

Covalent organic frameworks for photocatalytic hydrogen production

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Energy shortages and environmental issues have driven the exploration of renewable energy solutions, and the conversion of solar energy into clean energy has been considered as a sustainable approach to address the challenges of global warming and climate change. Since Honda and Fujishima laid the foundation for solar photocatalysis research by utilizing n-type semiconductor TiO₂ electrodes in the field of photoelectrochemical water splitting in 1972,¹ photocatalytic water splitting for hydrogen production has attracted tremendous efforts and a plethora of photocatalysts have been extensively developed, injecting vitality into the field.

Photocatalytic hydrogen evolution consists of three processes: (1) Light absorption. The absorption of photons with energy higher than the semiconductor bandgap generates photoexcited carriers. (2) Charge separation and transfer. Photoexcited carriers separate into free carriers, and then migrate to active sites on the surface of photocatalysts. (3) Redox reactions. Catalytic

sites accept electrons to reduce adsorbed protons from water into hydrogen, accompanied by the hole extraction with sacrificial electron donors. The optical and physicochemical properties of semiconductor materials determine light absorption and charge carrier mobility, which are crucial for photocatalytic efficiency.

Covalent organic frameworks (COFs) have emerged as highly crystalline porous materials with advanced functions and a wide range of potential applications. Owing to the well-ordered structure, high surface areas, structural versatility and tunable optical and physicochemical properties of COFs, they are promising heterogeneous photocatalysts for water splitting using solar energy. To enhance the photocatalytic performance, various strategies have been explored to design backbones with functional building blocks, including the design of donor-acceptor structures, extension of π -conjugation, preparation of ultrathin COF nanosheets, and construction of hybrid

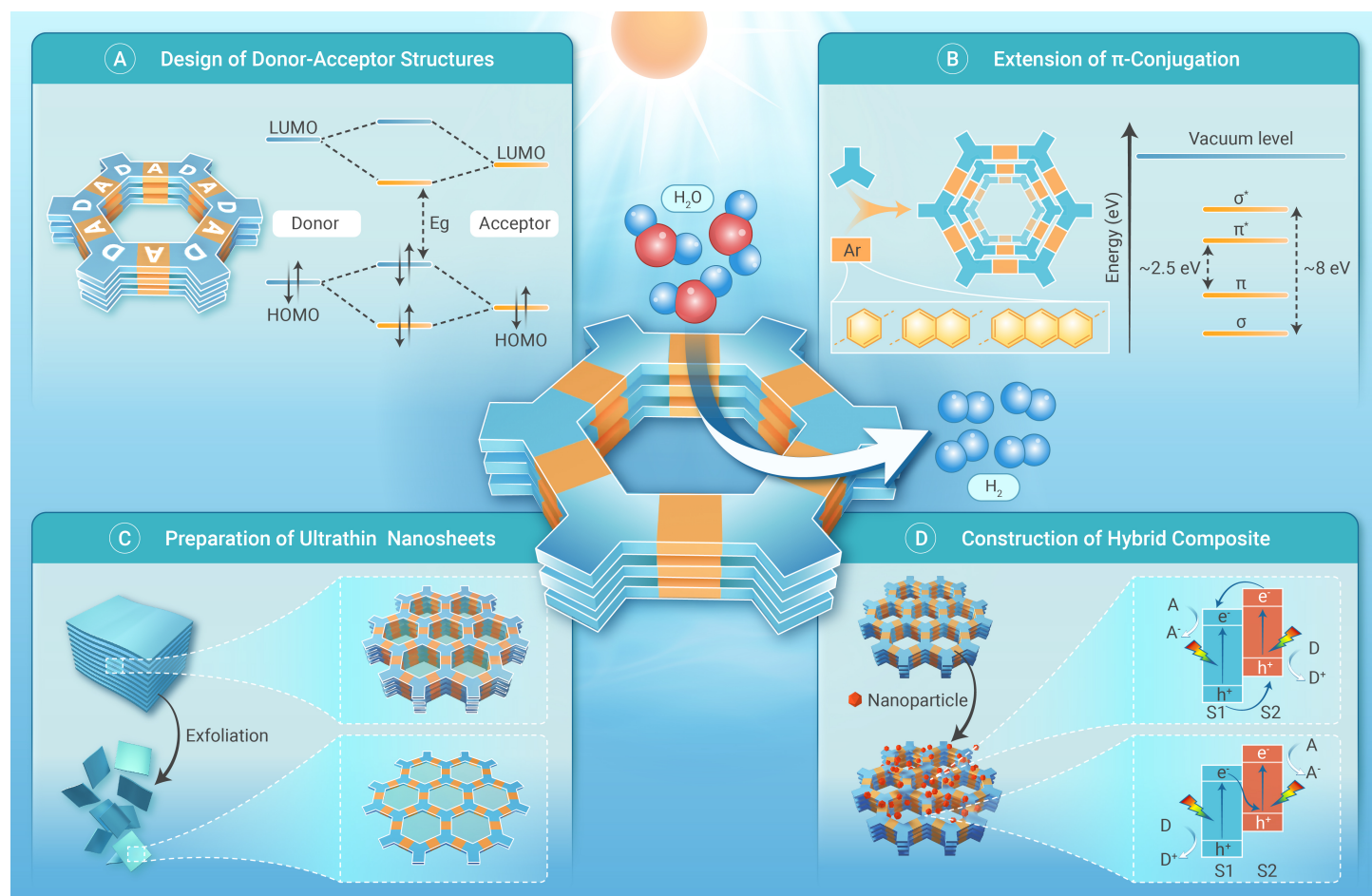


Figure 1. Common strategies for modulating the performance of photocatalytic hydrogen production Such as (A) design of D-A structure, (B) extension of π -conjugation; (C) preparation of ultrathin nanosheets, and (D) construction of hybrid composite.

composite.

DESIGN OF DONOR-ACCEPTOR STRUCTURES

The incorporation of donor-acceptor (D-A) structures into COFs can introduce an internal electric field by establishing a difference in charge density between the donor and acceptor, and facilitate rapid charge separation and

directional charge transfer on the frameworks (Figure 1A). The separation of excitons into free charge carriers requires overcoming the exciton binding energy. Therefore, the rational preparation of photocatalysts with low exciton binding energy is of great importance for the realization of efficient photocatalysis. Recently, Jiang et al. evaluated the band arrangement and charge transfer characteristics of potential D-A COFs using density-functional theory

(DFT) calculations. With 1,3,5-tris (4-aminophenyl) triazine (TAPT) or 1,3,5-tris(4-aminophenyl)benzene (TAPB) as acceptors, and terephthalaldehyde containing different groups as donors, DFT calculations show that TAPT-OMe has the strongest D-A interaction. Under theoretical guidance, Jiang et al. synthesized the corresponding D-A COFs, and TAPT-OMe-COF indeed delivered the best photocatalytic hydrogen production activity among several COFs. Notably, the activity trends for the other COFs are consistent with the calculated exciton binding energy (E_b) trends for the D-A pairs.²

EXTENSION OF π -CONJUGATION

The conjugation in the skeleton of COFs plays an important role not only in light harvesting but also in structural stability, which in turn is closely related to the stability of the charged state. For different conjugated systems, the π - π^* transition energy gap narrows as the conjugation expands, resulting in a broader light absorption range (Figure 1B). Recently, Baek et al. designed four covalent organic skeletons (COFs) based on benzotrithiophene (BTT) by controlling the conjugation of structural units, and investigated the relationship between the conjugated structural units and the photocatalytic hydrogen production activity. The synthesized BTT-COFs all featured sliding parallel stacked structures, high crystallinity, and high specific surface area. All the BTT-COFs were able to generate hydrogen from water under visible light irradiation with platinum (Pt) as a co-catalyst and ascorbic acid as a hole scavenger. By increasing the number of polycycles in the aromatic amine unit, the absorption undergoes a redshift. By the electron spin resonance (ESR) test and electron affinities (EAs) calculation, it was found that the extended π -conjugation of electron acceptor units resulted in the formation of more stable radicals, and effective charge separation, which can improve the catalytic activity.³

PREPARATION OF ULTRATHIN COF NANOSHEETS

Researchers have demonstrated that stripping 2D COF into ultrathin nanosheets effectively improves photocatalytic performance. This is because more reactive active sites are exposed and short diffusion distances allow for less charge carrier complexation (Figure 1C). Yang et al. developed a method for self-exfoliation of COF colloids on SiO₂ nanorods and prepared a series of COF layers and near-monolayer of COFs with adjustable thickness distributed on the surface of SiO₂ nanorods. In the photocatalytic hydrogen production half-reaction, it was found that the hydrogen production rate increased dramatically from 19.8 $\mu\text{mol/h}$ to 76.6 $\mu\text{mol/h}$ with the decrease of COF layer thickness, and the apparent quantum efficiency (AQE) increased significantly. The transient absorption spectra (TAS) characterizations revealed that all of the photogenerated long-lived electrons within the near-SLCOF engaged in photocatalysis, yet this proportion notably declined as the layer thickness increased, suggesting that reducing the number of 2D COF layers to nearly a single layer can significantly improve the carrier separation efficiency.⁴

CONSTRUCTION OF HYBRID COMPOSITE

It is believed that hybrid materials with synergistic effects will provide multifunctional properties for photocatalysis. Designing heterojunction systems with appropriate energy band levels, wide light absorption range, and efficient charge separation can effectively improve photocatalytic performance (Figure 1D). Li et al. constructed an efficient 2D/2D Z-scheme heterojunction for photocatalytic overall water splitting by in situ growth of COFs on O-vacancy WO₃ nanosheets (Ov-WO₃) through W-O-C chemical bonding. Due to the synergistic effect between the built-in electric field enhanced by interfacial W-O-C bonds, the strong water oxidizing ability of Ov-WO₃, and the ultrathin

structure of TSCOF, the charge separation and charge carrier transfer efficiencies are significantly improved. The optimal photocatalytic hydrogen evolution rate of TSCOFW can reach 593 $\text{mmol h}^{-1} \text{g}^{-1}$, which was four times higher compared to that of pure TSCOF, and the AQE at 420 nm was as high as 56.1%. Such AQE is superior to most of the reported photocatalysts.⁵

CONCLUSION AND PERSPECTIVE

This commentary highlights four approaches including the design of donor-acceptor structures, extension of π -conjugation, preparation of ultrathin COF nanosheets, and construction of hybrid composite for tuning the photocatalytic hydrogen production performance of COFs. Although much progress has been made in this field, there remain challenges that need to be addressed. First, most COFs exist in polycrystalline rather than single-crystal forms, which makes it hard to precisely investigate the catalytic mechanisms; Second, there are fewer detailed studies on the strong or weak interactions between donors and acceptors; furthermore, it is difficult to maintain structural stability, porosity and crystallinity for most photocatalysts. To address these challenges, it is necessary to develop efficient and versatile synthesis methods to prepare single-crystal COF materials with specific functionalities; to obtain detailed information on the nature and strength of the interactions utilizing computational methods; and to introduce novel building blocks and dynamic linkages to overcome the stability issues of COFs. Nevertheless, COFs and COF-based photocatalysts are still in their infancy, and these new initiatives will greatly simplify the synthesis of COF materials, and the combination of theory and experimentation can accurately predict the relationship between the structure and function of COF materials.

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AUTHOR CONTRIBUTIONS

X. Luo, G.-H. Ning and D. Li co-wrote the manuscript. J. Luo and J.-T. Lin read and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.