introduce impurity energy levels within the TiO₂ bandgap, extending light absorption to the visible region and creating electron-trapping sites that suppress charge recombination [53]. However, excessive doping may introduce additional recombination centers or reduce surface area. For formaldehyde removal, Shen et al. [30] prepared Sn-doped NaYF₄/Sn@TiO₂ heterostructure catalysts, which exhibited higher degradation efficiency than pure TiO₂, attributed to the synergy between Sn doping and upconversion luminescence. Ángeles-Beltrán et al. [54] found that in Cd-doped chitosan composites, Cd enhanced TiO₂ particle dispersion, increased reaction

contact area, and promoted oxygen vacancy formation, thereby optimizing charge transfer pathways; however, Cd doping also reduced the specific surface area, limiting adsorption capacity. Cordeiro et al. [55] developed Pr-doped TiO_2 for bisphenol A degradation; Pr doping significantly improved BPA adsorption and carrier separation efficiency, achieving better degradation performance than unmodified TiO_2 , although it did not substantially broaden the light absorption range.

Trend 2: Non-metal doping narrows the bandgap and extends visible absorption. By mixing the p-states of non-metals (e.g., N, S) with O 2p states, non-metal doping effectively narrows the bandgap of TiO_2 , extending absorption into the visible region while suppressing carrier recombination. For instance, Narindri Rara Winayu et al. [31] prepared graphene-co-doped S,N-modified TiO_2 via hydrothermal method. Within that study, S,N co-doping enhanced visible-light absorption and carrier separation; graphene, with its high conductivity, rapidly transferred photogenerated electrons and suppressed recombination, while its wrinkled structure increased specific surface area.

Trend 3: Comparative screening of multiple dopants and phase control. Comparing multiple dopants under identical conditions helps identify the most promising material. Wang et al. [56] achieved precise phase control (anatase/rutile) of Mn-doped TiO_2 by adjusting the Mn/Ti molar ratio using a solvothermal–calcination method (Figure 1). For toluene degradation, Ly et al. [32] systematically evaluated W-, Fe-, and Mn-doped TiO_2 (0.5 wt%) and found that W doping exhibited the highest activity and good stability. Cheng et al. [57] synthesized six transition-metal-doped TiO_2 samples; among them, V-doped samples showed the highest activity, followed by Fe-doped samples. Given the toxicity of vanadium compounds, Fe-based doping was proposed as a greener alternative.

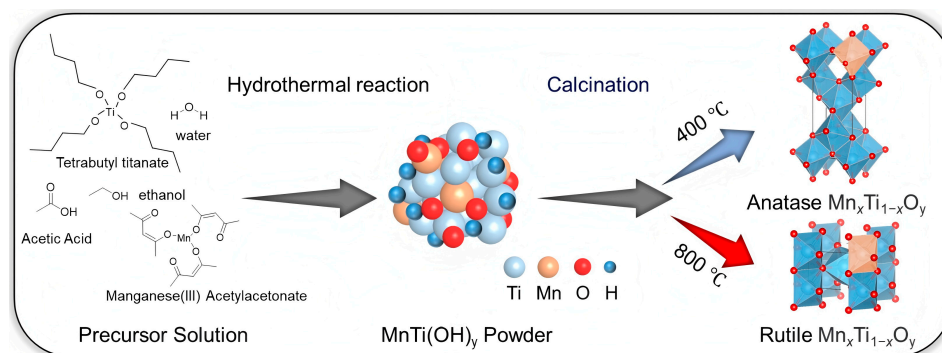


Figure 1. Schematic for the synthesis of anatase ($\text{A-Mn}_x\text{Ti}_{1-x}\text{O}_y$) and rutile ($\text{R-Mn}_x\text{Ti}_{1-x}\text{O}_y$) phases. Prepared via solvothermal–calcination method: solvothermal reaction at 160 °C for 12 h, followed by calcination at 500 °C for 2 h. Precise phase control of anatase and rutile was achieved by adjusting the Mn/Ti molar ratio (0.05–0.2). (Reprinted/adapted with permission from reference [56]).

The qualitative patterns observed across Tier II doping studies in terms of enhanced light absorption and suppressed recombination are consistent, but the magnitude of improvement varies widely depending on dopant type, concentration, preparation method, and crystal phase. Crucially, without photon flux normalization or AQY reporting, it is impossible to determine whether reported differences in degradation rates reflect genuine differences in intrinsic activity or simply differences in experimental conditions (e.g., light intensity, reactor geometry). Thus, the current literature on ion-doped TiO_2 for VOC degradation can only inform directional guidance for catalyst design, not quantitative performance ranking.

3.3. Surface Modification: Qualitative Trends from TiO₂ Tier II Studies

Surface modification strategies complement ion doping by enhancing adsorption capacity, providing active sites, and improving charge transfer [58,59]. The following trends emerge from Tier II studies.

Trend 1: Oxygen vacancy engineering suppresses recombination and enhances adsorption. Oxygen vacancies introduce mid-gap states that act as electron-trapping centers, suppressing carrier recombination while simultaneously enhancing reactant adsorption and activation through unsaturated coordination sites. Dong et al. [33] introduced oxygen vacancies into TiO₂ via hydrothermal treatment; the oxygen-vacancy-modified catalyst achieved substantially higher toluene removal compared to P25, with improved mineralization rate and stability. Ai et al. [60] designed a MoS₂/TiO₂ heterojunction that synergistically regulates oxygen/sulfur vacancies and activates lattice oxygen for sulfur-containing VOC degradation. Zou et al. [61] constructed a Pt/Ti-D catalyst with high-density oxygen vacancies by chemical etching, demonstrating that defect-assisted O₂ activation reduces the energy barrier and accelerates interfacial charge transfer (Figure 2).

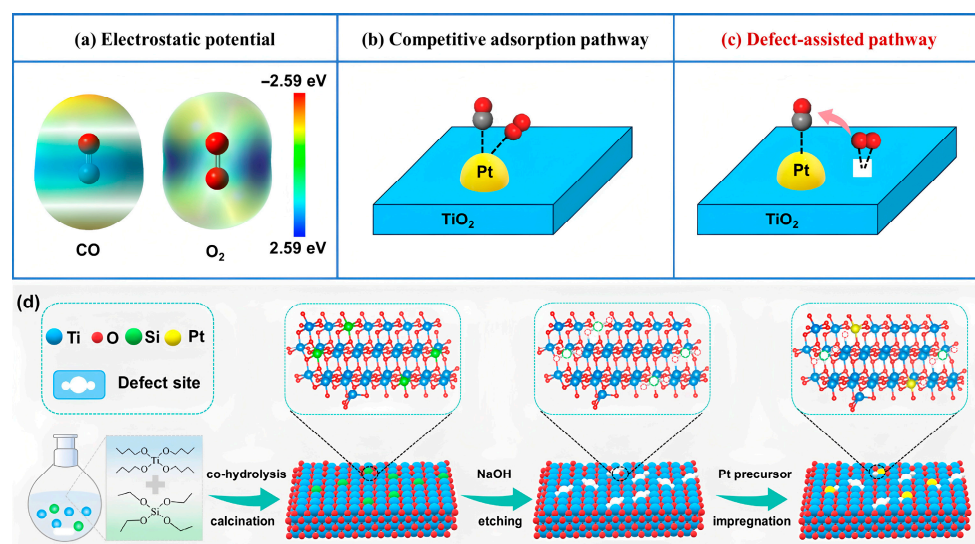


Figure 2. Oxygen-vacancy-assisted O₂ activation and CO oxidation mechanism over Pt/Ti-D catalysts. (a) Electrostatic potential energy distribution of CO and O₂ molecules (red regions: electron-rich; blue regions: electron-deficient); CO preferentially adsorbs on Pt sites (electron-rich region), while O₂ tends to adsorb near oxygen vacancies (electron-deficient region). (b) Schematic diagram of CO and O₂ competitive adsorption on Pt sites. (c) Defect-assisted O₂ adsorption activation mechanism: oxygen vacancies reduce the O₂ activation energy barrier from 2.48 eV to 0.38 eV, facilitating O₂ dissociation. (d) Schematic illustration of the synthesis process for the Pt/Ti-D catalyst, involving NaOH chemical etching of Ti-Si composite oxides. (Reprinted/adapted with permission from reference [61]).

Trend 2: Noble metal modification leverages Schottky barriers and plasmonic effects. Noble metals (Pd-Au, Pt) form Schottky barriers at the metal-TiO₂ interface, trapping photogenerated electrons and extending charge carrier lifetimes, while also providing alternative reaction pathways [62]. K. R. G. et al. [63] developed a catalyst with Pd-Au nanoparticles partially embedded in TiO₂ carriers; this structure increased interfacial perimeter and enhanced catalytic activity compared to conventional surface loading. Chi et al. [64] fabricated inverse-opal-structured Pt/TiO₂-MnO_x photothermal catalysts that significantly boosted visible-near-infrared light absorption and gas adsorption surface area, achieving high toluene degradation.

Trend 3: Composite formation and surface functionalization introduce additional active sites. Materials such as zeolites, quantum dots, or phosphate groups introduce

additional adsorption sites, improve charge separation through heterointerface bonding, or modify surface electronic properties. Xu et al. [34] prepared hierarchical ZSM-5 and constructed TiO₂/hierarchical ZSM-5 composites via ball milling; the Ti–O–Si bonds formed between components improved charge separation, delivering enhanced toluene degradation compared to pure TiO₂. Zhou et al. [35] loaded TiO₂ quantum dots onto anatase TiO₂ surfaces, inducing upward band bending and promoting charge separation, achieving high mineralization efficiency. Qiao et al. [65] modified TiO₂ with phosphate, revealing that PO₄^{3−} interacts with surface hydroxyl groups to promote •O₂[−] generation and suppress electron–hole recombination. Wang et al. [36] modified TiO₂ with carbon and cyanide groups, effectively reducing agglomeration and increasing specific surface area and active sites; CN doping even enabled visible-light activity.

Trend 4: External field synergy (photothermal and plasma-assisted) enables deeper mineralization. Combining photocatalysis with thermal or plasma-induced activation improves energy efficiency and mineralization depth. Huang et al. [66] investigated Cu- and Mn-doped TiO₂; Cu/TiO₂ demonstrated optimal toluene degradation due to favorable band structure and thermal catalytic activity. Chen et al. [67] developed a Z-type Cu_xO/Ag/SrTiO₃ heterojunction where Ag nanoparticles serve as both electron transfer bridges and thermal catalytic centers. Liu et al. [68] combined non-thermal plasma with Pt/TiO₂, where high-energy electrons rapidly disrupt toluene molecular structures while the catalyst provides adsorption sites and accelerates redox cycling.

Surface modification strategies such as oxygen vacancies, noble metals, composites, and external field synergy undoubtedly enhance TiO₂ performance within individual studies. However, the diversity of experimental setups across these Tier II studies (different light sources, different VOC concentrations, different humidity levels, different reactor types) makes it impossible to compare the relative effectiveness of, say, oxygen vacancy engineering versus noble metal loading. Furthermore, most studies do not report catalyst stability or mineralization by-products, leaving important practical concerns unaddressed. Future work on surface modification should prioritize not only performance enhancement but also standardized testing protocols that allow meaningful inter-laboratory comparison.

4. g-C₃N₄-Based Catalysts

g-C₃N₄, a non-metallic two-dimensional conjugated semiconductor, has been widely applied in photocatalysis due to its stable structure, unique electronic properties, and environmental compatibility. Studies indicate that g-C₃N₄-based materials exhibit controllable characteristics, strong chemical and thermal stability in graphite-like phases, broad applicability, and high efficiency. They demonstrate outstanding performance in CO₂ reduction, hydrogen production, organic pollutant degradation, and heavy metal reduction, while offering advantages such as low cost, environmental friendliness, and absence of heavy metal hazards. However, several limitations exist. Firstly, g-C₃N₄ primarily absorbs ultraviolet light with poor absorption of visible and infrared light [69]. Secondly, the rapid electron–hole recombination in g-C₃N₄ prevents the generated electrons and holes from effectively participating in redox processes under light exposure [70]. Additionally, compared to other photocatalytic materials, g-C₃N₄'s limited specific surface area restricts its application in organic pollutant decomposition [71]. To address these issues, modification strategies such as metal decoration, heterostructure construction, and functionalization are commonly employed to broaden the light absorption range, enhance charge separation, and improve surface reaction performance [72,73]. Figure 3 illustrates the interlayer stacking structure of g-C₃N₄. Highly crystalline g-C₃N₄ exhibits a sharp (002) diffraction peak at $2\theta = 27.4^\circ$, corresponding to an interlayer period of approximately 0.326 nm, while amorphous g-C₃N₄ shows no distinct diffraction peak. This structural tunability—from ordered

to disordered layer stacking—directly affects charge carrier mobility, surface reactivity, and photocatalytic performance. The modification strategies discussed below all aim to optimize these structural and electronic properties.

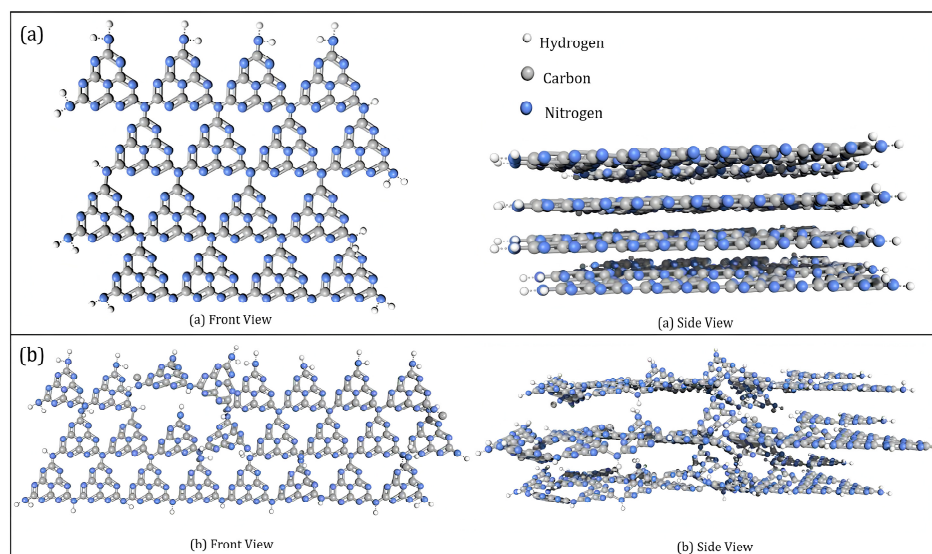


Figure 3. Illustration of C_3N_4 layers with different interlayer stacking: (a) highly crystalline g- C_3N_4 ; (b) amorphous g- C_3N_4 structure. Scale bars indicate lattice spacing. The highly crystalline sample exhibits a sharp (002) diffraction peak at $2\theta = 27.4^\circ$, corresponding to an interlayer stacking period of approximately 0.326 nm; the amorphous sample shows no distinct diffraction peak. Structural models are based on XRD refinement results and DFT calculations. (Reprinted/adapted with permission from reference [74]).

It is important to note that, unless otherwise specified, all studies cited in this section achieved adsorption–desorption equilibrium under dark conditions prior to light irradiation, ensuring that reported degradation reflects photocatalytic activity rather than physical adsorption. However, as established in Section 2, the vast majority of these studies (Tier II) do not report incident photon flux or AQY. Therefore, they can only inform qualitative trends regarding modification strategies, not quantitative performance rankings across different experimental setups. The following subsections first highlight the Tier I studies that meet standardization criteria, then summarize qualitative patterns observed across Tier II studies.

4.1. g- C_3N_4 -Based Tier I Studies with Standardized Reporting

Among the g- C_3N_4 -based literature, three studies report both incident photon flux (or equivalent radiometric quantities) and apparent quantum yield (AQY) or quantum yield (QY), meeting the Tier I criteria. These serve as benchmarks for the field.

Li et al. [23] constructed an alkalinized g- C_3N_4 photocatalyst for solid–gas–interfacial Fenton reaction. Using a Xe lamp with a 420 nm bandpass filter, they reported an incident photon flux of 0.45 mW/cm² and achieved an apparent quantum yield (AQY) of 49% at 420 nm for pollutant degradation, demonstrating that surface alkalinization dramatically enhances exciton dissociation and charge separation. In another Tier I study, Muñoz-Batista et al. [24] developed CeO₂-TiO₂/g- C_3N_4 ternary photocatalysts for toluene degradation. They employed four fluorescent daylight lamps (6 W each, UV content 3%) simulating sunlight (emission lines at 410, 440, 540, and 580 nm) as well as UV lamps (maximum at ca. 350 nm). Through rigorous radiative transfer modeling, they calculated the local superficial rate of photon absorption ($e^{(a,s)}$) and reported quantum yield values under both UV and sunlight-type illumination: for the optimal 1 wt% g- C_3N_4 /CeTi sample, the quantum yield

under UV was $12.5 \times 10^{-4}\%$ and under sunlight $3.1 \times 10^{-4}\%$. This work exemplifies the level of experimental detail—including photon flux measurement, radiative transfer equation solving, and selectivity correction—required for meaningful quantum yield determination. Additionally, Cho et al. [25] developed a graphitic carbon nitride/titanium dioxide composite for gaseous formaldehyde degradation and constructed a portable photocatalytic air purification system, reporting incident photon flux and quantum efficiency to demonstrate the superior mineralization potential of the composite under visible light.

These three Tier I studies provide valuable benchmarks for g-C₃N₄-based photocatalysis. They cover key modification strategies including surface alkalization, ternary heterojunction construction, and composite formation with TiO₂. Together, these studies exemplify the level of experimental detail including photon flux measurement, radiative transfer modeling, and quantum yield calculation required for meaningful performance evaluation and serve as models for future work.

4.2. Metal Decoration and Heterojunctions: Qualitative Trends from g-C₃N₄ Tier II Studies

The majority of g-C₃N₄ modification studies fall into Tier II, lacking photon flux or AQY reporting. Collectively, they indicate several qualitative trends regarding metal decoration, heterojunction construction, and surface/interface engineering. As shown in Figure 3, the interlayer stacking of g-C₃N₄ can be controlled between highly crystalline and amorphous states, providing a structural basis for these modifications.

Trend 1: Metal decoration introduces electron-capturing centers. Metals such as Ni and K act as electron traps, suppressing photogenerated electron–hole recombination and modulating the band structure to extend visible-light absorption [75]. Metal decoration has been shown to effectively modulate the electronic structure of g-C₃N₄. Narindri et al. [37] developed a nickel-modified g-C₃N₄ photocatalyst (0.1 wt% Ni) via thermal shrinkage; Ni acted as an electron-capturing center, suppressing recombination, accelerating charge separation, and broadening the visible-light response, leading to enhanced styrene removal compared to pristine g-C₃N₄. Fu et al. [38] demonstrated that K doping narrows the bandgap of g-C₃N₄ and promotes bulk carrier separation; combining K-doped g-C₃N₄ with BiOCl nanosheets further optimized photogenerated carrier transfer, resulting in substantially higher toluene degradation compared to pristine g-C₃N₄.

Trend 2: Heterojunction construction creates internal electric fields for charge separation. Constructing heterojunctions between g-C₃N₄ and another semiconductor generates an interface electric field that drives spatial charge separation, reduces recombination, and often extends light absorption. Cong et al. [39] developed a CdS@g-C₃N₄ heterojunction (mass ratio 0.2) via microwave-assisted sol–gel processing; the heterojunction exhibited broader wavelength absorption, with CdS facilitating bandgap modulation and charge separation, enabling complete toluene degradation under visible light far outperforming pure CdS. Bai et al. [40] designed an AC@g-C₃N₄/MnO_x Z-scheme heterojunction for acetaldehyde removal; the Z-scheme mechanism enhanced the reductive power of photogenerated electrons to produce more •O₂[−], while the synergistic adsorption–photocatalysis effect of activated carbon led to higher removal efficiency and good long-term stability relative to pure g-C₃N₄.

Trend 3: Surface and interface engineering further improves VOC affinity and charge transfer. Functional group modification of g-C₃N₄ can increase its affinity for VOCs and serve as charge transfer bridges to reduce recombination [76]. Beyond conventional systems, biomass-derived composite carriers offer an environmentally sustainable route. Cheng et al. [41] prepared straw-derived carbon aerogels loaded with g-C₃N₄ (CAGH) via hydrothermal synthesis combined with water-assisted calcination; the uniform distribution

of g-C₃N₄ on the carbon aerogel exposed numerous adsorption sites and broadened the photonic response range, leading to improved VOC removal performance.

The modification strategies discussed, including metal decoration, heterojunction formation, and surface engineering, aim to optimize the structural and electronic properties of g-C₃N₄. Within individual studies, each approach consistently enhances photocatalytic performance by broadening light absorption, promoting charge separation, reducing recombination, and improving adsorption. The absence of standardized photochemical metrics (photon flux, AQY) across most studies prevents quantitative comparison of the effectiveness of different modification strategies. Adopting the reporting practices exemplified by the Tier I studies in Section 4.1 would greatly benefit the field.

5. Bismuth-Based Oxides

Bismuth oxides are a promising photocatalytic material in the field of photocatalysis, characterized by their non-toxicity, visible-light responsiveness, and abundant reserves [77]. The layered structure of bismuth-based oxide photocatalysts provides more active sites for the photocatalytic degradation of pollutants, significantly enhancing their photocatalytic activity [78]. However, challenges remain including limited visible-light utilization, carrier recombination, and stacking issues in two-dimensional structures.

It is important to note that, unless otherwise specified, all studies cited in this section achieved adsorption–desorption equilibrium under dark conditions prior to light irradiation, ensuring that reported degradation reflects photocatalytic activity rather than physical adsorption. As established in Section 2, the vast majority of these studies (Tier II) do not report incident photon flux or AQY. Therefore, they can only inform qualitative trends, not quantitative cross-study comparisons.

5.1. Bismuth-Based Tier I Studies with Standardized Reporting

Bismuth-based oxides have emerged as promising photocatalysts for VOC degradation due to their unique layered structures, visible-light responsiveness, and abundant active sites. However, the lack of standardized photochemical parameters, such as incident photon flux and apparent quantum yield (AQY), has hindered meaningful cross-study comparisons and the rational design of high-performance materials.

Early work by Amano et al. [26] demonstrated that crystalline Bi₂WO₆ (russellite) exhibits remarkable visible-light activity for the complete mineralization of gaseous acetaldehyde (2000 ppm), whereas amorphous Bi₂WO₆ is nearly inactive. Using visible light ($\lambda > 400$ nm) and measuring the action spectrum, they reported an AQY of approximately 8% at 400 nm. The superior activity of the crystalline sample was attributed to the significantly prolonged lifetime of photogenerated charge carriers, as confirmed by time-resolved infrared absorption spectroscopy. This work provided early evidence that crystallization dramatically reduces electron–hole recombination and enhances photocatalytic efficiency, setting a benchmark for bismuth-based photocatalysts under visible light. More recently, Zhang et al. [27] met the Tier I criteria by reporting both incident photon flux and quantum yield for BiOCl with controlled surface defects (BiOCl-R) in the degradation of toluene (5 ppm) under UV light. Their study reported an incident photon flux of 0.076 W and a quantum yield of 1.04×10^{-3} , demonstrating that surface defect engineering enhances charge separation and activity.

These Tier I studies provide benchmarks for bismuth-based photocatalysis, demonstrating the value of reporting incident photon flux and AQY. The work on crystalline Bi₂WO₆ illustrates how crystallization dramatically reduces electron–hole recombination and enhances visible-light activity, while the study on BiOCl with controlled surface defects shows how defect engineering can improve charge separation. Both studies exemplify the

use of action spectrum analysis and quantum yield measurement to establish structure–activity relationships, offering a template for future investigations.

5.2. Self-Doping and Microstructure: Qualitative Trends from Bismuth-Based Tier II Studies

The majority of bismuth-based oxide studies fall into Tier II, lacking photon flux or AQY reporting. While their reported degradation rates are not comparable across different setups, they collectively indicate several qualitative trends regarding self-doping, microstructural design, and heterojunction construction.

Trend 1: Bi self-doping enhances visible-light absorption and charge separation. Introducing Bi⁰ species acts as electron acceptors and extends visible-light absorption through surface plasmon effects [79]. Guo et al. [42] prepared a type II Bi₂O₃/Bi/TiO₂ heterojunction with an embedded Bi interlayer via stepwise hydrothermal synthesis. The Bi interlayer broadened the photoreactive range of TiO₂, promoted active species generation, and prevented active site blockage by intermediates, leading to excellent photocatalytic activity and stability for toluene degradation compared to pure TiO₂.

Trend 2: Microstructural design resolves nanosheet stacking and exposes active facets. Constructing 1D/2D or 0D/1D/2D hierarchical architectures increases accessible active sites, exposes high-activity crystal planes, and improves light harvesting [80]. To address the stacking issue of two-dimensional nanosheets, Chen et al. [43] developed a flexible Bi₂WO₆ (BWO) thin film structure via electrospinning followed by calcination, featuring a 1D nanofiber/2D nanowire interpenetrating network (Figure 4); this unique architecture resolved the stacking problem and selectively exposed {010} crystal planes with high hole oxidation performance, enabling rapid acetaldehyde degradation and excellent stability over multiple cycles. Building on this, Chen et al. [44] further transformed the 1D/2D BWO structure under H₂/Ar reduction, reducing Bi³⁺ to Bi⁰ to form a dynamically evolving 0D/1D/2D Bi-BWO metal-defect system, achieving faster acetaldehyde degradation compared to conventional 1D/2D BWO.

Trend 3: S-type heterojunction construction promotes interfacial charge separation while preserving redox potential. The staggered band alignment in S-type heterojunctions facilitates recombination of useless carriers while retaining more powerful electrons and holes on opposite sides [81]. Kong et al. [82] introduced Pt and Bi into Bi₂WO₆/CeO₂, creating an S-type heterojunction that promoted interfacial charge separation and enhanced redox capacity, leading to increased photocatalytic reaction rates. Borjigin et al. [45] developed an S-type CuBi₂O₄/CeO_{2–x} heterojunction with abundant oxygen vacancies; interfacial synergy generated more superoxide and hydroxyl radicals, achieving high toluene degradation and CO₂ yield with stable cycling performance compared to pure CeO₂. Wu et al. [46] prepared a Bi₂MoO₆/WO₃ S-type heterojunction for formaldehyde degradation. Within the same study, significantly reduced interfacial charge transfer resistance led to enhanced degradation efficiency for high-concentration formaldehyde compared to pure Bi₂MoO₆.

In summary, self-doping (e.g., Bi), microstructural engineering (e.g., 1D/2D, 0D/1D/2D architectures), and S-type heterojunction construction consistently enhance the photocatalytic performance of bismuth-based oxides within individual studies by improving light absorption, charge separation, and surface reactivity. However, the near-absence of Tier I studies, with only one identified, severely limits quantitative understanding. Future research on bismuth-based oxides should prioritize reporting incident photon flux and calculating AQY.

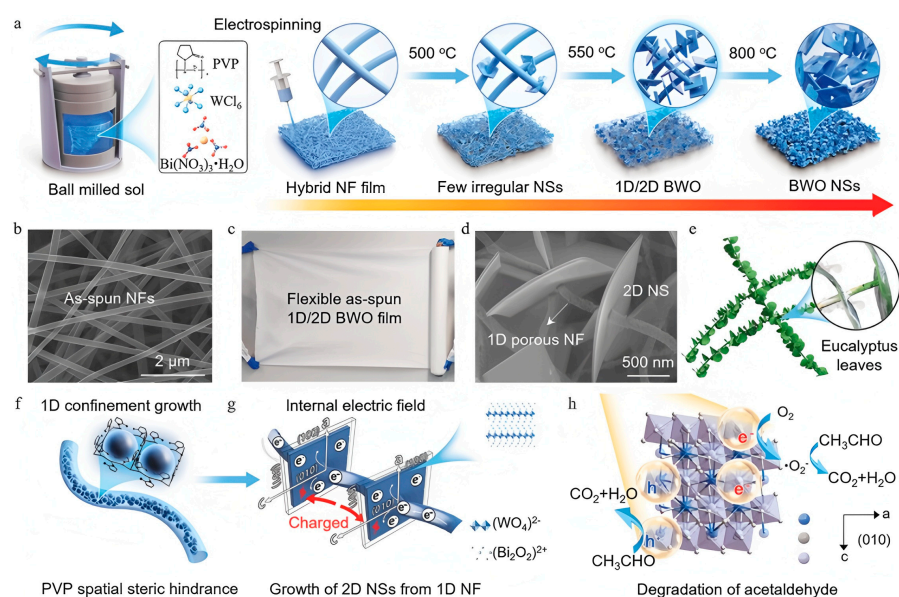


Figure 4. Synthesis strategy and photocatalytic mechanism of biomimetic interpenetrating 1D/2D Bi_2WO_6 films. (a) Synthesis process: fabrication of an interpenetrating network structure composed of 1D nanofibers and 2D nanowires via electrospinning followed by calcination, resolving the stacking issue of 2D nanosheets. (b) Under light excitation, this unique structure promotes charge separation and selectively exposes crystal planes with high hole oxidation performance, enabling rapid degradation of acetaldehyde. (c) Photographs of the as-spun NFs and flexible film. (d) SEM image of the 1D/2D structure. (e) Photograph of eucalyptus leaves for comparison; (f,g) Schematic of multiscale confinement and electrostatic forces. (h) Illustration of the enhanced photocatalytic degradation mechanism. (Reprinted/adapted with permission from reference [43]).

6. Metal–Organic Frameworks (MOFs)

Metal–organic frameworks (MOFs) have garnered significant attention in the field of photocatalysis due to their tunable pore structures and exceptionally high specific surface areas. However, conventional MOFs commonly exhibit limitations such as narrow light response ranges, slow charge transfer rates, and suboptimal stability, which hinder their practical applications [83]. Through strategies like ligand functionalization, structural derivatization, and composite construction, MOFs can be effectively modified to regulate their band structures, enhance light absorption, and improve charge separation, thereby significantly boosting their photocatalytic performance [84,85].

It is important to note that, unless otherwise specified, all studies cited in this section achieved adsorption–desorption equilibrium under dark conditions prior to light irradiation. This experimental practice is particularly critical for MOFs due to their exceptionally high specific surface areas, where adsorption-induced concentration decreases can significantly exceed photocatalytic contributions. Strict dark equilibrium ensures that reported degradation rates accurately represent photocatalytic activity rather than adsorption effects. As established in Section 2, the vast majority of these studies (Tier II) do not report incident photon flux or AQY. Therefore, they can only inform qualitative trends, not quantitative cross-study comparisons.

6.1. MOF-Based Tier I Studies with Standardized Reporting

Metal–organic frameworks (MOFs) have garnered significant attention in photocatalysis due to their tunable pore structures, exceptionally high specific surface areas, and the ability to integrate light-harvesting organic linkers with metal-oxo clusters. However, conventional MOFs often suffer from narrow light response ranges, slow charge transfer rates, and limited stability, which hinder their practical applications. Moreover, the lack

of standardized photochemical reporting, particularly incident photon flux and apparent quantum yield, has severely limited cross-study comparisons and the rational design of MOF-based photocatalysts for VOC degradation.

Among MOF-based literature, Yang et al. [28] met the Tier I criteria by reporting both incident photon flux and apparent quantum efficiency. They constructed a CeO₂-chelated Ce-MOF isogenous S-scheme heterojunction for acetaldehyde purification. Using a Xe lamp with a 420 nm bandpass filter and an incident photon flux of 100 mW/cm², they achieved an apparent quantum efficiency (AQE) of 7.15% at 420 nm. This work demonstrates that isogenous heterojunction design can achieve efficient exciton dissociation and charge separation, providing a quantitative benchmark for MOF-based photocatalysis. More recently, Lu et al. [29] constructed a mediator-assisted hybridized step (MAH-S)-scheme heterojunction by combining Ag-doped WO₃ (AW) with an amine-functionalized NH₂-MIL-125 (M), denoted as AWM-10, for the mineralization of gaseous formaldehyde (5 ppm) in a portable air purifier. Under a 1 W UV-LED ($\lambda_{\text{max}} = 370$ nm), AWM-10 achieved 100% removal of FA with a clean air delivery rate of 11.48 L·min⁻¹ and an apparent quantum yield (AQY) of 0.238%. The enhanced performance is attributed to the dual role of Ag nanoparticles: they act as an electron mediator to facilitate directional charge separation and as a plasmonic photosensitizer to generate hot electrons, extending light absorption and boosting charge carrier density. The complete mineralization pathway from HCHO to CO₂ was confirmed by in situ DRIFTS and GC-FID analysis.

These Tier I studies provide quantitative benchmarks for MOF-based photocatalysis. The work on CeO₂/Ce-MOF isogenous S-scheme heterojunction demonstrates that isogenous heterojunction design can achieve efficient exciton dissociation and charge separation. The study on Ag-WO₃/NH₂-MIL-125 MAH-S heterojunction shows that even for high-surface-area, adsorption-sensitive materials, rigorous reporting of photon flux and AQY is feasible. Both works highlight the critical importance of verifying dark adsorption equilibrium and measuring quantum efficiency to distinguish true photocatalysis from adsorption effects.

6.2. Ligand Functionalization and Composites: Qualitative Trends from MOF-Based Tier II Studies

The majority of MOF studies fall into Tier II, lacking photon flux or AQY reporting. While their reported degradation rates and ζ_r values are not comparable across different experimental setups, they collectively indicate several qualitative trends regarding ligand functionalization, heterojunction construction, and composite formation.

Trend 1: Ligand functionalization modulates electronic structure and enhances VOC capture. Introducing donor or acceptor groups (e.g., NH₂, Fc-CHO) narrows the bandgap, extends light absorption, enhances “ligand-to-metal” charge transfer, and improves VOC capture through specific interactions [47,86]. Yang et al. [87] synthesized NH₂-functionalized MIL-125 with varying degrees of modification via solvothermal method; NH₂ functionalization broadened the light absorption range and optimized charge separation pathways, leading to enhanced degradation of o-xylene and acetaldehyde compared to unmodified MIL-125. The NH₂ groups act as adsorption sites via H bonding for o-xylene and Lewis acid–base interactions for acetaldehyde, while also facilitating ROS generation. Yu et al. [48] employed ferrocenecarboxaldehyde (Fc-CHO) for post-synthetic modification of reo-NH₂-UiO-66; functional group introduction introduced Fe-OH and cyclopentadienyl rings as new adsorption sites, enhancing LMCT, electron–hole separation, and ROS generation, while π - π stacking promoted toluene ring-opening.

Trend 2: MOF-derived materials and heterojunctions combine high surface area with conductivity. MOF-derived metal oxides and heterojunctions leverage the high surface area of MOFs and the conductivity of functional materials (e.g., graphene, TiO₂) to form efficient

interfacial charge transfer pathways. Uppara et al. [88] synthesized MOF-derived Ce-Cu oxides via solvothermal synthesis; compared with pure phase oxides, the derived material exhibited narrower band gap, higher specific surface area, and better visible-light absorption, leading to enhanced pollutant degradation [89]. Shah et al. [49] developed a highly conductive, defect-rich nanohybrid material by bridging NH₂-MIL-125 with 3D graphene through an amino-ionic liquid strategy (IL-3DGr/NM(Ti)); this created abundant coordinatively unsaturated sites and oxygen vacancies, with activity increasing with relative humidity up to 80%, and excellent stability. Wang et al. [50] constructed a Z-type heterojunction (Zr₁₀Ti₁-U6N-300@TiO₂) using bimetallic MOF derivatives and TiO₂; through efficient interfacial charge separation, the material maintained stable toluene removal and selectivity over extended operation.

Trend 3: Plasma-assisted systems create synergistic degradation cascades. Coupling non-thermal plasma with MOF-derived catalysts leverages non-selective active species from plasma and specific active sites on the catalyst surface. Lu et al. [90] achieved significant synergistic effects by combining La₂O₃-CeO₂ catalysts (with MOF precursors) with pulsed plasma. Within their study, non-selective active species generated by plasma interacted with specific active sites on the catalyst surface, forming an efficient degradation cascade that completely mineralized pollutants while reducing harmful by-products.

Ligand functionalization, MOF-derived heterojunctions, and plasma-assisted systems consistently enhance MOF photocatalytic performance within individual studies by broadening light absorption, improving charge transfer, and creating synergistic effects. The exceptionally high surface areas of MOFs make dark adsorption equilibrium particularly critical; future research must ensure rigorous dark equilibrium protocols. The field urgently needs standardized reporting of photon flux and AQY to enable meaningful quantitative comparison across studies.

7. Conclusions

This review critically assesses the state of photocatalytic VOC degradation across four catalyst families. The most significant finding is not a performance ranking but a methodological crisis: among over 80 studies surveyed, the vast majority lack essential photochemical parameters—incident photon flux, apparent quantum yield (AQY), or rigorous dark adsorption equilibrium. Consequently, most published work consists of non-comparable case studies. Within individual studies under identical conditions, modification strategies (doping, heterojunctions, surface engineering) consistently enhance activity relative to controls. However, without standardized metrics, any claim of superior performance based solely on degradation percentages or mass-based rate constants is scientifically unverifiable across different reactors, light sources, or laboratories.

Only a handful of Tier I studies report photon flux and AQY, proving that rigorous standardization is feasible but far from routine. These exemplars provide genuine benchmarks, yet they remain exceptional. Moreover, most studies are conducted under simplified, single-component, steady-state conditions that ignore real-world VOC mixtures, humidity fluctuations, and temperature variations. Few identify degradation intermediates or assess by-product toxicity.

To advance the field, future research must adopt unified reporting standards as a minimum requirement: (1) systematically report light source characteristics, incident photon flux, reactor geometry, and operating conditions; (2) always verify dark adsorption equilibrium; (3) calculate AQY or within-study ζ_r against a clear benchmark (e.g., P25 under identical conditions). Literature evaluations should explicitly distinguish standardized (Tier I) from non-standardized (Tier II) studies, treating the latter as qualitative, hypothesis-generating observations rather than quantitative evidence. Mechanistic studies using

operando characterization and engineering evaluations under realistic, long-term, multi-component conditions are urgently needed. Only through such a cultural shift from performance advocacy to reproducible, photochemically rigorous science can photocatalytic VOC degradation mature into a credible technology for environmental protection.

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