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Carbon–TiO_2 Hybrid Ph otocatalysts: Roles of Carbon Types in Enhancing Photocatalytic Performance

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Highlights

- *Hybrid carbon–TiO_2 enhances photocatalytic efficiency through improved charge transfer and reduced electron–hole recombination.*
- *Different carbon types exhibit distinct roles, establishing a clear structure–function–performance relationship*
- *Adsorption–photocatalysis synergy significantly improves pollutant degradation efficiency.*
- *Carbon–TiO_2 systems show strong potential for sustainable water treatment and environmental remediation*

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ABSTRACT

Titanium dioxide (TiO_2) *is one of the most extensively studied semiconductor photocatalysts due to its chemical stability, non-toxicity, and strong oxidizing ability. However, its practical application is hindered by a wide band gap* (approximately 3.2 eV *for anatase), rapid charge carrier recombination, and limited visible-light response. The integration of various carbon-based materials with* TiO_2 *has emerged as a highly effective strategy for overcoming these limitations. This review systematically examines the distinct roles played by different carbon allotropes and carbon-based materials including graphene, reduced graphene oxide* (rGO), *carbon nanotubes* (CNTs), *carbon quantum dots* (CQDs), *graphitic carbon nitride* (g-C_3N_4), *activated carbon* (AC), *and biochar when hybridized with* TiO_2. *The mechanisms by which each carbon type enhances photocatalytic performance are critically analyzed, encompassing improved charge carrier separation, extension of light absorption to the visible region, elevated pollutant adsorption through synergistic effects, and the formation of unique heterojunction architectures. Furthermore, recent advances in synthesis methodologies, key photocatalytic applications in environmental remediation and energy conversion, and structure–activity relationships are comprehensively reviewed. Challenges pertaining to scalability, stability, and carbon loading optimization are identified, and future research directions are proposed. This review provides a unified framework for understanding how the structural and electronic properties of carbon materials govern the photocatalytic behavior of* Carbon–TiO_2 *hybrids, guiding the rational design of next-generation photocatalysts.*

1. Introduction

The growing challenges of environmental pollution and the global energy crisis have stimulated intense research into sustainable and efficient technologies for pollutant remediation and clean energy production. Semiconductor photocatalysis has attracted enormous scientific interest as a green technology capable of harnessing solar energy to drive chemical reactions, including the degradation of organic pollutants, hydrogen evolution, CO_2 reduction, and the disinfection of pathogenic microorganisms [1, 2]. Among the various semiconductor photocatalysts investigated, titanium dioxide (TiO_2) occupies a central position due to its exceptional combination of properties: chemical inertness, non-toxicity, low cost, photostability, and potent oxidizing capacity when irradiated by ultraviolet (UV) light. Upon photoexcitation, TiO_2 generates electron–hole (e^-/h^+) pairs that initiate a series of redox reactions, ultimately producing reactive oxygen species (ROS) such as hydroxyl radicals ($\bullet OH$) and superoxide anions ($O_2\bullet^-$) capable of mineralizing diverse organic contaminants [3-5].

Despite these advantages, the practical deployment of TiO_2 in solar-driven applications is severely constrained by two fundamental drawbacks. First, the large band gap of anatase TiO_2 (approximately 3.2 eV) restricts photoexcitation to the UV region, which comprises only approximately 4% of the solar spectrum, limiting solar energy utilization efficiency. Second, the rapid recombination of photogenerated charge carriers (e^- and h^+) occurring on the nanosecond timescale drastically reduces quantum efficiency and, consequently, photocatalytic activity. Bridging these gaps is therefore a primary research objective in the field [6-8]. Numerous strategies have been explored to address these limitations, including metal doping (e.g., N, C, S, Fe), noble metal deposition (Au, Pt, Ag), sensitization with visible-light-absorbing dyes, and engineering of heterojunction architectures with other semiconductors. Among these, the hybridization of TiO_2 with carbon-based materials has emerged as a particularly versatile and effective approach. Carbon materials offer a remarkable diversity of structural forms from zero-dimensional (0D) carbon quantum dots to one-dimensional (1D) carbon nanotubes, two-dimensional (2D) graphene and graphitic carbon nitride, and three-dimensional (3D) porous activated carbon and biochar each endowing TiO_2 hybrids with distinct functional advantages [9, 10].

The integration of carbon materials with TiO_2 can simultaneously address multiple limitations: (i) the extraordinary electrical conductivity of graphene and CNTs facilitates rapid extraction of photogenerated electrons, suppressing recombination; (ii) the introduction of new energy states through chemical bonding at the C–TiO_2 interface extends light absorption to the visible range; (iii) the high surface area and functional groups of activated carbon and biochar concentrate pollutants near catalytic sites, amplifying degradation rates; (iv) the unique photoluminescence and up-conversion properties of CQDs enable harvesting of near-infrared

(NIR) radiation; and (v) the formation of Z-scheme or Type-II heterojunctions in g-C_3N_4–TiO_2 systems spatially separates oxidation and reduction sites, preserving strong redox potentials [11-15].

While numerous reviews have addressed carbon–TiO_2 photocatalysts, they have predominantly focused on a single carbon allotrope in isolation for instance, graphene-TiO_2 composites, CQD-sensitized TiO_2, or g-C_3N_4/TiO_2 heterojunctions treating each system as a distinct research thread rather than as variations of a common design principle. Consequently, the field lacks a unified framework that maps how carbon dimensionality (0D to 3D) systematically governs the dominant charge-transfer mechanism, whether through interfacial energy-level coupling, direct electron conduction pathways, photoluminescent down/up-conversion, or adsorption-mediated pollutant enrichment. This fragmentation makes it difficult for researchers to rationally select a carbon modifier based on target application (e.g., pollutant type, light source, reactor configuration) rather than by precedent or material availability.

This review addresses that gap by providing the first systematic, dimensionality-based comparative analysis of carbon–TiO_2 hybrids, explicitly correlating the structural and electronic properties of 0D (CQDs), 1D (CNTs), 2D (graphene, g-C_3N_4), and 3D (activated carbon, biochar) carbon materials with their mechanistic function in suppressing charge recombination, extending visible-light absorption, and enhancing pollutant/substrate interaction. Beyond summarizing synthesis routes and applications as in prior reviews, this work proposes structure mechanism performance correlations that can guide the rational, application-specific design of next-generation carbon–TiO_2 photocatalysts.

2. Method

This study employed a systematic literature review to evaluate the roles of different carbon materials in enhancing the photocatalytic performance of carbon–TiO_2 hybrid photocatalysts. Literature was retrieved from *Google Scholar, ScienceDirect, and SpringerLink* using relevant keywords. An initial 60 articles were identified, and after screening based on relevance, publication year, full-text availability, and inclusion criteria, 38 articles were selected for analysis. The selected studies were compared based on carbon types, synthesis methods, physicochemical properties, photocatalytic mechanisms, and performance.

3. Results and Discussion

3.1 TiO_2 as a Photocatalyst: Fundamentals and Limitations

3.1.1 Crystal Phases and Band Structure

TiO_2 exists predominantly in three naturally occurring polymorphs: anatase, rutile, and brookite. Anatase and rutile are by far the most technologically relevant phases. Anatase exhibits a tetragonal structure with a band gap of approximately 3.2 eV (corresponding to a wavelength

threshold of approximately 387 nm), while rutile is also tetragonal but with a narrower band gap of approximately 3.0 eV (approximately 413 nm threshold). Brookite possesses an orthorhombic structure with a band gap of approximately 3.3 eV and is generally less photocatalytically active due to difficulties in phase-pure synthesis [16]. Anatase is generally considered the most photocatalytically active phase, primarily because of its higher conduction band edge potential (enabling stronger reduction reactions), its lower density of recombination centers compared to rutile, and the higher surface hydroxyl group density on its surface. The commercial benchmark photocatalyst P25 (Evonik-Degussa) consists of approximately 75–80% anatase and 20–25% rutile, and its superior activity compared to either pure phase has been attributed to the formation of a phase junction that facilitates charge carrier separation through vectorial electron transfer from anatase to rutile [17].

3.1.2 Photocatalytic Mechanism

The fundamental photocatalytic mechanism of TiO_2 proceeds through well-defined steps. Upon irradiation with photons of energy exceeding the band gap ($h\nu \geq Eg$), electrons are excited from the valence band (VB) to the conduction band (CB), generating electron–hole pairs:

$$TiO_2 + h\nu \rightarrow TiO_2 (e^-CB + h^+VB)$$

The photogenerated holes (h^+VB; E = +2.7 V vs. NHE) and electrons (e^-CB; E = −0.5 V vs. NHE) can follow multiple pathways: (i) direct oxidation of adsorbed organic species by h^+, (ii) generation of highly reactive •OH radicals through oxidation of surface –OH groups or water, (iii) reduction of dissolved O_2 to superoxide radicals ($O_2^{\bullet -}$), and (iv) non-productive recombination. The efficiency of photocatalysis is fundamentally governed by the competition between productive charge utilization and recombination, with recombination rates in bare TiO_2 typically occurring within nanoseconds [18].

3.1.3 Key Limitations

The two primary limitations of bare TiO_2 photocatalysts are: (1) The large band gap restricts activity exclusively to UV light, which constitutes only approximately 4–5% of the solar spectrum, meaning that under solar irradiation, the vast majority of photon energy is unutilized. This renders outdoor, solar-driven applications of pure TiO_2 highly inefficient. (2) The rapid recombination of photogenerated e^-/h^+ pairs, occurring through radiative and non-radiative pathways, leads to quantum yields that are often below 10% under optimal conditions. The short lifetime of charge carriers (approximately nanoseconds) severely limits the probability of productive surface redox reactions [19].

Additional limitations include: inadequate adsorption affinity for certain pollutants, poor activity in the absence of dissolved oxygen, photocorrosion under strongly reductive conditions,

and particle aggregation at high concentrations, which reduces effective surface area. Carbon based modification strategies directly and simultaneously address most of these challenges, as elaborated in subsequent sections.

3.2 Carbon-Based Materials: Properties and Classification

Carbon is unique among the elements in its ability to form stable structures across all dimensionalities, from 0D fullerenes and CQDs, through 1D carbon nanotubes, to 2D graphene and graphene-derived materials, and 3D networks such as activated carbon, biochar, and carbon aerogels. This remarkable structural versatility, coupled with exceptional electronic properties, chemical tunability, and surface functionalization possibilities, underpins the diverse roles of carbon materials in hybrid photocatalysis. Table 1 provides a systematic comparison of the key carbon types used in TiO_2 hybrid photocatalysts.

Table 1. Comparative properties of carbon materials used in TiO_2 hybrid photocatalysts.

Carbon Type	Structure	Band Gap (eV)	Surface Area	Electron Mobility	Key Role	Reference
Graphene	2D sp^2 lattice	≈ 0 (semimetal)	≈ 2,630 m^2/g	≈ 200,000 cm^2/Vs	Charge transport	[11]
rGO	2D, oxygen defects	0.5–2.2 (tunable)	≈ 400–1500 m^2/g	≈ 1,000–10,000 cm^2/Vs	Visible light absorption	[20]
CNT (SWCNT)	1D hollow cylinder	0–2 (chirality dep.)	≈ 100–900 m^2/g	≈ 100,000 cm^2/Vs	Electron sink & scaffold	[21]
CQDs	0D quantum dots	1.0–3.5 (size dep.)	≈ 50–400 m^2/g	Moderate	Up-conversion & sensitiz.	[12] [18]
g-C_3N_4	2D polymeric network	≈ 2.7	≈ 8–68 m^2/g	Low moderate	Heterojunction formation	[13]
Activated Carbon	Amorphous porous	N/A (conductor)	500–3,000 m^2/g	Low	Adsorption + concentration	[22]
Biochar	Amorphous + aromatic	Variable	10–1,000 m^2/g	Low	Sustainable scaffold	[23]

Note: SSA = specific surface area; dep. = dependent; N/A = not applicable. Values are representative ranges from the literature.

3.2.1 Graphene and Reduced Graphene Oxide (rGO)

Graphene a single atomic layer of sp^2-hybridized carbon atoms arranged in a hexagonal lattice was first isolated in 2004 by Novoselov and Geim, earning them the 2010 Nobel Prize in Physics. Its extraordinary electron mobility (approximately 200,000 $cm^2/V.s$), theoretical specific surface area (approximately 2,630 m^2/g), zero band gap (semimetallic character), and outstanding mechanical strength (approximately 130 GPa) make it an ideal platform for interfacing with semiconductors [24, 25]. In the context of photocatalysis, pristine graphene serves as a highly efficient electron acceptor and transporter, drawing photogenerated electrons from TiO_2 through the formation of a Schottky-like barrier at the interface. This suppresses electron–hole recombination and extends charge carrier lifetime. Reduced graphene oxide (rGO), derived from the chemical, thermal, or photochemical reduction of graphene oxide (GO), retains many properties of graphene but introduces residual oxygen-containing functional groups (epoxide, hydroxyl, carboxyl) and structural defects that serve as anchoring sites for TiO_2

nanoparticles and as additional photocatalytic active sites. Furthermore, the partial band gap opening in rGO (approximately 0.5–2.2 eV, tunable via degree of reduction) extends visible light absorption, contributing to broadened photocatalytic response [20, 26].

3.2.2 Carbon Nanotubes (CNTs)

Carbon nanotubes are cylindrical nanostructures formed by rolling graphene sheets into seamless tubes, existing as single-walled (SWCNTs) or multi-walled (MWCNTs) variants. Their diameter typically ranges from 0.4 to 2 nm (SWCNT) or 2 to 100 nm (MWCNT), with lengths of micrometers to millimeters. The electronic properties of CNTs are uniquely chirality-dependent: armchair SWCNTs are metallic, while zigzag and chiral tubes can be semiconducting with band gaps of 0.4–2 eV [27]. In CNT–TiO_2 composites, CNTs function as one-dimensional electron highways, facilitating long-range electron transport across the composite scaffold. Their tubular geometry provides an extended heterojunction interface with TiO_2, while their surface chemistry can be tailored through acid treatment or functional group grafting to improve TiO_2 nucleation and adhesion. MWCNTs are particularly preferred for environmental applications due to their lower cost, greater chemical stability, and ease of functionalization compared to SWCNTs [21].

3.2.3 Carbon Quantum Dots (CQDs)

Carbon quantum dots are quasi-spherical carbon nanoparticles with diameters typically below 10 nm, first discovered serendipitously during the purification of single-walled carbon nanotubes in 2004 [28]. CQDs exhibit strong photoluminescence (PL) with excitation-dependent emission, high quantum yields, biocompatibility, and tunable optical properties. Their band gap is size-dependent (approximately 1.0–3.5 eV), and crucially, CQDs demonstrate unique up-conversion luminescence converting near-infrared or visible photons into higher-energy UV/visible emission through multi-photon absorption processes (Tian et al., 2018). In CQDs–TiO_2 hybrids, multiple concurrent roles have been identified. CQDs sensitize TiO_2 to visible and even NIR radiation by absorbing lower-energy photons and transferring energy to TiO_2 via up-conversion or resonance energy transfer mechanisms. They also function as efficient electron reservoirs, accepting photogenerated electrons from TiO_2 and suppressing recombination, while their nitrogen or sulfur dopants (in heteroatom-doped variants) introduce additional mid-gap states that further narrow the effective optical band gap [29].

3.2.4 Graphitic Carbon Nitride (g-C_3N_4)

Graphitic carbon nitride (g-C_3N_4) is a metal-free, two-dimensional polymeric semiconductor composed of interconnected tri-s-triazine (heptazine) ring units linked by tertiary amines, forming a layered structure analogous to graphite. With an intrinsic band gap of approximately 2.7 eV and a VB edge at approximately +1.6 V vs. NHE and CB edge at

approximately −1.1 V vs. NHE, g-C_3N_4 is capable of absorbing visible light (λ < 460 nm) while maintaining thermodynamic capacity for both water oxidation and hydrogen evolution [30]. The formation of g-C_3N_4–TiO_2 heterojunctions is particularly impactful. Due to the staggered band alignment (Type II) between TiO_2 and g-C_3N_4, electrons and holes are vectorially separated: photogenerated electrons from g-C_3N_4 transfer to the TiO_2 conduction band, while holes migrate from TiO_2 to g-C_3N_4, physically separating reduction and oxidation sites. More advanced Z-scheme configurations further preserve the strong redox potentials of each semiconductor while still achieving charge separation. This architecture has enabled near-complete degradation of recalcitrant pollutants such as bisphenol A and tetracycline under visible light [13].

3.2.5 Activated Carbon (AC) and Biochar

Activated carbon is a highly porous, predominantly amorphous carbon material produced through the controlled pyrolysis and chemical or physical activation of carbonaceous precursors such as wood, coal, coconut shells, or agricultural waste. Its defining characteristic is its extraordinarily high specific surface area (500–3,000 m^2/g), predominantly arising from a hierarchical network of micropores, mesopores, and macropores, which confers exceptional adsorption capacity for organic contaminants [31, 32]. Biochar, while structurally similar to activated carbon, is specifically defined as the carbonaceous solid produced by pyrolysis of biomass under low-oxygen or oxygen-free conditions (slow pyrolysis, fast pyrolysis, or hydrothermal carbonization). Biochars derived from diverse agricultural residues including rice husks, sugarcane bagasse, palm shell, and coconut fiber have gained attention as sustainable, low-cost supports for TiO_2 in photocatalysis. Their surface chemistry is rich in oxygen-containing functional groups, and their physicochemical properties are highly tunable through precursor selection and pyrolysis conditions [23, 32].

In AC–TiO_2 and Biochar–TiO_2 composites, the primary mechanism of enhancement is adsorption synergy: pollutant molecules are concentrated in the vicinity of TiO_2 active sites through strong adsorption on the carbon matrix, effectively increasing the local reactant concentration and dramatically accelerating degradation rates. This 'concentrator-reactor' mechanism is particularly effective for dilute pollutant solutions where direct interaction with TiO_2 would be kinetically limited. Secondary contributions include the provision of a structural scaffold that prevents TiO_2 sintering, as well as limited charge transport facilitated by the partially graphitized domains in biochar [22].

3.3 Mechanisms of Photocatalytic Enhancement

The diverse structural and electronic properties of carbon materials translate into a rich array of mechanisms by which they enhance TiO_2 photocatalysis. Understanding these mechanisms at a molecular level is essential for the rational design of optimized hybrids. Table 2

summarizes the key enhancement mechanisms, the carbon types primarily responsible, and the associated photocatalytic effects.

Table 2. Mechanisms of photocatalytic enhancement in Carbon–TiO_2 hybrid systems.

Mechanism	Key Feature	Carbon Type	Photocatalytic Effect	Performance Gain	References
Charge Transfer	High conductivity	Graphene, CNT, rGO	Suppresses e^-/h^+ recombination	Up to 5–10× ↑	[33]
Visible Light Absorption	Narrowed optical gap	rGO, CQDs, g-C_3N_4	Extends solar spectrum use	Eg: 3.2→2.4 eV	[20]
Adsorption Synergy	High SSA, functional groups	AC, Biochar, rGO	Concentrates pollutants	3–8× faster degradation	[22]
Up-conversion	NIR→UV/Vis conversion	CQDs	Enables NIR photocatalysis	approximately 2× solar activity	[12]
Heterojunction	Z-scheme / Type-II	g-C_3N_4, rGO	Spatially separated redox	Near-complete degradation	[13]

Note: SSA = specific surface area; e^-/h^+ = electron/hole pair; NIR = near-infrared. Performance gains are approximate and vary with experimental conditions.

3.3.1 Charge Carrier Separation and Transport

The suppression of electron–hole recombination is arguably the most universally impactful mechanism through which carbon materials enhance TiO_2 photocatalytic activity. In graphene–TiO_2 and CNT–TiO_2 systems, the photogenerated electrons in TiO_2 rapidly migrate to the carbon scaffold driven by the favorable energetic alignment of the TiO_2 conduction band (approximately −0.5 V vs. NHE) relative to graphene's work function (approximately −4.4 eV). This ultrafast electron transfer occurring on femtosecond timescales as demonstrated by transient absorption spectroscopy effectively decouples the electron from the hole, dramatically extending the lifetime of photogenerated h^+ that can then engage in surface oxidation reactions [11, 33]. The formation of a Schottky barrier at the graphene–TiO_2 interface has been proposed as the driving force for unidirectional electron transfer. Photogenerated electrons accumulate on graphene, where they can either reduce dissolved O_2 to form superoxide radicals or be subsequently consumed in multi-step reduction processes. The spatial separation of electrons on carbon and holes on TiO_2 provides an extended temporal window (approximately microseconds to milliseconds) for productive redox chemistry, representing an improvement of 3–5 orders of magnitude compared to bare TiO_2 [34].

3.3.2 Visible-Light Absorption Extension

Extending the optical response of TiO_2 into the visible spectrum is a critical prerequisite for efficient solar photocatalysis, where UV radiation constitutes less than 5% of the incoming photon flux. Carbon based modifications achieve this through multiple distinct mechanisms. In rGO–TiO_2 composites, the partial restoration of sp^2 conjugation and the presence of residual oxygen functional groups introduce new energy levels within the TiO_2 band gap, enabling sub-band-gap photoexcitation. Chemical C–O–Ti and C–C–Ti bond formation at the interface creates a sensitization pathway where visible-light-excited electrons in rGO are injected into the TiO_2

conduction band, effectively functioning as a 'carbon sensitizer' analogous to organic dye sensitization but with superior stability [20]. Carbon quantum dots exhibit a complementary mechanism: their unique up-conversion photoluminescence converts NIR and visible photons into higher energy UV emission that can directly excite TiO_2. This process, attributed to multi-photon absorption and anti-Stokes emission, enables harvesting of the most abundant portion of the solar spectrum (approximately 700–900 nm) that is entirely inaccessible to bare TiO_2. Nitrogen doped CQDs have demonstrated particularly efficient up conversion yields, approximately doubling the apparent solar photocatalytic activity of CQDs–TiO_2 composites relative to undoped CQDs systems [12].

3.3.3 Adsorption-Enhanced Photocatalysis

The role of adsorption in photocatalysis is often underappreciated but fundamentally important. According to the Langmuir Hinshelwood kinetic model, the photocatalytic degradation rate is proportional to the surface concentration of the substrate. Carbon materials with high surface areas particularly activated carbon and biochar dramatically increase the local concentration of organic pollutants in the immediate vicinity of TiO_2 active sites, accelerating mass transfer from the bulk solution to the photocatalytic interface [22]. In AC–TiO_2 systems, the 'concentration effect' can produce apparent degradation rates 3–8 times higher than those achievable with TiO_2 alone for dilute pollutant solutions, even without any improvement in the intrinsic photocatalytic quantum efficiency. This synergistic effect is maximized when TiO_2 nanoparticles are deposited directly on the carbon surface at the interface between adsorption and reaction zones, allowing photocatalytically generated ROS to intercept adsorbed molecules with minimal diffusion limitations. Functional groups on the carbon surface (–COOH, –OH, –NH_2) further enhance selectivity toward specific pollutant classes through electrostatic and π–π interactions [31].

3.3.4 Heterojunction Formation

The deliberate engineering of semiconductor heterojunctions represents the most sophisticated mechanistic approach to photocatalytic enhancement. In g-C_3N_4–TiO_2 Type-II heterojunctions, the staggered band alignment drives spatial charge separation: upon dual photoexcitation, photogenerated electrons accumulate in the more negative TiO_2 CB while holes accumulate in the more positive g-C_3N_4 VB. This configuration maximizes charge separation at the cost of reducing the effective redox potentials available at each interface [13].

More elegantly, Z-scheme g-C_3N_4–TiO_2 configurations particularly those mediated by carbon or metallic conductors preserve the strong oxidation potential of TiO_2 holes and the strong reduction potential of g-C_3N_4 electrons while still achieving efficient charge separation. In this arrangement, the less energetic electrons from TiO_2 and holes from g-C_3N_4 recombine at the

mediator interface, effectively 'short-circuiting' the less productive carriers while retaining the most energetically valuable ones. Photocatalytic systems based on this Z-scheme architecture have demonstrated near-complete mineralization of recalcitrant pharmaceutical pollutants including tetracycline, ciprofloxacin, and bisphenol A under simulated solar irradiation [35].

3.4 Synthesis Methodologies

3.4.1 Hydrothermal and Solvothermal Methods

Hydrothermal synthesis is the most widely employed method for preparing Carbon–TiO_2 composites due to its simplicity, scalability, and the high crystallinity of products obtainable under mild conditions (120–200°C). In a typical procedure for rGO–TiO_2 synthesis, graphene oxide (prepared by Hummers' method) and a TiO_2 precursor such as titanium isopropoxide (TTIP) or $TiCl_4$ are dispersed in aqueous media and subjected to hydrothermal treatment. During the reaction, TiO_2 nucleates preferentially at the oxygen-functional sites of GO, while the simultaneous reduction of GO to rGO is achieved by the hydrothermal reducing environment or through the reducing action of the evolving H_2 at elevated temperatures [36].

Solvothermal methods, employing organic solvents such as ethanol, dimethylformamide (DMF), or benzyl alcohol, offer additional control over TiO_2 crystal phase, morphology, and particle size. The use of benzyl alcohol as both solvent and capping agent in the nonaqueous solvothermal route yields highly crystalline anatase TiO_2 nanoparticles with narrow size distributions, which when combined with pre-formed carbon materials, produce composites with intimate interfacial contact superior to that achievable by simple physical mixing [37].

3.4.2 Sol-Gel and Impregnation Methods

Sol-gel synthesis offers exceptional compositional flexibility and low processing temperatures. In the preparation of CNT–TiO_2 composites, acid-functionalized MWCNTs are dispersed in an alcohol-water mixture, to which TTIP is added dropwise under vigorous stirring. Controlled hydrolysis and condensation of the titanium alkoxide precursor deposit TiO_2 nanoparticles uniformly along the CNT surface. Subsequent calcination at 400–500°C under inert atmosphere (to prevent carbon oxidation) yields well-crystallized anatase TiO_2 strongly anchored to the CNT scaffold. The covalent C–O–Ti bonding formed during calcination ensures intimate electron transfer at the heterojunction interface [21].

3.4.3 Photodeposition and In-Situ Reduction

Photodeposition represents an elegant, one-step approach for simultaneously reducing graphene oxide and depositing TiO_2 nanoparticles. In this method, a suspension of GO and TiO_2 (P25) is irradiated with UV light under an inert atmosphere. Photogenerated electrons in TiO_2 are captured by GO, progressively reducing it to rGO while anchoring TiO_2 nanoparticles at the

interface. This approach produces rGO–TiO_2 composites with exceptionally strong interfacial coupling because the electron transfer pathway is established during the very process of composite formation. The degree of GO reduction and the final C/Ti ratio can be modulated by controlling irradiation time, incident photon flux, and initial C/Ti stoichiometry [33].

3.4.4 Thermal Calcination Routes for g-C_3N_4–TiO_2

g-C_3N_4 is most commonly prepared by the thermal polycondensation of nitrogen-rich precursors such as melamine, urea, dicyandiamide, or cyanamide at temperatures of 500–600°C under inert or N_2 atmosphere. For the synthesis of g-C_3N_4–TiO_2 heterostructures, several strategies have been developed: (i) calcination of physical mixtures of g-C_3N_4 and TiO_2 under N_2, (ii) thermal treatment of TiO_2 coated on g-C_3N_4 nanosheets, (iii) simultaneous pyrolysis of g-C_3N_4 precursors in the presence of TiO_2 nanoparticles, and (iv) co-calcination with sacrificial templates for controlled morphology. The interfacial Ti–N and Ti–O–C bonds formed during high-temperature treatment ensure intimate heterojunction contact crucial for efficient charge transfer [13].

3.5 Photocatalytic Applications

Carbon–TiO_2 hybrid photocatalysts have been applied across a broad spectrum of environmental remediation and energy conversion applications. Table 3 summarizes representative photocatalytic performance data for key composite systems in environmental applications.

Table 3. Representative photocatalytic performance of Carbon–TiO_2 hybrids in environmental applications.

Carbon Type	Composite	Pollutant	Light Source	Degradation	Conditions	References
rGO	rGO–TiO_2 (P25)	MB dye	Visible	approximately 98% / 90 min	0.5 wt% rGO	[20]
Graphene	GR–TiO_2	Methylene Blue	UV+Visible	approximately 95% / 60 min	1 wt% GR	[11]
CNT	MWCNT–TiO_2	Phenol	UV	approximately 85% / 120 min	2 wt% CNT	[21]
CQDs	CQDs–TiO_2	Tetracycline	Simulated solar	approximately 91% / 60 min	5 wt% CQDs	[12]
g-C_3N_4	g-C_3N_4–TiO_2	Bisphenol A	Visible	approximately 88% / 120 min	Z-scheme	[13]
Biochar	Biochar–TiO_2	Atrazine	UV	approximately 92% / 90 min	5 wt% Biochar	[23]

3.5.1 Degradation of Organic Dyes and Emerging Pollutants

The photocatalytic degradation of synthetic dyes including methylene blue (MB), rhodamine B (RhB), methyl orange (MO), and reactive red has been extensively studied as a model system for evaluating Carbon–TiO_2 performance. These cationic and anionic dyes represent a class of environmentally significant textile wastewater pollutants that are resistant to conventional biological treatment. Across multiple studies, Carbon–TiO_2 composites particularly rGO–TiO_2 and graphene–TiO_2 consistently outperform bare TiO_2 by 2–10 fold under both UV and

visible irradiation. The superior performance under visible light is a particularly critical advantage for practical solar applications [20].

Of increasing environmental concern are emerging pollutants, including pharmaceutical and personal care products (PPCPs), endocrine-disrupting compounds (EDCs), and antibiotic residues. Antibiotics such as tetracycline, ciprofloxacin, and sulfamethoxazole have been detected at µg/L concentrations in surface waters and have been linked to the proliferation of antibiotic-resistant bacteria. CQDs–TiO_2 and g-C_3N_4–TiO_2 composites have demonstrated excellent activity toward antibiotic degradation under simulated solar irradiation, with removal efficiencies exceeding 90% within 60–120 minutes at environmentally relevant concentrations [12, 13].

3.5.2 H_2 Evolution and CO_2 Reduction

Photocatalytic water splitting for hydrogen evolution represents one of the most impactful applications of Carbon–TiO_2 hybrids for clean energy production. In graphene–TiO_2 systems, the efficient extraction of photogenerated electrons by graphene dramatically increases the flux of electrons available for proton reduction ($2H^+ + 2e^- \rightarrow H_2$), while the retention of holes on TiO_2 drives water oxidation. Graphene–TiO_2 composites modified with Pt co-catalysts have achieved H_2 evolution rates up to 450 µmol/h/g under UV irradiation, representing a 2–5 fold enhancement over Pt–TiO_2 without carbon [11]. Photocatalytic CO_2 reduction to solar fuels (CH_4, CH_3OH, CO) is a thermodynamically challenging reaction requiring highly negative reduction potentials sustained over extended periods. g-C_3N_4–TiO_2 Z-scheme composites have demonstrated remarkable activity in CO_2 reduction, primarily due to the strong reducing CB potential of g-C_3N_4 (−1.1 V vs. NHE) that is preserved in Z-scheme configurations. CO production rates of 10–25 µmol/g/h have been reported under UV-vis irradiation, with selectivity tunable through surface engineering and defect modulation [35].

3.5.3 Antibacterial Applications

The ROS generated by Carbon–TiO_2 photocatalysts are potently bactericidal, enabling the photocatalytic inactivation of pathogenic microorganisms including Escherichia coli, Staphylococcus aureus, and drug-resistant strains. rGO–TiO_2 composites have shown synergistic antibacterial activity combining the membrane-penetrating toxicity of rGO sheets with the ROS generation of TiO_2, achieving >6 log reduction in E. coli viability within 30 minutes under solar irradiation. This dual mechanism makes Carbon–TiO_2 composites particularly attractive for water disinfection applications in resource-limited settings where UV lamp systems are impractical [38].

3.6 Challenges and Future Perspectives

3.6.1 Carbon Loading Optimization

A critical and recurrent challenge in Carbon–TiO_2 composite design is the optimization of carbon loading. While carbon materials confer multiple benefits at low to moderate loadings, excessive carbon content invariably leads to performance deterioration through two primary mechanisms: (i) shielding effect, whereby opaque carbon layers intercept incident photons before they can reach TiO_2, reducing the rate of photoexcitation; and (ii) competitive adsorption of ROS on the carbon surface rather than their delivery to target pollutants. The optimal carbon loading is thus a delicate balance that varies with the specific carbon type, TiO_2 morphology, target pollutant, and light source, and must be empirically determined for each composite system. For graphene–TiO_2, optimal loadings of 0.5–5 wt% have been most frequently reported, while for AC–TiO_2, higher loadings (10–30 wt%) may be beneficial due to the adsorption-dominated mechanism [10].

3.6.2 Long-Term Stability and Recyclability

The practical deployment of Carbon–TiO_2 photocatalysts in continuous-flow water treatment systems requires sustained activity over multiple operational cycles. Stability concerns include: (i) photocorrosion of carbon under prolonged UV irradiation in the presence of ROS, leading to gradual loss of carbon content and structural modification; (ii) deactivation of TiO_2 active sites through fouling by reaction intermediates or inorganic species in real wastewater matrices; (iii) agglomeration of nanoparticles reducing active surface area over time; and (iv) catalyst loss during recovery in slurry-phase systems. Immobilization on solid substrates (ceramic membranes, glass beads, polymer fibers) and the development of magnetically recoverable Carbon–TiO_2–Fe_3O_4 ternary composites represent promising strategies for facilitating catalyst recovery and reuse [7].

Beyond simple recovery, regeneration of spent Carbon–TiO_2 photocatalysts remains comparatively underexplored. Reported approaches include thermal calcination to burn off adsorbed organic foulants and restore surface activity, although this risks partial oxidation or loss of the carbon phase itself, particularly for CQDs and graphene, which are more thermally labile than activated carbon or biochar. Solvent washing and mild acid treatment have been used to desorb inorganic foulants without damaging the Carbon–TiO_2 interface, while UV/ozone regeneration has shown promise for restoring activity without significant carbon loss. However, most regeneration studies report activity retention only over 3–5 cycles, and systematic data on long-term (>20 cycles) performance decay, structural degradation mechanisms, and the cumulative economic cost of regeneration versus catalyst replacement remain scarce. Establishing standardized protocols for reporting cyclic stability ideally normalized against both

photocatalytic efficiency and carbon content retention would substantially improve comparability across studies.

3.6.3 Scalable Synthesis and Cost Analysis

The majority of high-performance Carbon–TiO_2 photocatalysts reported in the literature are synthesized via multi-step batch processes employing high-purity chemical precursors and energy-intensive conditions (e.g., hydrothermal, solvothermal, or CVD routes operated at elevated temperature and pressure), raising significant questions about economic viability and scalability. Translating these gram-scale laboratory protocols to the ton-scale production required for municipal or industrial wastewater treatment introduces additional challenges, including batch-to-batch reproducibility of Carbon–TiO_2 interfacial quality, heat and mass transfer limitations in scaled-up reactors, and the need for continuous rather than batch synthesis to be economically competitive [23].

The cost of pristine graphene and SWCNTs remains prohibitive for large-scale environmental applications, and current graphene production methods (mechanical exfoliation, CVD) are not amenable to industrial-scale manufacturing. In contrast, biomass-derived carbon precursors offer a substantially more favorable cost structure: activated carbon and biochar from agricultural waste can be produced at a fraction of the cost of synthetic carbon nanomaterials, while still providing high surface area and tunable surface chemistry. Preliminary techno-economic estimates in the literature suggest that AC–TiO_2 and biochar–TiO_2 composites can achieve treatment costs approaching those of conventional UV/H_2O_2 or ozonation processes when precursor costs and catalyst lifetime are factored in, whereas CQD or graphene–TiO_2 systems remain economically viable primarily for high-value, low-volume applications (e.g., point-of-use disinfection) rather than bulk water treatment [23].

3.6.4 Environmental Release and Nanotoxicity Considerations

A dimension largely absent from the current Carbon–TiO_2 literature is the potential environmental release of carbon nanomaterials and TiO_2 nanoparticles during photocatalytic operation, catalyst degradation, or improper disposal. Photocorrosion and mechanical attrition in slurry-phase reactors can generate nanoscale fragments or free CQDs that are not fully immobilized within the composite matrix, raising concerns about their fate in treated effluent and downstream aquatic ecosystems. Carbon nanotubes and graphene-family materials in particular have been associated with cytotoxicity and oxidative stress in aquatic organisms in independent nanotoxicology studies, while the environmental behavior of CQDs despite their generally favorable biocompatibility profile in biomedical contextsunder prolonged UV/ROS exposure in real wastewater matrices remains poorly characterized [33].

Mitigating this risk requires two complementary strategies: (i) robust immobilization architectures (membrane-supported, magnetically recoverable, or covalently anchored composites) that minimize nanoparticle leaching during operation, and (ii) post-treatment quality monitoring protocols capable of detecting trace nanomaterial release in treated water, which are not yet standardized for Carbon–TiO_2 systems. Future reviews and primary studies should report not only photocatalytic efficiency but also effluent nanoparticle concentration and ecotoxicological screening data, as regulatory acceptance of Carbon–TiO_2 technologies for real-world deployment will likely hinge on demonstrating environmental safety alongside performance[38].

3.6.5 Future Directions

Several research directions hold transformative potential for the next-generation of Carbon–TiO_2 photocatalysts. (i) Ternary and quaternary composite systems incorporating multiple carbon types (e.g., CQDs–rGO–TiO_2, g-C_3N_4–biochar–TiO_2) may synergistically combine the complementary advantages of different carbons. (ii) Defect engineering in carbon materials specifically the controlled introduction of N, S, P, or B dopants offers a rational pathway for fine-tuning interfacial charge transfer and optical response. (iii) Machine learning and high-throughput computational screening of Carbon–TiO_2 interfaces can accelerate the discovery of optimal compositions and morphologies beyond what is accessible through trial-and-error experimentation. (iv) Integration with membrane filtration for continuous flow photocatalytic reactors addresses the practical challenge of slurry separation while simultaneously limiting nanoparticle release. (v) Exploration of natural and bio-derived carbon precursors from Indonesian agricultural biomass (palm shell, rice husk, sugarcane bagasse, candlenut shell) presents a significant opportunity for sustainable, locally sourced photocatalyst development, provided it is paired with the techno-economic and environmental safety assessments outlined above [10].

4. Conclusions

The hybridization of TiO_2 with carbon-based materials effectively overcomes the wide band gap and rapid charge recombination of pristine TiO_2. Different carbon materials contribute through distinct mechanisms: graphene and CNTs enhance electron transport, rGO and CQDs extend visible-light absorption, activated carbon and biochar improve pollutant adsorption, while g-C_3N_4 forms efficient heterojunctions for charge separation. Photocatalytic performance strongly depends on carbon type, loading, synthesis method, and interfacial contact, highlighting the need for careful optimization. Future research should focus on developing multifunctional ternary composites, utilizing sustainable biomass-derived carbons, and integrating computational and machine learning approaches to accelerate material design. These advances

will support the practical application of Carbon–TiO_2 hybrid photocatalysts in environmental remediation and solar energy conversion.

CRediT Authorship Contribution Statement

D. Lestari: Conceptualization, methodology, literature search, data curation, formal analysis, writing original draft, visualization, and corresponding author; **I. Masriah:** Literature screening, data validation, formal analysis, and writing review & editing; **J.N. Sari:** Literature analysis, writing review & editing, and proofreading. **A. Daulay:** Conceptual validation, critical review, and project administration.

Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this research. The research was conducted independently, and no financial, personal, or professional relationships influenced the study design, data collection, analysis, interpretation, or manuscript preparation.

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