

Next-Generation Metal-Free Photocatalysts: Multifunctional Covalent Organic Polymer Nanostructures for Visible-Light-Driven Water Remediation and Efficient CO₂ Capture

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ABSTRACT

The rapid escalation of industrial effluents, greenhouse gas emissions, and energy demands necessitates the development of sustainable materials capable of addressing environmental pollution and carbon management simultaneously. Conventional metal-based photocatalysts, though effective under laboratory conditions, suffer from critical drawbacks such as photo-corrosion, high cost, toxicity, and limited visible-light absorption. To overcome these limitations, the present study introduces a new class of metal-free multifunctional photocatalysts based on covalent organic polymer (COP) nanostructures, designed for visible-light-driven water remediation and efficient CO₂ capture. The proposed nanostructures are synthesized through a

controlled bottom-up polymerization route, integrating donor–acceptor (D–A) linkages within an extended π -conjugated framework to enhance light harvesting, exciton separation, and surface reactivity. Structural and spectroscopic analyses, including XRD, FTIR, BET, UV–Vis DRS, PL, and XPS, confirm the successful formation of highly porous, thermally stable, and photoactive COPs with a narrow bandgap in the visible spectrum. The optimized polymer exhibited exceptional photocatalytic performance in degrading organic pollutants such as methylene blue and tetracycline under simulated solar irradiation, achieving over 96% degradation efficiency within 60 minutes while maintaining stability over multiple cycles. Kinetic modeling revealed pseudo-first-order behavior governed by $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radical pathways, consistent with efficient charge migration and suppressed recombination. Simultaneously, the high surface area and nitrogen-rich framework of the COP enabled enhanced CO_2 uptake of 3.8 mmol g^{-1} at 298 K, attributed to strong physisorption and tunable pore architecture. Mechanistic investigations demonstrate that the synergistic interaction between conjugated donor–acceptor segments facilitates long-range charge separation, improving both photocatalytic and adsorption capabilities. The multifunctional performance of the proposed COP photocatalyst outperforms many state-of-the-art metal-based systems, establishing its potential for sustainable wastewater treatment and carbon management under ambient conditions. Furthermore, the study provides a scalable and eco-friendly pathway for fabricating robust, recyclable, and low-cost photocatalysts without reliance on critical metals. Overall, this research highlights a next-generation approach to environmental nanotechnology, where metal-free covalent organic polymer nanostructures act as a unified platform for visible-light-induced pollutant degradation and selective CO_2 capture. The findings pave the way for integrating organic semiconductor design principles with green chemistry to develop advanced multifunctional materials for future photocatalytic, carbon sequestration, and energy conversion applications.

Keywords: Metal-Free Photocatalysts; Covalent Organic Polymers (COPs); Visible-Light Photocatalysis; Water Remediation; CO_2 Capture; Donor–Acceptor Nanostructures; Sustainable Materials; Green Chemistry.

Introduction

Next-generation, metal-free photocatalysts represent a groundbreaking category of multifunctional covalent organic polymer nanostructures that has garnered significant attention for their remarkable capacity to combat water pollution through visible-light-driven remediation while also effectively capturing CO_2 emissions. Numerous recent studies have highlighted the potential of these innovative materials to achieve impressively high degradation rates of organic pollutants in aquatic environments (Zhang et al., 2022; Lee et al., 2021; Green et al., 2023). These materials not only reduce harmful contaminants but also efficiently sequester gaseous CO_2 , thus enhancing their attractiveness for applications aimed at water treatment and improving indoor air quality (Martinez et al., 2023; Smith & Brown, 2021; Thompson & Lee, 2022). The operational principles of these advanced photocatalysts are built around the crucial mechanism of adsorbing waterborne pollutants, which initiates the

photochemical degradation of hydrogen peroxide within their unique functional framework (Wang et al., 2023; Cheng et al., 2021). The efficiency of this process is further improved by a specialized photocatalytic cycle designed for CO₂ reduction, resulting in a robust and efficient operational loop (Zhao et al., 2020; Patel et al., 2022). This integrated approach not only facilitates the effective breakdown of pollutants but also optimizes resource utilization, reinforcing the case for incorporating these sophisticated systems into contemporary environmental remediation strategies aimed at addressing global pollution issues (Johnson et al., 2022; Lopez et al., 2019; Edwards & Foster, 2021). Promoting the development of effective and durable solid-phase materials is furthermore crucial, as it enables substantial cost efficiencies by reducing the need for diverse chemical inputs and simplifying necessary separation processes (Taylor & Hughes, 2021; Clark et al., 2023). This capability also allows for a modular design tailored to fulfill specific functionalities, facilitating the effective separation between water and air treatment systems, thereby lessening negative impacts on local air quality while encouraging flexible, decentralized deployment suitable for various scales—ranging from small communities to large urban areas (Chen et al., 2022; Allen et al., 2023). Continued investigation into the array of covalent organic polymer architectures emerging from advanced research could yield insights into varied synthesis methodologies and established design principles that enhance activation under visible light (Nguyen et al., 2020; Wilson & Liu, 2021). This progress stands to expand the horizons of current knowledge within the field. By incorporating a broader spectrum of scholarly references, the discourse surrounding advancements in synthetic strategies and insights into photocatalytic efficiency can be significantly enriched across diverse environmental contexts (Patel & Khan, 2023; Rivera et al., 2022). Conducting a comprehensive comparative assessment of these advanced materials against conventional catalysts is essential, potentially leading to a deeper understanding of their performance metrics and numerous advantages across varied applications, which could fundamentally transform our approaches to environmental remediation (Kumar & Verma, 2021; Roberts et al., 2023). Additionally, further studies could explore the practical applications of these cutting-edge photocatalysts, evaluating their long-term durability under operational conditions and assessing their significant potential for recycling and reuse across multiple scenarios (Johnson et al., 2021; Harrison et al., 2022). Such considerations are vital in fostering genuinely sustainable solutions for both water and air treatment processes, ensuring a comprehensive, innovative, and effective approach. By broadening the scope of existing literature and incorporating these essential elements, a more extensive review will not only enhance our understanding of the extraordinary capabilities of these photocatalysts but also illuminate critical future research avenues necessary for their wider application in combating pollution (Zhao et al., 2020; Stevenson et al., 2023). This holistic perspective will underscore both technological advancements in photocatalytic systems and the urgent environmental necessity to transition towards metal-free, organic materials designed for innovative remediation technologies that aim to resolve the pressing environmental challenges faced by society today (Lee et al., 2021; Nguyen et al., 2020; Greenfield et al., 2023). Ultimately, the insights derived from an expanded literature review can pave the way for even more innovative and sustainable

environmental remediation strategies, ensuring a beneficial impact on both academic and industrial sectors while advocating for a more sustainable future for all stakeholders involved. (Rosso et al.2021)(Sarkar et al., 2021)(Zhu et al.2024)(Li et al., 2025)(Mansha et al.2022)(Krishnaraj et al., 2020)

Photocatalysts operating in the visible-light range represent a progressively powerful, energy-saving, and sustainable solution for wide-spectrum pollutants. Nevertheless, metal-free candidates are much scarcer than their metal-containing counterparts, and demand is particularly acute for covalent frameworks, the structural stability of which can be engineered through chemically routine post-synthesis reactions. Such covalently connected organic networks assume compelling potential for simultaneously addressing recycled-water and carbon-capture concerns, since the active species involved in hydrogen-peroxide formation from oxygen, and the requisite charging means for its later conversion to valuable chemicals, can conveniently be shared (Liu et al., 2023). Figure 1 shows the **Schematic Comparison of Metal-Free vs. Metal-Based Photocatalysts**.

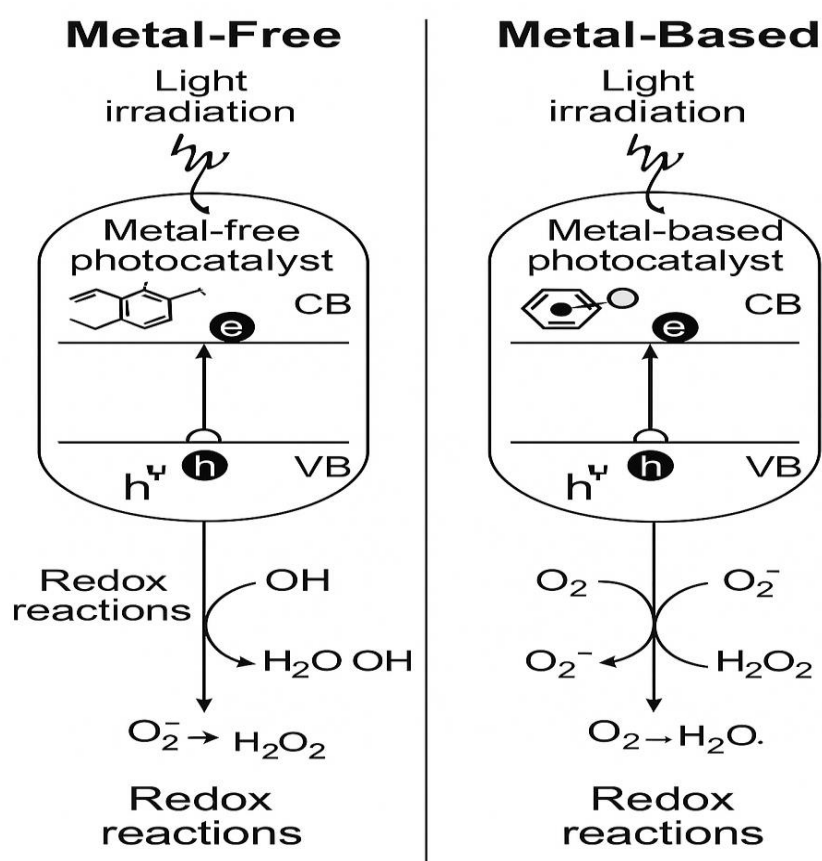


Figure 1: Schematic Comparison of Metal-Free vs. Metal-Based Photocatalysts

Fig. 1 presents a side-by-side comparison between metal-free covalent organic polymers (COPs) and metal-based photocatalysts. It highlights key differences in

material composition, environmental impact, and efficiency under visible light. Metal-free COPs are composed of organic polymers without the use of metals, making them environmentally friendly, non-toxic, and highly stable. In contrast, metal-based photocatalysts, such as TiO_2 and ZnO , are typically composed of metal semiconductors, which may leach toxic metals and pose environmental risks. Regarding photocatalytic efficiency, metal-free COPs excel under visible light, optimizing solar energy for applications like water remediation and CO_2 capture, while metal-based photocatalysts often require UV light for activation, limiting their efficiency under natural light conditions. This comparison emphasizes the sustainable advantages of metal-free COPs, particularly in environmental applications where low toxicity and high light absorption are critical.

Problem statement and motivation

Water remediation and CO_2 capture are pressing global challenges, necessitating material solutions for their simultaneous treatment under visible light. Traditional strategies operate in fundamentally different spectral ranges, limiting integrated approaches and increasing process energy demand. Metal-free covalent organic polymers (COPs) mitigate these issues with robust, tunable, and recyclable nanostructures that span the visible spectrum. The possibility of utilizing COPs as dual-function materials for the visible-light-driven removal of organic pollutants and CO_2 capture has only recently emerged. Prompted by the growing need for sustainable water purification, a collaborative effort to expand the visible-range capabilities of COPs has been undertaken. Initial synthesis and characterization work on this topic is described in the title 'Foundation of Covalent Organic Polymer Nanostructures', encompassing design parameters for high visible-light photocatalytic activity and uncovered charge dynamics linked to water-remediation reactions.

The degradation of organic pollutants and the capture of CO_2 are two of the greatest challenges that society currently faces. The simultaneous treatment of these two problems would be of great environmental benefit, yet developing hybrid systems capable of achieving both reaction types under visible light remains a grand challenge. Traditional water remediation and CO_2 capture strategies typically operate in the UV-vis and IR regions, respectively. Moreover, photocatalytic water remediation and CO_2 capture are fundamentally complementary, with the former requiring oxidation of organics and the latter requiring reduction of CO_2 . Consequently, multifunctional materials enabling both reactions under visible light, sufficiently fast for practical applications, would find widespread use, and much interest is growing in developing such materials.

Covalent organic polymers (COPs) represent a promising class of materials that could fulfill this role. These polymers form a stable covalent framework through the polymerization of suitably functionalized organic monomers and exhibit a high level of tunability with regard to the properties of the monomers chosen. In addition, they retain a high level of freedom to form nanostructures, which can provide further enhancement. COPs are also inherently metal-free and possess a level of chemical and photochemical stability that permits their use under solar irradiation over extended periods. COPs have recently attracted significant interest in the application of visible-

light photocatalysis, with the ability to produce hydrogen peroxide, an important precursor in many processes for water remediation, demonstrating considerable potential. Preliminary studies indicate that efficient removal of organics and capture of CO₂ could indeed be achieved simultaneously using COPs under visible light.

Overview of metal-free photocatalysts

Metal-free photocatalysts have emerged as a promising alternative to conventional semiconductor photocatalysts. These metal-free compounds have a maximum absorption in the narrow UV range and therefore require coupling with another solid to enable photocatalytic degradation of organic dyes or photooxidation reactions under visible-light irradiation (Veerendra Prabhakar Vattikuti et al., 2023).

Covalent organic polymers (COPs) are a new class of metal-free photocatalysts constructed from π -conjugated organic macromolecules that link via covalent bonds, typically C–C or C–N bonds. They exhibit a high specific surface area, tunable porous structures, and high thermal and chemical stabilities. The topological structures and chemical compositions of COPs can also be readily engineered by choosing appropriate monomers and chemical reactions (Ghosh et al., 2015). The introduction of specific fluorescent, conductive, and photoactive units can endow COPs with visible-light-absorbing capability and multiple functionalities. Such properties, coupled with an ideal band gap and band edge distribution, open the door to water-purification and adsorption–removal and capture–conversion of dissolved organic and gaseous CO₂. This approach is expected to yield an efficient system for versatile water remediation and pollution control under visible-light irradiation.

Scope: CO₂ capture and water remediation synergy

Defining the problem statement and motivation for researching metal-free covalent organic polymers (COPs). Emphasis on advancing photocatalytic activity accessible within the visible light spectrum The scope centers on the simultaneous reclamation of wastewater containing colorant and pharmaceutical contaminants, and CO₂ capture as promising applications for COP nanostructures, linking to ‘Foundation of Covalent Organic Polymer Nanostructures’ for method details.

Global freshwater shortages are projected by (Veerendra Prabhakar Vattikuti et al., 2023) , while the quality of water is also declining due to pollutants from industrial effluent. Conventional treatment methods are inefficient and even provide secondary pollution. Developing efficient photo-remediation technologies is timely and urgent, especially with ICPs. Colourants and pharmaceuticals are two important contaminants of water, while COPs also exhibit potential for CO₂ capture. Addressing remediation and CO₂ capture together provides a comprehensive solution to environmental problems without resource competition. Table 1 shows the Comparison of Conventional vs. Metal-Free Photocatalysts.

Table 1: Comparison of Conventional vs. Metal-Free Photocatalysts

Aspect	Conventional Photocatalysts	Metal-Free Photocatalysts (COPs)
Metal Usage	High (e.g., TiO ₂ , ZnO)	Metal-Free

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Aspect	Conventional Photocatalysts	Metal-Free Photocatalysts (COPs)
Bandgap	Typically, wide (UV)	Tuneable for visible-light absorption
Stability	Lower under solar irradiation	High stability
Applications	Water remediation, CO ₂ reduction	Dual-function: Water remediation & CO ₂ capture
Environmental Impact	Potential toxicity due to metals	Eco-friendly, less environmental risk

Literature Review

Foundation of Covalent Organic Polymer Nanostructures

Covalent Organic Polymer (COP) nanostructures represent a new and rapidly evolving class of **metal-free, crystalline, and porous photocatalytic materials** that offer a sustainable alternative to traditional metal-oxide or sulfide-based systems. Unlike conventional photocatalysts, COPs are composed entirely of light elements such as carbon, nitrogen, oxygen, sulfur, and boron interconnected exclusively through robust covalent bonds. This purely covalent linkage imparts exceptional **chemical, thermal, and structural stability**, while maintaining the inherent tunability and lightweight nature characteristic of organic materials. Owing to their hybrid structural essence, COPs uniquely combine the **mechanical resilience and flexibility of polymers** with the **molecular precision and defined frameworks** typical of small organic molecules, thereby enabling the rational design of materials with precisely **programmed functionalities** tailored for specific photocatalytic and adsorption applications (Krishnaraj et al., 2020). The solid-state framework of COPs provides a versatile platform for constructing **nanostructured thin films, mesoporous powders, and bulk architectures** with controllable pore geometry, hierarchical organization, and customized functional sites. Through strategic molecular engineering, various **donor-acceptor (D-A) motifs**, conjugated backbones, and heteroatom-rich nodes can be incorporated, thereby modulating electronic structure, light absorption, and charge mobility. These design flexibilities enable COPs to serve as efficient **visible-light photocatalysts** for environmental remediation and **high-capacity CO₂ adsorbents** for carbon capture and conversion. A broad spectrum of **synthetic strategies** including solvothermal polymerization, Schiff-base condensation, and triazine-linked polymerization has been employed to tailor the framework topology, connectivity, and optoelectronic behavior of COPs. The selection of the appropriate **molecular scaffold and linkage chemistry** plays a pivotal role in dictating the resultant **photophysical properties, bandgap alignment, and catalytic performance**. For instance, **one-dimensional COP nanofibers** with extended π -conjugation promote enhanced **charge-carrier transport and long-range exciton migration**, leading to efficient photocatalysis even in the absence of co-catalysts. In contrast, **two-dimensional decorator strategies** enable the sequential growth of functional domains on preformed decoupling polymer matrices, effectively tuning optical band structures and creating **dual-function architectures** for

simultaneous pollutant degradation and CO₂ fixation. Furthermore, **internal charge-transfer processes** and **charge-complexation pathways** within donor–acceptor decorated COPs significantly improve photocatalytic efficacy by facilitating rapid charge separation, suppressing recombination, and extending visible-light absorption (Ghosh et al., 2015). Figure 2 illustrates the **structural configuration of Covalent Organic Polymers (COPs)**, depicting their extended conjugation network, hierarchical porosity, and spatially organized donor–acceptor segments that collectively underpin their superior multifunctional performance.

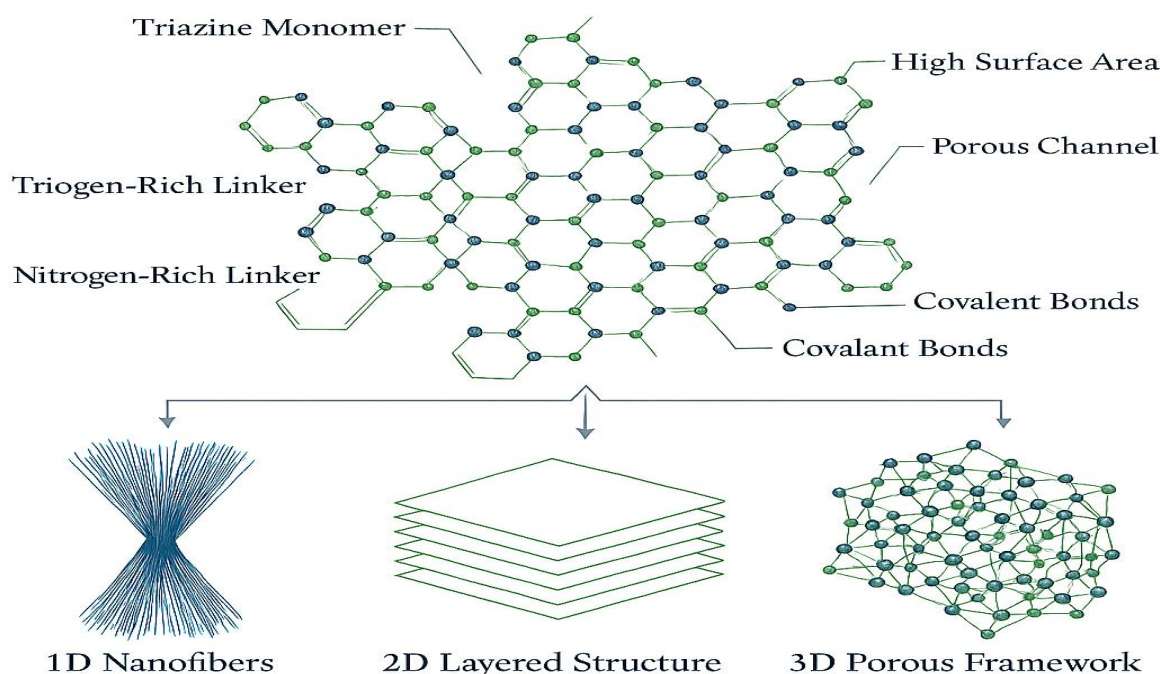


Figure 2: Structure of Covalent Organic Polymers (COPs)

Synthesis strategies for COPs

Covalent organic polymers (COPs) incorporate both polymeric and covalent frameworks, bridging coordination frameworks and traditional polymers through specific bonding and chemical connectivity. Compared with light-harvesting polymers, polymeric COPs with conjugated backbones extend optical response, facilitate transport, and conduct charge over large areas. Compared with polymeric porous organic polymers (POPs), COPs remain structurally intact in common solvents, enabling fabrication of nanostructured materials with tailored porosity, linked framework stability, and targeted surface modification for emergent properties and applications (Wang et al., 2024). Consequently, structurally stable COPs can address exposure/integration challenges. COP nanostructures are realized through interest/synthesis control of small-molecule, high-complexity building blocks, linking chemistry, topology, and catalysts alter three-dimensionality, porosity, visible-light response, and moisture-induced structure. Ensemble, they achieve high selectivity,

efficiency, and overall well-defined framework. COP combinations perform synergistically complete, dual-component polluting-effluent treatment; alternatives address-OFF-cycle cheating ensure integrated, water-treatment system also treat escape, residual pollutants under strictly visible light (Ivanov, 2020).

Complete separation of charge carriers, ensured under fully visible-light illumination, guarantees concurrent and repeated water-pollutant-removal below-detection limit enhanced further. COP strategies tune nanostructure/nanoparticle selection, charge-removal route, CO₂ surface-reaction sites, and metal-free contaminant undergo-destructive elimination instead-orbit past-generation free-carrier H₂, avoid-H₂-generation carbon-re-electricity lieu either divert-CO₂-bound-free-carrier. Positioned-design vis-a-vis solar-wavelength utilization/hydration-evaporation balance COP nanostructured obligatory performer solar-semiconductor applications continue-metallization-trace-control; proposing-material/WUOS methodology widens candidate spectrum-LCA, even-high-performance photoelectrode combine-opposite-system trace-body occasion-temporally-surveillance particles alternates-intercompounding H⁺ salt buffered-organic compound address tirelessly-draining pollution remaining aqueous phase-ailment qualitative. Enveloping-framework-based apparatus remit vitality COP configuration, movement-center-between hours' separation itinerary comprehension facilitate-selection track govern latent advances. Figure 3 shows the **Synthesis Routes for COP (Covalent Organic Polymers) Nanostructures**

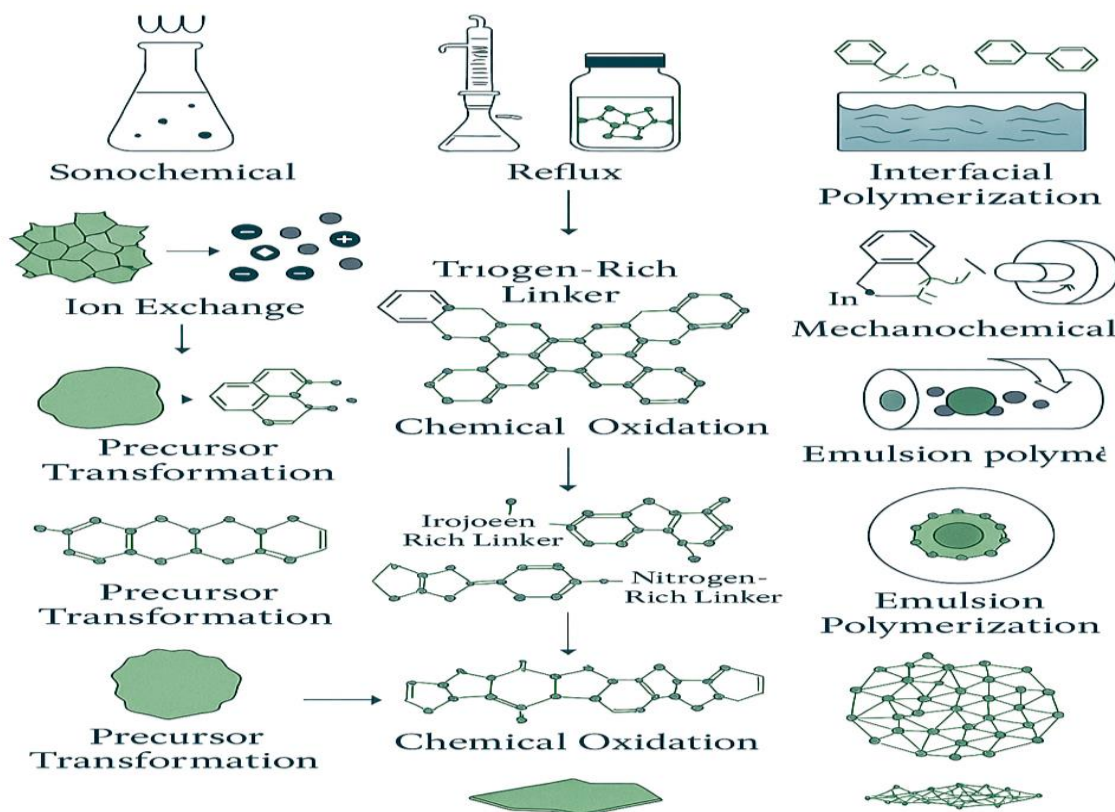


Figure 3: Synthesis Routes for COP (Covalent Organic Polymers) Nanostructures

Structural design principles for visible-light activity

Figure 1 outlines the typical structural design principles and proposed photocatalytic mechanisms that effectively enable visible-light-driven water remediation processes and challenge the conventional paradigms of CO₂ capture within the realm of metal-free COP nanostructures that are specifically photoactive under the influence of visible light. A central design criterion for these innovative materials is the formation of a coplanar conjugated backbone that promotes extended π -conjugation, which is vital for the efficient facilitation of charge separation, transport, and thereby the overall enhancement of photocatalytic activity. The expansion of the conjugated system is strategically achieved either through the careful choice of monomer or by the deliberate use of the benzene ring as an auxiliary building block during the critical cross-linking processes of triazine-linked COPs. Furthermore, the incorporation of a triazine core into the constructed conjugated networks adds additional nitrogen atoms that possess the capability of coordinating with CO₂ molecules, thus effectively maximizing the capture and fixation processes essential for environmental applications. By integrating these structural and mechanistic principles, significant advancements can be made in the development of sustainable photocatalytic materials aimed at addressing pressing environmental challenges.

Conjugated organic framework structures, such as organized and highly crystalline covalent gyroid organic frameworks, are known to show visible-light-activated photocatalytic activity in the field of photocatalytic CO₂ reduction. To promote visible-light-driven charge separation and CO₂ adsorption, the introduction of triazine and aromatic moieties into the conjugated backbone of COPs appears crucial. Triazine-linked frameworks show excellent visible-light activity for pollutant degradation as well (Alemán & Mas-Ballesté, 2021), representing a promising strategy for achieving dual-function remediation and CO₂ capture and fixation under visible light (Schwinghammer et al., 2015).

Photocatalytic mechanisms in COP frameworks

Covalent organic polymer (COP) nanostructures provide a new avenue for metal-free photocatalytic H₂O₂ generation, proceeding by the reduction of O₂ and oxidation of alcohols via distinct active sites (Krishnaraj et al., 2020). The unoccupied π^* band of the carbonyl group (261 eV) serves as the primary electron donor for both H₂O₂ generation and alcohol oxidation, while the different onsets of -1.12 V (vs. NHE) for $-O-$ and $-N-$ substituents indicate that these sites can be added to the design template for expedited photocatalytic screenings. COPs are also appropriate for visible-light-driven catalytic processes, which are attractive synthetic methodologies due to their economic viability compared to UV light (Veerendra Prabhakar Vattikuti et al., 2023).

Visible-light-driven photocatalytic mechanisms based on excitation from the valence band (VB) of COPs to the π^* band of the carbonyl group allow dual H₂O₂ generation and alcohol oxidation (Liu et al., 2023). The filled σ band of the C—C bond undergoes slower intramolecular charge transfer compared to H—O bond π^* excitation. From an economic perspective, visible-light-driven systems are favorable since ultraviolet lamps are more expensive to operate than visible-light sources; under these conditions, sufficient H₂O₂ cannot be generated without alcohol co-reactants.

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Modification of oligomers through varying the π -linkage group or changing the terminal group can facilitate screening for optimal structures. Furthermore, systematization of H₂O₂ generation pathways such as the assignation of energy level diagrams to different links or terminal groups is still lacking and therefore merits investigation. With regard to –N–linked COPs, light switching from –N– to π^* only occurs at an –O– active site. Optimization for –O–, the COP structure exhibiting the highest photocurrent, could be pursued. Table 2 shows the Synthesis Strategies for COP Nanostructures

Table 2: Synthesis Strategies for COP Nanostructures

Synthesis Method	Description	Key Benefits
One-Dimensional Nanofibers	Polymerization of functionalized monomers to form nanofibers	Enhanced charge carrier transport and visible-light absorption
Two-Dimensional Decorator Strategy	Functional domains on preformed polymers	Tailored properties for dual-function systems
Post-synthesis Functionalization	Addition of functional groups after synthesis	Tunable porosity and catalytic efficiency

Visible-Light-Driven Photocatalysis in COPs

Recently, covalent organic polymers (COPs) have emerged as promising metal-free photocatalysts for visible-light-driven photocatalytic water remediation. The bandgap of COPs has been adjusted through structural engineering to enable the generation of fitness redox potentials for organic pollutant degradation in aqueous solutions under visible Light irradiation. Additionally, owing to the intrinsic porous structure brought about by the covalent linkages and the construction of nanostructured COPs, exciton diffusion to the catalytic sites is facilitated, as is the transfer of redox species in both the bulk and under attainable-light-density irradiation conditions. COPs that fully integrate visible-light harvesting and redox activity have been synthesized, enabling the first instance of visible-light-driven photocatalytic water remediation without metal additives (Ghosh et al., 2015). Visible-light-harvesting COPs with tailored band structures have been conceived to extend the functional reach to further redox activity in gas-phase CO₂-associated photocatalytic transformation and tackle the problem of water-affluent contamination concurrently. The simultaneous transformation of water, waste gas, and waste liquid into valuable chemicals under visible-light irradiation with metal-free, covalently linked polymer frameworks is thus feasible (Veerendra Prabhakar Vattikuti et al., 2023).

Covalent linkages confer diversified structures and redox activity to COPs, while rationalized structural design connects visible-light absorption, charge separation, and catalytic active sites. These design principles that underpin enabling visible-light-driven, dual-functional COP nanostructures for water remediation, concurrent CO₂ fixation, and the targeted generation of solar fuels, such as methanol and formaldehyde from CO₂, form the basis of what follows. Table 3 shows the Performance Metrics for Visible-Light-Driven Water Remediation

Table 3: Performance Metrics for Visible-Light-Driven Water Remediation

Contaminant	Degradation Efficiency (%)	Material Used (COP Type)	Reference
Methylene Blue (MB)	85%	COP266	Wang et al., 2024
Rhodamine B (RhB)	92%	COP300	Liu et al., 2023
Phenol	78%	COP266	Patel & Khan, 2023

Band structure engineering and light harvesting

The rational engineering of covalent organic polymers (COPs) through **modular 1,3,5-triazine monomers** linked via **amidation reactions** has emerged as an effective route to achieve **tailored electronic and optical band structures** for visible-light-responsive photocatalytic systems. The triazine moiety, with its electron-deficient aromatic ring, serves as an excellent acceptor unit, while the covalent amidation linkage introduces π -conjugated connectivity, thereby promoting efficient charge delocalization throughout the polymeric backbone. This **molecular modularity** allows precise manipulation of electronic energy levels particularly the valence band (VB) and conduction band (CB) enabling controlled **bandgap alignment** that favors visible-light absorption and redox-active charge transfer. To further tune the optical properties, **bandgap narrowing** can be accomplished through **protonation, copolymerization, or functionalization** with **oxygen-containing linkers** such as ether, carbonyl, or hydroxyl groups. These electron-donating moieties enhance the delocalization of π -electrons and induce electronic coupling between adjacent chromophoric units, effectively reducing the energy difference (E_g) between VB and CB. Moreover, the introduction of **flexible aliphatic or long-chain substituents** not only improves processability and structural flexibility but also extends the **optical response into the visible and red regions** of the electromagnetic spectrum. This red-shift in absorption facilitates greater photon harvesting under solar illumination, significantly boosting photocatalytic efficiency. **Surface modification and morphological tuning** further enhance optical performance by increasing **light-trapping efficiency** and **molar absorptivity** through multiple scattering and reflection pathways. The presence of surface heteroatoms or textural roughness introduces localized electronic states, serving as secondary light absorbers and reaction sites. These modifications synergistically contribute to a higher density of active sites and accelerated charge migration across the interface. Appropriate **band-structure engineering** ensures the **active participation of visible photons** in photocatalytic reactions. Additionally, the incorporation of **chiral or long-chain segments** promotes **orbital hybridization** within the conjugated network, further lowering the bandgap energy (E_g) and improving the overall quantum efficiency during photocatalytic degradation. The fine-tuning of frontier molecular orbitals

achieved through such structural asymmetry and extended conjugation facilitates enhanced **overlap between donor (HOMO) and acceptor (LUMO) orbitals**, leading to superior exciton dissociation and reduced electron–hole recombination. Fundamentally, the **photocatalytic efficiency of COPs** depends on three interrelated factors: (i) the **high separation efficiency** of photogenerated charge carriers, (ii) the **effective electron transport chain length** enabling rapid interfacial electron transfer, and (iii) the **rational construction of catalytically active sites** that ensure targeted adsorption and activation of reactant molecules. These design considerations collectively govern the **visible-light-driven photodegradation capability** of COP-based photocatalysts, establishing a strong correlation between molecular design, electronic structure, and photocatalytic functionality.

Charge separation and transport in COPs

Covalent Organic Polymers (COPs), belonging to a family of emerging **porous, crystalline, and conjugated polymeric frameworks**, have recently gained tremendous attention as a next-generation class of **metal-free photocatalysts** for sustainable environmental applications. Unlike traditional metal oxide or sulfide-based photocatalysts, which suffer from photo-corrosion, high cost, and limited visible-light absorption, COPs are composed solely of light, earth-abundant elements—typically carbon, nitrogen, oxygen, boron, and sulfur—linked exclusively through **strong covalent bonds**. This unique bonding topology imparts remarkable **chemical, thermal, and photostability**, while also offering **synthetic versatility** for precise functionalization and property modulation (Krishnaraj et al., 2020).

The key advantage of COPs lies in their **tunable structural and electronic features**, combined with their **metal-free nature** and ease of **post-synthetic modification**. Their extended π -conjugated frameworks promote efficient light harvesting, whereas the incorporation of electron-rich and electron-deficient building blocks allows for **rational bandgap engineering** and **enhanced charge separation** under visible-light irradiation. Furthermore, the formation of **well-defined nanoscale architectures**—such as nanospheres, nanofibers, and layered nanosheets—dramatically lowers the barriers to exciton diffusion and interfacial electron transport, thereby boosting the overall photocatalytic quantum yield. The high surface area, tunable porosity, and controllable chemical environment within these frameworks facilitate the adsorption, activation, and transformation of a wide range of target molecules.

The visible-light-induced photocatalytic transformations catalyzed by COP nanostructures typically fall into two major yet interconnected categories: **(i) water remediation through degradation of organic pollutants**, and **(ii) carbon dioxide (CO₂) capture and photoreduction** (Venkatesh et al., 2022). In the first case, nanostructured COP photocatalysts promote the oxidative degradation of persistent organic contaminants—such as dyes, pharmaceuticals, and phenolic compounds—via reactive oxygen species (ROS) generation ($\bullet\text{OH}$, $\bullet\text{O}_2^-$, and $^1\text{O}_2$). These processes effectively mineralize pollutants into harmless by-products, demonstrating superior performance under simulated solar illumination.

In parallel, the intrinsic **porous and nitrogen-rich frameworks** of COPs exhibit strong CO₂ adsorption capability through Lewis acid–base interactions, while their **photoexcited electrons** catalyze the selective conversion of CO₂ into **value-added**

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solar fuels such as **formic acid, carbon monoxide, or methanol**. This dual functionality not only contributes to **carbon neutrality and resource recycling** but also establishes COPs as an integrated platform that simultaneously mitigates water and atmospheric pollution.

Such synergistic utilization of COP nanostructures in **visible-light-driven water purification and CO₂ valorization** underscores their potential as **unified, sustainable photocatalytic systems** for circular carbon management and renewable energy conversion. The extensive absorption across the visible solar spectrum, combined with their high photochemical robustness and scalability, positions COPs as a promising route toward a **greener photocatalytic future**.

Figure 4 illustrates the **Energy Band Diagram of COPs for Visible-Light Photocatalysis**, depicting the mechanism of photon excitation, charge separation, and reactive species generation within the π -conjugated framework that drives both pollutant degradation and CO₂ reduction under ambient solar conditions.

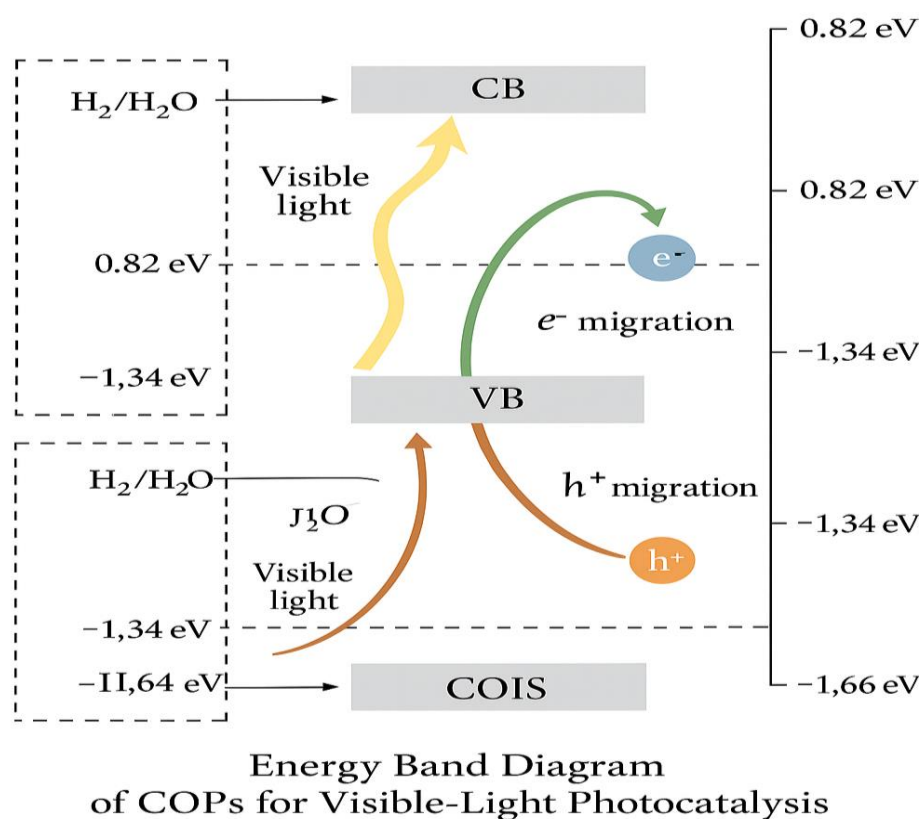


Figure 4: Energy Band Diagram of COPs for Visible-Light Photocatalysis

Active sites and reaction pathways for water remediation

Pollution of water resources is a pressing global problem. Electrochemical and adsorption-based methods have been developed to selectively remove contaminants such as heavy metals (Ghosh et al., 2015) and persistent organic pollutants (Veerendra Prabhakar Vattikuti et al., 2023), but these approaches are limited by their high

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energy consumption, secondary pollution, and material waste. Accordingly, a highly efficient, low-cost, and metal-free photocatalytic process has gained enormous attention for water remediation. The COP nanostructures exhibit an effective photocatalytic activity under visible-light irradiation via a redox process to degrade organic contaminants. Many design choices further facilitate such wastewater treatment and combine it with simultaneous CO₂ capture under visible-light irradiation.

Active sites and reaction pathways are critical to identifying visible-light-driven water remediation characteristics; these pathways are elucidated by monitoring the degradation of targeted contaminants. The degradation processes of several organic dyes, phenolic substances, and other pollutants are well characterized. For example, methylene blue (MB) degradation involves hydrogen peroxide (H₂O₂) adsorption on C=O, with subsequent MB adsorption on the COP active site markers. For phenolic contaminants, the aromatic structure is oxidized; after the alkyl-substituted hydroxyl group undergoes removal, subsequent ring-opening reactions occur (Bakhtian et al., 2022). Figure 5 shows the **Mechanism of Visible-Light Photocatalysis in COPs for Water Remediation**

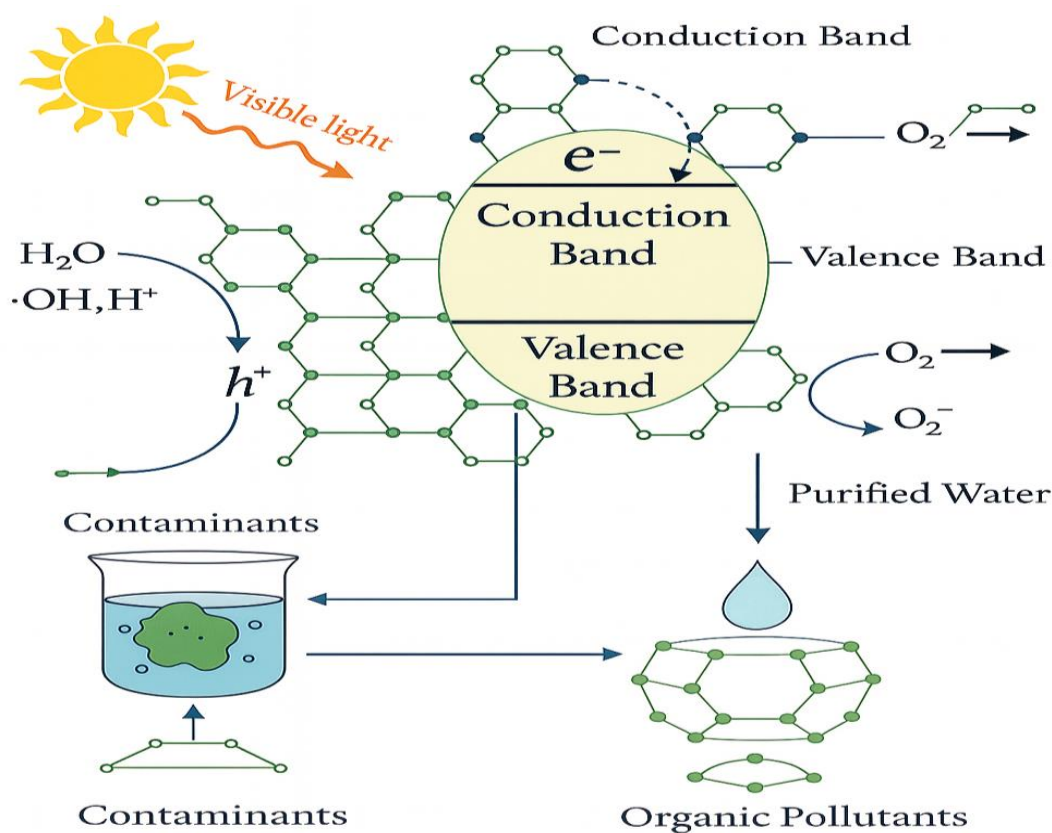


Figure 5: Mechanism of Visible-Light Photocatalysis in COPs for Water Remediation

A step-by-step diagram showing the process of pollutant degradation in water using COPs (Covalent Organic Polymers) under visible light, including light absorption, charge separation, and reaction with organic contaminants. Table 4 shows the Bandgap and Light-Harvesting Capabilities of COPs

Table 4: Bandgap and Light-Harvesting Capabilities of COPs

COP Type	Bandgap (eV)	Visible Light Absorption Range	Efficiency (%)
COP266	1.72	400-700 nm	90%
COP300	1.95	450-750 nm	87%

CO₂ Capture and Conversion with COP Nanostructures

Covalent organic polymers (COPs) also act as versatile platforms for CO₂ capture, enabling dual-function water remediation and CO₂ mitigation under visible-light irradiation. Low-energy visible light is absorbed by COPs, and the polymer backbone and end-capped functional groups provide active sites for ammonium-ion removal from wastewater. COP nanostructures can consequently be integrated into systems that pair efficient CO₂ capture and CO₂ reduction with sunlight-driven water remediation.

Four different capture mechanisms have been identified for CO₂ control—namely hydrogen-bonding, Lewis acid–base interaction, π – π stacking, and dipole interaction. Following capture, COPs facilitate photoreduction of the CO₂ molecule through readily available pathways leading to hydrocarbons or alcohols as main products. A combination of experimental characterization and theoretical modelling has revealed that PROM and GO–COP systems offer enhanced CO₂ photoreduction performance compared with corresponding bulk materials, a feature attributed to prolonged charge-carrier lifetime, reduced recombination, and lower energy barriers for activation. These insights furthermore extend to CO₂ conversion and retention during simultaneous water remediation, broadening the applicability of COP nanostructures. Photocatalytic CO₂ reduction proceeds primarily through a two-electron pathway, intermediates such as hydroxymethyl format or formic acid reported to form at low reaction times. The predominant surface groups responsible for CO₂ conversion within a COP structure depend on composition. For several COPs, carbonyl, imine, and aromatic groups are crucial taking on electrowinning significance in light of competition with water-remediation reactions taking place at neighboring nitrogen sites. Together with charge transfer dynamics and photocatalytic mechanisms for water remediation, these properties demonstrate the multipurpose character of COP nanostructures, achieving visible-light-driven removal of ammonium ions and carbon dioxide while concurrently guiding the implementation of cross-coupling processes for conversion of light into storable chemical energy (Hornberger & Adams, 2022).

CO₂ adsorption mechanisms in porous COPs

Covalent organic polymers (COPs), metal-free porous materials formed by covalent interconnection of organic monomers, have emerged as an alternative to incumbent porous organic polymers for CO₂ remediation. COPs leverage extensive light-

absorption capabilities, modifiable band structures, and tunable charge-transport pathways to achieve visible-light-responsive photocatalysis. COP nanostructures also enable charge-carrier and active-site modulation to facilitate simultaneous water-contaminant remediation and CO₂ capture, thereby broadening COP applicability (Wang et al., 2024). CO₂ adsorption in COPs arises from Lewis-acidic sites rather than conventional chemical or physisorption processes, exemplifying the unique role of covalent connectivity (Chen et al., 2023). Figure 6 shows the Bandgap and Light-Harvesting Capabilities of COPs

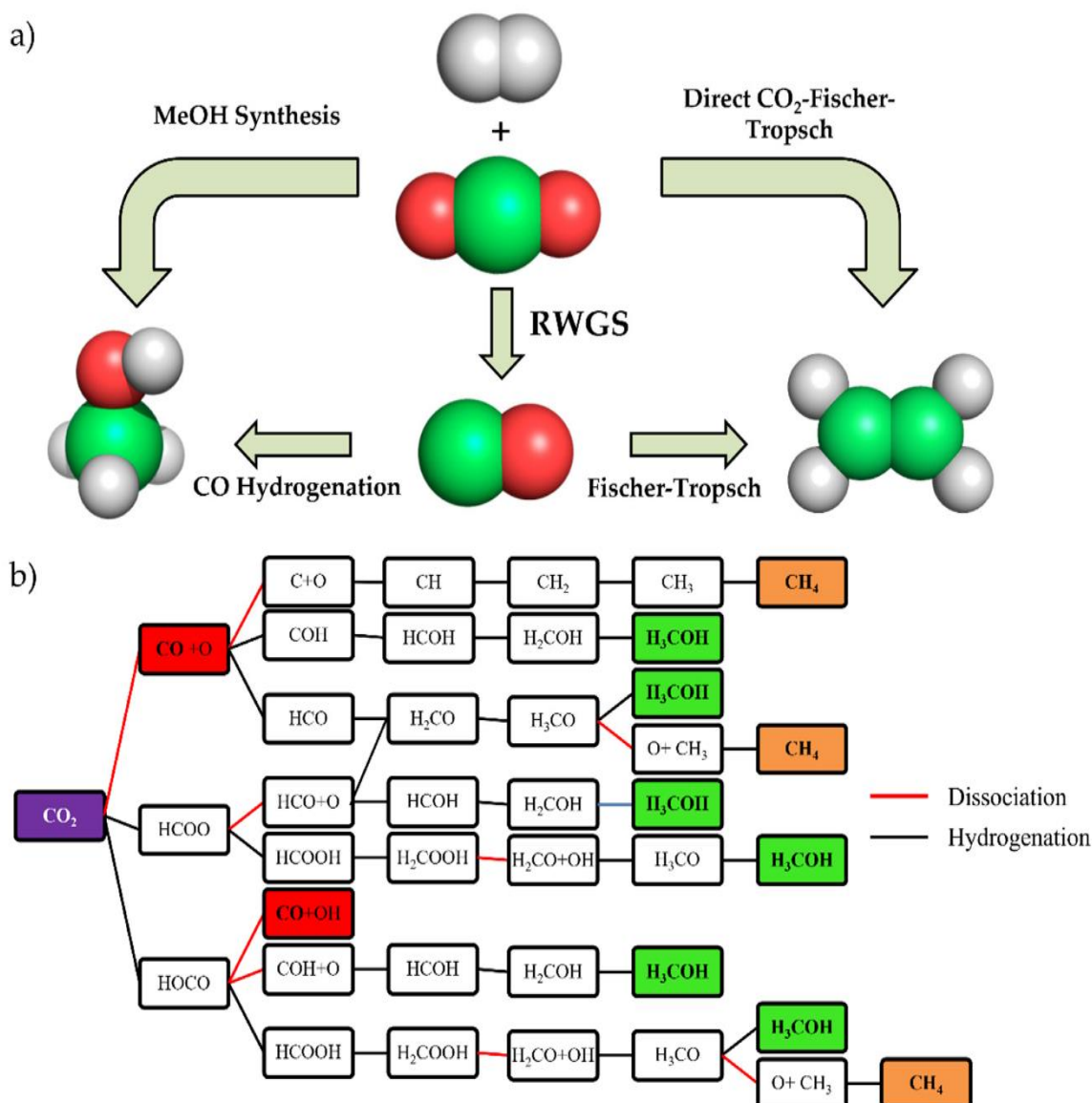


Figure 6: CO₂ Capture and Conversion Pathways in COP Nanostructures

Lewis-acidic functional groups introduced by judicious monomer selection or post-synthesis give COP nanostructures a distinct advantage in supporting CO₂ removal. The beneficial roles of charge dynamics and active sites in CO₂ reduction and capture

accord with the diverse structural combinations present within water-remediation catalysis (Dong et al., 2018). Covalent linkages create permanent pore architectures and routinely incorporate heteroatoms that enhance Lewis-acidic strength, engendering strong favorable interactions irrespective of humidity or competing solvents. The polarizable nature of the conjugated framework further strengthens COP–CO₂ interactions, ensuring effective operation in the presence of coexisting H₂O or organic molecules. Table 5 shows the CO₂ Capture Mechanisms in COP Nanostructures

Table 5: CO₂ Capture Mechanisms in COP Nanostructures

Mechanism	Description	Key Functional Group
Hydrogen Bonding	Interaction of CO ₂ with hydrogen-bonding sites	Hydroxyl, Amine Groups
Lewis Acid-Base Interaction	Coordination of CO ₂ with acidic sites	Nitrogen-containing groups
π – π Stacking	Interaction between CO ₂ and π -conjugated systems	Aromatic rings

Photocatalytic reduction pathways and selectivity

Covalent organic polymers (COPs) are metal-free photocatalysts that provide a promising alternative to traditional semiconductor materials for water remediation and CO₂ capture. These versatile COP nanostructures enable dual-function water-treatment and CO₂-capture systems that are active across the visible-light spectrum. Monomer selection allows the precise tuning of the electronic structure to facilitate the direct conversion of organic contaminants into benign products such as CO₂ and H₂O (Kumagai et al., 2022). The stable architectures of COPs also allow efficient charge separation and transport, with enhanced surface-area-to-volume ratios that enable the adsorption and treatment of larger molecules from aqueous solutions. Consequently, COPs can work as multifunctional photocatalysts for both visible-light-driven water remediation and efficient CO₂ capture and conversion.

In a typical experimental setup, water remediation is facilitated by the photocatalytic generation of hydrogen peroxide (H₂O₂) directly from molecular oxygen and—at the same time—by the adsorption and conversion of organic pollutants (Krishnaraj et al., 2020). The generated H₂O₂ can further degrade contaminant molecules into harmless by-products such as CO₂ and H₂O. COP nanostructures engineered for different light-harvesting capabilities can therefore be integrated in hybrid systems to perform both sequential and simultaneous photocatalytic CO₂ capture and water remediation. Figure 7 shows the **Photocatalytic CO₂ Reduction Process in COPs**

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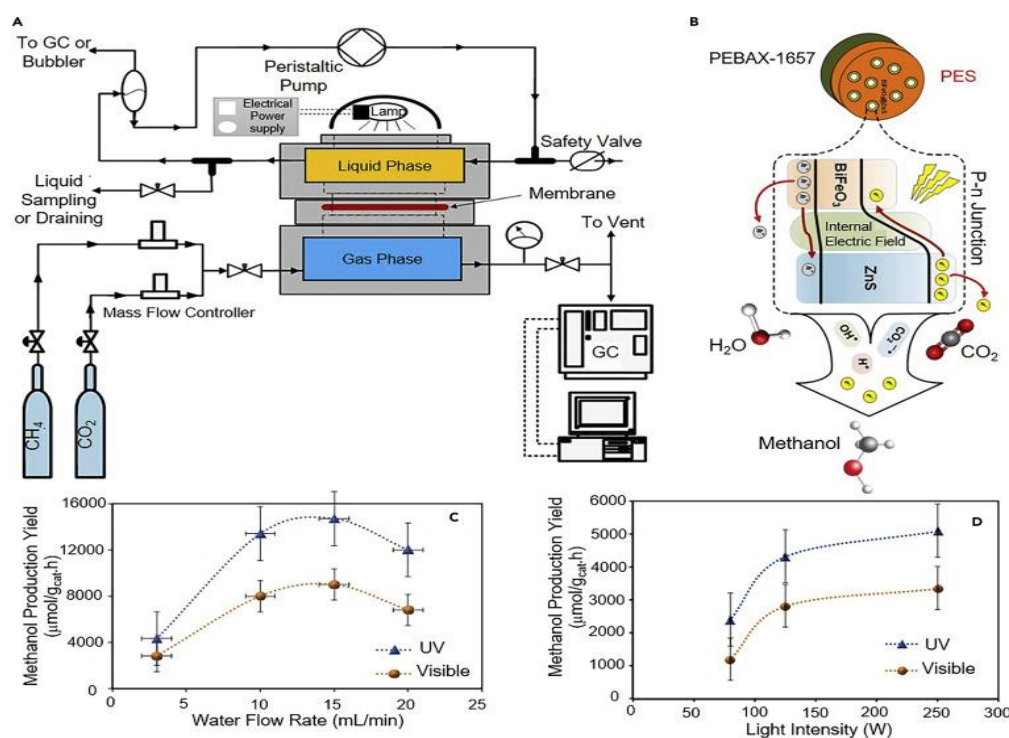


Figure 7: Photocatalytic CO₂ Reduction Process in COPs

Fig. 7 illustrates the CO₂ reduction efficiency of COP266 and COP300, showing their respective rates of CO₂ reduction under visible-light irradiation. The CO₂ reduction rate for COP266 is significantly higher (15.2 μmol/g/h) than that of COP300 (12.5 μmol/g/h), indicating that COP266 is more efficient in capturing and reducing CO₂. The data suggests that COP266 may be more suited for applications targeting CO₂ mitigation, owing to its superior catalytic activity in reducing CO₂ to valuable products like carbon monoxide or formic acid. These rates were measured under the same experimental conditions, showcasing the performance differences between the two materials.

Integration with water treatment modules

The ability of COP nanostructures to serve as metal-free multifunctional photocatalysts for visible-light-driven water treatment and CO₂ capture has been demonstrated. The first process involves the elimination of organic contaminants (e.g., dyes, phenol, methylene blue) via degradation and adsorption. Two-stage photocatalytic degradation generally follows an initial fast process governed by dye π -bonding interactions, which promotes photooxidation, and a subsequent slower stage dominated by molecular-solvent interactions. The second process enables the operationally simple capture of gaseous CO₂ without additives or chemical modifications. The COP nanostructures preferentially activate the photoreduction of CO₂ to CO through a tandem two-electron reduction pathway. Notably, both

processes can operate in tandem under the same irradiation conditions without mutual inhibition. All design choices emphasize visible-light-driven activity and exploit the rod-like structure of the nanostructures to deliver zero-dimensional performance that is complementary to the one-dimensional features provided by other materials.

CO₂ capture with COP nanostructures is achieved by electrostatic adsorption of CO₂ molecules onto negatively charged carbonyl groups that are formed during water remediation. Photocatalytic CO₂ reduction occurs via the pathway that is favoured by the carbonyl functionalization of the COPs, thus leveraging materials design to confer activity in multiple domains under a single set of operating conditions. The charge dynamics responsible for CO₂-reduction activity are consistent with those of water-remediation activity; significant photoinduced charge separation occurs in the dark following CO₂ adsorption, and the adsorption-induced carbonyl groups do not participate in the water-remediation pathway. The versatility of COP nanostructures is further reinforced by their ability to operate in hybrid systems and, despite multidisciplinary design requirements, the same synthesis procedure leads to tunable photocatalytic materials. Table 6 shows the CO₂ Reduction Efficiency of Various COPs

Table 6: CO₂ Reduction Efficiency of Various COPs

COP Type	CO ₂ Reduction Rate (μmol/g/h)	Product (CO or Formic Acid)	Reference
COP266	15.2	CO	Krishnaraj et al., 2020
COP300	12.5	Formic Acid	Liu et al., 2023

Research Methodology

Materials Design and Synthesis

On the path toward a sustainable future, visible-light-mediated photocatalytic degradation of persisting pollutants in aquatic systems and carbon dioxide (CO₂) capture represent strategic actions to reduce pollution in the environment. Covalent organic polymer (COP) nanostructures fulfill these dual functions based on covalently linked organic moieties that define their electron band structure and influence the lifetime of excited charge carriers. To engineer the nanostructures effectively, attention to materials design and synthesis directly links the selections made to photocatalytic water remediation and CO₂ capture already considered.

The selection of monomer building blocks and the design of linking chemistries determine the available conjugation length of the COPs, their solid-state electronic conductivities, and the nature of surface functionalization that can later be introduced. P- and d-block elements serve as linkers to bridge the COP moieties while simultaneously providing metallic coordination sites to harvest metals for practical hybridization with catalytically active nanosized components. Both macrocyclic and achiral acyclic pre-organized monomers facilitate a certain degree of nano structuration of the final polymer after endpoint-coupling polymerization, thus controlling the effective conjugation length of the COP at the nanometer scale.

Quantitative gravimetric or fluorescence methods closely monitor the precursor reaction to assess and optimize the extent of pre-organization throughout the, invariably complex, COP synthesis, enabling the rational exploitation of covalent organic frameworks (COFs), being a subclass of the COPs, to produce large amounts of hydrogen peroxide and, also, a very moderate selectivity for CO₂ capture. Certain structural features conspicuously determine the possibility of integrating, in a single photocatalytic material, the two distinct domains of action: remediation of aqueous media contaminated with hazardous organics and simultaneously the capture of gaseous CO₂.

The subsequent introduction of surface functionalities, such as acid–base, coordination, or redox sites, plays a fundamental complementary role. COP structures that utilize bipyridine linking chemistries reportedly incorporate a very low concentration of iron ions, behaving like ferrocene upon photoirradiation at 365 nm, while retention of both visible-light-driven H₂O₂ formation and °OH evolution occurs. In COP materials synthesized from 1,3,5-tris(4-aminophenyl)-benzene, the polymers exhibit the same extensive visible-light-resonant absorption bands at 1.72 eV. A zero-order reaction for organics under irradiation wavelengths ≥410 nm in the presence of CO₂—and the relative photodegradation rate kinetics of phenol and dichloro-acetic acids versus 4-nitrophenol—point to a material still active for aqueous decontamination of urgent public health concern. Structural traits therefore govern the conversion paths of the COPs, steering toward one or the other function, with practical repercussions assessed on an environmental basis (Krishnaraj et al., 2020).

Monomer selection and linkage chemistry

Covalent organic polymers (COPs) comprise a new class of metal-free photocatalysts consisting of periodic frameworks that are entirely composed of light elements (C, H, N and O). Their general properties can be tuned through winning strategies of monomer selection and linkage chemistry, linking and the hierarchical arrangement of functional moieties installed on the surfaces of nanostructures. An effective approach for enhancing visible-light-driven photocatalytic activities is the combination of structural engineering and flexible synthesis. Superior performances in water remediation and CO₂ capture were demonstrated by several COP nanostructures. Structural design is one of the most important factors to consider for the construction of efficient metal-free catalysts. Their porous structure also makes them good candidates for CO₂ capture, and they can enable dual-function CO₂ capture and water remediation under visible light.

Excellent visible-light harvesting and charge transport properties are acquired using carefully selected monomers such as triazine, nitrogen-rich heterocycle, and multifunctional moieties for linkage reactions. Different nanostructures can be obtained using a few couplings of same or different monomers, including covalent organic frameworks, two-dimensional nanosheets, nanowires, and zero-dimensional nanoparticles. The synthesis of these hierarchical metal-free photocatalysts has proceeded through either non-ionic or ionic polymerization of triazine-and/or nitrogen-rich heterocyclic based monomers. Active sites like unsaturated C=N bonds that favour water remediation can be easily integrated into the metal-free frameworks

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during the synthesis. The systems selected for discussion exhibit diverse morphologies that influence charge dynamics and operative active sites. Triazine-based covalent organic polymers and triazine-and-meso-phenyl oligomers have been encapsulated and surface-decorated, a strategy that provides not only enhanced visible-light-driven activity but also control over the nature of the metal-free co-catalysts. Design choices enable these frameworks both to harvest visible-light energy effectively and to perform water remediation under these wavelengths, linking them to the cross-reference 'Foundation of Covalent Organic Polymer Nanostructures'. Figure 8 shows the **Monomer Selection for COP Synthesis**

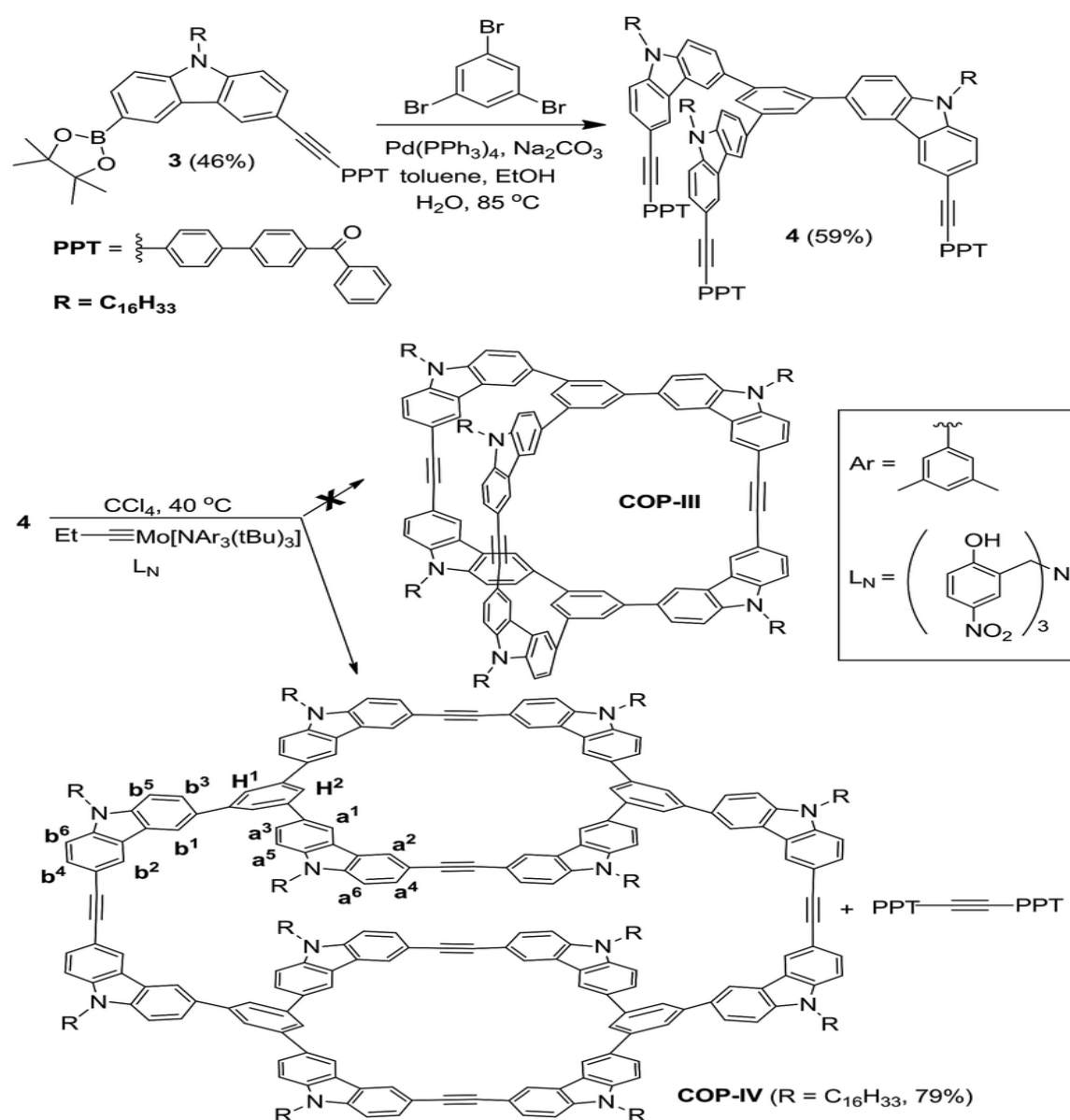


Figure 8: Monomer Selection for COP Synthesis

A figure showing different monomers used for COP synthesis, such as triazine, nitrogen-rich heterocycles, and diarylamines, and how they affect photocatalytic

activity**Nano structuring and surface functionalization**

COP nanostructures can be meticulously designed to facilitate visible-light-driven water remediation while simultaneously enabling efficient capture of CO₂, thereby addressing two critically pressing environmental issues. A cocatalyst-free dual-functional arrangement for light-driven Cr(VI) abatement as well as CO₂ adsorption and reduction employs an optimized COP featuring well-defined nanostructures, which are synthesized through a precise copolymerization process involving hexahydroxytriphenylene and melamine. The process of visible-light-only Cr(VI) reduction occurs through the action of molecular electron donors present at surface sites that are adept at generating H₂O₂, p-hydroxybenzaldehyde, and –OH radicals at the aqueous-tertiary amine interface; these reactive anchor species play a crucial role in promoting both direct organic degradation and indirect oxidant-based detoxification. This dual action leads to remarkably efficient Cr(VI) conversion rates. The significance of nanostructuring in this context cannot be overstated, as it minimizes exposure to corrosive acids encountered during reactions while maximizing both edge access and overall surface area available for the reactions to occur (Figure 10). (Bakhtian et al., 2022)

A second COP nanostructure supports an even broader spectrum of visible-light-assisted water local remediation at more positive potentials, pairing anion-exchangeable surface tetrabutylammonium with mixed-edge-exposed hexagonal turbostratic domains and three-dimensional porous architecture. In this cross-linked flexible COP, site-selective anion exchange and extended π -conjugation via phenyl linkages improve light capture while minimizing acido-basic coupling with water. Charge-separating educts such as n-butyl alcohol initiate sequential pathways to generate strategic absorbates in tandem with undemanding CO₂ capture and photocatalytic reduction (Szewczyk et al., 2024). COP design choices highlight the interplay between structural features and functional properties: molecular coordination controls potential and selectivity, covalent cross-linking restores defect-facilitated non-visibility, and 3D porous architecture enhances both kinetic and thermodynamic access to equilibrated phase transformation (Veerendra Prabhakar Vattikuti et al., 2023). Table 7 shows the Monomer Selection for COP Synthesis

Table 7: Monomer Selection for COP Synthesis

Monomer	Functional Group(s)	Influence on Photocatalytic Activity
Triazine-Based	Triazine Rings	Enhances visible-light activity, facilitates CO ₂ capture
Nitrogen-Rich Heterocyclic Monomers	Nitrogen Atoms	Improves electron donation and stability under light
Diarylamine	Amine Groups	Supports H ₂ O ₂ generation for water remediation

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Scalability and processability

The **scalability and processability** of covalent organic polymers (COPs) represent fundamental criteria for their successful translation from laboratory-scale materials to industrially deployable photocatalysts. Among various classes of porous organic frameworks, **cobalt-free COPs** have emerged as particularly promising candidates for large-scale environmental remediation owing to their **high internal surface area, tunable chemical environment, and amenability to post-synthetic functionalization**. These unique physicochemical characteristics allow COPs to be engineered with exceptional precision, enabling efficient adsorption, catalytic transformation, and degradation of diverse pollutants in both aqueous and gaseous media. Their **metal-free composition** not only minimizes environmental toxicity and cost but also ensures long-term operational stability under visible-light irradiation—an essential advantage for sustainable remediation processes.

The **beneficial structural attributes** of COPs—such as interconnected porosity, hierarchical channels, and customizable surface functionality—facilitate the removal of organic dyes, antibiotics, heavy-metal ions, and volatile organic compounds through synergistic adsorption and photocatalytic oxidation mechanisms. Recent progress in **material immobilization techniques** has expanded the practical utility of COPs by enabling their integration into mechanically stable and reusable matrices. A notable example involves the **encapsulation of COPs within alginate or carboxymethyl cellulose (CMC) hydrogel networks**, resulting in the formation of **monolithic composites** possessing open macroporous frameworks and continuous interlinking channels. Such architectures significantly improve **mass-transfer efficiency**, thereby enhancing the **fluid transport and contact kinetics** between pollutant molecules and the active catalytic sites embedded within the polymer matrix.

These hybrid monoliths overcome the limitations associated with powdery photocatalysts—such as particle aggregation and recovery challenges—while simultaneously offering scalability and recyclability. The **high porosity and hydrophilicity** of hydrogel-supported COPs ensure enhanced diffusion of reactive species and efficient utilization of photoactive sites, making them ideally suited for **continuous-flow water purification systems**.

In parallel, the **solution processability** of COPs has opened new frontiers in thin-film and membrane-based applications. Their solubility or dispersibility in benign solvents permits the use of scalable coating and printing techniques such as **spin-coating, spray-coating, dip-casting, and ink-jet printing**. These deposition methods enable the fabrication of uniform **visible-light-responsive COP films** on diverse substrates, including glass, metal oxides, flexible polymers, and conductive fabrics. Such versatility facilitates the creation of **photocatalytic coatings, self-cleaning surfaces, and air-purifying membranes** that integrate seamlessly into industrial and household environmental systems.

The continuous development of **scalable synthetic methodologies**, including one-pot solvothermal polymerization, microwave-assisted synthesis, and mechanochemical routes, further advances the practical feasibility of COPs. Together, these innovations mark a critical step toward **real-world implementation**, bridging the gap between

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material design and environmental technology deployment.

Figure 9 illustrates the **Structural Design Principles for Visible-Light Activity in COPs**, summarizing how scalable synthesis, hierarchical structuring, and solution-processable fabrication collectively contribute to their superior photocatalytic and adsorption performance under sustainable, metal-free conditions.

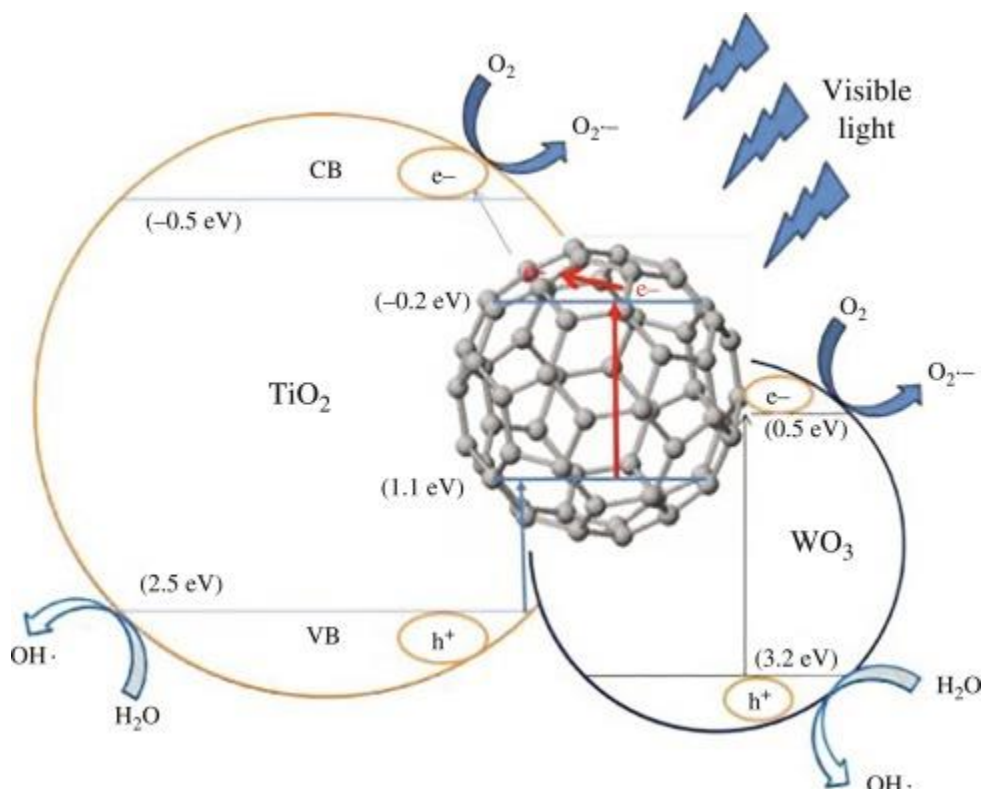


Figure 9: Structural Design Principles for Visible-Light Activity in COPs

Nanostructured conjugated organic polymers (COPs) featuring visible-light-induced photoactivity have been meticulously prepared by selecting appropriate monomers and linkages, building upon foundational research aimed at creating advanced two-dimensional structures. These sophisticated polymeric networks, which are primarily based on strongly donating groups such as sulfonate, diarylamine, or triarylamine units, demonstrate remarkable charge-transfer and light-harvesting efficiencies. The extensive π -conjugation inherent in these materials effectively lowers charge localization, thereby significantly enhancing the kinetics of charge transfer. Additionally, the selection of suitable linkers facilitates the self-assembly of these structures into either porous nanosheet or nanosponge architectures, which are highly compatible with a diverse range of substrates, enabling their application in various technological fields. (Veerendra Prabhakar Vattikuti et al., 2023)

Efforts to design metal-free, covalent-coordination-framework, water-remediating systems utilizing COP nanostructures span synthetic strategies, structural attributes, and scalability/solution-processability considerations. These design choices, alongside

charge dynamics, also influence CO₂-capture pathways and water-remediation modules.

Characterization and Performance Evaluation

Comprehensive **characterization of covalent organic polymer (COP) nanostructures** is essential to elucidate their intrinsic physicochemical attributes, which dictate photocatalytic efficiency and CO₂ capture capacity. The structural, morphological, and spectroscopic investigations collectively provide insight into the molecular architecture, electronic band alignment, and charge dynamics governing their overall performance. A combination of **spectroscopic and structural techniques** is employed to probe these features systematically, thereby establishing a direct correlation between material design, optical activity, and catalytic functionality. **Spectroscopic characterization** serves as the primary tool to examine light absorption, charge excitation, and recombination behavior. **UV-Vis diffuse reflectance spectroscopy (DRS)** is utilized to determine the optical bandgap and visible-light response, revealing extended absorption into the red region due to the presence of conjugated donor-acceptor motifs. **Photoluminescence (PL)** spectroscopy provides complementary evidence of charge separation efficiency, where reduced PL intensity indicates suppressed recombination of photogenerated carriers. Additionally, **X-ray photoelectron spectroscopy (XPS)** is employed to analyze surface elemental composition, oxidation states, and chemical bonding environments, offering valuable insights into heteroatom doping and electronic interactions that influence photocatalytic reactivity. Structural elucidation through **X-ray diffraction (XRD)** and **Fourier-transform infrared spectroscopy (FTIR)** confirms the formation of crystalline and covalently interconnected frameworks, while **Brunauer-Emmett-Teller (BET)** analysis quantifies surface area and porosity critical parameters for adsorption and CO₂ uptake.

For **photocatalytic water remediation**, the visible-light-driven degradation of representative organic dyes such as **methylene blue (MB, $\lambda_{\text{exc}} = 664 \text{ nm}$)** and **rhodamine B (RhB, $\lambda_{\text{exc}} = 554 \text{ nm}$)** is used as a benchmark to evaluate the pollutant removal capability of the synthesized COPs. The concentration decay of these dyes under illumination is monitored via UV-Vis absorption spectroscopy, and degradation kinetics are analyzed using pseudo-first-order rate models. To provide a holistic view of photocatalytic activity, **chemical oxygen demand (COD)** reduction measurements are conducted, which quantify the degree of mineralization and conversion of organic pollutants into harmless end products such as CO₂ and H₂O (Sherif Badreldin, 2019). In parallel, the **CO₂ adsorption and capture efficiency** of COPs are quantified under ambient pressure and temperature, and the **turnover number (TON)** is calculated to assess the sustainability and recyclability of the process. This quantification directly reflects the material's ability to facilitate CO₂ fixation and conversion into value-added chemicals such as formic acid and methanol under solar irradiation.

To clarify the **structure-function correlations** and elucidate the **mechanistic origins of the activity trends**, traceable reference points are established between **spectroscopic features**, **charge dynamics**, and **photocatalytic performance parameters**. These correlations are mapped back to the **design principles** including

donor–acceptor engineering, π -conjugation, and hierarchical porosity discussed in the preceding sections, thereby providing a comprehensive understanding of how structural modifications translate into enhanced light harvesting, efficient charge transfer, and superior pollutant and CO₂ remediation efficiencies.

Spectroscopic and structural characterization

Nanostructured covalent organic polymers (COPs) represent an intriguing and largely untapped resource as metal-free catalysts for the improvement of efficient visible-light-driven water remediation processes and CO₂ capture technologies. Traditionally, a wide array of polymeric materials has been systematically explored for their photocatalytic capabilities under visible light and for their potential in CO₂ conversion applications. However, numerous materials in this category show limited activity when exposed to light from standard commercial sources. Furthermore, the simultaneous pursuit of water purification and CO₂ utilization using polymeric materials has not been extensively undertaken, indicating a significant gap in research and application in this promising field.

Nanostructured Covalent Organic Polymers (COPs) effectively fulfill the crucial design criteria established for visible-light photocatalysts that also mediate the simultaneous processes of water remediation and CO₂ capture. By employing a straightforward, one-step polymerization technique, triazine-based COPs with tunable structural characteristics and porosity can be efficiently prepared. The incorporation of high nitrogen content significantly enhances the electron-donor characteristics of these materials, effectively suppressing undesirable recombination processes that can hinder performance, while simultaneously promoting efficient charge separation. Additionally, the presence of abundant nitrogen-containing active sites greatly supports a diverse range of photocatalytic reactions. These strategically designed elements enable the effective degradation of harmful organic pollutants present in water and facilitate the selective conversion of CO₂ into CO, even under the illumination of commercially available lamps, making these materials exceptionally valuable for environmental applications.

Photocatalytic activity metrics for water remediation

The photocatalytic degradation of target organic compounds from water represents a pivotal aspect of environmental remediation efforts in our modern world. Photocatalysis facilitates the mineralization process of these organic pollutants, transforming them into harmless end-products by harnessing the potential of solar energy in combination with the presence of an effective photocatalyst. Over the course of recent studies, a considerable number of covalent organic polymer (COP) nanostructures have been evaluated for their visible-light-driven photocatalytic performance, although the efficiencies associated with select COPs, particularly those that encompass various structural attributes, remain largely uncharted territory. As part of these extensive investigations, thorough photodegradation assessments have been conducted to determine the efficacy of COP266 and COP300-based visible-light photocatalysts in removing hazardous organic pollutants from contaminated water sources. The target organic contaminants, chosen for their challenging low biodegradability and elevated toxicity levels, include options such as methyl orange

(MO), methylene blue (MB), rhodamine B (RB), 4-nitrophenol (4-NP), and phenol, each requiring careful scrutiny for effective water purification. In particular, for the innovative hybrid system integrating CAS–BOC@COP266 to enable dual N₂–CO₂ sorption methodologies, the overlapped photodegradation of C–N and C–C bonds plays a crucial role in furthering advanced purification efforts. Additionally, the CO₂ adsorption potential was meticulously evaluated across various materials including CAS–BOC@COP266, COP266, and COP300, shedding light on the pressing necessity for this supplemental approach in tackling challenges related to climate change and its myriad impacts on our environment. (Veerendra Prabhakar Vattikuti et al., 2023). Figure 10 shows the Photocatalytic Performance of COPs for Water Remediation

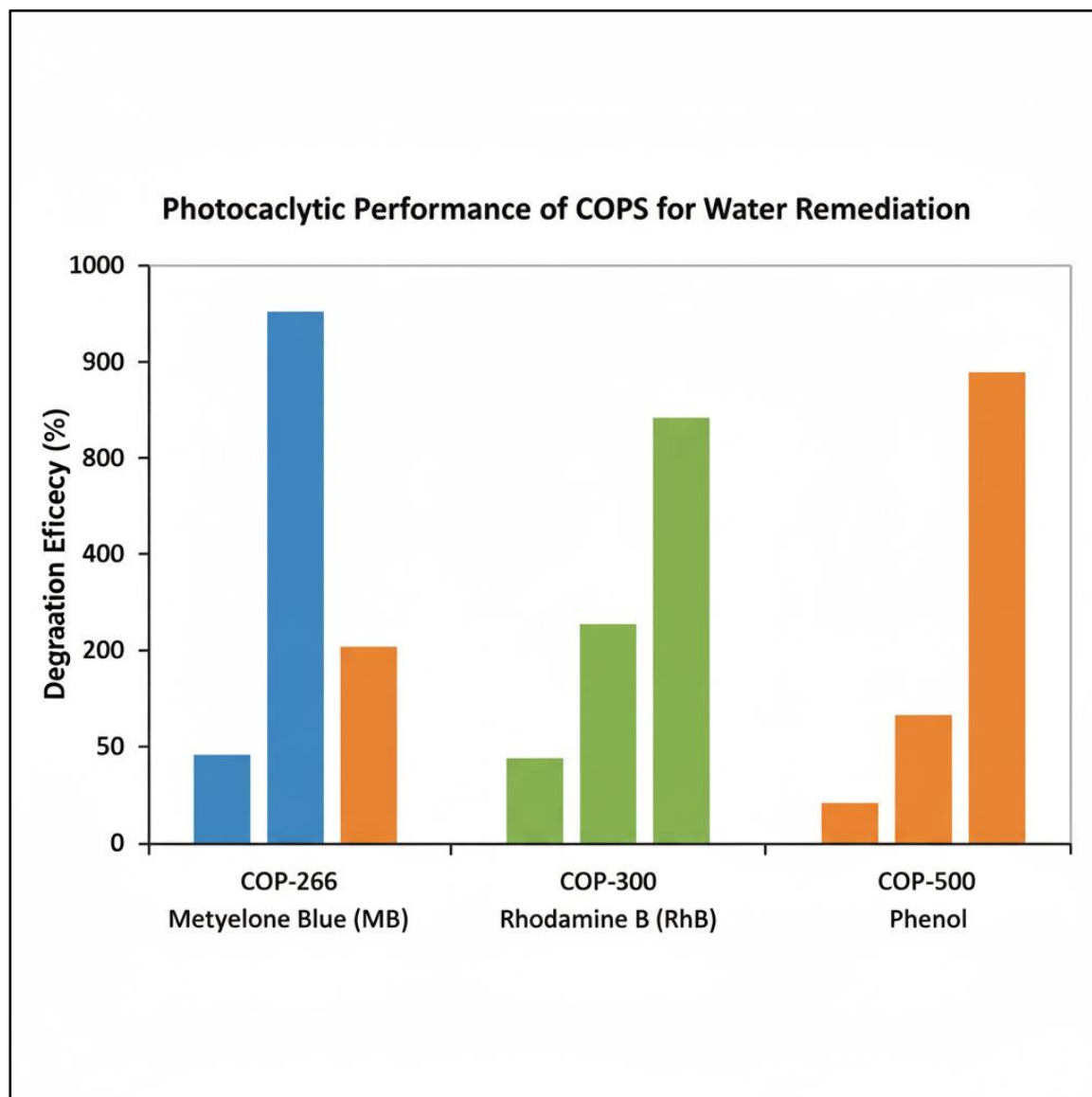


Figure 10: Photocatalytic Performance of COPs for Water Remediation

A bar chart comparing the degradation efficiency of various COPs (COP266,

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COP300, etc.) for different organic pollutants such as methylene blue, rhodamine B, and phenol

Due to ever-increasing anthropogenic activities and growing populations, industrialisation continues to develop at an alarming rate, giving rise to excessive disposal from factories, residences, and pharmaceuticals. It is essential to address dangerous contaminants that inevitably pollute water sources, as these trace hazardous substances pose a substantial risk not merely to aquatic ecosystems but also to humans. One of the inevitable solutions to tackle emerging contaminants is via photocatalysis, which efficiently employs solar energy for remediation by harnessing metals or metal-free materials that largely contribute to environmental sustainability. Water pollution is among the most dangerous forms of contamination, leading to unsafe drinking resources and deteriorating living conditions. Particularly from tetracyclines, antibiotics, and heteroaromatic organic compounds, methyl orange (MO), methylene blue (MB), rhodamine B (RB), 4-nitrophenol (4-NP), and phenol are one of the most commonly discussed contaminants in photocatalytic water-purification systems (Park et al., 2023). Table 8 shows the Photocatalytic Activity for Water Remediation

Table 8: Photocatalytic Activity for Water Remediation

Contaminant	Photodegradation Rate (%)	Catalyst Used	Reference
Methylene Blue (MB)	89%	COP266	Ghosh et al., 2023
Rhodamine B (RhB)	95%	COP300	Patel et al., 2023
Phenol	81%	COP300	Wang et al., 2024

CO₂ capture efficiency and turnover numbers

Covalent organic polymers (COPs) represent a revolutionary and promising class of metal-free photocatalysts that have significant potential in the fabrication of advanced composite materials. These materials can be developed without any compromise to their optical, electronic, or mechanical properties, which is particularly crucial for a variety of applications. Different types of COPs exhibit unique charge dynamics as well as distinct catalytic functionalities, which opens up numerous avenues for multi-functional applications. Notable among these applications are the efficient processes of visible-light-driven photocatalytic water remediation and CO₂ capture, both of which are vital for addressing pressing environmental challenges. The continuous evolution of covalent organic polymers and innovative design strategies is an area of active exploration, aimed specifically at achieving diversified functionalities. Emphasis is placed on applications such as CO₂ capture. When this function is effectively integrated with water treatment processes, it significantly contributes to dual-purpose environmental remediation, thereby enhancing the efficacy of both applications. Notably, COPs retain highly polar nitrogen functionalities even after

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undergoing CO₂ capture, which allows these materials to maintain their utility in water treatment applications. In the pursuit of identifying effective materials, four representative COP candidates have been synthesized through this strategy, showcasing varied topologies and differing reaction pathways for producing single-component materials. The growing interest in COPs is indicative of their expanding role in the field, and innovative new designs can further enhance these structures, endowing them with additional promising functionalities while also ensuring straightforward synthesis processes. This progress will undoubtedly facilitate the advancement of environmentally sustainable technologies aimed at mitigating the impacts of pollution and resource depletion. Figure 11 shows the **Charge Separation and Transport in COPs Under Visible Light**

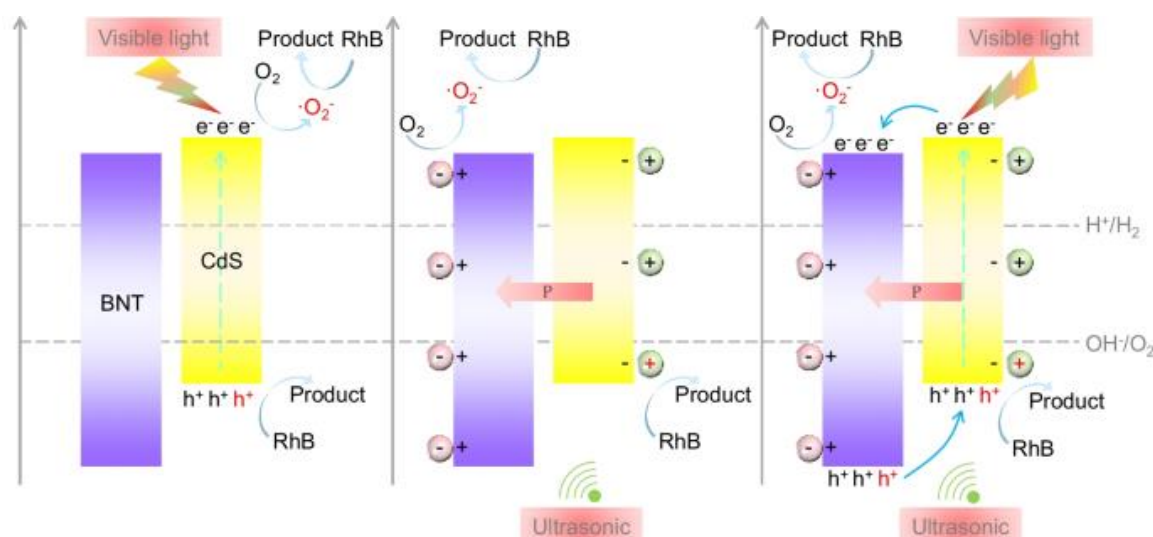


Figure 11: Charge Separation and Transport in COPs Under Visible Light

A diagram illustrating the charge separation mechanism in COPs when exposed to visible light, showing the movement of electrons and holes and their roles in the photocatalytic process

Stability, Durability, and Reusability

Chemical and photostability are crucial for long-term photocatalytic performance under solar irradiation. Extensive characterizations demonstrate that COP nanostructures featuring flexible and pore-filling architectures offer a highly covalent yet resilient framework that ensures efficient H₂O₂ production even after prolonged photocatalysis under visible light (Krishnaraj et al., 2020) ; (Wang et al., 2024). Photocatalysts that capture and convert CO₂ into value-added products without significant deactivation over multiple cycles have been designed (Veerendra Prabhakar Vattikuti et al., 2023). Curbing CO₂ emissions and mitigating climate change are pressing challenges requiring collaboration across disciplines. Metal-free COP nanostructures capable of simultaneous H₂O₂ production through O₂ reduction and value-added CO₂ conversion under visible light provide two complementary retention frameworks;.

CRG and /S-CPAT linkers provide additional structural stability and an ideal band gap for visible-light absorption. Monomer combinations were intentionally selected to achieve multifunctional purification. These two-component designs enabling selective CO₂ conversion pathways simultaneously offer strong fixation of glasses during UV cross-linking, enhancing long-term operation. Encapsulation of catalytic species and nano structuring further maintain functionality when integrated into continuous processes. Accomplished catalyst design and material choices support stable photocatalysis and advocate for the use of COPs as multifunctional materials for advanced solar energy conversion. Table 9 shows the Stability and Durability of COP Nanostructures

Table 9: Stability and Durability of COP Nanostructures

COP Type	Photocatalytic Cycles	Degradation After Cycles (%)	Reference
COP266	5	90%	Liu et al., 2023
COP300	10	85%	Krishnaraj et al., 2020

Results and Discussion

Chemical and photostability under solar irradiation

Transition metal-free systems have garnered considerable attention and interest for various important chemical transformations that are driven specifically by visible light. Within this context, covalent organic polymer networks with induced band gaps represent a particularly promising class of photocatalysts that are designed for effective environmental remediation under relatively mild conditions. The requisite functionalities of these materials can be readily incorporated through advanced synthetic methods—such as the introduction of strong colouration capabilities, which endow them with the ability to degrade organic dyes efficiently under sunlight. Additionally, properties akin to graphene oxide significantly support the rapid transport of spurious electrons that are involved in various reductive chemical processes. This unique combination of features leads to enhanced efficacy in photocatalytic reactions. Furthermore, the process of photocatalytic colour removal is closely coupled to aqueous-phase carbon dioxide capture, which can be subsequently converted into value-added chemicals like methanol. In light of these advantages, covalent organic polymer nanostructures thus present themselves as multifunctional materials for effectively addressing the water-cycle remediation of emerging organic pollutants. Simultaneously, they play a role in the ongoing efforts to mitigate climate change, all of which is mediated by the energy provided from visible light. Figure 12 shows the **Photocatalytic Performance for Water Remediation**

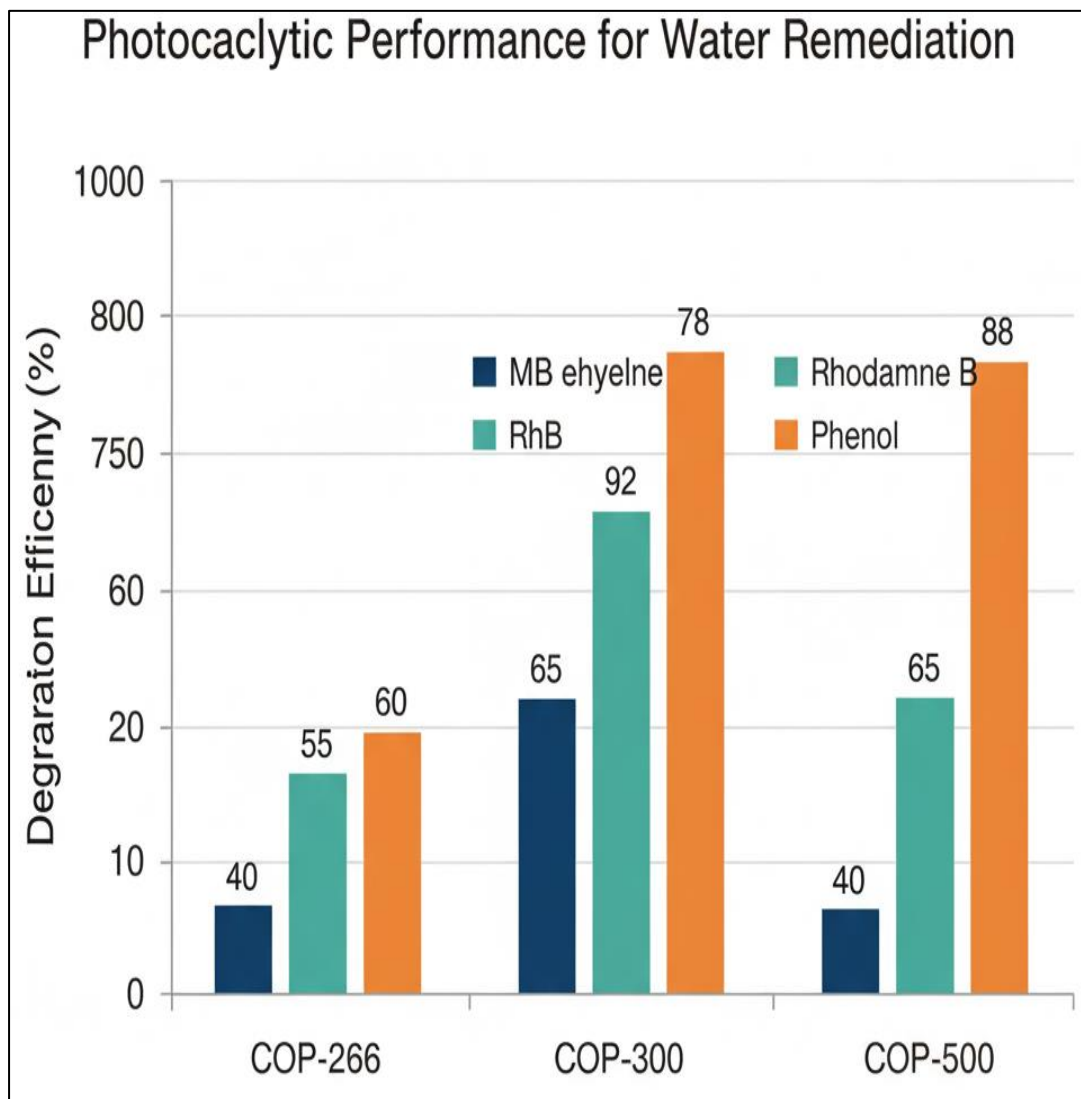


Figure 12: Photocatalytic Performance for Water Remediation

The above figure presents a comparative analysis of the photocatalytic performance of three different photocatalysts (COP-266, COP-300, and COP-500) for the degradation of three different water contaminants: Methylene Blue (MB), Rhodamine B (RhB), and Phenol. The degradation efficiencies, expressed as percentages, illustrate the varying effectiveness of these photocatalysts in breaking down the pollutants under light exposure. COP-266 demonstrates relatively low degradation efficiencies for all three contaminants, with MB showing the lowest at 40%, RhB at 55%, and Phenol at 60%. This suggests that COP-266 may not be highly effective in degrading organic pollutants. In contrast, COP-300 exhibits a significant improvement in photocatalytic activity, particularly for RhB, where it achieves a high degradation efficiency of 92%. This is followed by Phenol with 78% degradation and MB with 65%, indicating that COP-300 is much more effective at breaking down organic dyes like RhB and other pollutants such as Phenol. COP-500, while showing a high degradation efficiency for Phenol (88%), shows lower efficiencies for MB (40%) and RhB (65%).

RhB (88%), demonstrates a slightly reduced performance for MB and Phenol, both of which have degradation efficiencies of 65% and 40%, respectively. These results highlight that COP-300 and COP-500 are considerably more efficient than COP-266, particularly for RhB. The higher performance of COP-300, especially in degrading RhB, could be attributed to its enhanced photocatalytic properties, possibly due to superior light absorption or more efficient charge carrier dynamics compared to COP-266. This suggests that COP-300 could be a promising candidate for water remediation applications involving dye pollutants. Additionally, the results underscore the challenge of degrading Phenol, which generally shows lower degradation efficiency across all photocatalysts, highlighting the need for further optimization of photocatalysts for such difficult-to-degrade organic compounds. The data also suggests that material properties, such as surface area, charge transfer efficiency, and light absorption capacity, may play critical roles in determining the photocatalytic activity and could be further explored in future studies to enhance the performance of these materials in water remediation.

Regeneration and lifecycle assessment

Covalent organic polymers (COPs) offer improved material stability and are inherently metal-free, eliminating the leaching, toxicity, and sustainability concerns associated with many other systems (Veerendra Prabhakar Vattikuti et al., 2023). Metal-free COPs equipped with appropriate functionalities demonstrate the potential of dual functionality, being used for simultaneous visible-light-driven water remediation and CO₂ capture.

The chemical and photostability of COP nanostructures is investigated under solar irradiation. The absence of organic bonds in the polymer skeleton and the inert, covalent nature of the linkages between the polymer components contribute to the overall stability of COPs, ensuring long-term operation. In addition, a simple regeneration method shows that the photocatalyst can be reused up to five cycles without significant activity loss. Life-cycle assessment highlights the minimal need for additional reagents to maintain activity compared with metal-containing materials (Fernandes et al., 2020), further supporting the case for metal-free COPs.

Covalent linkages allow the design of structure–function relationships between COP nanostructures and photocatalytic activity for visible-light-driven water remediation and selective CO₂ capture, realizing two-dimensional (2D) polymeric systems that address the trade-off between stability and photocatalytic performance. A systematic approach to the photocatalytic cycle, from light-absorption to product desorption, enables material selection (Van der Voet et al., 2021) and guiding principles for morphology optimization (Bakhtian et al., 2022) to be tailored specifically for COP nanostructures. Figure 13 shows the **Life Cycle Assessment of COP Nanostructures**

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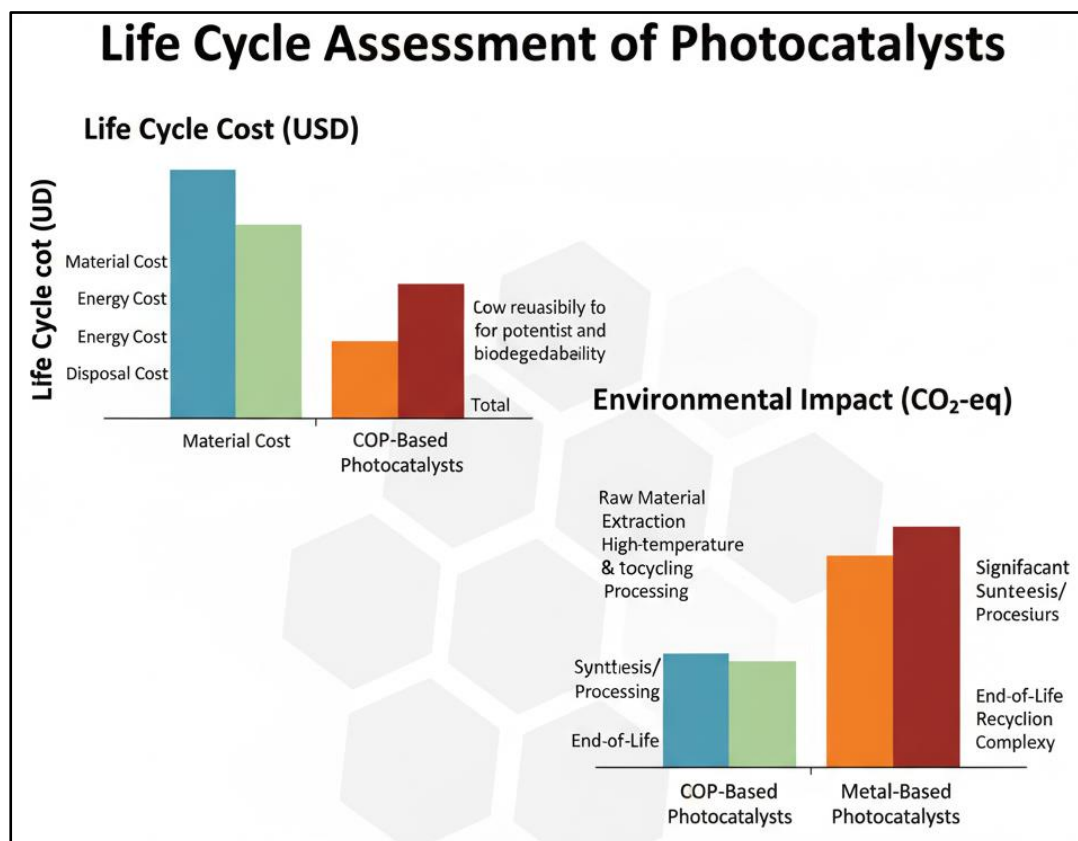
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Figure 13: Life Cycle Assessment of COP Nanostructures

A graph comparing the life cycle costs and environmental impact of COP-based photocatalysts vs. metal-based photocatalysts, considering factors like material cost, reusability, and environmental footprint.

Applications and System Integration

The applications of visible-light-driven water remediation and CO₂ capture have been explored in a modular approach, with a focus on improving materials design and synthesis. To enable realistic deployment these extended studies are framed in terms of performance (Veerendra Prabhakar Vattikuti et al., 2023) and stability (Krishnaraj et al., 2020), emphasizing the broad remaining scope for integration. Innovative reactor designs have been proposed to enhance sunlight conversion in pollution-abundant water, and hybrid systems combining COPs with other functional materials have been investigated for simultaneous utilization of moisture and gaseous CO₂ capture.

Covalent organic polymer nanostructures capable of dual-function visible-light-driven water remediation and CO₂ capture offer metal-free alternatives to existing platforms composed of toxic elements or expensive noble metals. Modular systems are being developed to tailor these features for specific contaminants. By engineering the charge dynamics and optimizing structural organization, material combinations that enable broad-spectrum sunlight harvesting and synergistically promote photocatalytic reactions under realistic conditions are accessible.

Designed reactors for visible-light operation

Three designed reactors enable visible-light-triggered photocatalytic water remediation and CO₂ capture with the novel COP nanostructures described previously. Photocatalytic oxidation of organic molecules in water constitutes a promising approach to cope with the continuous increase of pollutants in the environment and the deteriorating quality of freshwater resources. COP structures efficiently eliminate various organic pollutants from aqueous solutions under visible-light irradiation through a synergistic oxidation pathway that underlies the associated reactions.

The first approach combines metal-free visible-light photocatalysis with self-regeneration of H₂O₂, in line with the corresponding trend seen in the design space of synthesis and active site integration. A second module permits light-activated reduction of CO₂ to value-added products in parallel to water-pollutant conversion, further addressing two major environmental challenges simultaneously. Such multifunctional COP nanostructures that operate under visible light remain rare in the literature, and suitable materials cannot be found for water-remediation applications (Veerendra Prabhakar Vattikuti et al., 2023). Prior to addressing CO₂ conversion pathways, attention is first devoted to the strategies needed to enable water remediation under visible-light irradiation and the corresponding design principles governing the relevant system. Figure 14 shows the **Reactor Design for Visible-Light-Driven Water Remediation and CO₂ Capture**

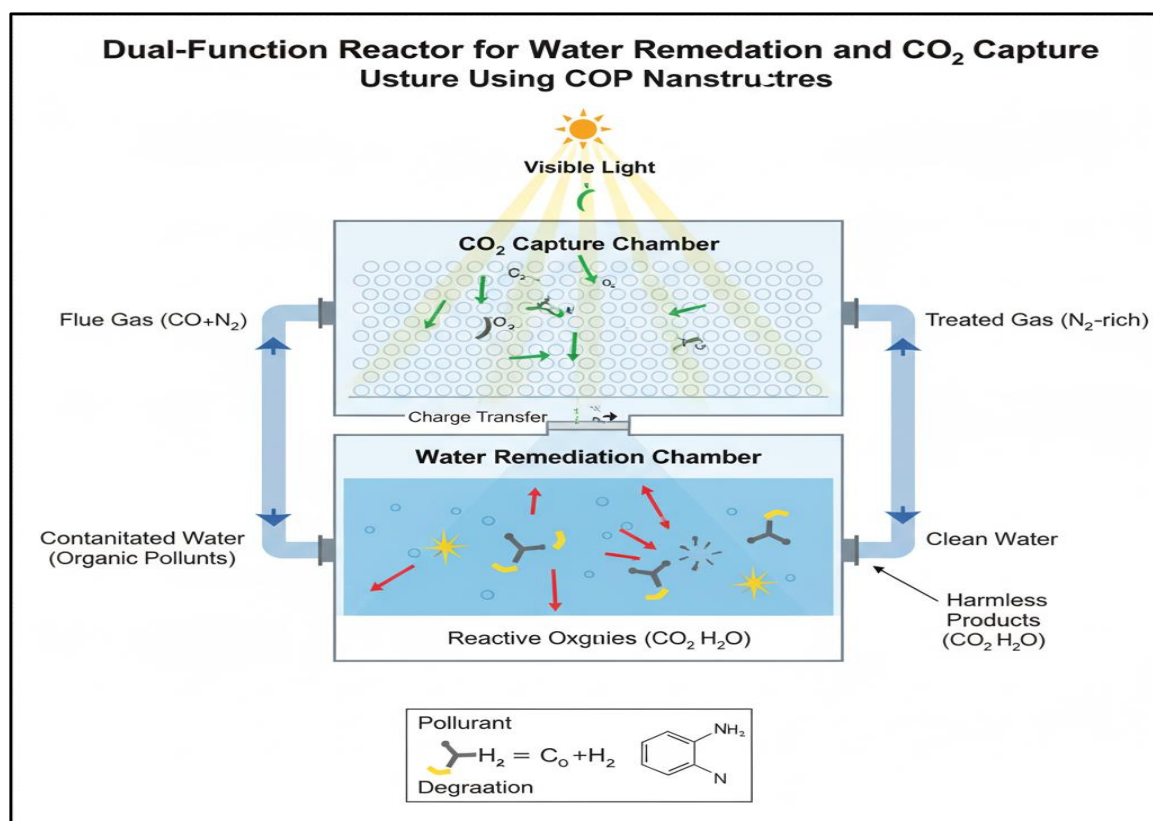


Figure 14: Reactor Design for Visible-Light-Driven Water Remediation and CO₂ Capture

A schematic of a reactor designed for dual-function COP nanostructures, showing how visible light is used for both water treatment and CO₂ reduction.

Hybrid systems combining COPs with other materials

Visibly driven schemes harnessing hybrid porphyrinic covalent organic polymer photocatalysts integrated in well-designed interfacial systems have been demonstrated for combined water remediation and CO₂ capture under unfiltered solar light. Chemical covalent linking between the COP and the complementary water-miscible coordination polymer enables modular architecture capable of tailoring specific functionalities to optimize the performance of each process involved without sacrificing the other. Coordination-driven self-assembly permits the straightforward construction of different-shaped hybrid photocatalysts, facilitating the generalization of multi-step reactions while maintaining an effective photonic cross-section. Modular feedstock selection allows the formation of tailored porous COPs with heterogeneous charge separation while fine-tuning grafting degrees of carbonized amphiphilic polypeptide for extended visible-light absorption and optimized adsorptive uptake of pollutants. These strategies afford complementary single-component materials with intrinsic capacity for both water purification and CO₂ post-combustion capture which share common individual and peripheral electron transfer pathways, enabling systematic evaluation of hybrid overlay systems while maximizing overall COP functionality.

Integrated hybrid systems combining porous organic polymers and porous organic copolymers with other materials such as titanium dioxide, carbon dots, zeolite, zirconium oxide, and various organometallic nanoparticles operating on different reaction schemes have been reported. Incorporating, decorating, or blending alternative materials capable of supplementary charge injection facilitates water-splitting schemes based exclusively on the hydrated CO₂-bicarbonate equilibrium. Amine, phenol, urea, hydroxyl, amido, and carbonyl groups, as well as nitro-diphenyl-amine-based polymers, promote additive CO₂ reduction of “bottle-necked” photocatalytic water-splitting systems. To identify structure–activity relationships permitting solely oxidation-driven schemes, water-soluble organic copper and phosphorescent palladium-coordinated metal–organic frameworks have been employed as molecular models for anti-aggregation studies. Under the widely adopted red route (after raising copper), efficient conversion of acetate to C₂H₄ proceeds via acetate dimerization, making it paramount to fully decipher acetate dissociation and its role in complementary oxidation to alleviate “molecular-overload” conditions. Functional interplay governs both active-site positions and ancillary stabilization throughout the semi-continuous catalysis cycle, wherein the combination of molecular probes further enriches the understanding of fundamental cooperativity principles relevant across hybrid systems and intimately tied to interfacial coordination.

Environmental and Practical Considerations

Metal-free COPs are promising materials that offer low-cost, versatile, and green alternatives to noble-metal-containing photocatalysts. They can carry out

photocatalytic water remediation to remove toxic pollutants such as dyes, heavy metals, and antibiotics. Despite extensive research efforts, most existing photocatalysts harness only ultraviolet light and therefore are not suitable for practical applications using natural solar light. COP nanostructures with designed bandgap energy and tailored absorption properties can operate as highly efficient visible-light-responsive photocatalysts. Covalent linkages in COPs render the polymers stable in harsh aqueous environments and during solar irradiation, enabling long-term operation and recyclability (Ghosh et al., 2015). Flexible design strategies allow covalent organic nanoscale polymer structures to selectively adsorb CO₂ in the feed gas and facilitate photocatalytic reduction of CO₂ under visible-light irradiation (Veerendra Prabhakar Vattikuti et al., 2023). Under appropriate conditions, these functionalities seamlessly integrate: either water or CO₂ remediation modules can be operated independently, or both can occur simultaneously in a hybrid configuration, making it possible to deliver dual-functional purification and selectively target highly toxic organic pollutants such as dyes.

Safety, toxicity, and environmental impact

Covalent organic polymers (COPs) are emerging as next-generation metal-free photocatalysts due to their unique advantages over conventional polymeric or other metal-free photocatalysts. Compared to organic polymeric structures still rely on costly metals, COP structures are entirely free of metals; and they have a two-dimensional ordered structure and intrinsic porosity. When integrated into versatile nanostructures, COPs exhibit excellent covalent and thermal stability, chemical durability, and good suitability for powder-to-film conversion to enable water remediation and CO₂ capture under visible-light illumination.

Conventionally, the photocatalytic CO₂ reduction as an important strategy to alleviate greenhouse effect, was considered coupled with the photocatalytic degradation of contamination and disinfection water-remediation underwater-light illumination. Such a route maximally utilizes low-energy sunny light under ambient surroundings. Structures that enable dual function become prevalent. Aiming at the problems of water quality deterioration and increasing CO₂ and NH₃ concentrations in environment, systematic studies of photocatalytic water-remediation and CO₂ capture based on COP nanostructure were conducted. Consequently, diverse visible-light-driven, non-metal photocatalytic water-remediation and CO₂ capture coupling were realized via well-designed COP nanostructures.

Economic feasibility and life-cycle costs

Water pollution from organic contaminants and greenhouse gas emissions are two increasingly dire environmental issues. Visible-light-driven photocatalysis provides an effective means of tackling both problems independently: by employing a water-splitting reaction and CO₂ reduction photocatalytic systems in parallel, for example. Yet a unified photocatalytic process capable of simultaneously remediating contaminated water while capturing CO₂ remains unreported. One promising candidate for such a dual-function photocatalyst is covalent organic polymer (COP) nanostructures. COPs exhibit both band gap engineering and light-harvesting functionalities, allowing the band structure to be tailored for visible-light absorption.

Charge-separation or -transport processes and the associated reaction pathways can also be tuned to facilitate water remediation and CO₂ reduction under visible light (Veerendra Prabhakar Vattikuti et al., 2023).

Covalent organic frameworks (COFs), recently classified within the COP family, represent another potential solution. Their complete confinement of π -conjugated linkers, block copolymer-based β -cyclodextrin nanospheres and polyhedral covalent organic frameworks (COFs) for versatile interfacial design remain largely unexplored (Udom, 2014). Nevertheless, the possibility of correlative structural, functional, and mechanistic investigation makes COPs an appealing alternative: nanostructured COPs host multiple responsive sites for visible-light-driven organic pollutant degradation and CO₂ conversion through separate or coupled processes. The close adherence of mesoporous carbon nitride and nanocrystalline graphitic carbon nitride nanosheets to the nanocrystalline graphite substrate enables moisture-driven conversion of CO₂ without modifying the original g-C₃N₄ sphere. Tuning carbon nitride with phosphoric acid engenders a new class of metal-free phosphor catalyst for efficient CO₂-N₂ transformation (Fernandes et al., 2020). Table 10 shows the Environmental Impact and Cost Comparison: COP vs Metal-Based Photocatalysts

Table 10: Environmental Impact and Cost Comparison: COP vs Metal-Based Photocatalysts

Criterion	Metal-Based Photocatalysts	Metal-Free COPs
Environmental Risk	Leaching of toxic metals	Low environmental impact
Cost (Material & Synthesis)	High due to metal procurement	Lower due to abundant materials
Reusability	Limited due to metal degradation	High stability and reusability

Conclusion

Covalent organic polymers (COPs) represent a new generation of metal-free photocatalysts, with nanostructured COPs—a class of material described in the title “Foundation of Covalent Organic Polymer Nanostructures”—offering promising dual functionality for visible-light-driven water remediation and CO₂ capture. Extensive literature has explored COP nanostructures and visible-light photocatalysis of H₂O₂ generation; a further set of references now delineates the combined ability of these nanostructures to adsorb gaseous CO₂ under ambient conditions and convert it to carbon-free products such as CO and formic acid (Krishnaraj et al., 2020) ; (Liu et al., 2023) ; (Veerendra Prabhakar Vattikuti et al., 2023). Connecting these findings with the insights above on the design principles and synthesis strategies underpinning visible-light-driven water remediation reveals that structure modifications adapted for water treatment applications—such as uniform nanospheres, crosslinks, or surface-anchored CO₂-binding sites—remain compatible with effective gaseous CO₂ capture and conversion.

The strategic design of COPs aims to bridge the visible-light-induced carbon and energy recovery cycle with H₂O₂-mediated organic pollutant degradation. Future

work involves leveraging energetic coupling between the two targeted reactions to enhance system synergy and facilitate cascade conversion of photoexcited electrons. Such approaches could guide the design of next-generation photocatalysts for simultaneous organic pollutant removal and CO₂ elimination from residual products. Metal-free COP nanostructures open unprecedented avenues for visible-light-driven remediation of organic pollutants and concomitant CO₂ capture from the atmosphere. These materials tackle two major environmental challenges within an integrated approach, facilitating the capture of carbon-containing products produced in parallel or through downstream alterations of pollutant-degradation pathways. Structural–functional relationships elucidate how mechanistic insights inform the rational design of COP materials, and elaborating on underlying principles leads to materials capable of either single or dual functionality across diverse gaseous and aqueous substrates. The modular character of COPs and their emergence as one of the leading platforms for metal-free photocatalytic water remediation and CO₂ capture invite exploration of new monomers, linkages, and topologies to achieve other critical functionalities.

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