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Review

Recent research progress on perylene diimide-based photocatalytic materials

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ABSTRACT

Perylene diimide (PDI) is an organic semiconductor with outstanding optical and electronic properties, including a rigid π -conjugated structure, high electron affinity, and chemical stability, which have garnered significant attention in the field of photocatalysis. This review provides a comprehensive overview of recent advancements in PDI-based photocatalytic materials, focusing on their structural characteristics and photocatalytic mechanisms. Despite their promise, PDI-based materials face challenges in practical applications, such as poor light absorption and high charge recombination rates. To address these issues, several strategies have been developed to enhance their photocatalytic performance, including the molecular design of various PDI polymer systems, the incorporation of co-catalysts to boost activity, the construction of heterostructures, synergistic Fenton reactions, and carbon-coupled PDI supramolecular photocatalysts. These approaches have led to significant improvements in the stability and efficiency of PDI-based photocatalysts. These approaches have led to significant improvements in the stability and efficiency of PDI-based photocatalysts. In practical applications, PDI-based materials show great potential in critical areas such as photocatalytic sterilization, environmental pollutant degradation, water splitting for hydrogen production, CO₂ reduction to renewable fuels, nitrogen fixation, and cancer treatment. These applications highlight the vast potential of PDI-based materials in both environmental remediation and renewable energy development. Finally, the review discusses future research directions, emphasizing the need for rational molecular design, optimization of heterostructure, and the development of novel composite materials as key strategies to further enhance performance. With continued research and development, PDI-based photocatalysts are poised to become a key technology in tackling global challenges such as energy shortages and environmental pollution.

1. Introduction

With the rapid advancement of the global economy and modern industry, humanity has made significant progress, but is also confronted with unprecedented environmental and energy crises [1]. Environmental pollution and energy shortages have become two of the most pressing issues worldwide [2]. Semiconductor-based photocatalysis is a cutting-edge technology with dual potential for environmental remediation and energy conversion [3]. It shows considerable promise in the efficient transformation of clean solar energy into chemical energy [4]. Photocatalysis, through the absorption of light and energy conversion, enables a series of green chemical reactions under ambient conditions, such as pollutant degradation, CO₂ reduction, and water splitting for H₂ production [5]. These reactions not only effectively reduce environmen-

tal pollution but also facilitate the clean and renewable utilization of energy [6].

An ideal photocatalyst should possess several core characteristics: a high redox potential to drive photocatalytic reactions, a broad light absorption range to fully utilize solar energy, and excellent carrier separation and migration efficiency to minimize energy losses due to carrier recombination [7]. Therefore, the search for semiconducting materials with these properties has become a focal point in photocatalysis research [8]. Over the past few decades, various organic and inorganic photocatalysts have been developed, including metal oxides, sulfides, carbon nitrides, covalent organic frameworks, and metal-organic frameworks [9]. TiO₂, one of the most extensively studied photocatalytic materials, is renowned for its chemical stability, non-toxicity, and superior oxidative properties [10]. It has shown considerable promise in a range of appli-

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cations, including the degradation of organic pollutants, water splitting for hydrogen production, and air purification [11,12]. However, TiO_2 suffers from a relatively large band gap (~ 3.2 eV), limiting its activation to UV light and thereby reducing its efficiency in harnessing solar energy [13,14]. To address this limitation, there has been increasing interest in alternative photocatalysts that respond to visible light, such as graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [15]. With a narrower band gap (~ 2.7 eV), $\text{g-C}_3\text{N}_4$ can absorb visible light and is cost-effective to synthesize using straightforward methods [16]. Despite these advantages, $\text{g-C}_3\text{N}_4$'s photocatalytic performance is compromised by low charge separation efficiency and rapid recombination of photogenerated charge carriers [17].

Organic semiconductors have garnered increasing attention in the field of photocatalysis due to their unique structures and properties [18]. Among the diverse range of organic semiconductors, materials such as perylene diimide (PDI), polypyrrole (PPy), and polyaniline (PANI) serve as prominent examples [19–21]. These materials not only exhibit excellent optoelectronic properties but also possess advantages such as light weight, ease of processing, and environmental friendliness [22]. Among them, PDI stands out as a promising organic photocatalyst, owing to its simple preparation process, low cost, and stable chemical properties [23].

In comparison to conventional photocatalysts such as TiO_2 and $\text{g-C}_3\text{N}_4$, PDI demonstrates significant advantages. TiO_2 is constrained by its large band gap and reliance on UV light for activation, while $\text{g-C}_3\text{N}_4$ suffers from poor charge separation and rapid recombination rates. In contrast, PDI effectively addresses these limitations. The backbone of PDI molecules features rigid, planar π -conjugated aromatic heterocycles, fostering strong π - π interactions that endow PDI with distinctive electronic and optical characteristics, as well as notable electron affinity [24]. PDI has demonstrated excellent performance in various photocatalytic applications [25]. For instance, in the degradation of organic pollutants, PDI can effectively decompose pollutants into harmless small molecules through photocatalytic oxidation; in water splitting for oxygen generation, PDI can significantly enhance the oxygen generation rate; additionally, PDI has been widely applied in selective organic synthesis and photocatalytic cancer cell destruction [26]. However, the rigid planar conjugated system in PDI molecules, while imparting unique properties, also results in strong intermolecular interactions that limit its solubility and increase the carrier recombination rate, thereby restricting its practical applications in photocatalysis [27].

To address these challenges, the development of efficient PDI-based photocatalysts has become a key area of research. In recent years, the construction of PDI-based heterostructure has been considered an effective approach to overcome the limitations of PDI materials [28]. By combining PDI with other functional materials, heterostructure can not only significantly suppress the recombination of photogenerated electron-hole pairs but also impart new properties to the photocatalyst through synergistic effects [29]. For example, combining PDI with inorganic semiconductors that have broad light absorption ranges can extend its light response range, while incorporating metal oxides can improve its catalytic activity and stability [30]. These strategies based on heterostructure have effectively overcome the bottlenecks in the photocatalytic applications of PDI materials [31]. Specifically, PDI-based heterostructure can be categorized into three main types: Type II, Type Z, and Type S heterostructure [32–34]. Type II heterostructure achieve the separation of electrons and holes through band alignment; Type Z heterostructure enhance photocatalytic efficiency by providing a pathway for the transfer of photogenerated electrons between two semiconductors; and Type S heterostructure further optimize carrier separation and migration efficiency while maintaining high redox ability. The construction and optimization of these heterostructure require an in-depth understanding of the interaction mechanisms between the components and precise control over the structure and performance of the materials [35].

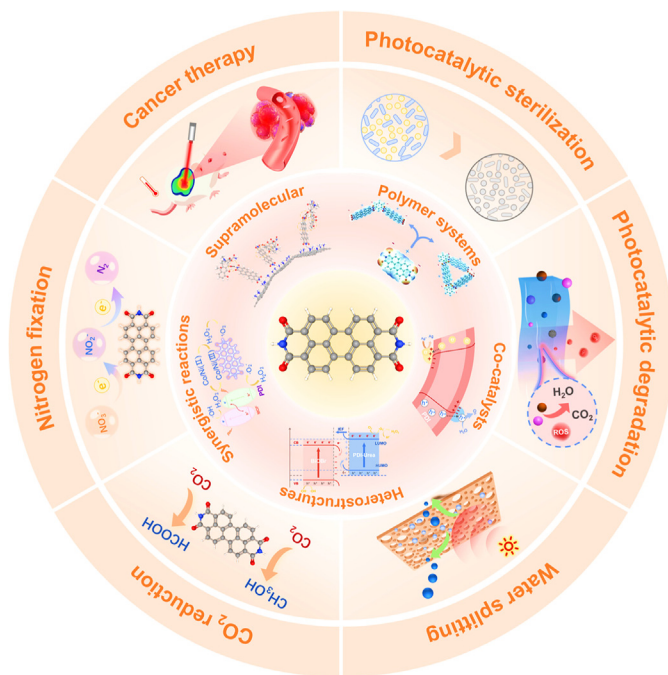


Fig. 1. Regulation strategies and applications of PDI-based photocatalytic materials.

Moreover, the study of PDI-based heterostructure provides new insights for the development of efficient, visible-light-driven photocatalysts [36]. In practical applications, these photocatalysts can be widely used in water treatment, air purification, greenhouse gas emission reduction, and renewable energy development [37]. For example, by utilizing PDI-based heterostructure for CO_2 reduction, CO_2 can be converted into high-value chemical fuels; in water splitting for H_2 production, their efficient photogenerated carrier separation properties provide technological support for clean energy production [38,39].

In conclusion, the rational design and optimization of PDI-based heterostructure are key to achieving efficient photocatalysis [40]. Future research should focus on several directions: first, introducing novel materials and structures to further enhance the light absorption range and carrier separation efficiency of PDI-based photocatalysts; second, combining theoretical simulations and experimental studies to explore the formation mechanisms of heterostructure and their impact on photocatalytic performance; third, developing low-cost, scalable PDI-based photocatalysts to meet the demands of practical applications. As research deepens, PDI-based heterostructure are expected to play an even greater role in environmental remediation and renewable energy development, providing new technological support to address global environmental and energy challenges [41].

This review systematically summarizes the research progress of PDI-based photocatalytic materials and analyzes their unique molecular structures and photocatalytic mechanisms in depth (Fig. 1). In response to the challenges of poor light absorption and high carrier recombination rates in practical applications, a series of performance optimization strategies have been proposed, including the molecular design of diversified PDI polymers, the introduction of co-catalysts, the design of heterostructure, synergistic Fenton reactions, and carbon-coupled PDI supramolecular photocatalysts. These optimization methods have significantly improved the stability and catalytic efficiency of PDI-based photocatalysts. In practical applications, PDI-based photocatalytic materials have been widely used in photocatalytic sterilization, pollutant degradation, water splitting for hydrogen production, CO_2 reduction, photocatalytic nitrogen fixation, and cancer treat-

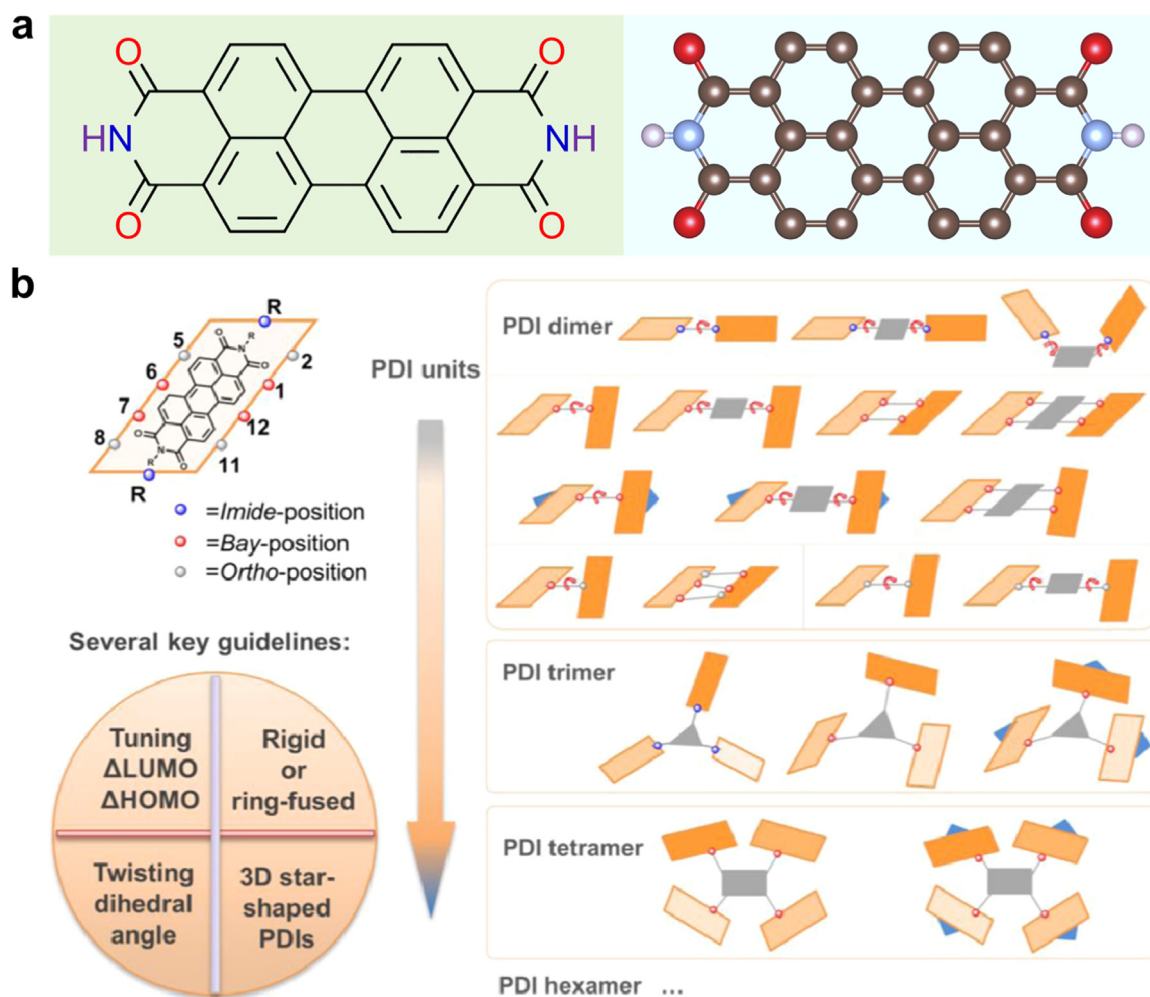


Fig. 2. Molecular structure of PDI. (a) Single molecule structure and ball-and-stick model of PDI. (b) PDI derivatives with functional active sites. (Reproduced with permission [46]. Copyright 2020, Elsevier).

ment, demonstrating significant potential in environmental remediation and renewable energy development. The research outcomes provide strong evidence for the important role of PDI-based materials in addressing the dual challenges of energy and environmental issues.

2. Molecular structure and photocatalytic mechanism of PDI

PDI represents an emerging class of non-covalent, self-assembled supramolecular n-type organic semiconductors [42]. By fine-tuning the molecular dipole moment and leveraging frontier molecular orbital theory, the energy band structure and internal electric field of PDI-based photocatalysts can be precisely engineered [43]. As a photocatalyst, PDI supramolecules form robust hydrogen bonds and π - π stacking networks through the introduction of functional groups at amine sites, facilitating electron transport [44]. Additionally, PDI readily generates reactive anionic radicals that drive pollutant degradation and water splitting processes [45]. The planar, rigid π -conjugated heteroaromatic architecture of PDI underpins pronounced π - π intermolecular interactions (Fig. 2a), imparting distinctive optoelectronic characteristics and remarkable electron affinity.

Moreover, PDI derivatives [46] are diverse, with straightforward synthesis routes and readily available raw materials, creating favorable conditions for their development (Fig. 2b). The supramolecular architecture of PDI commonly adopts a one-dimensional nanofiber morphol-

ogy, characterized by a large specific surface area that amplifies its photocatalytic efficiency [47]. Beyond serving as an organic semiconductor, PDI functions as a sensitizer for inorganic semiconductors, broadening light absorption [48]. With absorption spanning 400–760 nm, high fluorescence quantum yield, structural stability, and exceptional photovoltaic properties, PDI's adaptable molecular framework has positioned it as a key organic semiconductor photocatalyst in photocatalysis [49,50].

3. Methods for enhancing the photocatalytic performance of PDI-based materials

Despite their potential, PDI supramolecules face notable challenges as photocatalysts, including rapid recombination of photogenerated electron-hole pairs, sluggish charge transport, and a low valence band (VB) potential [51]. These factors constrain their efficiency in environmental remediation [52]. To overcome these limitations, researchers have explored approaches such as π - π composite frameworks, heterostructure architectures, co-catalyst integration, synergistic Fenton reactions, and carbon-coupled PDI supramolecular photocatalysts [53–55]. These approaches target multiple aspects, such as molecular structure optimization, interface regulation, and carrier behavior management, leading to significant improvements in the photocatalytic efficiency of PDI-based materials [56]. The following sections discuss these strategies in detail.

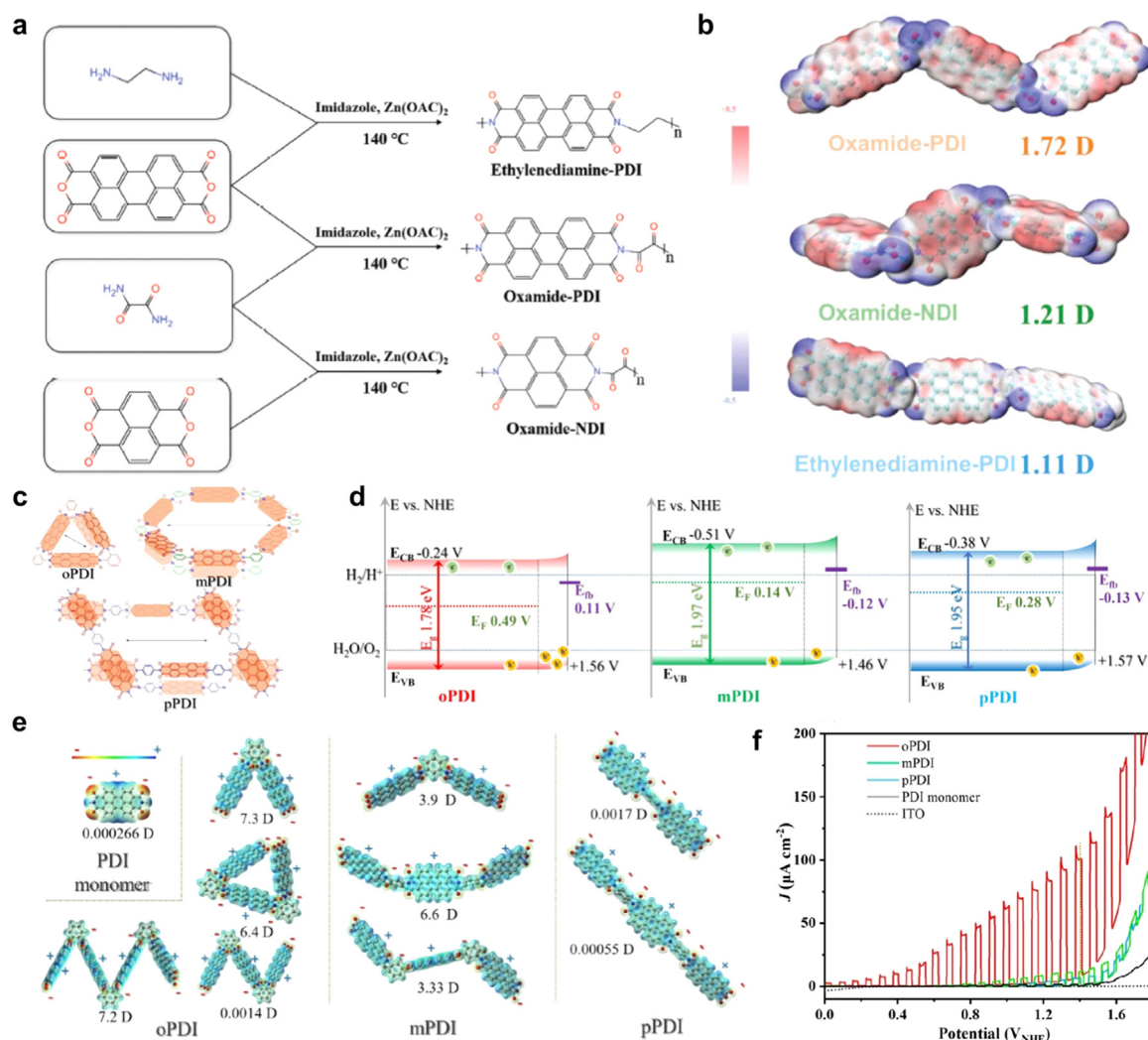


Fig. 3. Construction of various PDI polymer systems. (a) Synthetic pathways for three linear conjugated polymers. (b) The MESP and ground-state dipole moments across three repeating units. (Reproduced with permission [60]. Copyright 2023, Wiley-VCH). (c) Diagram illustrating nanopore structures formed through π - π stacking and molecular folding. (d) Band structures, photogenerated carriers, and transport pathways in oPDI, mPDI, and pPDI. (e) Surface electrostatic potential and dipole moments. (f) LSV curves under intermittent illumination. (Reproduced with permission [61]. Copyright 2024, Wiley-VCH).

3.1. Construction of various PDI polymer systems

PDI, as a prototypical class of polycyclic aromatic hydrocarbons, features a molecular scaffold composed of a perylene core symmetrically flanked by imide groups, giving rise to an extended π -conjugated architecture [57]. The intrinsic electronegativity of the perylene core, coupled with the electron-withdrawing nature of the terminal imide groups, synergistically facilitates efficient charge carrier separation and migration [58]. In recent years, precise molecular design and modulation of PDI building blocks have emerged as powerful strategies to enhance their photocatalytic performance [46]. Notably, tuning the conjugation length of the aromatic core and tailoring the type of bridging units not only optimizes the internal electric field distribution but also critically influences the dynamics of photogenerated charge carriers, offering promising avenues for performance enhancement and practical application [59].

Liu et al. [60] reported the successful synthesis of three linear conjugated polymer analogs by tailoring the aromatic core and covalent linkage groups (Fig. 3a). A comparative analysis of these materials underscores the critical influence of conjugation length and the nature of the bridging groups on performance optimization. Notably, Oxamide-PDI, characterized by robust π - π stacking and favorable dipole-dipole

interactions (Fig. 3b), exhibits highly ordered molecular alignment, elevated crystallinity, a wide light absorption spectrum, and outstanding stability. The larger molecular dipoles, combined with a well-ordered crystalline structure, induce a strong internal electric field, which significantly enhances the separation and migration of charge carriers. This results in remarkable full-spectrum photocatalytic water splitting performance, further underscoring the potential of this material for efficient solar energy conversion. Furthermore, Jian et al. [61] synthesized three PDI polymers-oPDI, mPDI, and pPDI-by incorporating distinct phenyl diamine bridging agents (Fig. 3c). The study revealed that variations in the spatial arrangement of PDI units markedly affected energy level alignment, light absorption, and the separation and transport of photogenerated carriers (Fig. 3d). Notably, oPDI, characterized by a larger molecular dipole moment and an enhanced internal electric field (Fig. 3e), demonstrated exceptional performance in solar-driven water splitting (Fig. 3f). This study provides a critical strategy for designing efficient solar energy conversion systems through the control of polymer building unit orientation.

3.2. Design and application of co-catalysts

The enhancement of photocatalytic performance can be effectively achieved through the introduction of co-catalysts. Co-catalysts play mul-

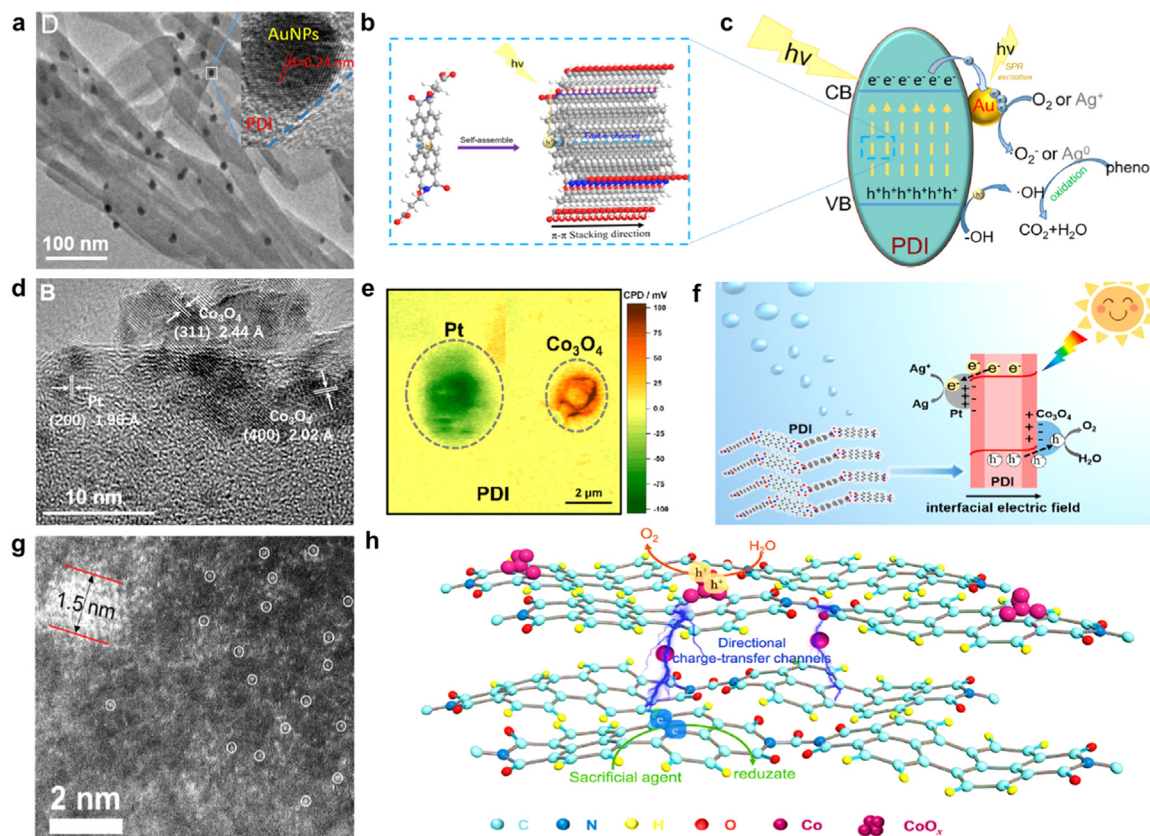


Fig. 4. Design and application of co-catalysts. (a) HRTEM image and of PDI/Au. (b) Mechanism of charges separation of PDI. (c) Photocatalytic oxidation process of phenol on PDI/Au. (Reproduced with permission [62]. Copyright 2018, Elsevier). (d) HRTEM image of PDI/Co₃O₄/Pt. (e) Contact potential difference mapping of Co₃O₄ and Pt particles relative to the PDI. (f) The band structure and charge transfer pathways. (Reproduced with permission [63]. Copyright 2023, American Chemical Society). (g) HAADF-STEM image of Co-PDI. (h) The charge-transfer process in Co-PDI upon light irradiation. (Reproduced with permission [64]. Copyright 2022, Wiley-VCH).

multiple roles in the photocatalytic process, such as facilitating the separation of photogenerated electron-hole pairs, lowering reaction activation energy, improving light absorption efficiency, and enhancing reaction stability. The inclusion of co-catalysts typically depends on their unique physicochemical properties, such as high electrical conductivity, suitable Fermi levels, and surface structures rich in active sites. These properties enable co-catalysts to form synergistic effects with photocatalysts, thereby optimizing the reaction dynamics.

Surface plasmon resonance (SPR) effects from Au nanoparticles (NPs) significantly enhance the absorption efficiency of visible light. Zhu et al. [62] successfully synthesized a PDI/Au photocatalyst with visible light response using an electrostatic adsorption method (Fig. 4a). Compared to pure PDI nanowires, the PDI/Au exhibited a 1.7-fold increase in the rate constant (*k*) for visible light degradation of phenol. This enhanced photocatalytic performance was primarily attributed to the SPR effect of Au NPs. Specifically, the SPR effect of Au NPs and the energy feedback transfer process between Au and PDI significantly improved the utilization efficiency of visible light, making PDI/Au outperform PDI nanowires in photocatalytic performance (Fig. 4b). Additionally, the lower Fermi level of Au effectively enhanced the separation of photogenerated electron-hole pairs, promoting efficient charge carrier migration (Fig. 4c). Moreover, the low reduction potential of Pt makes it an ideal candidate for coupling with PDI to enhance photocatalytic activity. In further research, Zhu et al. [63] selected a PDI polymer with a wide light absorption range and deep VB position and constructed a photocatalytic system with an interface electric field by introducing dual co-catalysts, Co₃O₄ and Pt (Fig. 4d). The interface electric field generates a directional driving force that promotes the

migration of photogenerated holes and electrons towards Co₃O₄ and Pt, greatly enhancing the spatial charge separation efficiency in water oxidation (Fig. 4e). Furthermore, Co₃O₄ serves as an active site for water oxidation, further optimizing the utilization of photogenerated holes at the surface (Fig. 4f). This system exhibited remarkable photocatalytic water oxidation performance under visible light irradiation.

Enhancing atomic utilization can be achieved by reducing the size of metal NPs and improving their distribution across the semiconductor surface. In particular, the use of single-atom metals enables optimal atom efficiency and provides numerous active sites for surface catalysis. Shen et al. [64] employed a two-step immersion-calcination method to incorporate Co single atoms and CoO_x clusters into polymer diacetylene PDI (Fig. 4g). The resulting PDI/Co photocatalyst demonstrated exceptional water oxidation activity under visible light. The single Co atom facilitated efficient charge transfer, while the CoO_x clusters enhanced O₂ evolution kinetics, leading to a significant boost in photocatalytic performance (Fig. 4h).

3.3. Construction and optimization of heterostructures

Heterostructures significantly enhance photocatalytic performance through material integration and interface band engineering, with their key roles reflected in several aspects [65]. First, heterostructures can effectively promote the separation of photogenerated electron-hole pairs by reducing carrier recombination through interface band alignment and built-in electric fields, thereby improving photocatalytic efficiency [66]. Second, by combining semiconductors with different band gaps,

heterostructures can broaden the light absorption range, enabling the utilization of additional wavelengths, such as visible and near-infrared (NIR) light [67]. Furthermore, the interfaces of heterostructures often provide more active sites, facilitating surface reactivity and optimizing the adsorption and dissociation processes of reaction intermediates [68]. They also play a crucial role in suppressing photocatalyst photocorrosion, thereby extending the material's service life under harsh conditions [69]. PDI-based heterostructured photocatalysts can be classified into conventional Type II, Z-scheme, and S-scheme heterostructure, according to the transfer mechanisms of photogenerated carriers between PDI and the coupled components [70].

In type-II heterostructure photocatalysts, the overall energy levels of semiconductor A are higher than those of semiconductor B [71]. Upon contact, an internal electric field is established at their interface, acting as a driving force that facilitates charge separation under light irradiation [72]. Specifically, when the photocatalyst absorbs photons, photogenerated electrons in semiconductor A are driven towards semiconductor B, while photogenerated holes in semiconductor B migrate in the opposite direction into semiconductor A. This spatial separation of electrons and holes effectively suppresses their recombination, thereby significantly enhancing the photocatalytic efficiency. Zhang et al. [73] constructed a PDI/Bi₂WO₆ Type II heterostructure photocatalyst via a simple water-bath heating method. Bi₂WO₆, a layered chalcogenide semiconductor with a narrow band gap, plays a significant role in photocatalysis due to its strong visible light absorption and photo corrosion resistance. Under illumination, electrons from the PDI conduction band are injected into the conduction band of Bi₂WO₆ (Fig. 5a). Electron spin resonance (ESR) experiments show that the 50% PDI/Bi₂WO₆ heterostructure significantly enhances the •O₂[−] yield, improving its electron-accepting capacity and thereby enhancing its oxidation ability. g-C₃N₄, a promising new visible-light-responsive photocatalyst, was used by Guo et al. in a one-step iridization reaction with perylene tetracarboxylic dianhydride (PTCDA) to form a PDI/g-C₃N₄ heterostructure (Fig. 5b) [74]. The surface hybridization of PTCDA with g-C₃N₄ through O=C–N–C=O covalent bonding accelerates the migration and separation of photogenerated charge carriers, generating more active species, which is the key to its enhanced photocatalytic activity. Gao et al. [75] also used acetic acid to induce the self-assembly of PDI supramolecules on the surface of Bi₅O₇I. Additionally, multiple oxygen vacancies were formed during solvothermal treatment, which not only enhanced visible light capture but also modified the band structure of Bi₅O₇I (Fig. 5c). Under visible light irradiation, the PDI/Bi₅O₇I composite exhibited significantly enhanced photocatalytic degradation of organic pollutants. This improvement is attributed to the strong hole oxidation ability of the metastable Bi₅O₇I and the introduction of oxygen vacancies.

Inspired by natural photochemical processes in plant photosynthesis, scientists designed a Z-scheme heterostructure photocatalytic system [76]. In contrast to type-II heterostructure, this structure enhances the redox potential, promoting more efficient charge separation while preserving robust redox capacity. As a result, its photocatalytic activity surpasses that of single-component catalysts. Constructing PDI-based Z-scheme heterostructure has proven to be a promising strategy for enhancing PDI's photocatalytic efficiency [77]. He et al. [78] anchored ZnIn₂S₄ nanosheets onto high-crystallinity PDI nanorods, forming a unique layered branched structure that enhanced surface area, pore size, pore volume, and light absorption properties (Fig. 5d). The covalent bonds formed between the organic high-crystallinity PDI and the inorganic ZnIn₂S₄ provide a rapid charge transfer channel. Furthermore, the formed PDI/ZnIn₂S₄ built-in electric field and Z-type heterostructure not only promoted the transfer and separation of photogenerated charges but also removed water oxidation reactions from ZnIn₂S₄, further improving the system's photocatalytic activity and stability. This work offers a new approach for exploring high-performance photocatalysts.

Zhu et al. [79] developed PDI/naphthalimide (NDINH) supramolecular photocatalysts using a rapid solution dispersion technique. By adjusting the large local dipoles, they generated a significant internal electric field, greatly accelerating charge separation and achieving longer carrier lifetimes, resulting in high photocatalytic activity (Fig. 5e). Furthermore, incorporating NDINH substantially decreased the reflected electric field on PDI, thereby improving its response to UV light. The findings demonstrated that under full-spectrum illumination, the PDI/NDINH system could efficiently split water into H₂ and O₂. In this Z-type photocatalytic system, the inclusion of electron mediators was essential for promoting the transfer of photogenerated electrons between the semiconductor interfaces. However, the use of noble metal electron mediators raises both fabrication complexity and cost. Ji et al. [80] introduced a PDI/boron nitride (BN) composite, where theoretical calculations revealed the formation of π - π stacking interactions between BN and PDI. Compared to pure PDI and BN, the PDI/BN photocatalyst demonstrated enhanced charge separation efficiency and improved tetracycline (TC) degradation performance under visible light. The study revealed that PDI/BN follows a direct Z-type charge transfer mechanism (Fig. 5f), where holes in the PDI VB recombine with electrons in the BN conduction band.

Moreover, Zeng et al. [81] utilized Cu as an electron mediator to construct a PDI/Cu/WO₃ Z-type photocatalytic system. In this system, self-assembled PDI supramolecules are tightly bound to WO₃ and small Cu NPs, favoring the photocatalytic process. The interface charge transfer in the PDI/Cu/WO₃ composite follows a Z-type mechanism, where Cu serves as a conductive electron mediator, promoting carrier transfer between WO₃ and PDI. Electrons from the WO₃ conduction band transfer via the Cu intermediary to the PDI VB, where they recombine with holes, while electrons in the PDI conduction band accumulate, enhancing reduction capacity, and holes in the WO₃ VB boost oxidation potential.

The S-type heterostructure consists of a reduced-type semiconductor (RP) and an oxidized-type semiconductor (OP) with interlaced band structures [82]. RP has higher CB and VB positions compared to OP, and a smaller work function. When these two semiconductors come into contact, electrons from RP spontaneously diffuse into OP, forming an electron depletion region and an electron accumulation region near the interface [83]. Simultaneously, an internal electric field is established from RP to OP, which drives the migration of photogenerated electrons from OP to RP. Upon contact, the Fermi levels of OP and RP align to the same energy level, causing the Fermi levels of OP and RP to shift upward and downward, respectively [84]. The resulting band bending facilitates the recombination of photogenerated electrons in the CB of OP with holes in the VB of RP at the interface. The Coulombic attraction between the electrons and holes further promotes this recombination. Together, the internal electric field, band bending, and Coulombic attraction act as driving forces for the recombination of electrons in OP's CB and holes in RP's VB, eliminating unnecessary electrons and holes. Meanwhile, the high-energy photogenerated electrons in the RP's CB and holes in OP's VB are retained for photocatalytic reactions. This S-type heterostructure effectively removes unwanted electrons and holes while preserving the advantageous oxidation potential of the VB in OP and the reduction capability of the CB in RP. It enhances the photogenerated carrier separation efficiency and the solar response range of the composite, while maintaining the material's inherent strong redox properties [26]. This significantly improves the photocatalytic activity and solar light utilization efficiency of the heterostructure, demonstrating considerable potential for future applications [85].

Wang et al. [86] developed a novel organic/inorganic PDI/BiOBr S-type heterostructure photocatalyst through a straightforward solvothermal reaction and an in-situ growth approach (Fig. 5g). Due to the Fermi level differences between BiOBr and PDI, electron transfer occurs at the interface, causing electron accumulation and depletion, and generating band bending, a key feature of S-type heterostructure. This charge transfer mechanism retains the oxidizing holes on BiOBr and the reducing

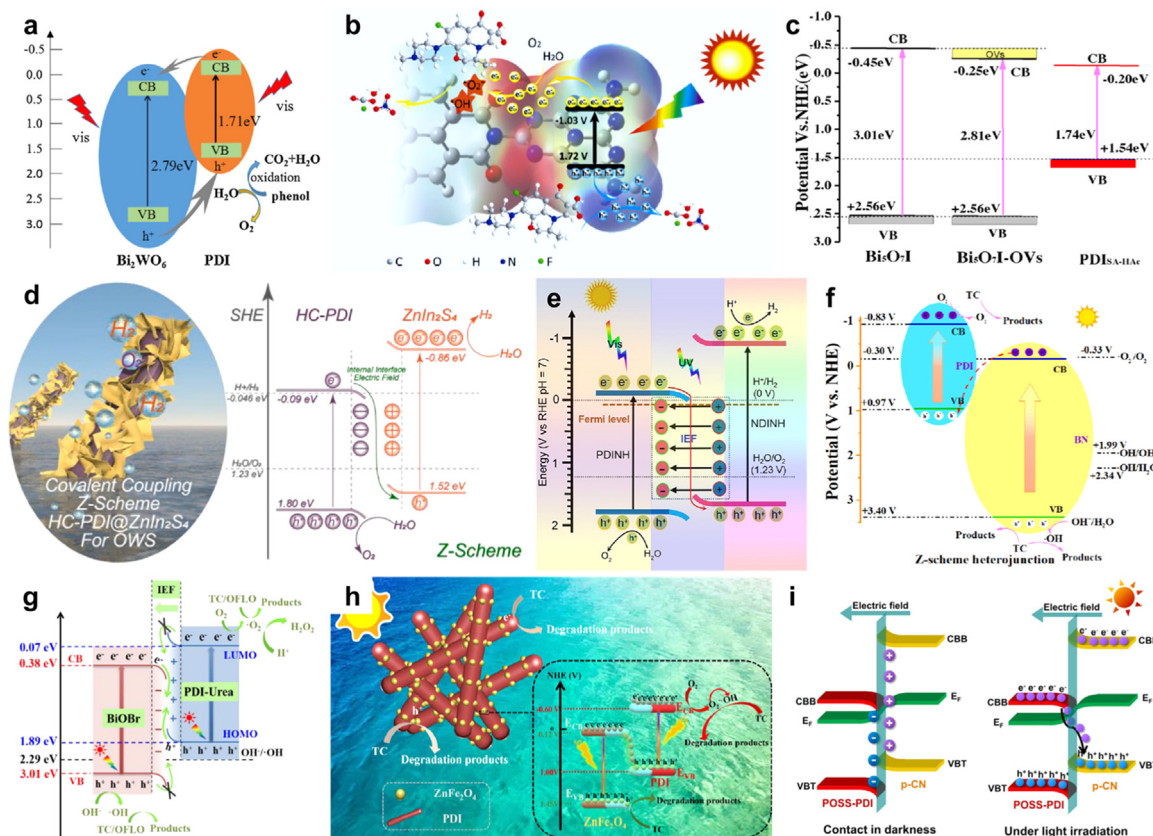


Fig. 5. Heterostructure based on PDI. (a) The potential reaction mechanism of PDI/Bi₂WO₆. (Reproduced with permission [73]. Copyright 2018, Elsevier). (b) Schematic depiction of the visible-light photocatalytic degradation mechanism over the PDI/g-C₃N₄. (Reproduced with permission [74]. Copyright 2019, American Chemical Society). (c) Band structure of PDI/Bi₂O₇I. (Reproduced with permission [75]. Copyright 2020, Elsevier). (d) Schematic illustration of PDI/ZnIn₂S₄ photocatalyst. (Reproduced with permission [78]. Copyright 2023, Elsevier). (e) Schematic representation of the interface charge transfer pathway in the NDINH/PDI. (Reproduced with permission [79]. Copyright 2024, Wiley-VCH). (f) Charge transfer mechanisms in PDI/BN for TC photodegradation. (Reproduced with permission [80]. Copyright 2021, Elsevier). (g) Photocatalytic mechanism in the PDI/BiOBr. (Reproduced with permission [86]. Copyright 2022, Elsevier). (h) The photocatalytic mechanism of degradation of TC by PDI/ZnFe₂O₄. (Reproduced with permission [84]. Copyright 2022, Elsevier). (i) Schematic illustration of S-scheme charges transfer process. (Reproduced with permission [87]. Copyright 2023, Wiley-VCH).

electrons on PDI-urea, enabling their migration to the surface where they engage in redox reactions with free radicals. Xu et al. [84] synthesized a magnetic PDI/ZnFe₂O₄ S-type heterostructure photocatalyst via HCl modulation, which exhibited excellent magnetic separation performance and stable recyclability. This approach effectively controlled the morphology of the PDI/ZnFe₂O₄ structure. The rod-like morphology of PDI and the small size effect of ZnFe₂O₄ facilitate efficient carrier migration to the composite surface (Fig. 5h). The resulting PDI/ZnFe₂O₄ heterostructure establishes an internal electric field at the interface, with the energy bands of both semiconductors bending. Electrons move to the PDI surface for reduction reactions, while holes in the ZnFe₂O₄ VB degrade pollutants directly, thereby enhancing the photocatalytic performance of the system.

Lignin constitutes 15%–25% of natural cellulose biomass and holds potential as an alternative to fossil resources for the production of aromatic chemicals, offering a sustainable solution to the global resource scarcity. Li et al. [87] functionalized both ends of PDI by grafting polyhedral oligomeric silsesquioxane (POSS) cage groups, improving its photo-physical properties, and obtaining POSS-PDI catalysts. Simultaneously, they selected polymeric carbon nitride (p-CN) nanosheets with an appropriate band gap to form an S-type heterostructure with POSS-PDI for the photocatalytic depolymerization of lignin C–C bonds. As a shape-persistent molecular nanoparticle, POSS effectively prevents crystallization on the surface of p-CN, enhancing its electrochemical stability and solubility in organic solvents, thereby promoting electron conduction.

The band structure of POSS-PDI aligns with that of p-CN, forming an S-type heterostructure (Fig. 5i), which improves the catalyst's redox ability and significantly boosts the photocatalytic performance of p-CN/PDI Table 1.

3.4. Synergistic Fenton reactions

As one of the oldest advanced oxidation processes, Fenton and Fenton-like reactions are widely employed in pollutants remediation due to their low cost, ease of implementation, and ability to thoroughly degrade organic contaminants [92]. In the Fenton reaction, •OH are considered the primary reactive species [93]. By generating highly oxidative •OH, the Fenton reaction effectively attacks organic molecules, oxidizing them into carbon dioxide and water [34].

To address this issue, Lu et al. [94] constructed a PDI/g-C₃N₄@NH₂-MIL-53(Fe) heterostructure photocatalyst, successfully achieving the synergistic enhancement of photocatalysis and Fenton-like reactions. Under light irradiation, photogenerated electrons from PDI/g-C₃N₄ transfer to NH₂-MIL-53(Fe), effectively suppressing charge recombination and enhancing electron separation efficiency. Simultaneously, Fe³⁺ in NH₂-MIL-53(Fe) is reduced to Fe²⁺, further catalyzing H₂O₂ to generate •OH, which accelerates the degradation of organic pollutants (Fig. 6a). Additionally, Zhu et al. [95] proposed an innovative photo-assisted Fenton system based on graphene oxide/self-assembled phthalocyanine diimide (GO/SA-PDI) catalysts for efficient removal of

Table 1
Summary of the different types of PDI-based heterostructure.

Heterostructure	Type	Application	Performance	Advantage	Ref.
PDI/Bi ₂ WO ₆	II	degradation of pollutants phenol	65% (180 min)	n–n heterojunction with optimized band alignment for efficient charge separation	[73]
PDI/Bi ₂ O ₄	II	degradation of pollutants RhB	98.6% (25 min)	Tight interfacial contact enabling fast carrier migration	[88]
PDI/CuS	II	degradation of pollutants TC	90% (120 min)	Efficient charge separation via π – π stacking and p–n junction and broad-spectrum light absorption including NIR region	[89]
PDI/BiOI	Z	degradation of pollutants sulfadimidine (SM2)	100% (20 min)	Diffusion-controlled charge separation beyond built-in field limitations	[69]
PDI/Cu/WO ₃	Z	degradation of pollutants TC	76% (15 min)	Z-scheme electron transfer for efficient carrier separation and retention of redox ability	[81]
PDI/ZnPc	Z	CO ₂ reduction	16- fold higher than PDI	Phosphate-modulated assembly enhancing charge transfer and photocatalytic efficiency	[90]
PDI/BiOBr	S	degradation of pollutants TC	93% (150 min)	S-scheme heterojunction enhancing efficient charge separation and active species generation	[86]
PDI/ZnFe ₂ O ₄	S	degradation of pollutants TC	66.7% (60 min)	Regulated morphology enhancing carrier migration and separation	[84]
PDI/g-C ₃ N ₄	S	degradation of pollutants TC	90% (90 min)	Well-matched band structure and strong interfacial bonding	[91]
PDI/TiO ₂	S	water splitting production of H ₂	9766 mmol h ^{–1} g ^{–1}	π – π stacking structure enhancing light harvesting and photocatalytic activity	[85]

antibiotic-resistant pollutants from water (Fig. 6b). The introduction of GO significantly enhanced the light absorption and charge transfer rate of SA-PDI. The synergistic effect of photocatalysis and Fenton reactions accelerated the Fe³⁺/Fe²⁺ cycle, improved H₂O₂ utilization, and generated more oxidative species, significantly enhancing the removal of antibiotics, antibiotic-resistant bacteria, and antibiotic resistance genes.

Furthermore, Zhou et al. [96] prepared ultra-thin nanofiber PDI by self-assembly of commercial PDINH and constructed an innovative Co/Ni-MOF-74@PDI Z-scheme heterostructure photocatalytic material using a solvothermal method, significantly enhancing photocatalytic performance. This effect was attributed to the matching bandgap structures of Co/Ni-MOF-74 and PDI. The construction of the Z-scheme heterostructure effectively reduced the recombination rate of photogenerated carriers (Fig. 6c). The further developed Co/Ni-MOF-74@PDI/H₂O₂/visible light system, utilizing the Fenton-like properties of bimetallic Co/Ni, enhanced the activation of H₂O₂ to generate •OH, thereby further improving the degradation efficiency of TC hydrochloride, achieving a degradation rate of 87% within 90 min. Zhang et al. [92] designed an iron-modified PDI/g-C₃N₄ composite material, with the successful introduction of iron enhancing its visible light absorption and carrier separation. Furthermore, under visible light, it generates H₂O₂, and based on this, an *in situ* Fenton system was constructed for the removal of p-nitrophenol. To overcome the issue of iron ions competing with oxygen, ethylenediaminetetraacetic acid was added as a reducing agent, improving removal efficiency while maintaining excellent stability, with high activity retained even after five cycles of reuse.

3.5. Carbon-coupled PDI supramolecular photocatalysts

The coupling of PDI-based photocatalysts with carbon materials has emerged as a promising strategy to enhance catalytic performance [97,98]. Carbon materials such as graphene, carbon nanotube (CNT), and activated carbon exhibit exceptional conductivity, facilitating the migration of photogenerated electrons and suppressing electron-hole recombination, thereby improving charge separation and boosting photocatalytic activity and stability [53,99,100]. Zhu et al. [101] synthesized a PDI-anchored three-dimensional reduced GO (rGO) structure via electrodeposition-impregnation, leveraging π – π stacking interactions to uniformly anchor PDI nanorods on the graphene surface (Fig. 7a). This unique architecture promotes charge separation and migration, closely associated with electron delocalization along the π – π stacking direction, leading to superior photoelectrocatalytic degradation in both static and dynamic systems (Fig. 7b).

The porous structure and large surface area of carbon materials also contribute to the adsorption of reactants, enriching their local concentration and accelerating reaction rates, particularly in organic pollutant degradation [102]. Lu et al. [24] reported a nitrogen-doped carbon framework modified with PDI and manganese-doped ZnO, achieving remarkable TC adsorption and nearly complete degradation within 40 min (Fig. 7c). The synergistic effect of enhanced adsorption and efficient charge separation facilitated the generation of reactive oxygen species (ROS), significantly boosting photocatalytic activity (Fig. 7d). Moreover, the high chemical stability and mechanical strength of carbon materials ensure prolonged catalytic performance [103,104]. Bai et al. [105] developed PDA/PDI@CNT confined materials, where carbon nanotubes stabilized PDI through π -electron conjugation, forming a 3D electron transport pathway that accelerated electron-hole separation (Fig. 7e). The confined structure exhibited a pseudo-first-order rate constant 6.11 times higher than pure PDI in diclofenac degradation (Fig. 7f).

In summary, the integration of PDI with carbon materials effectively enhances photocatalytic performance by promoting charge separation, facilitating electron transfer, and enriching reactant adsorption. These synergistic effects drive the practical applications of PDI-based photocatalysts in environmental remediation and energy conversion, presenting a cost-effective and sustainable approach for advanced photocatalysis.

4. Application of PDI-based photocatalytic materials

With the development of PDI photocatalytic materials featuring various structures, their applications have expanded across a broader range of catalytic reactions and processes. In this review, the applications of PDI-based photocatalytic materials are categorized into six areas: photocatalytic antibacterial, photocatalytic pollutant degradation, photocatalytic water splitting, photocatalytic CO₂ reduction, photocatalytic nitrogen fixation, and photocatalytic cancer treatment.

4.1. Photocatalytic sterilization

Bacteria present in the environment cause diseases, and bacteria on wounds lead to infections [106]. These issues have long plagued healthcare professionals worldwide [107]. In the face of diseases and wound infections, the excessive use of antibiotics has led to the emergence of antibiotic-resistant “superbugs” [108]. Consequently, the development of more effective antibacterial methods has become a key research fo-

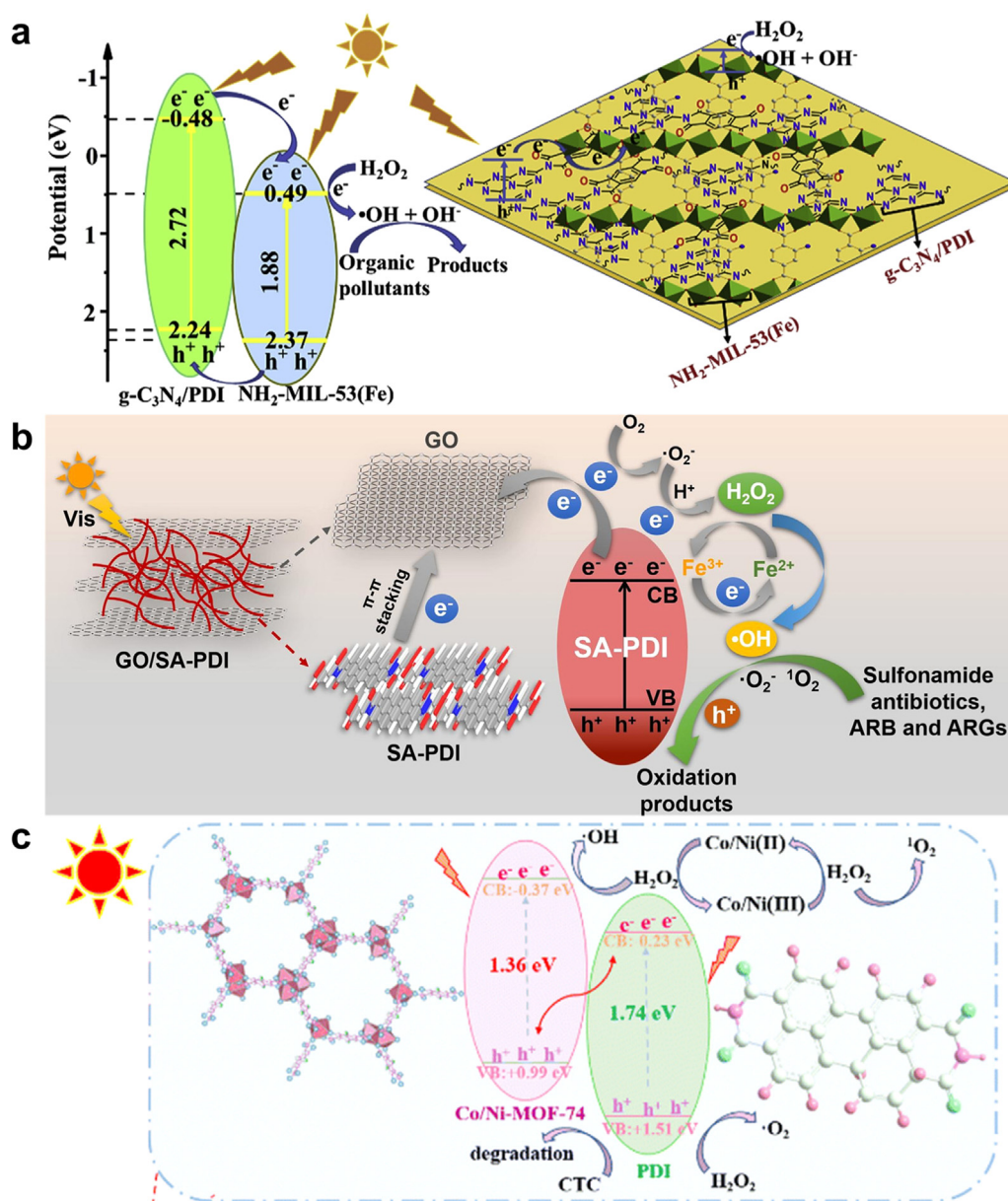


Fig. 6. Synergistic Fenton reactions. (a) Schematic illustration of the photocatalytic mechanism of the PDI/g-C₃N₄@NH₂-MIL-53(Fe). (Reproduced with permission [94]. Copyright 2019, Elsevier). (b) The mechanism diagram of the GO/SA-PDI-PSF. (Reproduced with permission [95]. Copyright 2025, Elsevier). (c) Schematic illustration of the Co/Ni-MOF-74@PDI system activating H₂O₂ to degrade contaminants. (Reproduced with permission [96]. Copyright 2023, Royal Society of Chemistry).

cus [109]. Photocatalytic antibacterial therapy has been proven to effectively combat resistant bacteria [110]. However, many common photocatalytic materials contain heavy metals, which may pose toxicity risks, limiting their further application [111,112]. As a result, organic nanomaterials have been increasingly developed for photocatalytic bacterial infection treatment. Organic semiconductor photocatalysts, with their excellent biocompatibility, tunable semiconductor structures, diverse microarchitectures, appropriate band gaps, and low cost, have attracted significant attention.

Wang et al. [113] developed an all-organic semiconductor heterostructure, PDI/g-C₃N₄, through *in situ* recrystallization of PDI onto the surface of g-C₃N₄ nanosheets. This structure extended the absorption spectrum from UV to NIR light, significantly enhancing photocatalytic performance and enabling efficient generation of ROS. The material exhibited excellent inactivation of both Gram-negative and Gram-positive bacteria (Fig. 8a). Being free of metal elements, it demonstrated good bi-

ological safety, with no toxicity to normal tissue cells, and significantly promoted the healing of dermal wounds infected with *Staphylococcus aureus* (*S. aureus*) in mice.

Furthermore, Yang et al. [114] utilized hydrogen bonding interactions between materials to self-assemble PDI onto the surface of Sn₃O₄, creating an inorganic-organic hybrid PDI/Sn₃O₄ heterostructure. This heterostructure not only enhanced photocatalytic performance but also formed a “hook-and-loop” sticky surface via hydrogen bonds on PDI, interacting with bacterial surface functional groups to capture bacteria, allowing ROS to act directly on the bacterial surface and significantly improving bactericidal efficiency (Fig. 8b). Building on this, researchers introduced GO during the recrystallization of PDI to prepare a PDI/GO supramolecular composite (Fig. 8c) [115]. The rich surface functional groups of GO shifted the HOMO and LUMO energy levels of the composite, improving its stability, and by introducing intermediate energy levels, extended the absorption spectrum to

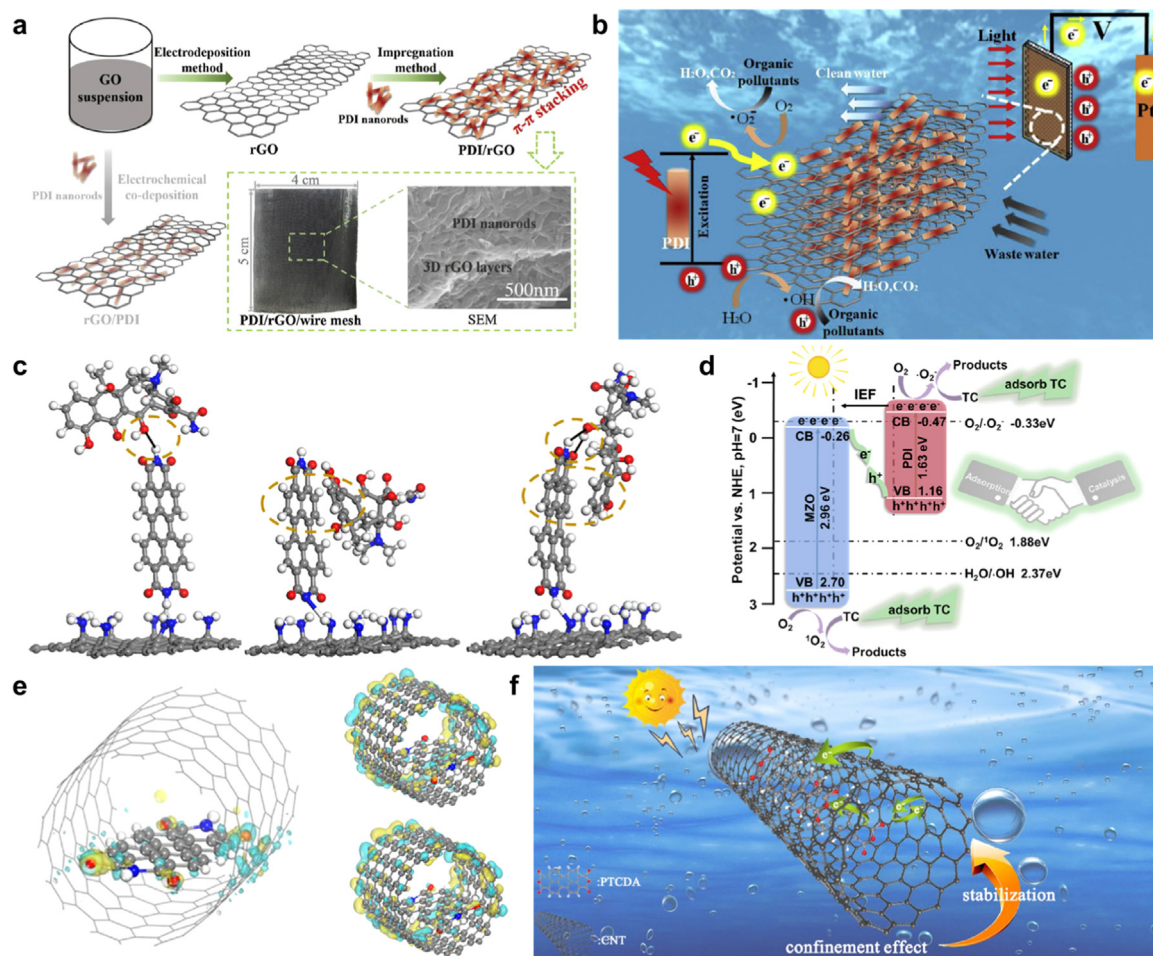


Fig. 7. Carbon-coupled PDI supramolecular photocatalysts. (a) Diagrammatic representation of the synthesis process of PDI/rGO. (b) The diagram illustrating the photoelectric degradation process of PDI/rGO. (Reproduced with permission [101]. Copyright 2020, Elsevier). (c) Adsorption models: hydrogen bond adsorption, π - π adsorption, and co-adsorption of π - π interactions and hydrogen bonds. (d) Photocatalytic process for the degradation of TC. (Reproduced with permission [24]. Copyright 2024, Elsevier). (e) The charge density of PDI@CNT. (f) Enhancement mechanisms for the performance of CNTs-stabilized PDA. (Reproduced with permission [105]. Copyright 2022, Elsevier).

the NIR range of 750–1,200 nm, further enhancing photocatalytic performance. Under light irradiation, protonated carboxyl groups on the GO surface formed highly active carboxyl radicals that reacted with amines on the bacterial cell wall to generate amide compounds, enabling efficient bacterial capture (Fig. 8d). Both *in vitro* and *in vivo* experiments showed that the PDI/GO composite exhibited excellent antibacterial activity and wound healing capabilities, making it an innovative photocatalytic antibacterial material with broad light spectrum response, high carrier separation efficiency, and efficient bacterial capture performance.

Additionally, to address bacterial contamination in the environment, PDI materials have also been developed for environmental remediation. Chen et al. [116] integrated p-type Cu_2O and n-type PDI materials to design an inorganic-organic PDI/ Cu_2O heterostructure. This structure improved photocatalytic antibacterial efficiency by promoting the separation of photogenerated carriers and the generation of singlet oxygen, while effectively reducing the environmental toxicity of Cu_2O , making it a promising eco-friendly marine antifouling agent. Through defect engineering, PDI was loaded onto Ga-doped Cu_2O , and the resulting p-n junction structure and Ga-doped defects significantly redshifted the optical absorption edge of Cu_2O . The optimized PDI/ $\text{Cu}_{1.8}\text{Ga}_{0.2}\text{O}$ material exhibited enhanced photocurrent density and ROS generation capacity, achieving over 91% inhibition of *S. aureus* and *Pseudomonas aeruginosa* (*P. aeruginosa*) (Fig. 8e). Meanwhile, Wang et al. [117] prepared a

PDI/ NH_2 -UiO-66 (PNU) Z-type heterostructure by ball milling. This material outperformed pure PDI and UiO-66 in photocatalytic performance, with the Z-type mechanism effectively promoting the separation of photogenerated carriers and generating a large amount of ROS, significantly improving antibacterial performance.

4.2. Photocatalytic degradation of pollutants

Photocatalytic degradation technology is widely applied in the removal of organic pollutants from industrial and domestic wastewater [67]. For instance, wastewater from industries such as papermaking, rubber, and textiles often contains significant amounts of phenolic compounds, while chemical and pharmaceutical wastewaters pose serious environmental threats due to their high toxicity and poor degradability [118]. Additionally, medical wastewater, food processing effluents, and organic waste from decaying plants and animals not only cause foul odors but can also foster bacterial growth and disease transmission [119]. These harmful substances pose significant risks to aquatic environments and ecosystems, and threaten human health. The photocatalytic degradation process effectively breaks down and removes pollutants through oxidation reactions, offering a green and sustainable solution for water purification [120].

PDI serves as an efficient visible-light photocatalyst, effectively facilitating the cleavage of organic compounds. Xu et al. [121] synthe-

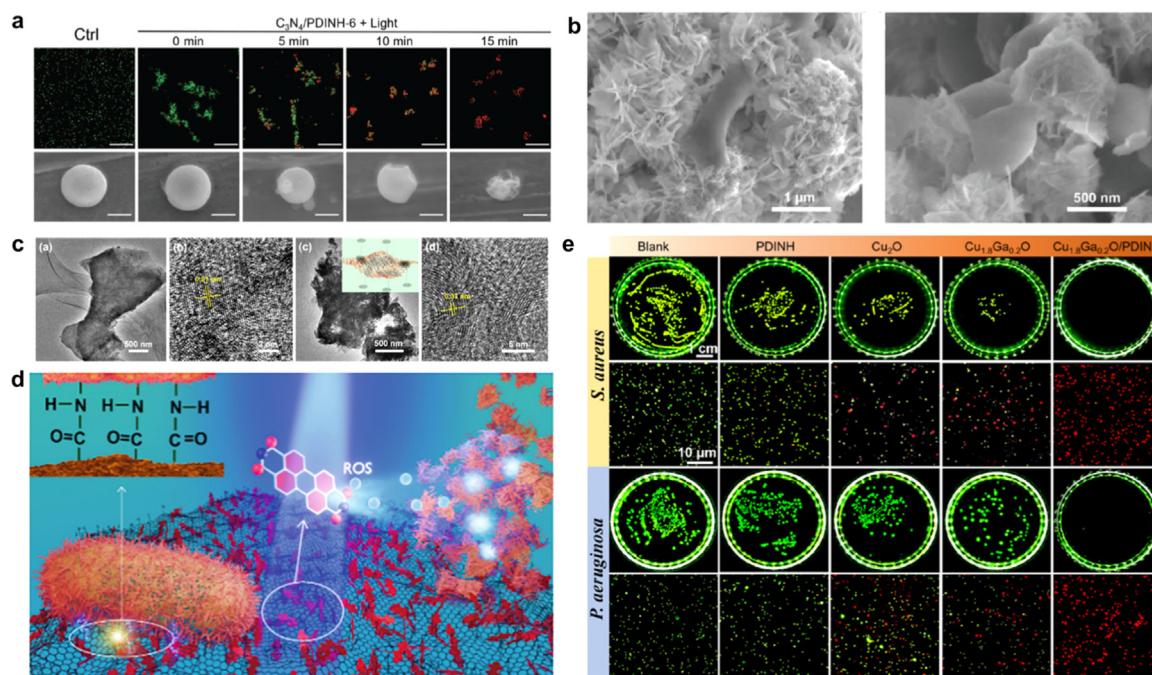


Fig. 8. Photocatalytic sterilization. (a) The bacterial viability of *S. aureus* at various time intervals was assessed using the PDI/C₃N₄, accompanied by corresponding SEM images. (Reproduced with permission [113]. Copyright 2019, Wiley-VCH). (b) SEM images of bacteria treatment with PDI/Sn₃O₄. (Reproduced with permission [114]. Copyright 2021, Wiley-VCH). (c) TEM and HRTEM images of PDI and PDI/GO. (d) Schematic diagram of antibacterial. (Reproduced with permission [115]. Copyright 2023, Elsevier). (e) The antibacterial performance of PDI/Cu_{1.8}Ga_{0.2}O. (Reproduced with permission [116]. Copyright 2024, Elsevier).

sized a magnetic separation-type photocatalyst by *in situ* self-assembly of ZIF-67 derivatives onto PDI supramolecules, which was used for organic pollutant removal. The 1D SA-PDI nanofibers interact through π - π and hydrogen bonding with the 3D Co-N-C structure, forming a 3D/1D heterostructure. Co-N-C, with its porous structure, high surface area, excellent conductivity, and strong magnetism, serves as a multifunctional co-catalyst, broadening the light absorption range of SA-PDI, increasing the active reaction sites, and improving the separation efficiency of photogenerated charge carriers. This enhances the photocatalytic performance in H₂O₂ synthesis (Fig. 9a).

Building on oxidation processes, Li et al. [122] employed highly dispersed PDI to generate electron-rich PDI^{•−} under visible light, thereby enhancing the rapid activation of peroxydisulfate (PDS) for bisphenol A (BPA) degradation. By covalently attaching PTCDA to the surface of SiO₂ NPs, a highly dispersed π - π stacked supramolecular layer was formed. The resulting PDI-SiO₂ composite not only enhanced the interaction between PDS and pollutants, reducing charge transfer distance, but also generated electron-rich PDI^{•−} radicals under visible light. These radicals were captured by PDS, facilitating efficient activation. Additionally, photogenerated electron transfer to PDS improved charge carrier separation, promoting hole involvement in oxidative degradation reactions (Fig. 9b). In the PDI-SiO₂-activated PDS system, the synergistic action of multiple active species enabled the rapid degradation of BPA. This method, driven by powerful oxidative free radicals, presents a promising approach for the treatment of organic wastewater.

Considering the favorable band alignment between MIL-88A and PDI, Yi et al. [123] synthesized a PDI/MIL-88A composite via a simple ball milling method and constructed a PDI/MIL-88A/PDS/visible light system for performance testing with chloroquine (CQ) as a model pollutant. The study revealed that both active free radicals and non-radical singlet oxygen participated in the degradation of CQ. LC-MS analysis and DFT calculations provided insights into the degradation pathway of CQ and the toxicity assessment of intermediates. This study offers deep insights into the mechanism of selective free radical advanced oxidation processes activated by photocatalytic Fe-MOFs for organic pollutant degradation (Fig. 9c). Additionally, Zhang et al. [124] introduced an in-

novative and effective visible light-driven photocatalytic method for the selective degradation of lignin model compounds and organic solvent lignin, utilizing PDI as a non-metallic organic catalyst. At room temperature, under visible light irradiation, this process efficiently degraded the oxidized lignin model into phenolic and ketone decomposition products with high selectivity. Additionally, using a self-made continuous-flow photocatalytic reactor, the reaction time was effectively shortened to less than one hour (Fig. 9d). Even organic solvent lignins were degraded to low molecular weight mono- and di-aromatic products in nearly 86% yield.

In summary, PDI-based photocatalysts exhibit significant potential in pollutant degradation. Through various synthesis strategies and system optimizations, researchers have successfully enhanced the photocatalytic performance of PDI, improved the separation efficiency of photogenerated charge carriers, expanded its light absorption range, and effectively degraded a variety of organic pollutants via multiple synergistic mechanisms. PDI not only effectively decomposes toxic and harmful substances but also holds broad applicability in the treatment of industrial wastewater, medical wastewater, and organic solvents, offering a green and sustainable solution for water pollution remediation. As research progresses, PDI-based photocatalytic technology is expected to play an increasingly pivotal role in environmental protection and resource recovery, advancing photocatalysis towards more efficient and widespread applications Table 2.

4.3. Water splitting reactions

H₂, as a clean and efficient energy carrier, has garnered significant attention due to its pollution-free and sustainable characteristics [103]. Photocatalytic overall water splitting for H₂ and O₂ production not only reduces dependence on sacrificial agents but also offers the advantages of zero consumption and pollution-free processes, making it a prominent research focus [131]. The core challenge lies in developing highly efficient and stable photocatalysts [132]. An ideal photocatalyst should be able to fully absorb sunlight, generate photogenerated charge carriers, suppress their recombination, and promote interface reactions [104].

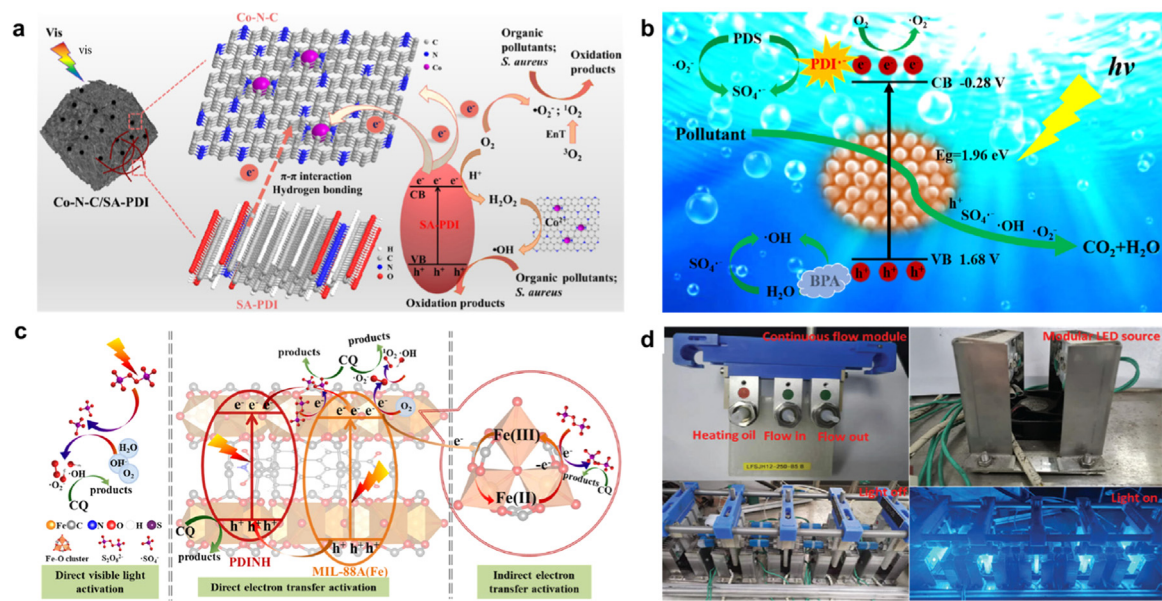


Fig. 9. Photocatalytic degradation of pollutants. (a) The interactions between SA-PDI and Co-N-C in composite system. (Reproduced with permission [121]. Copyright 2023, Elsevier). (b) A schematic illustration depicting the degradation mechanism of PDI-SiO₂ photocatalytically activating PDS. (Reproduced with permission [122]. Copyright 2024, Elsevier). (c) A depiction of the proposed mechanism for photocatalytic SR-AOP oxidation of CQ using P25M175. (Reproduced with permission [123]. Copyright 2021, Elsevier). (d) Photograph of the photocatalytic continuous-flow set-up. (Reproduced with permission [124]. Copyright 2020, Royal Society of Chemistry).

Table 2
Summary of the photocatalytic degradation of PDI-based materials for various pollutants.

Photocatalyst	Pollutant	Light source (Xenon lamp)	Performance	Ref.
PDI/g-C ₃ N ₄	phenol	500 W	57% (240 min)	[70]
PDI/rGO	phenol	500 W	86% (320 min)	[125]
	5 mg/mL	(λ > 420 nm)		
PDI/graphene	phenol	500 W	94% (360 min)	[53]
	5 mg/mL	(λ > 420 nm)		
PDI/Au	phenol	500 W	93% (180 min)	[62]
	5 mg/mL	(λ > 420 nm)		
PDI/BiOCl	phenol	800 W	57% (240 min)	[72]
	5 mg/mL	(λ > 420 nm)		
PDI/Cu/WO ₃	TC	300 W	76% (15min)	[81]
	20 mg/mL	(λ > 420 nm)		
PDI/g-C ₃ N ₄	NO	300 W	47% (10 min)	[126]
	0.6 mg/L	(λ > 420 nm)		
PDI/rGO/C ₃ N ₄	NO	300 W	60% (10 min)	[127]
	0.6 mg/L	(λ > 420 nm)		
PDI/C ₃ N ₄	RhB	300 W	95% (90 min)	[128]
	20 μM	(λ > 420 nm)		
PDI/TiO ₂	MB	500 W	96.4% (120 min)	[129]
	10 mg/L	(λ > 420 nm)		
PDI/P25	MO	500 W	65% (360 min)	[130]
	20 μM	(λ > 450 nm)		

Zhang et al. [133] successfully developed a highly crystalline PDI polymer (urea-PDI) as a photocatalyst (Fig. 10a). Thanks to its extensive conjugated system, Urea-PDI exhibits a broad light absorption range. Experimental results show that under visible light irradiation, Urea-PDI, without any catalyst, demonstrated the highest oxygen production rate to date (Fig. 10b). Its strong oxidative capability arises from the deep VB contributed by the covalent bonding of conjugated molecules. Moreover, Urea-PDI's high crystallinity and large molecular dipole moment facilitate the formation of a strong internal electric field, which enhances the separation and transportation of photogenerated charge carriers (Fig. 10c). The direct conversion of solar energy into H₂ using purely organic heterogeneous catalysts still faces challenges. Two key

challenges exist: first, low-frequency photons in the solar spectrum are ineffective in exciting the unified S₁ state for water splitting; second, the H₂ evolution reaction is impeded by a high overpotential on organic surfaces. To address these issues, Lin et al. [134] self-assembled spin-double radical anions along with their tautomeric spin-zero closed-shell quinone isomers, successfully creating organic molecular crystal nanoribbons (Fig. 10d). The self-assembled PDI²⁻/PDI²⁻ crystal nanoribbons modified the evolution of spin-related excitations, resulting in spin-allowed singlet fission from S₀S₁ → ¹(TT) → T₁ + T₁ under visible light (420–700 nm), and a spin-forbidden transition from S_n → T₁ in the NIR (700–1100 nm) range. Through triplet-triplet annihilation, the newly formed S₁ excitation state on the bi-radical quinone hybrid undergoes

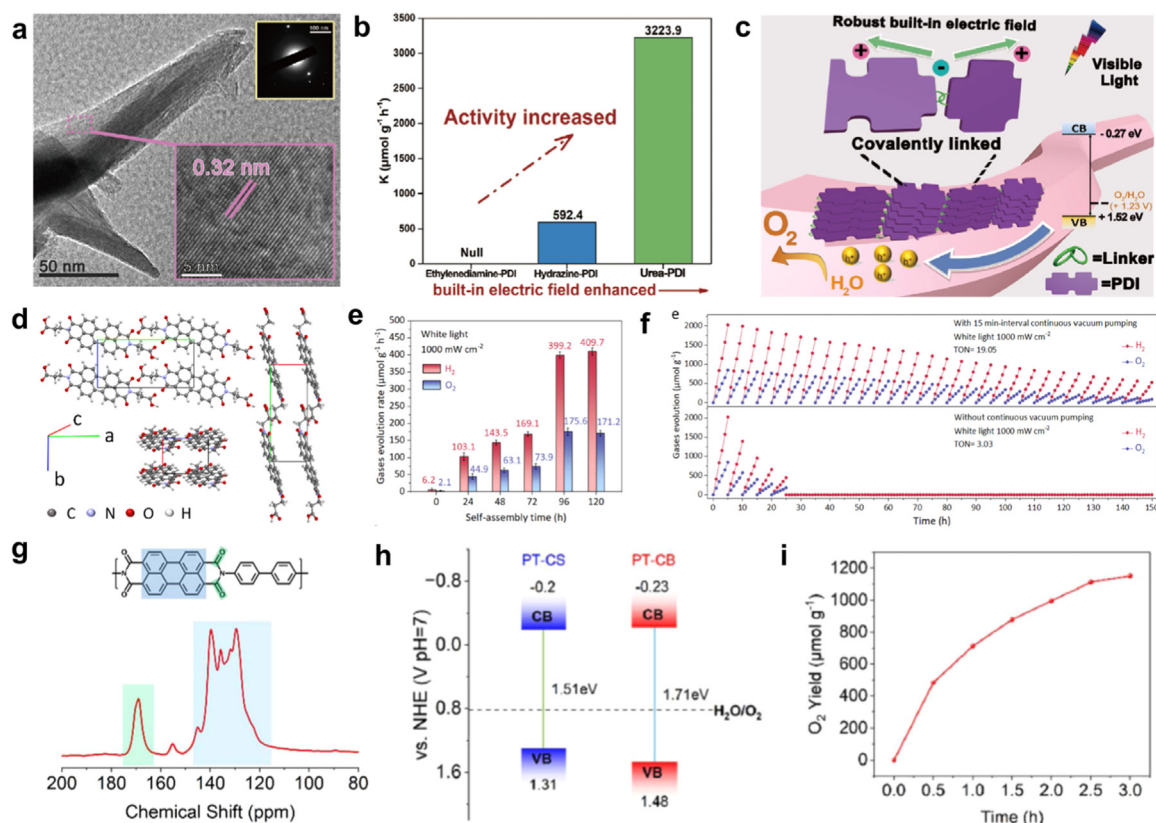


Fig. 10. Water splitting reactions. (a) HRTEM image of Urea-PDI. (b) Enhanced photocatalytic O₂ evolution attributed to the improved built-in electric field. (c) Schematic illustration of the photocatalytic mechanism of the Urea-PDI. (Reproduced with permission [133]. Copyright 2020, Wiley-VCH). (d) A simulated structural model of the PDI²⁻/PDI²⁻ crystal arrangement. (e) Comparison of H₂ and O₂ production from pure H₂O using PDI²⁻/PDI²⁻ catalysts with varying self-assembly durations under white light illumination. (f) Long-term gas production performance of PDI²⁻/PDI²⁻ nanobelts under white light over 150 h (Reproduced with permission [134]. Copyright 2024, Springer Nature). (g) Characterization of PT-CB solid-state ¹³C nuclear magnetic resonance spectra. (h) Energy level and performance diagram of PT-CB and PT-CS. (i) Photocatalytic O₂ evolution performance of PT-CB. (Reproduced with permission [135]. Copyright 2025, Royal Society of Chemistry).

electron transfer mediated by the hydrophilic bi-radical, inducing H⁺ reduction, enabling simultaneous H₂ and O₂ production from pure water under both visible and NIR light, with an average apparent quantum efficiency exceeding 1.5% (Fig. 10e) and excellent cycling stability (Fig. 10f). The design of organic polymers with efficient charge transfer properties is a critical area of research in photocatalytic systems, particularly for applications in energy storage and conversion. However, the structural characteristics of these polymers often hinder the optimal separation of charge carriers. To address this challenge, Wang et al. [135] developed linear conjugated organic polymers incorporating PTCDA as a fundamental building block, with p,p'-diaminobiphenyl and 3,7-diaminodiphenylene sulfone as linkers, resulting in the formation of PT-CB and PT-CS polymers (Fig. 10g). In PT-CB, charge carriers primarily migrate along the polymer backbone, with higher mobility along the chain direction compared to inter-chain transport, confirming its ability for directional electron transfer. These polymers not only exhibit directional charge transfer but also demonstrate exceptional performance in photocatalytic water oxidation reactions (Fig. 10h). Notably, PT-CB achieved an oxygen evolution rate of 966.28 mmol g⁻¹h⁻¹ (Fig. 10i), highlighting its outstanding charge separation efficiency.

In summary, PDI-based photocatalysts have demonstrated significant potential in water splitting reactions. Through various design strategies and system optimizations, researchers have successfully enhanced the photocatalytic performance of PDI, including expanding its light absorption range, improving the separation efficiency of photogenerated charge carriers, and enhancing the stability of the catalyst. Furthermore, under visible and NIR light irradiation, PDI-based photocatalysts can effectively promote water splitting reactions to generate H₂ and O₂, pro-

viding a feasible solution for clean energy production. Looking ahead, PDI-based photocatalytic technology is expected to play an increasingly important role in solar energy conversion, hydrogen production, and other green energy applications.

4.4. CO₂ reduction reactions

Energy shortages and environmental issues represent two of the most pressing challenges facing humanity, with the global energy consumption still heavily reliant on non-renewable fossil fuels [136]. The growing scale of human activities and global economic expansion not only accelerates the depletion of fossil fuels but also exacerbates the increase in greenhouse gas emissions, disturbing the natural "carbon equilibrium" [137]. The efficient reduction of atmospheric CO₂ and its subsequent utilization has emerged as a key area of global research [138]. Solar energy, as a sustainable and clean energy source, holds great potential for CO₂ conversion into valuable fuels like CO, CH₄, and HCOOH through photocatalysis, offering a promising solution to both the global energy crisis and environmental challenges.

Inspired by the porous structures of photosynthetic organelles, Shan et al. [139] employed chemical polymerization and layer-by-layer modification methods to stably load photosensitive components and catalytic components onto the surface of a porous network through zirconium-sulfonic acid-based coordination bridging (Fig. 11a). As a novel organic photoelectrode substrate, MCN demonstrated superior performance compared to conventional inorganic photoelectrodes: its porous network structure provides a higher surface area for loading dense photocatalytic components, and the surface's rich functional groups fur-

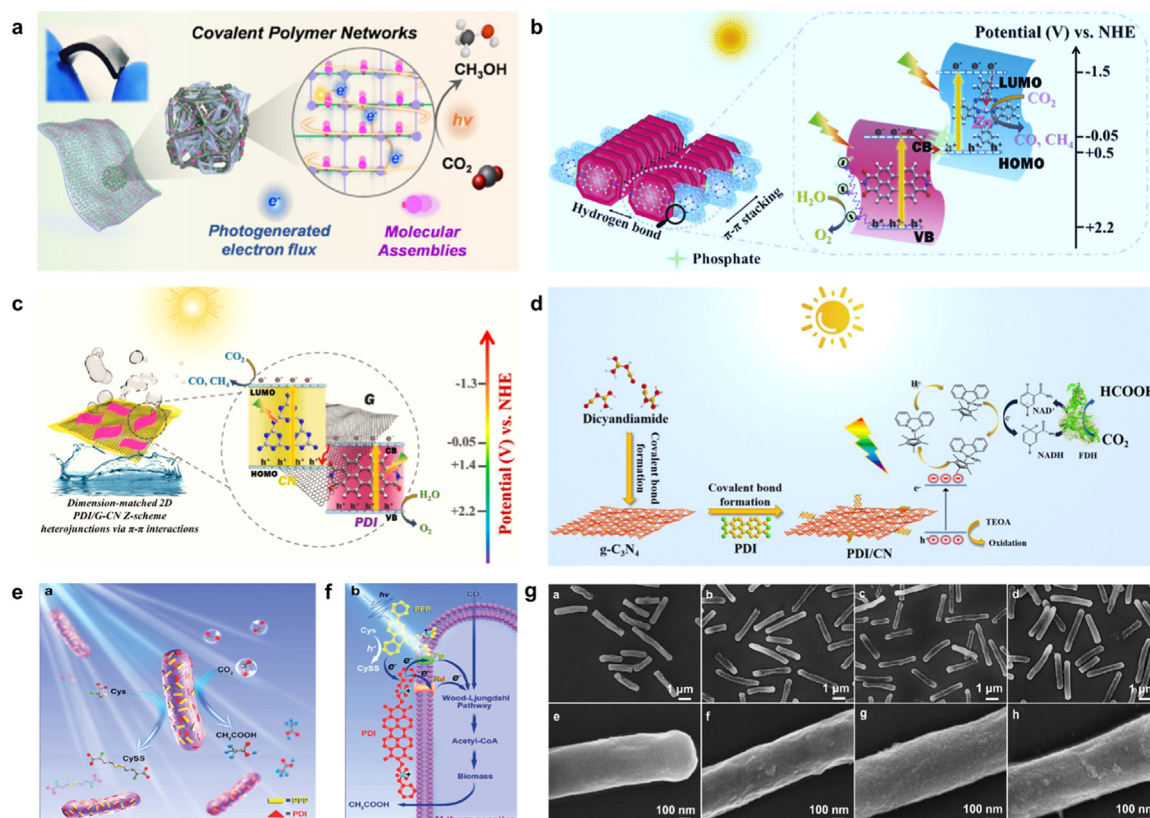


Fig. 11. CO₂ reduction reactions. (a) Photoelectrocatalytic reduction of CO₂ to methanol using molecular self-assemblies encapsulated within covalent polymer networks. (Reproduced with permission [139]. Copyright 2024, American Chemical Society). (b) Schematic of the package assembly structure in the phosphate-modulated PDI/ZnPc heterostructure, illustrating the Z-scheme charge transfer mechanism and induced reactions. (Reproduced with permission [90]. Copyright 2021, Elsevier). (c) Diagram of S-scheme-based photogenerated charge transfer and separation, showing the redox reactions occurring on the PDI/g-C₃N₄ heterostructure. (Reproduced with permission [140]. Copyright 2021, American Chemical Society). (d) Visible-light-driven CO₂-to-formic acid conversion in a semiconductor-enzyme hybrid photocatalytic system. (Reproduced with permission [141]. Copyright 2021, American Chemical Society). (e) Illustration of the PDI/PFP/*M. thermoacetica* photosynthetic hybrid system and (f) the transfer of photoexcited electrons from PDI/PFP to membrane proteins, ultimately passing through the Wood-Ljungdahl pathway for CO₂ reduction. (g) SEM images of *M. thermoacetica*, PFP/*M. thermoacetica*, PDI/*M. thermoacetica*, and PDI/PFP/*M. thermoacetica* with enlarged views. (Reproduced with permission [142]. Copyright 2020, Wiley-VCH).

ther modulate the physicochemical properties of the electrode material. The electrode's excellent hydrophilicity facilitates aqueous-phase catalytic reactions, while its high transparency effectively reduces competition for light absorption with the photosensitive components. Moreover, its high conductivity aids in the rapid transport of photogenerated charges. The effective separation of photogenerated charge carriers plays a crucial role in improving photocatalytic CO₂ reduction efficiency. Sun et al. [90] developed an ultrathin supramolecular Z-type heterostructure composed of phosphoric acid-regulated zinc phthalocyanine and PDI (PDI/ZnPc) for efficient visible-light-driven photocatalytic CO₂ reduction. Phosphoric acid treatment enhanced the hydroxyl group density on the surface of PDI nanosheets, fostering the formation of hydrogen bonding interactions between PDI and ZnPc. This improved the dispersion of ZnPc on the PDI surface (Fig. 11b). The PDI/ZnPc composite exhibited CO and CH₄ production rates of 6.26 and 1.88 μmol/g, respectively, showing a photocatalytic efficiency roughly 30 times higher than that of pure PDI. After four cycles, XRD, FT-IR, and TEM analyses of the recovered composite revealed no significant structural changes, confirming the heterostructure's excellent stability during photocatalytic reactions.

Furthermore, Jing et al. [140] developed an all-organic photocatalyst for CO₂ reduction by creating size-matched PDI/g-C₃N₄ S-type nanoflake heterostructure. This composite effectively reduces CO₂ to CO and CH₄, achieving a 16-fold increase in performance compared to the original CN nanoflakes. Using steady-state and transient photoluminescence spectroscopy, ESR, and Kelvin probe measurements, it was deter-

mined that the enhanced photoactivity was primarily due to the interface modulation with graphene, which improved S-type charge transfer and separation efficiency. Additionally, the π - π interactions optimized the dispersion of PDI (Fig. 11c). Inspired by artificial photosynthesis and leveraging the high efficiency and specificity of biological enzymes, Li et al. [141] integrated photocatalysis with enzymatic catalysis to create a metal-free PDI/g-C₃N₄ heterostructure. This system exhibited excellent visible-light response, enabling a highly efficient photocatalytic enzyme cascade (Fig. 11d). This system effectively regenerates nicotinamide adenine dinucleotide (NADH) and selectively reduces CO₂ to HCOOH. The PDI/g-C₃N₄ composites achieved an NADH generation efficiency of up to 75%, with a HCOOH production rate of 1.269 mmol g⁻¹ h⁻¹ and nearly 100% selectivity, significantly surpassing previous materials. The remarkable photocatalytic performance can be attributed to the unique photocatalytic enzyme cascade system, the heterostructure effects, the superior conductivity, and the wide solar light absorption range of the PDI/g-C₃N₄ heterostructure.

Further, Wang et al. [142] developed an organic semiconductor-microbe hybrid photosynthetic system and achieved efficient CO₂ conversion to acetic acid, with a conversion efficiency of 1.6%, comparable to current reports on inorganic hybrid biosynthesis systems (Fig. 11e). The cationic n-type organic semiconductor PDI and p-type polyfluorene derivative (PFP) formed a p-n heterostructure as a photosensitizer, demonstrating excellent light capture ability and high hole/electron separation efficiency. The cationic organic semiconductor was uniformly adsorbed onto the surface of non-photosynthetic bacterium *Moorella*

thermoacetica (*M. thermoacetica*) via electrostatic interactions (Fig. 11f), with the cationic side chains embedding into the bacterial cell membrane, effectively preventing electron loss across the membrane, ensuring efficient transfer of photogenerated electrons from the organic conjugated molecules to the bacteria, and successfully driving the Wood-Ljungdahl metabolic pathway within the bacteria, resulting in CO₂ reduction (Fig. 11g). This work opens a new direction for the application of organic semiconductors in bioenergy and provides a novel biomaterial manufacturing strategy for designing efficient solar-to-chemical energy conversion systems.

In summary, PDI-based photocatalysts exhibit significant potential in CO₂ reduction reactions. These photocatalysts efficiently catalyze CO₂ reduction under visible and NIR light irradiation, producing valuable fuels such as CO, CH₄, and HCOOH, offering a practical solution to the global energy crisis and environmental pollution. Looking ahead, PDI-based photocatalytic technology is expected to play an increasingly important role in CO₂ conversion, hydrogen production, and solar energy conversion, contributing to the sustainable utilization of energy and the achievement of environmental protection goals.

4.5. Nitrogen fixation reactions

Ammonia is a critical raw material for fertilizers, pharmaceuticals, fibers, and explosives, making it indispensable to modern society's development. However, the widely used Haber-Bosch process, which requires high temperatures and energy consumption, presents significant environmental and economic challenges. In recent years, photocatalytic nitrogen fixation has been regarded as a promising low-energy and sustainable alternative for producing nitrogen-containing compounds, with photocatalysts playing a vital role in this process.

PDI has garnered significant interest owing to its stability and robust absorption in the visible light spectrum. The efficiency of photogenerated charge separation and photocatalytic nitrogen fixation can be notably improved by tuning supramolecular structures that incorporate intrinsic electric fields. Yin et al. [143] integrated microfunctional hydrogen-based triazole units into a rigid PDI-based hydrogen-bonded organic framework (NPDI), designing a novel hydrogen-bonded organic framework. Experimental and theoretical studies revealed that the flexible, polar microfunctional groups embedded in the rigid framework not only significantly enhanced the framework's stability but also strengthened local polarization, electron delocalization, and the intensity of the built-in electric field, thereby effectively promoting exciton dissociation and charge carrier transport (Fig. 12a). NPDI exhibited excellent photocatalytic nitrogen fixation rates and NIR light ammonia production in pure water at room temperature. In further studies, Wang et al. [144] the authors employed a solution-dispersed supramolecular self-assembly technique to prepare PDI-triazine-based supramolecular materials. These supramolecular materials exhibited a significant enhancement in photocatalytic nitrogen fixation rates and NIR yields, achieving up to 10 times that of the original PDI. DFT calculations and experimental results showed that the introduction of triazine units effectively modulated the HOMO and LUMO energy levels and light absorption properties, enabling the material to absorb NIR light and efficiently activate N₂ molecules (Fig. 12b). Additionally, the tunable π - π stacking arrangement and intrinsic molecular dipole characteristics significantly enhanced the formation of the built-in electric field, further improving charge carrier separation efficiency.

In the context of regulating flexible geometries, optimizing the spatial twisting angle to enhance the spatial overlap and electronic transport channels of organic semiconductors represents another critical strategy. However, high molecular polymers with flexible geometries and complex compositions often face the limitation of restricted charge carrier migration rates. Peng et al. [145] designed and synthesized a donor-acceptor (D-A) type PDI polymer. The experiments demonstrated that high crystallinity and the coplanar molecular polarity of the semi-

conductor material enabled differentiated charge distributions and carrier transport sites, laying the foundation for efficient charge transport and exciton dissociation (Fig. 12c). The unique π -conjugated D-A structure not only provided a smooth electronic transport channel but also significantly enhanced the adsorption, diffusion, and electron exchange capabilities of nitrate, while lowering the energy barrier for hydrogenation reactions. Furthermore, Yang et al. [146] proposed a new approach to enhance photocatalytic performance by constructing a PDI-based polar bridge D-A unit composite (BOPDI) (Fig. 12d). The enhanced BOPDI demonstrated remarkable photocatalytic nitrogen fixation rates without requiring co-catalysts or sacrificial agents, achieving an efficiency 11 times greater than that of the original PDI. DFT calculations and experimental data revealed that the polar bridging units strategically tuned the HOMO and LUMO energy levels and light absorption properties, enabling BOPDI to effectively absorb NIR light and activate N₂ molecules. Furthermore, these bridging units strengthened the built-in electric field, facilitating carrier separation and exciton dissociation by overcoming Coulomb potential barriers.

In summary, significant progress has been made in the research of PDI-based photocatalysts for nitrogen fixation reactions. By optimizing molecular structures and built-in electric fields, the performance of photocatalysts can be effectively enhanced, facilitating the activation and conversion of N₂ molecules under low-energy conditions. These optimization strategies are expected to provide critical theoretical insights for the development of more efficient photocatalysts and promote the advancement of low-energy, sustainable nitrogen fixation technologies in the future.

4.6. Photocatalysis in cancer therapy

NIR light-mediated therapies, including photothermal therapy (PTT) and photodynamic therapy (PDT), have attracted significant interest due to their high efficacy and non-invasive nature. Nevertheless, developing single-component therapeutic agents with precise structural and molecular weight control to enable effective synergistic photothermal and photodynamic treatments remains a challenge. Wu et al. [147] tackled this issue by combining PDI with methylene violet, leading to the creation of an innovative, intelligent photosensitizer (PRX). The D-A architecture of methylene violet effectively shifts its absorption into the NIR region (Fig. 131a). The amphiphilic PRX self-assembled into uniform NPs, leading to a significant enhancement and broadening of its absorption spectrum. MTT assays demonstrated the excellent biocompatibility of PRX NPs with A549 cells (Fig. 13b). Upon 808 nm laser irradiation, PRX NPs efficiently produced ROS and generated heat, achieving a photothermal conversion efficiency of 59%. Additionally, PRX NPs exhibited strong interactions with DNA, causing plasmid DNA damage upon light exposure (Fig. 13c). Thus, PRX NPs show great potential as a nanomedicine for anti-tumor therapies through synergistic photothermal and photodynamic treatments.

Further research by Guan et al. [148] explored the impact of H-type and J-type stacking on the photocatalytic performance and mechanisms of PDI. H-type aggregates, which align face-to-face, exhibit enhanced π -electron conjugation (Fig. 13d), leading to more prominent semiconductor properties. This structural arrangement promotes efficient charge carrier separation and migration upon light exposure. In contrast, J-type aggregates, characterized by head-to-tail stacking, show reduced π -electron conjugation and display more molecular-like characteristics. The study revealed that PDI in H-type aggregation primarily generates superoxide radicals and holes through electron transfer, while J-type aggregation mainly produces singlet oxygen via energy transfer. Due to the greater oxidative power of superoxide radicals and holes, H-type aggregates demonstrate superior efficiency in small molecule degradation and oxygen evolution photocatalysis under visible light. *In vivo* anti-cancer studies in female mice with subcutaneous breast cancer xenografts revealed that both H-PDI and J-PDI injections significantly suppressed tumor growth (Fig. 13e). However, J-PDI exhibited a more potent tumor-

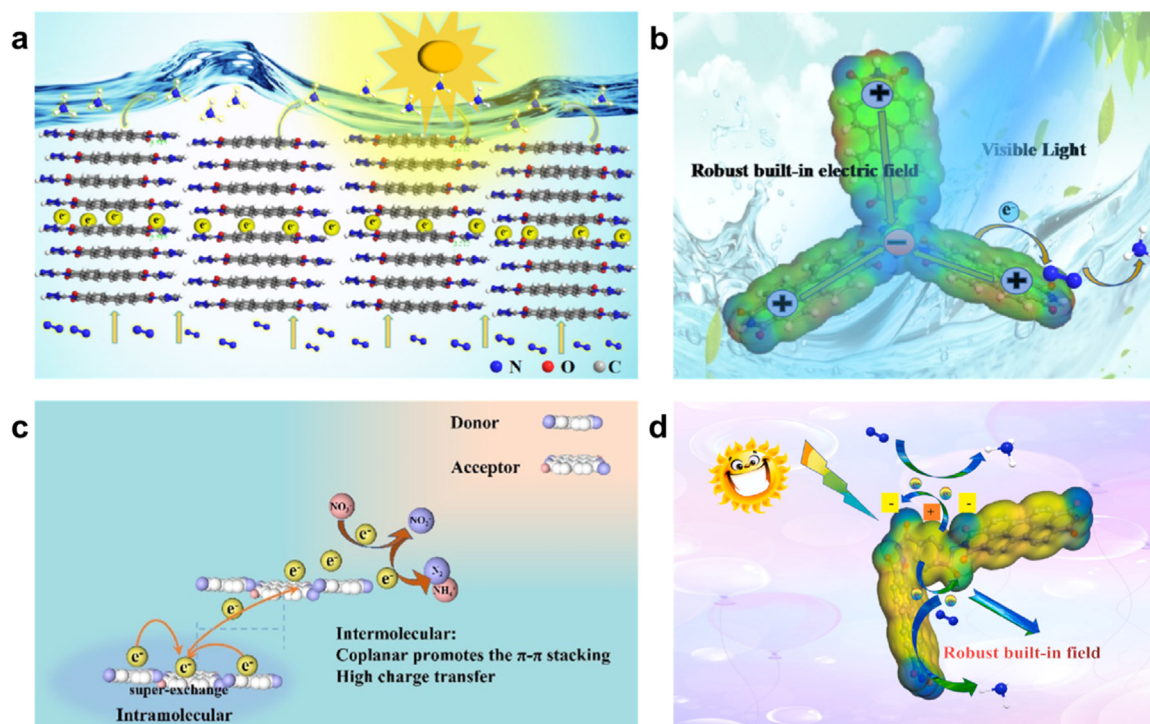


Fig. 12. Nitrogen fixation reactions. (a) Photocatalytic nitrogen fixation reaction mechanism over NPDI. (Reproduced with permission [143]. Copyright 2023, Elsevier). (b) Schematic of the photocatalytic nitrogen fixation process occurring over PDI-triazine-based supramolecular materials. (Reproduced with permission [144]. Copyright 2023, Elsevier). (c) Schematic mechanism of the PDI polymer. (Reproduced with permission [145]. Copyright 2024, American Chemical Society). (d) Proposed mechanism for photocatalytic N_2 fixation using BOPDI. (Reproduced with permission [146]. Copyright 2022, Elsevier).

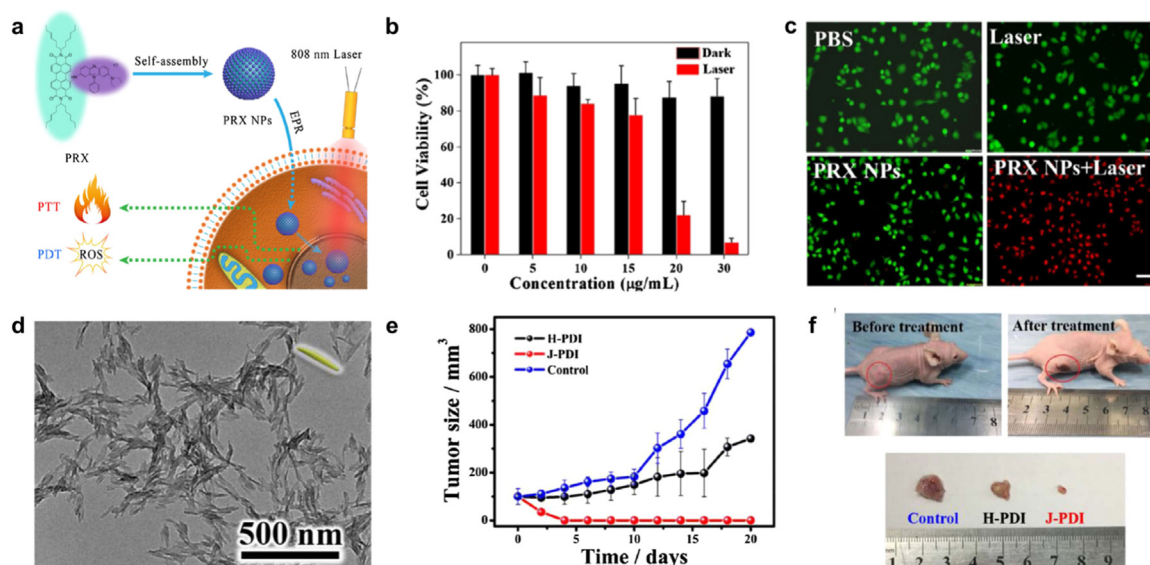


Fig. 13. Photocatalysis in cancer therapy. (a) A schematic representation of the self-assembly process of PRX NPs and their utilization in PTT and PDT. (b) Cell viability of A549 cells exposed to different concentrations of PRX, both with and without irradiation. (c) Fluorescence microscopy images of A549 cells treated with PBS, PRX NPs, laser irradiation, and PRX combined with laser irradiation. (Reproduced with permission [147]. Copyright 2020, Elsevier). (d) TEM image of J-PDI supramolecular nanomaterial. (e) Temporal changes in tumor growth in a mouse tumor model following treatment with H-PDI and J-PDI. (f) Photographic images of mice and tumors after treatment with H-PDI and J-PDI. (Reproduced with permission [148]. Copyright 2018, Elsevier).

inhibiting effect, resulting in tumor tissue ulceration and the smallest final tumor volume (Fig. 13f). These results underscore the promise of J-PDI in photocatalytic cancer therapy.

PDI-based photocatalysts have demonstrated promising potential for cancer therapy. By modulating molecular structures and aggregation states, researchers have effectively enhanced the photocatalytic performance of PDI, thereby strengthening its syner-

gistic effects in both photothermal and photodynamic therapies. These advancements suggest that PDI-based photocatalysts hold significant application potential in cancer treatment. As the technology continues to evolve, PDI-based photocatalysts are expected to emerge as a novel therapeutic strategy in precision medicine and tumor treatment, providing more effective solutions for clinical applications.

5. Summary and perspective

This review highlights the latest advancements in PDI-based photocatalytic materials, focusing on the structure, photocatalytic mechanisms, and strategies to enhance photocatalytic performance. The photocatalytic performance of PDI-based materials has been significantly enhanced through the design of various PDI polymers, the introduction of co-catalysts, the development of heterostructures, synergistic Fenton reactions, and the use of carbon-coupled PDI supramolecular photocatalysts. In terms of applications, PDI-based photocatalytic materials show considerable promise across a wide range of fields, including photocatalytic antibacterial, pollutant degradation, water splitting, CO₂ reduction, nitrogen fixation, and cancer treatment. By optimizing material design and reaction conditions, PDI-based photocatalysts have demonstrated excellent performance, particularly in the areas of environmental protection and sustainable energy, offering substantial potential for future advancements. However, despite these notable achievements, challenges remain in the ongoing research of PDI-based photocatalytic materials.

5.1. Further exploration of surface/structure

The surface properties and structural morphology of PDI require further investigation to enhance its optical and photocatalytic performance. Nanostructures with high surface areas and abundant active sites, including quantum dots, hollow tubes, and hollow spheres, require further investigation to fully harness their capabilities in photocatalytic applications.

5.2. Enhancing interface interactions and stability

PDI-based heterostructure are commonly coupled with semiconductors via electrostatic interactions, non-covalent bonds, covalent bonds, and physical adsorption. However, over extended photocatalytic cycles, the interactions between semiconductor components may degrade, leading to reduced charge transfer efficiency and diminished photocatalytic performance. Hence, there is a pressing need to devise strategies that strengthen interface interactions within PDI-based heterostructure, ensuring their stability and effectiveness for practical applications.

5.3. Deepening understanding of photocatalytic mechanisms

To optimize the design and performance of PDI-based heterostructure photocatalysts, it is crucial to develop a comprehensive understanding of their photocatalytic mechanisms. Beyond carrier transfer dynamics, the thermodynamics and kinetics of surface catalysis must also be thoroughly examined. *In situ* characterization methods and theoretical simulations provide valuable insights into the structure-performance correlations of heterostructure, guiding the development of high-efficiency photocatalysts.

5.4. Expanding NIR response

Currently, the majority of PDI-based composites are designed to absorb visible light, while NIR light accounts for approximately 43% of the solar spectrum. As such, future research will prioritize the development of PDI-based photocatalysts that can efficiently utilize NIR light, expanding their photocatalytic capabilities.

5.5. Improving photocatalytic mineralization and application

Photocatalytic mineralization technology uses photocatalysts under light conditions to completely oxidize and decompose organic compounds into inorganic small molecules. The core of this process is the complete degradation of organic pollutants, with no secondary pollution

in the final products. Although PDI-based photocatalysts show promising performance in pollutant degradation, their photocatalytic mineralization capacity and stability still require further optimization and improvement. Furthermore, most of the research on PDI-based photocatalysts is still in the laboratory stage, with significant gaps in their practical application for water pollution treatment. Future research should focus on improving the stability and performance of photocatalysts to meet the demands of practical wastewater purification, while also exploring the impact of natural organic matter and heavy metal ions on the water degradation process, thereby promoting the widespread application of this technology in practical environments.

5.6. Advancing CO₂ reduction and H₂ generation

Research on PDI-based photocatalytic systems for CO₂ reduction and hydrogen production is still in its early stages, underscoring the need for further investigation into PDI composites tailored for these reactions. Simultaneously, the development of PDI heterostructure photocatalysts for nitrogen fixation offers significant promise in tackling global greenhouse gas emissions and addressing the energy crisis.

In conclusion, PDI-based heterostructure photocatalytic systems exhibit substantial potential for solar energy conversion and environmental remediation. However, additional research is necessary to refine material design, optimize performance, and explore practical applications. This review seeks to offer valuable perspectives to researchers, supporting the advancement of PDI-based photocatalytic technologies for sustainable energy and environmental solutions.

CRedit authorship contribution statement

Huiyan Xu: Formal analysis, Conceptualization. **Jian Zhang:** Data curation. **Xiran Qiao:** Conceptualization. **Longhua Ding:** Conceptualization. **Aizhu Wang:** Writing – review & editing. **Hong Liu:** Writing – review & editing. **Xin Yu:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no conflicts of interest in this work.

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