

Research Progress and Application Exploration of Conjugated Microporous Polymers in Photocatalysis

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Abstract: Conjugated microporous polymers (CMPs) have garnered significant attention in the field of photocatalysis owing to their tunable structures at the molecular level, high specific surface areas, and excellent physicochemical stability. The most recent molecular design techniques for CMPs, such as donor-acceptor (D-A) regulation, heteroatom doping, and heterostructure assembly, which allow for precise modification of their photoelectric properties, are methodically reviewed in this study. Their uses in the synthesis of hydrogen by photocatalysis and the breakdown of organic contaminants like colors and antibiotics are thoroughly examined. Numerous improvement techniques, including as heterostructure creation, morphology control, and metal doping, are suggested to solve important issues such high photogenerated carrier recombination rates. Lastly, potential research avenues for developing CMPs-based photocatalytic devices for environmental remediation and sustainable energy conversion are described.

1. Introduction

As the global energy crisis intensifies and environmental pollution continues to worsen, developing clean, renewable energy alternatives has become a critical societal concern. Solar energy, through efficient conversion and utilization, holds profound implications for future sustainable development[1]. Among numerous solar energy conversion technologies, photocatalytic technology is regarded as one of the ideal pathways for addressing energy and environmental challenges due to its ability to drive key reactions, such as water splitting for hydrogen production, carbon dioxide reduction, and organic pollutant degradation under mild conditions. In recent years, conjugated microporous polymers (CMPs) have demonstrated tremendous application potential in the field of photocatalysis due to their tunable structure, high specific surface area, and excellent stability[2]. Consequently, against the backdrop of increasingly severe energy shortages and environmental pollution, conducting in-depth research on the photocatalytic properties of CMPs holds significant urgency and practical relevance.

This paper systematically reviews and summarizes the research progress and application explorations of CMPs, which is an emerging photocatalytic material within the academic community, based on the practical development of photocatalytic technology. Molecular structure design is a core

component of CMPs photocatalyst research. Clarifying the intrinsic relationship between molecular structure and photocatalytic performance is a prerequisite for achieving rational design and development of highly efficient photocatalysts. Failure to clarify this structure-function relationship not only directly impacts the targeted design and performance optimization of catalysts but also readily induces issues such as high recombination rates of photo-generated carriers, as well as sluggish surface reaction kinetics. These problems severely constrain the practical application of CMPs photocatalytic technology in energy conversion and environmental remediation fields. Based on this, this paper attempts a groundbreaking approach by starting from molecular design strategies. After systematically analyzing the principles of band structure modulation in CMPs, it reviews their application progress in photocatalytic hydrogen evolution, carbon dioxide reduction, and environmental pollutant degradation. Subsequently, it summarizes existing challenges and enhancement strategies, and proposes targeted future research directions[3].

2. Design Principles for the Photocatalytic Performance of Conjugated Microporous Polymers

The photocatalytic performance of conjugated microporous polymers (CMPs) lies in their tunable molecular structure. Modulating their band structure and redox potential through molecular design is the cornerstone of their application in photocatalysis. Currently, the academic community has primarily established three core design strategies: donor-acceptor (D-A) structural regulation, introduction of heteroatoms/functional groups, and construction of heterojunctions.

2.1. Donor-Acceptor (D-A) Structure Regulation

Constructing D-A type CMPs has become the mainstream design strategy for optimizing charge separation and transfer efficiency. By rationally selecting electron-donating donor units and electron-accepting acceptor units, researchers can precisely control frontier molecular orbital energy levels, narrowing the bandgap and broadening visible light absorption. Xie Linfu systematically investigated salen-based donor-triazine conjugate combinations, revealing that the rigidity and electron-donating ability of the donor unit determine the polymer's photophysical properties. Similarly, Xie et al.[4] pre-screened 16 D-A combinations via DFT calculations and validated the high efficiency of Zn-salen-TEPA in photocatalytic oxidation reactions, demonstrating optimal electron-hole separation.

To further enhance charge separation, researchers have developed more sophisticated copolymerization strategies involving D- π -A, D-A₁-A₂, and D₁-D₂-A ternary copolymers[5]. Experimental results demonstrate that introducing a thiophene π -bridge between the donor triphenylamine (TPA) and the acceptor dibenzothiophene sulfonide (BTDO) improves the coplanarity of the polymer backbone, facilitating charge transfer and enhancing photocatalytic hydrogen production efficiency. These studies demonstrate that increasing the dimensionality of intramolecular charge transfer pathways can effectively suppress the recombination of photogenerated carriers, thereby enhancing photocatalytic performance[6].

2.2. Introduction of Heteroatoms/Functional Groups

Integrating N, S, O and other heteroatoms into the CMPs framework or introducing specific functional groups is another effective approach for precisely tuning electronic structure and surface properties. In thiophene-based CMPs synthesized by Zhang Jin[7], sulfur-and nitrogen-rich heterocyclic structures not only modulate light absorption but may also provide additional active sites. Jin Shenglin et al.[8] confirmed that in furan-based D- π -A type CMPs, optimizing the donor/acceptor ratio enhances photocatalytic hydrogen production. Furthermore, Deng Zhaozhang's[9] research demonstrates that constructing five-membered heterocyclic structures through gradient-doped

nitrogen atoms modulates the local charge distribution and built-in dipole moment of CMPs, promoting exciton dissociation and offering a novel approach to enhancing photocatalytic performance.

2.3. Constructing a Heterojunction

To address challenges such as severe carrier recombination, constructing heterojunctions has emerged as a key interfacial engineering strategy for optimizing band structure and enhancing photocatalytic performance. By compositing CMPs with other semiconductor materials, an intrinsic electric field can be formed at the heterojunction interface, significantly enhancing the spatial separation of photo-generated electrons and holes while preserving their strong redox capabilities. Z-type heterojunctions have garnered significant attention due to their unique charge transfer pathways. Zhao et al.[10] designed a TpPa/C₆N₇S-type heterojunction via first-principles calculations, achieving efficient spatial separation of photogenerated carriers. By positioning the active sites for hydrogen evolution and oxygen evolution reactions on two distinct layers of the material, the structure demonstrates high potential for efficient overall water splitting. The Z-type heterojunction hollow spheres PzTP@BTTP constructed by Zheng et al.[11] exhibit significantly enhanced H₂O₂ production (8.19 mmol g⁻¹ h⁻¹) in pure water, providing an effective solution to high carrier recombination rates in single-component CMPs.

The design principles of CMPs have evolved from simple copolymerization to sophisticated band structure engineering through synergistic strategies like D-A regulation, heteroatom doping, and heterojunction construction. This enables the customization of catalysts with ideal optoelectronic properties, deepening theoretical understanding and propelling photocatalytic technology toward addressing energy and environmental challenges.

3. Progress in the Application of CMPs in Photocatalytic Hydrogen Evolution

Due to their tunable band structure, CMPs demonstrate significant potential in energy conversion fields like photocatalytic water splitting. Through precise molecular design, CMPs can regulate visible light response, redox potential, and charge separation to meet the requirements of various energy conversion reactions. Photocatalytic hydrogen evolution (HER) is currently a mainstream application direction.

Extensive research has focused on enhancing HER performance through structural optimization. In recent years, achieving efficient charge separation via D-A structure design has become pivotal. Researchers enhanced performance by modulating exciton binding energy and donor sites, achieving rates of 27 mmol g⁻¹ h⁻¹ and 9.3 mmol g⁻¹ h⁻¹, respectively. Xu et al.[12] constructed D-A₁-A₂ type CMPs, achieving spatial charge separation through dual receptor synergy. Their optimized Py-BTDO-TAME-2 exhibited a rate of 27.53 mmol g⁻¹ h⁻¹, while P-BTDO-EDOT reached 87.21 mmol g⁻¹ h⁻¹. Lang et al.[13] synthesized ternary CMPs (D₁-D₂-A) directly via C-H arylation polymerization, achieving a hydrogen production rate as high as 81.4 mmol g⁻¹ h⁻¹. Constructing multicomponent D-A systems with strong intramolecular electric fields effectively overcomes the HER performance bottleneck. Introducing strong electron-withdrawing groups to enhance intramolecular dipole moments has also been shown to significantly boost hydrogen production activity.

CMPs have made significant strides in the field of energy photocatalysis, evolving from initial fundamental investigations into hydrogen production capabilities to the current pursuit of complex catalytic objectives high efficiency, high selectivity, and multi-product conversion through sophisticated molecular engineering and active site construction.

4. Current Research Status of CMPs in the Degradation of Environmental Pollutants

CMPs demonstrate significant application potential in the photocatalytic degradation of organic pollutants due to their high specific surface area, tunable pore architecture, and stable conjugated framework. Especially for recalcitrant new pollutants such as antibiotics and dyes, CMPs can rapidly achieve deep degradation by generating reactive species like superoxide radicals ($\cdot\text{O}_2^-$) through highly efficient photochemical charge separation. Currently, enhancing the degradation efficiency and selectivity of photocatalysts toward specific pollutants through molecular design and morphology control has become a research hotspot in the field of photocatalytic environmental remediation.

4.1. Photocatalytic Degradation of Dyes by CMPs

CMPs exhibit outstanding adsorption-photocatalytic synergistic effects due to their high specific surface area and tunable pore structure. Zang et al. demonstrated that CMP nanowires/hollow nanospheres with phenolic hydroxyl or naphthyl groups exhibit exceptionally high degradation efficiency (> 99.9%) for cationic dyes like methylene blue and rhodamine B, with outstanding cycling stability. Mechanistic studies indicate $\cdot\text{O}_2^-$ is the primary reactive species. Additionally, research has developed hollow CMP microspheres and TiO_2 composite films. Leveraging multiple light scattering effects of the hollow structure combined with TiO_2 's electron transport capability significantly enhanced degradation efficiency for RhB and tetracycline[14].

4.2. Photocatalytic Degradation of Antibiotics and Other Emerging Pollutants Using CMPs

Research has focused on overcoming CMPs' intrinsic defects: high exciton binding energy and rapid carrier recombination. Studies systematically investigating donor polarization engineering, gradient nitrogen doping, and built-in dipole moment modulation have enhanced exciton dissociation and improved tetracycline (TC) degradation. Introducing the strong donor EDOT or constructing five-membered heterocyclic structures successfully reduced exciton binding energy to 99 meV, enabling EdtTz-CMP to achieve 94.6% TC degradation within 90 minutes[15]. Deng et al. used molecular isomerization to regulate carbonyl position, minimizing exciton binding energy and achieving up to 99% degradation for ofloxacin (OFL). Zhang et al.[16] focused on dielectric constant regulation, employing polarization engineering by introducing high-dipole-moment acceptors. This approach similarly effectively reduced exciton binding energy and enhanced degradation of OFL. Regarding degradation mechanisms, multiple studies have confirmed through radical scavenging experiments and electron paramagnetic resonance (EPR) techniques that $\cdot\text{O}_2^-$, singlet oxygen ($^1\text{O}_2$), and holes (h^+) are key active species in the photocatalytic degradation of antibiotics[17].

4.3. Photocatalytic Degradation of Oil Pollutants by CMPs

CMPs also demonstrate significant potential in degrading oil pollutants. Petroleum hydrocarbons and aromatic compounds are characterized by strong hydrophobicity and resistance to biodegradation, posing a serious threat to aquatic ecosystems. However, CMPs, with their high specific surface area, tunable pore structure, and π - π stacking interactions with aromatic molecules, not only efficiently adsorb oil pollutants but also generate reactive oxygen species ($\cdot\text{O}_2^-$) under light irradiation to achieve deep oxidative degradation. This offers a novel technological pathway for treating marine oil spills and oil-containing industrial wastewater[18]. Modifying CMPs to be hydrophobic/oleophilic or constructing specific pore structures enhances adsorption and enrichment capacity, enabling deep degradation via photocatalytic oxidation. Leveraging π - π stacking interactions, these materials achieve efficient capture and degradation of oil contaminants into CO_2 and H_2O [19].

Beyond dyes, antibiotics, and oil pollutants, CMPs demonstrate potential in broader environmental applications. CMPs can photocatalytically reduce highly toxic heavy metals like Cr(VI) and U(VI) into less toxic forms, and their photoactive species confer antibacterial properties. Researchers designed anthraquinone D-A type CMPs inspired by natural photosynthesis, achieving highly efficient photocatalytic U(VI) reduction under strongly acidic conditions[20].

Research on CMPs in the field of environmental pollutant degradation has established a complete chain encompassing mechanism exploration, performance enhancement, and practical application. The research focus has shifted from merely demonstrating degradation efficiency to gaining a deeper understanding and controlling the photogenerated charge behavior, particularly the exciton dissociation process. By employing various strategies such as doping, heterostructuring, and constructing composite films, the inherent limitations are being overcome, propelling the technology toward practical wastewater treatment applications.

5. Conclusions

Conjugated microporous polymers (CMPs) have demonstrated broad application prospects in photocatalysis due to their structure-tunable properties, high surface area, and excellent stability. This paper systematically reviews the design principles, energy conversion applications, and environmental pollutant degradation capabilities of CMPs, providing a comprehensive understanding of the research landscape. Research has established a framework from molecular design to application expansion. At the fundamental level, strategies like D-A construction, heteroatom introduction, and bonding mode control effectively tune band structure and optoelectronic properties. At the application level, CMPs have achieved significant progress in photocatalytic hydrogen evolution and environmental pollutant degradation. Hydrogen production rates have exceeded $80 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, with degradation efficiencies for emerging pollutants reaching over 95%. Nevertheless, challenges remain: high recombination rates of photo-generated carriers, slow surface reaction kinetics, and the need to validate performance in practical applications. To address these, researchers have developed enhancement strategies including heterojunction construction, metal doping, morphology control, and post-treatment modification, which often synergize to produce significant effects. Based on this, future research should focus on deepening applied studies within real-world environmental systems, concentrating on complex pollution scenarios and actual aquatic conditions. By leveraging high-throughput computing and machine learning to accelerate the rational design of high-performance CMPs, and advancing green, large-scale synthesis and forming processes, we can lay the foundation for practical engineering applications. It is foreseeable that with the advancement of fundamental research and engineering exploration, CMPs and their photocatalytic properties will play an increasingly vital role in solar energy conversion and environmental remediation.

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