



共轲聚合物光电催化析氢进展

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摘要 为应对传统化石燃料所引发的能源危机与环境污染, 光电催化制氢技术能够将太阳能转换为氢能, 被认为是获得清洁能源的有效策略之一. 尽管光电催化析氢性能目前已得到了极大地提升, 但传统无机半导体催化剂(如金属氧化物、金属硫化物)存在的光吸收范围窄、稳定性差、贵金属依赖性强等问题仍制约着其商业化应用. 近年来, 共轲聚合物凭借可调的分子结构、宽谱光响应、低成本及高稳定性等优势引起了广泛关注, 为开发高效光电活性材料提供了新方向. 因此, 本文系统综述了共轲聚合物(如氮化碳、炔基共轲聚合物、共价有机框架及共轲聚合物复合结构)在光电催化制氢方向上的研究进展, 并重点探讨其分子结构设计、电子分布和转移调控、光生载流子分离机制及催化活性提升策略. 最后, 本文简要展望了共轲聚合物在光电催化水分解制氢领域存在的问题和未来发展, 有望为其他光电催化反应的探索和研究提供参考和借鉴.

关键词 共轲聚合物, 氮化碳, 炔基共轲聚合物, 共价有机框架, 光电催化, 析氢

传统化石燃料的广泛使用引发了全球范围内的能源危机和环境污染, 可再生清洁能源的开发迫在眉睫^[1]. 太阳能具有绿色、价格低廉以及取之不尽等优点^[2,3], 但由于辐射到地表的太阳能能量密度较低, 因而难以直接使用和储存^[4,5]. 氢气在所有的化学燃料中具有最高的质量能量密度($\approx 140 \text{ kJ g}^{-1}$), 是环保、高效的清洁能源的理想选择^[6-8]. 然而传统的商业制氢方法会不可避免地产生含碳副产物, 导致环境污染和温室效应^[9-11]. 自1972年Fujishima和Honda首次通过光电催化水分解法生成氢气后, 将太阳能转化为氢能的光电催化制氢技术被认为是实现“绿色制氢”的高效途径^[12-17].

几十年来, 光电催化领域不断发展, 研究人员开发了各类适合用于光电催化水分解制氢气的光电催化剂^[18-21]. 早期的研究聚焦于无机半导体催化剂. 作为最

初被开发的光催化材料, 二氧化钛(TiO_2)凭借其高化学稳定性、相对较低的成本、无毒等优势得到了广泛的研究^[22-24]. 然而, 大多数 TiO_2 基催化剂仅吸收紫外线, 对太阳光的利用率低^[25]. 其他无机半导体催化剂如金属氧化物^[26,27]、硫化物^[28,29]、氮化物^[30,31]等虽然在光电催化制氢领域被广泛报道, 但由于其高昂的成本、高金属毒性、易发生光腐蚀导致活性快速衰减等局限, 影响了它们在长时间使用过程中的稳定性^[32,33]. 为了克服无机半导体存在的诸多问题, 研究者将目光转向了具有独特电子结构和优异光电性质的有机高分子半导体, 特别是具有连续离域的 π 电子共轲体系的共轲聚合物. 它们的 π 电子共轲体系有利于电荷的快速传递与分离; 同时, 共轲聚合物在分子水平上可进行结构设计, 使得它们的光吸收范围、带隙、能带结构甚至是催化活性易于调节. 基于上述优势, 共轲聚合物表现出了更

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加优秀的光电催化潜力^[34]. 因此, 共轭聚合物为开发高性能的光电催化析氢催化剂提供了新的思路和广阔的研究空间.

因此, 在本文中, 我们总结了包括氮化碳(carbon nitride, C_3N_4)、炔基共轭聚合物(conjugated acetylenic polymers, CAPs)、共价有机框架(covalent organic frameworks, COFs)以及共轭聚合物复合结构在内的共轭聚合物在光电催化析氢领域的最新进展, 旨在阐明共轭聚合物在光电催化析氢领域中的工作原理与优势(图1). 此外, 我们还总结了共轭聚合物在目前光电催化析氢领域存在的挑战和潜在的解决思路, 有望为设计合成高效实用的共轭聚合物光电催化剂提供指导和启发.

1 光电催化析氢原理

光电催化水分解析氢是一种先进的能源转换技术, 它利用光能, 在外加偏压条件下将水分子分解为氢气和氧气^[35]. 该过程的本质在于半导体的光电效应, 当光催化剂吸收能量大于或等于禁带宽度的入射光时, 半导体价带上的电子会吸收能量而跃迁到导带上形成光生电子, 同时在价带上则会留下光生空穴^[36]. 随后, 产生的电子和空穴从半导体催化剂中迁移到半导体的表面, 再进一步转移到光阴极和阳极界面, 进而驱动水分

子在半导体表面发生氧化还原反应, 分别生成氢气和氧气.

具体来说, 光电催化水分解析氢的反应过程主要涉及三个步骤: 光吸收、光生电子/空穴迁移和表面氧化还原反应^[37]. 其中, 半导体对太阳光谱的吸收范围取决于其能带结构. 为了提高光吸收效率, 需选择具有适当能带宽度的半导体, 以确保其能最大程度地吸收太阳光. 此外, 材料的表面形貌和微观结构也会影响光吸收性能, 优化这些参数有助于提高太阳光利用率. 在光吸收过程中产生的光生电子和空穴在半导体内迁移和扩散, 最终电子向光阴极移动, 空穴向阳阳极移动, 最终实现氧化/还原产物氧气和氢气的有效物理分离. 通过优化催化剂的晶体结构、表面性质、减少缺陷和复合中心的形成, 能够有效提高电荷分离效率. 此外, 光生电子和空穴在半导体材料表面分别与水分子发生反应生成氢气和氧气的过程需要克服较高的活化能垒, 因此选择和设计具有表面活性位点的催化剂和优化反应条件对于提高催化效率和反应速率至关重要^[38,39].

尽管目前光电催化水分解制氢的研究已经取得了一些成果, 但仍面临着光生电荷在半导体内部的分离和迁移过程中因复合和陷阱效应而导致电荷损失和催化效率下降、光电催化剂催化活性位点不足的问题, 这限制了催化剂的析氢性能^[40-43]. 因此, 未来仍然需要

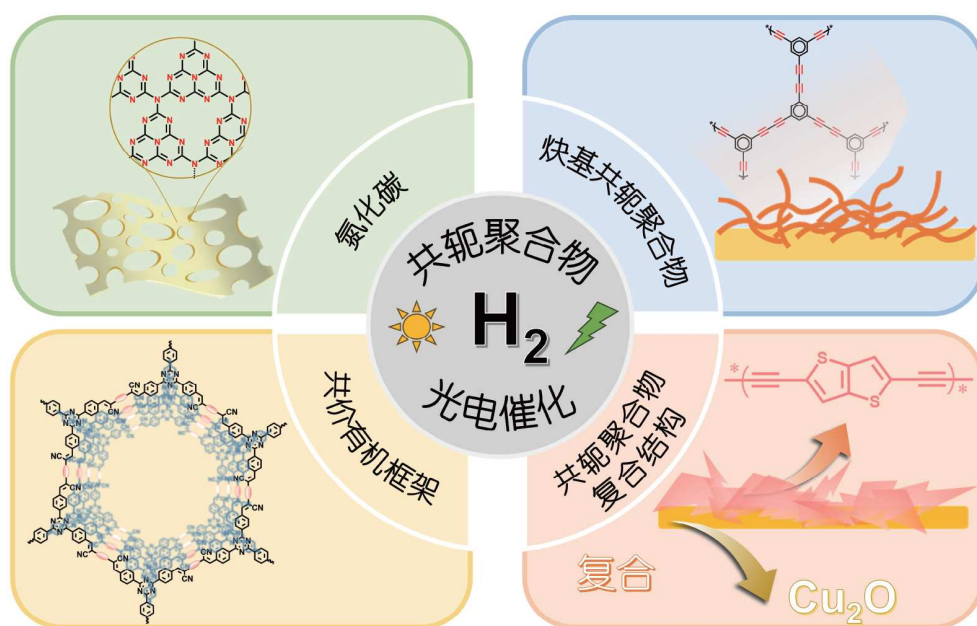


图1 (网络版彩色)用于光电催化析氢的有机共轭聚合物材料示意图

Figure 1 (Color online) Schematic diagram of organic conjugated polymer materials for photoelectrocatalytic hydrogen evolution

继续深入研究半导体催化剂的光电性质、优化其设计与制备方法、提高光生载流子的分离和转移效率,进而获得具有出色光电特性和析氢性能的催化剂。

2 用于光电催化析氢的共轭聚合物

共轭聚合物,如 C_3N_4 、CAPs、具有共轭效应的COFs及共轭聚合物复合结构等,是一类新型的光电催化剂。这些半导体具有丰富的离域电子、较窄的带隙、可调节的能级位置、多样化的结构设计、简便的合成方法和低廉的加工成本等优点,已在光电催化分解水制氢的应用中表现出巨大的应用潜力。

2.1 C_3N_4

自2009年由王心晨课题组首次报道通过模板法成功合成并应用于光催化制氢领域以来, C_3N_4 ,特别是类石墨相 C_3N_4 (g- C_3N_4)已经取得了显著的研究进展^[44,45]。这一里程碑式的发现不仅验证了g- C_3N_4 在水分解制氢中的可行性,推动了g- C_3N_4 在环境治理、能源转换和有机合成等多个领域的研究应用,还为后续的光催化剂和光电催化剂的设计提供了新思路^[46-49]。作为一类新型的非金属半导体光电催化剂,g- C_3N_4 采用简单的缩聚反应即可进行合成,具有无毒无害、成本低廉、制备方便和化学稳定性强等优点。其由3-均三嗪聚合而成的独特结构使得其中N和C产生的 sp^2 杂化构建出了高度离域的一类芳香环 π 电子共轭体系,可以有效促进光电催化反应过程中的光响应和电荷转移^[50]。更重要的是,g- C_3N_4 具有适中的禁带宽度(2.7~2.8 eV)和合适的能带位置,这使得它在水分解制氢过程中存在热力学优势,因此成为光电催化析氢领域的理想催化剂。同时,g- C_3N_4 在占据了太阳光谱大部分能量的可见光区有更好的光响应性能,能够显著提高太阳光利用率。其能够吸收可见光并产生大量的光生电子-空穴对,从而为后续的光电催化水分解析氢提供了充足的能量来源。此外,g- C_3N_4 的结构具有高度的可调控性,可以通过多种方式进行优化。比如,改变前驱体的种类、调整合成过程中的反应条件(温度、压力、反应时间等),或者通过后处理手段(如酸处理、碱处理等)进一步改性等^[51]。这些方式能够精准调控g- C_3N_4 的晶体结构、比表面积、孔隙率以及表面官能团等关键参数,进而显著影响其光电性能。这种结构可调控性使得研究人员可以根据具体的光电催化析氢需求,有针对性地对不同催化剂进行优化,例如增加活性位点数量、提高电荷分

离与传输效率等,从而不断提升其析氢性能。因此,凭借上述优势,g- C_3N_4 作为新型光电催化材料在光电析氢领域迅速崛起,为高效析氢催化剂的开发和利用开辟了新的途径。

尽管g- C_3N_4 具有共轭聚合物半导体的特性,但由于结晶度和导电性低、缺乏有效的氢气生成活性位点和光生电荷和空穴分离率低等固有缺陷,纯g- C_3N_4 在光电催化析氢中的效率相对较低,通常只能产生少量的氢气,几乎不能直接独立应用于光电催化水分解制氢。此外,当前对其光电转换机制的理解也较为有限。为提升g- C_3N_4 半导体催化剂在光电催化析氢中的性能,科研人员开发了多种改性方法。通过缺陷工程增加g- C_3N_4 的比表面积,并优化其能带结构,以促进电子传输并增强载流子迁移率^[52]。此外,适当的金属掺杂也是一种有效的改性方式。当金属离子进入g- C_3N_4 晶格后,不仅能够改变g- C_3N_4 的电子结构,使电荷分布更加均匀,还能够作为析氢的活性位点,加快析氢反应速率。不同的金属元素因其电子构型和化学性质的差异,对g- C_3N_4 性能的影响也有所不同,通过合理选择掺杂金属的种类及控制掺杂量,可以实现对g- C_3N_4 光电性能的精准调控,从而进一步提升其在光电催化析氢中的应用潜力^[53]。

例如,王艺璇等人^[54]通过碱辅助法在g- C_3N_4 中构建氮缺陷,再利用原位光还原法在富含氮缺陷的g- C_3N_4 表面负载Pt纳米颗粒(图2),制备出高效的光电催化析氢催化材料(Pt-NCN-CC),其 H_2 生产速率高达 $13.49 \text{ mmol h}^{-1} \text{ m}^{-2}$,表明氮缺陷和Pt纳米颗粒的引入显著提升了g- C_3N_4 的光电催化析氢性能。

此外,支凤梅及其合作者^[55]通过调节前驱体浓度和沉积时间,精确控制氮化碳(CN)层厚度,使其与载流子扩散长度(约90~100 nm)相匹配,从而减少了电荷复合。所制备的93 nm厚的CN纳米层在1.23 V(相对于可逆氢电极(vs. RHE))下达到了 $116 \mu\text{A cm}^{-2}$ 的光电流,并且起始电位低至0.2 V(1 mol L⁻¹ KOH溶液, AM 1.5G)。将沉积的NiFe层状双氢氧化物(LDH)作为助催化剂,能够使得光电流提升至 $210 \mu\text{A cm}^{-2}$,并且在400 nm处入射光子电流效率(IPCE)达12.8%。LDH促进了表面水氧化反应动力学,显著降低了反应的过电位。同时,g- C_3N_4 纳米层在长时间光照下表现出良好的化学稳定性,未观察到明显的光腐蚀或结构降解(图3(a)~(c))。在另一项工作中,黎明课题组^[56]首次报道了以廉价的氰尿酸氯为原料,在非真空条件下,通过UIL-

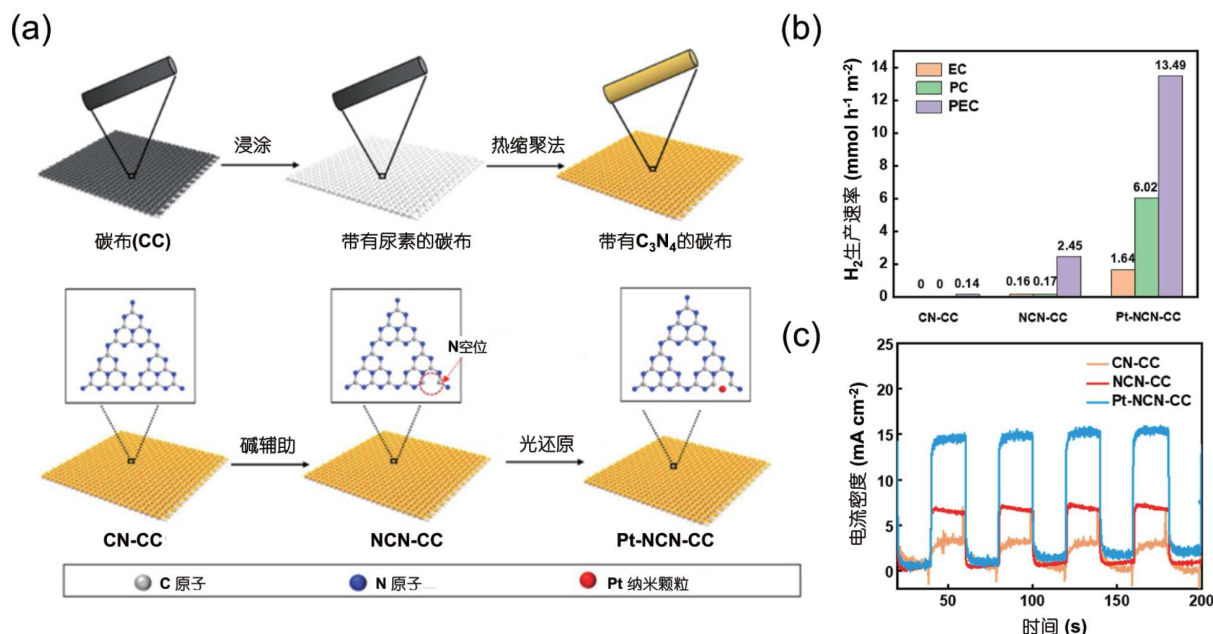


图2 (网络版彩色)富含氮缺陷的 $g-C_3N_4$ 及其析氢活性. (a) Pt-NCN-CC的制备示意图; (b) 不同催化剂在300 W Xe灯、1.23 V(vs. RHE)电压条件下电催化(EC)、光催化(PC)和光电催化(PEC)析氢活性; (c) 不同催化剂的瞬态光电流响应比较^[54]. Copyright © 2020, Elsevier

Figure 2 (Color online) Nitrogen-deficient $g-C_3N_4$ and its hydrogen evolution activity. (a) Schematic of preparation process of Pt-NCN-CC. (b) Comparison of electrocatalytic (EC), photocatalytic (PC) and photoelectrocatalytic (PEC) hydrogen production activities of different catalysts under 300 W Xe lamp and 1.23 V (vs. RHE) voltage. (c) Comparison of transient photocurrent responses of different catalysts^[54]. Copyright © 2020, Elsevier

mann聚合反应大规模合成了新型 C_3N_4 催化剂, 该催化剂在光电催化水分解反应中展现出良好的催化活性(图3(d), (e)). 此外, 它还可被剥离为二维聚合物薄膜, 进一步拓展了其在二维材料领域中的应用前景. 这些研究结果揭示了 $g-C_3N_4$ 基材料在光电析氢中的优化策略: 通过“结构缺陷激活-载流子路径优化-表面催化强化”的协同策略, 有效解决光吸收、电荷分离与表面反应动力学的匹配问题. 对 $g-C_3N_4$ 基光电催化材料进行改性和调控, 使得其在光电催化水分解制氢过程中的性能显著提升, 展现了 $g-C_3N_4$ 基光电催化剂在该领域巨大的应用潜力.

2.2 CAPs

CAPs是一类由炔基连接而成的共轲聚合物, 源于一个世纪前Baeyer为了合成纯 sp 杂化碳链而开发的乙炔Glaser氧化偶联反应^[57]. CAPs含有高度共轲的 $C\equiv C$ 结构, 这种由 sp^2 杂化和 sp 杂化的碳原子共同构成的共轲体系能够有效拓宽其光吸收范围, 可覆盖从紫外光到可见光的广泛光谱区域, 从而充分利用太阳能^[58]. 同时, 共轲结构为电荷传输提供了高效通道, 光生载流子(电子-空穴对)能够在聚合物链内快速迁移, 有效减少

复合几率, 提高了电荷分离效率, 这一特性为光电催化析氢反应提供了充足的活性载流子, 有效提升了析氢效率^[59]. CAPs还具有丰富的结构可设计性. 通过调节聚合反应条件、单体种类及比例, 可以精准调控CAPs的分子结构、共轲链长度和侧链基团等^[60]. 通过化学结构调控, 可以优化材料的能级结构, 使其更好地与水分解反应的氧化还原电位匹配. 此外, 这种化学结构调控还能够引入丰富的析氢活性位点, 改善光吸收特性和电荷传输性能, 从而获得可调带隙和可调电子属性的高活性催化剂, 进而满足不同光电催化析氢体系的需求^[61]. 相较于部分易在光电催化环境中发生降解的有机半导体, CAPs展现出良好的化学稳定性. 其共轲结构中的 $C\equiv C$ 具有较高的键能, 在长期光照和电解液作用下不易发生化学键的断裂和分子结构的破坏, 能够保证材料在光电催化析氢过程中长时间稳定运行, 为实际应用提供了可靠的材料基础^[62].

目前, 得益于CAPs的结构可调性, 通过设计不同的结构单元有利于抑制光生电荷和空穴的复合, 因此, CAPs已经被用作光阴极上的活性材料实现了光电催化水分解制氢气. 例如, 张涛及其合作者^[63]开发了一种铜表面介导的Glaser缩聚反应, 该反应能够在多种导电

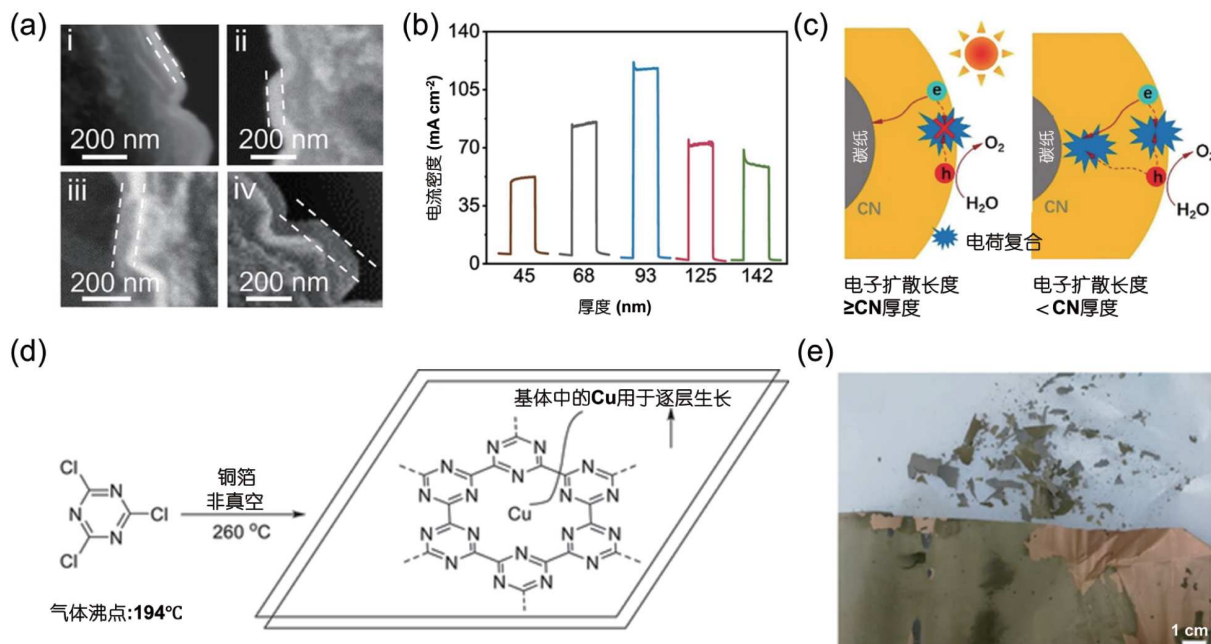


图 3 (网络版彩色)氮化碳基材料的可控合成. (a) 不同CN厚度CN/C的切面扫描电子显微镜(SEM)图像^[55]. (b) 不同CN厚度的CN/C的光电流比较^[55]. (c) CN纳米层中电子扩散和电荷复合的示意图^[55]. Copyright © 2024, Wiley-VCH. (d) C₃N₃Cl₃的聚合^[56]. (e) 铜箔上的C₃N₃^[56]. Copyright © 2020, Wiley-VCH

Figure 3 (Color online) Controllable synthesis of carbon nitride-based materials. (a) Cross-section SEM images of CN/C with different CN thicknesses^[55]. (b) The photocurrents of CN/C with different CN thicknesses^[55]. (c) Scheme of electron diffusion and charge recombination in CN nanolayer^[55]. Copyright © 2024, Wiley-VCH. (d) Polymerization of C₃N₃Cl₃^[56]. (e) C₃N₃ on copper foil^[56]. Copyright © 2020, Wiley-VCH

和非导电基底上大规模制备共轭聚合物纳米纤维(图4). 以1,3,5-三炔基苯(TEB)为前驱体聚合得到的聚(1,3,5-三炔基苯)(PTEB)可直接作为无金属光阴极进行光电析氢生产, 在0.3~0 V(vs. RHE)下, 其光电流密度能够达到10 $\mu\text{A cm}^{-2}$, 并且优于大多数已报道的无金属光电极. 通过引入噻吩[3,2-b]并噻吩单元来调节其光学带隙, 可以拓宽共聚物的光吸收范围, 进一步促进光电流密度的提升, 达到约21 $\mu\text{A cm}^{-2}$, 从而显著提升了催化剂的光电性能, 这为无金属光阴极催化剂的开发提供了新方向.

尽管已有许多研究者开发了有效的方法来获得CAPs基光电极并直接用于光电催化水分解, 但缺乏析氢活性位点仍然是制约它们析氢性能提升的一大障碍. 2019年, 孙瀚君等人^[64]提出了一种分子工程策略, 通过改变CAPs的芳香单元, 将其从苯环改变为噻吩环, 从而实现了聚合物结构和催化性能的精准调控(图5(a)~(c)). 研究表明, 所合成的噻吩基CAPs在0.3 V(vs. NHE)条件下, 光电流密度高达370 $\mu\text{A cm}^{-2}$, 超越了众多已报道的无助催化剂的有机和无机光阴极. 进一步

研究发现, 噻吩单元的引入不仅拓宽了半导体的光吸收范围, 还改变了电子的分布. 此外, 通过电化学-拉曼光谱和DFT计算, 研究者证实了C $\equiv$ C在光电催化水分解反应中作为高效的析氢活性位点, 极大提升了所合成CAPs的光电析氢性能. 因此, 通过分子工程策略设计的CAPs既能增强电荷分离与传输能力, 又能够通过噻吩结构活化C $\equiv$ C键作为高效催化活性位点, 为设计具有高光电催化性能的共轭聚合物提供了新思路.

在光电催化水分解的过程中, 中性或酸性条件通常更有利于共轭聚合物进行析氢反应, 这是因为大多数共轭聚合物缺乏必要的水解离位点, 导致其在碱性条件下的光电析氢性能较差. 为此, 冯新亮课题组^[65]开发了适用于碱性介质光电析氢的噻吩基CAPs, 通过设计不同的反应前驱体, 分别合成了具有不同结构的聚合物, 即聚(1,4-二炔基苯)(pDET)、聚(2,6-二炔基苯并[1,2-b:4,5-b']二噻吩(pBDT)和聚(二炔基二噻吩[3,2-b:2',3'-d]噻吩)(pDTT). 这种通过设计不同反应前驱体所带来聚合物分子骨架结构的改变, 通过电子效应和空间位阻效应在聚合物结构中同时引入了水分解与析氢

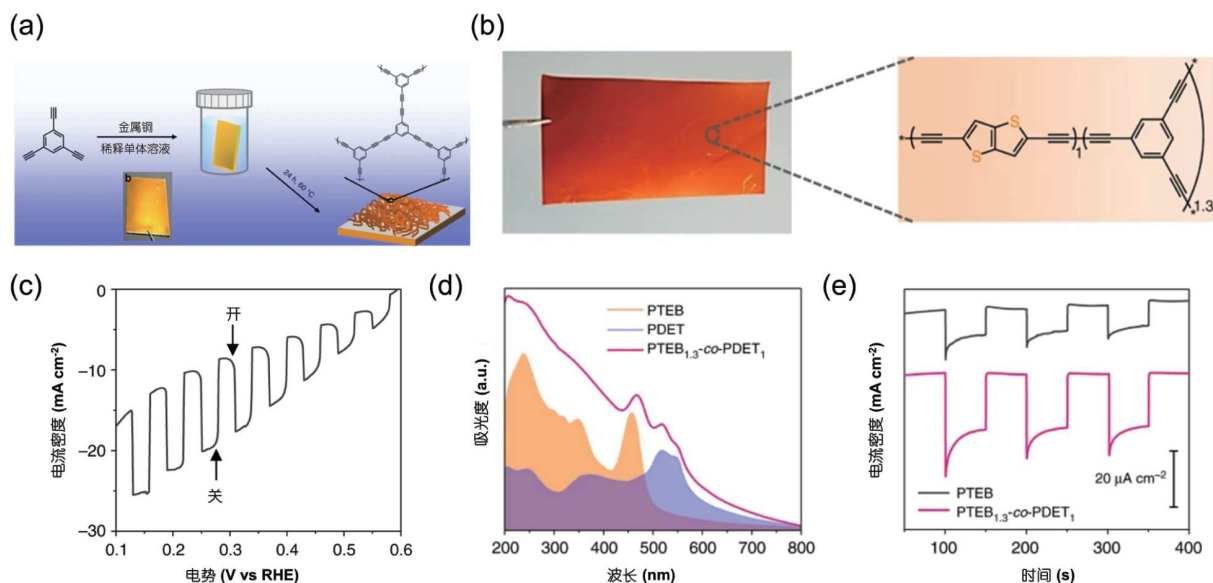


图 4 (网络版彩色)CAPs纳米纤维的合成及其光电性能。(a) PTEB纳米纤维的合成。(b) 在Cu表面生长的PTEB_{1.3}-co-PDET₁的照片(左)及其化学结构(右)。(c) 间歇性照射下PTEB的电流密度-电势曲线。(d) PTEB、PDET和PTEB_{1.3}-co-PDET₁的紫外-可见吸收光谱。(e) PTEB_{1.3}-co-PDET₁(红色曲线)和原始PTEB(黑色曲线)在间歇性照射下偏置为0 V(vs. RHE)的瞬态光电流密度与时间的关系图^[63]。Copyright © 2018, Springer Nature

Figure 4 (Color online) Synthesis and photoelectric properties of CAPs nanofibers. (a) Synthesis of PTEB nanofibers. (b) Photograph of PTEB_{1.3}-co-PDET₁ grown on a Cu surface (left) and its chemical structure (right). (c) Current density-potential curves of PTEB under intermittent irradiation. (d) UV-vis absorption spectra of PTEB, PDET and PTEB_{1.3}-co-PDET₁, respectively. (e) Transient photocurrent density vs. time at a bias of 0 V (vs. RHE) under intermittent irradiation for PTEB_{1.3}-co-PDET₁ (red curve) and pristine PTEB (black curve)^[63]. Copyright © 2018, Springer Nature

的活性位点,使得所合成的CAPs在碱性条件下仍然表现出优异的催化活性(图5(d)~(f))。值得注意的是,在0.3 V(vs. NHE)和pH 13的条件下,生长在铜基底上的pDTT和pBDT的光电流密度分别达到170和120 $\mu\text{A cm}^{-2}$,分别是pDET的4.2倍和3倍。此外,pDTT在连续光照10 h后,依旧展现出良好的稳定性。结合DFT计算和电化学原位拉曼光谱分析,研究揭示了在碱性条件下,双活性位点的协同作用提升了所合成CAPs的光电析氢活性,为进一步理解共轭聚合物的光电催化水分解反应提供了新视角。上述研究表明,CAPs的结构可调性使其成为光电催化析氢的理想材料,通过分子工程精准设计活性位点和优化能带结构,可显著提升其在不同环境中的催化性能。未来研究需进一步聚焦于多活性位点的原子级精准调控与协同效应以及复杂情况下(如宽pH范围、高杂质环境)的稳定性强化策略,以推动CAPs基光电极从概念验证向实际应用的跨越。

2.3 COFs

COFs是一类新型的有机多孔材料,具有高度有序的二维或三维多孔晶体结构,孔径大小均一且可在分子水平上精确调控。COFs较大的比表面积,能提供丰

富的活性位点,增加其与电解液的接触面积,使光催化剂与反应物充分接触,提高反应效率;高表面积的特点还有利于引入大量的活性位点,促进氢气的产生^[66]。COFs中由共价键连接而成的骨架结构赋予其良好的化学稳定性,能抵抗光电催化析氢复杂环境中电解液的侵蚀和光腐蚀,提升光电极的使用寿命^[67]。更重要的是,丰富的单体和拓扑结构可以灵活调节COFs的能带结构、光吸收范围和电荷传输性能,使其更好地满足光电催化析氢反应的需求^[68]。此外,COFs的有序结构为电荷传输提供了明确的通道,能够有效促进光生载流子迁移,减少其复合^[69]。

目前,得益于席夫碱缩合的高度可逆反应性质,亚胺连接的2D共轭COFs是光催化或者光电催化领域最为常见的COFs材料。但是,亚胺连接的2D COFs在反应过程中表现出的较弱的化学稳定性和较差的电子离域性,阻碍了其在光电催化领域的潜在应用。不同于传统亚胺键连接的COFs,sp²碳连接的共轭COFs具有较优的电子离域性以及耐酸/碱环境较高的耐受性。例如,冯新亮团队^[70]报道了首例噻吩桥连的D-A型2D sp²碳连接的COFs(CCP-Th),并将其用于光电催化水分解制氢(图6(a)~(c))。D-A结构的引入,使得所合成的2D

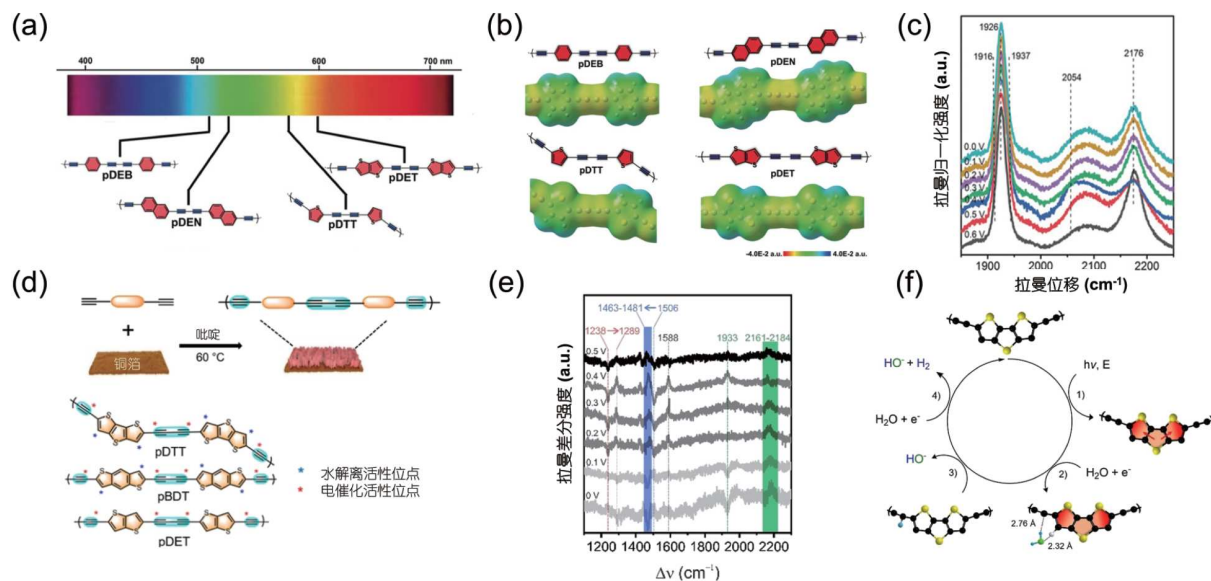


图 5 (网络版彩色)CAPs分子结构的设计与调控。(a) pDEB、pDEN、pDIT和pDET的吸收边示意图^[64]。(b) pDEB、pDEN、pDIT和pDET的化学结构和静电势表面(EPS)^[64]。(c) 594 nm激光作用下pDET的电化学-拉曼光谱^[64]。Copyright © 2019, Wiley-VCH。(d) 采用铜催化的Glaser缩聚法在泡沫铜上合成CAPs的示意图以及聚合物pDIT、pBDT和pDET的化学结构^[65]。(e) pDIT/Cu的电化学-拉曼光谱^[65]。(f) pDIT在碱性介质中的HER机理^[65]。Copyright © 2021, Wiley-VCH

Figure 5 (Color online) Design and regulation of CAPs molecular structure. (a) Schematic illustrations for the absorption edges of pDEB, pDEN, pDIT, and pDET^[64]. (b) Chemical structures and corresponding electrostatic potential surface (EPS) for pDEB, pDEN, pDIT, and pDET^[64]. (c) Potential-dependent Raman spectra of pDET under 594 nm laser^[64]. Copyright © 2019, Wiley-VCH. (d) Synthesis of CAPs using a copper-mediated Glaser poly condensation method on the Cu foam and chemical structures of the polymers pDIT, pBDT and pDET^[65]. (e) Potential-dependent difference Raman spectra of pDIT/Cu^[65]. (f) Proposed mechanism of HER in alkaline medium for pDIT^[65]. Copyright © 2021, Wiley-VCH

CCP-Th的光吸收范围拓宽至674 nm, 光学带隙窄至2.04 eV, LUMO能级高达-3.41 eV. 同时, 2D CCP-Th还展现出了优异的光电催化性能, 其饱和光电流密度在0.3和0 V(vs. NHE)下分别达到5.50和7.90 $\mu\text{A cm}^{-2}$, 且IPCE达6.1%. 这项研究为高效光电催化水解离制氢提供了新的催化剂选择。

然而, 缺乏有效的方法来实现COFs薄膜的有序结晶及均匀合成, 限制了COFs在光电器件中的应用. 为解决这一问题, Lotsch课题组^[71]以1,3,5-三(4-氨基苯基)苯(TAPB)和2,5-二甲氧基对苯二甲醛(MeOTP)为原料, 三氟甲磺酸铈($\text{Sc}(\text{OTf})_3$)为催化剂, 在室温下制备了TPB-MeOTP COF胶体(图6(d)~(f)). 该研究表明通过调整TAPB的浓度能够分别制备出纳米片(TPB-MeOTP-NP)和纳米球(TPB-MeOTP-NS), 采用旋涂法可以在氟掺杂氧化锡(FTO)等基底上制备出连续、均匀且厚度可调节的薄膜. 所构建的TPB-MeOTP-NP异质结光电极表现出优异的催化性能, 起始电位显著正移至+1.03 V(vs. NHE), 光电流密度在+0.7 V时达到21 $\mu\text{A cm}^{-2}$. 该研究实现了胶体亚胺COFs薄膜的可控生长。

此外, 孙瀚君课题组^[72]提出了铜表面介导的Knoevenagel缩聚反应(Cu-SMKP)原位制备光活性物质-导电基底集成光阴极的方法, 并用该方法制备出可用于光电催化析氢的 sp^2 碳共轭COF基光阴极(图6(g)~(i)). 该方法制备的COFTh-Cu光阴极在0.3 V(vs. NHE)下光电流密度高达56 $\mu\text{A cm}^{-2}$, 是传统旋涂法的4.5倍, 超过多数已报道的无助催化剂的COFs光阴极. 这一研究为制备高效稳定的COF光阴极提供了新思路及新途径. 因此, 通过键连结构优化、胶体化学调控和原位界面工程等方式实现材料可控设计, COFs在光电催化水解离中的活性和稳定性显著提升, 展现了多孔共轭材料的独特优势。

2.4 共轭聚合物复合结构

单一半导体材料存在的光生电荷和空穴复合严重的问题始终限制着其在光电催化析氢应用中的性能. 近年来, 研究者们探索了多种策略来促进共轭聚合物半导体的电荷分离, 构建具有电荷转移的共轭聚合物复合结构被认为是最有效的策略之一^[73~75]。

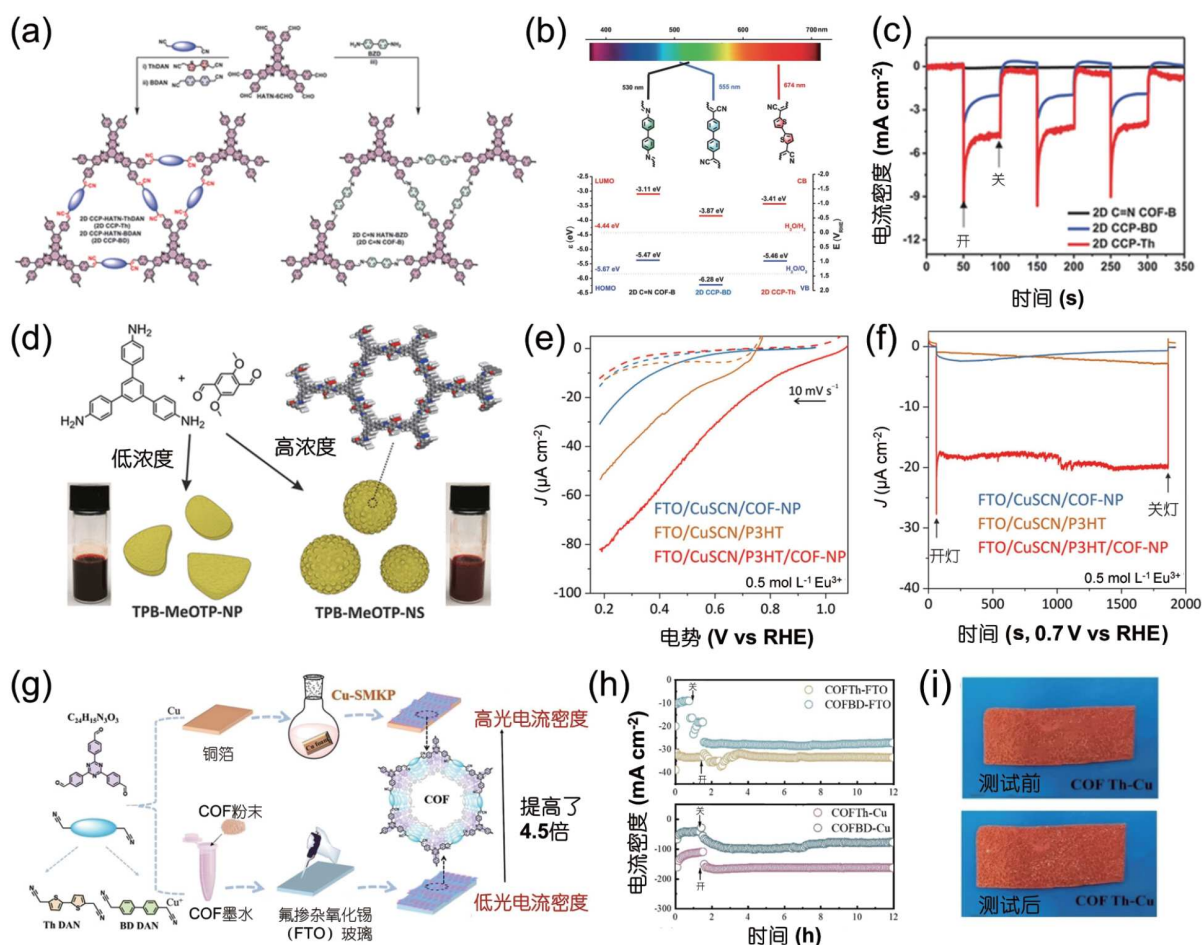


图 6 (网络版彩色)用于光电析氢的COFs设计与优化。(a) 2D CCP-Th、2D CCP-BD和2D C=N COF-B的合成路线图^[70]。(b) BDAN/ThDAN连接的2D CCP-Th、2D CCP-BD和亚胺连接的2D C=N COF-B的能带位置示意图^[70]。(c) 2D CCP-Th、2D CCP-BD和2D CN COF-B在0.3 V (vs. RHE)下的光电流-时间曲线^[70]。Copyright © 2020, Wiley-VCH。(d) TPB-MeOTP纳米片(TPB-MeOTP-NP)和纳米球(TPB-MeOTP-NS)的合成示意图^[71]。(e) TPBMeOTP-NP、P₃HT和P₃HT/TPB-MeOTP-NP光电阴极的线性扫描伏安(LSV)图^[71]。(f) TPBMeOTP-NP、P₃HT和P₃HT/TPB-MeOTP-NP光电阴极的CA图^[71]。Copyright © 2022, American Chemical Society。(g) 采用Cu-SMKP法和旋涂法在Cu衬底上制备sp²碳共轭COF光电阴极对比图^[72]。(h) COFTh-Cu、COFBD-Cu、COFTh-FTO和COFBD-FTO在0.3 V (vs. RHE)光电催化稳定性测试图^[72]。(i) 光电催化析氢测试前后COFTh-Cu的照片^[72]。Copyright © 2024, Wiley-VCH

Figure 6 (Color online) Design and optimization of COFs for photoelectric hydrogen evolution. (a) Scheme for the synthesis of 2D CCP-Th, 2D CCP-BD, and 2D C=N COF-B^[70]. (b) Schematic representation of the band positions of BDAN/ThDAN-linked 2D CCP-Th, 2D CCP-BD, and imine-linked 2D C=N COF-B^[70]. (c) Photocurrent-time plots for 2D CCP-Th, 2D CCP-BD, and 2D C=N COF-B at 0.3 V (vs. RHE)^[70]. Copyright © 2020, Wiley-VCH. (d) Schematic illustration of the synthesis of TPB-MeOTP nanoplates (TPB-MeOTP-NP) and nanospheres (TPB-MeOTP-NS)^[71]. (e) Linear sweep voltammetry (LSV) plots of TPBMeOTP-NP, P₃HT, and P₃HT/TPB-MeOTP-NP photocathodes^[71]. Copyright © 2022, American Chemical Society. (f) CA of TPBMeOTP-NP, P₃HT, and P₃HT/TPB-MeOTP-NP photocathodes^[71]. Copyright © 2022, American Chemical Society. (g) Schematic representation for the preparation of sp² carbon-conjugated COF films on Cu substrates through Cu-SMKP and spin coating method^[72]. (h) The photoelectrocatalytic stability test of COFTh-Cu, COFBD-Cu, COFTh-FTO and COFBD-FTO at 0.3 V (vs. RHE)^[72]. (i) Photographs of COFTh-Cu before and after photoelectrocatalytic hydrogen evolution test^[72]. Copyright © 2024, Wiley-VCH

例如,在前期工作基础上,孙瀚君等人提出了一种新颖的梯度同质结策略。该策略通过调控1,4-二烷基苯(DEB)和1,3,5-三烷基苯(TEB)的共聚,实现了同质结的梯度分布^[76]。实验结果表明梯度同质结的光电流密度、电荷分离效率和IPCE值均优于纯pDEB、传统pDEB同

质结以及其他已报道的有机光阴极(图7)。证实了梯度同质结策略为解决共轭聚合物在光电催化析氢反应中光生载流子复合严重的问题提供了有效途径,并且有助于提高光电催化水分解制氢的效率。

2020年,Oh-Shim Joo课题组^[77]首次报道了无机/聚

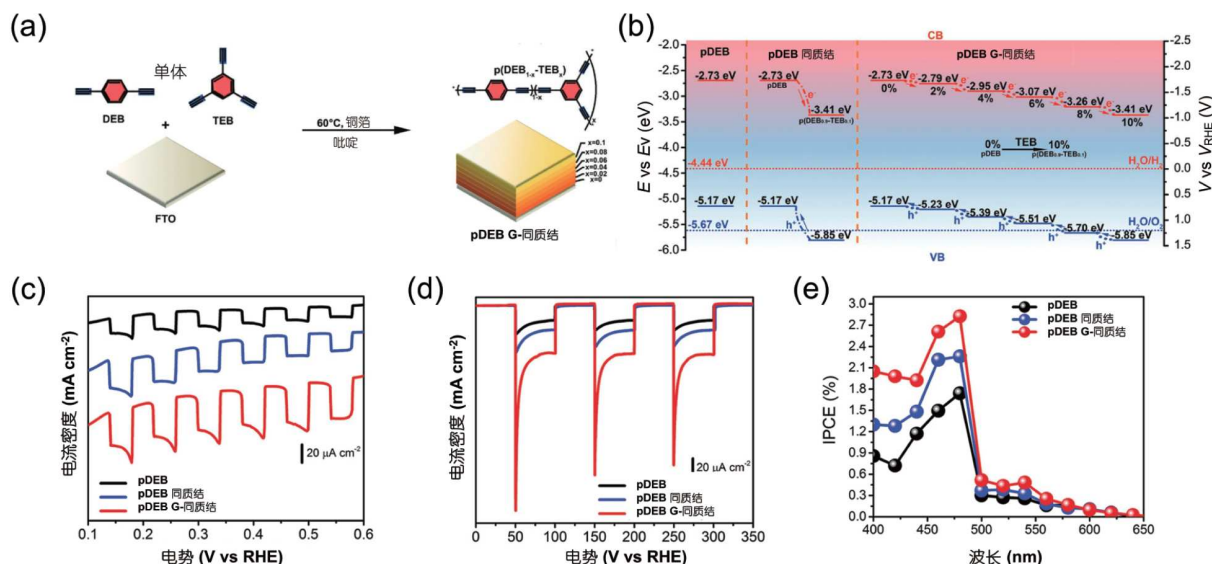


图 7 (网络版彩色)梯度同质结策略促进高效制氢。(a) 在FTO上合成pDEB G-同质结的示意图。(b) pDEB、pDEB同质结和pDEB G-同质结光电阴极的CB和VB能带图。(c) pDEB、pDEB同质结和pDEB G-同质结光电阴极的光电流-电位图。(d) pDEB、pDEB同质结和pDEB G-同质结光电阴极在0.3 V(vs. RHE)下的光电流-时间曲线。(e) pDEB、pDEB同质结和pDEB G-同质结光电阴极的IPCE谱^[76]。Copyright © 2019, Wiley-VCH

Figure 7 (Color online) Gradient homojunction strategy promotes efficient hydrogen production. (a) Schematic illustration for the synthesis of pDEB G-homojunction on FTO. (b) Band diagram representing the measured CB and VB levels of pDEB, pDEB homojunction, and pDEB G-homojunction photocathodes. (c) Photocurrent-potential plots for the pDEB, pDEB homojunction, and pDEB G-homojunction photocathodes. (d) Photocurrent-time plots for the pDEB, pDEB homojunction, and pDEB G-homojunction photocathodes at 0.3 V (vs. RHE). (e) The IPCE spectra of pDEB, pDEB homojunction, and pDEB G-homojunction photocathodes^[76]. Copyright © 2019, Wiley-VCH

合物半导体的p-n结, 将p型CuInS₂与n型聚合物半导体(PNDI3OT-Se1和PNDI3OT-Se2)结合, 用于光电催化水分解制氢(图8(a), (b)). 结果表明, p-n结的构建显著改善了催化剂的电荷转移特性, 使得所合成的异质结在光电催化析氢中表现出优异的性能。研究发现, 当CuInS₂的价带最大值(VBM)、聚合物的HOMO能级和TiO₂的VBM呈现级联结构时, 在实际反应过程中有利于载流子迁移, 从而提高催化剂的光电催化活性。研究无机/聚合物半导体异质结的电荷转移行为, 有助于深入了解材料的能级结构对电荷转移和复合的影响, 为设计和开发具有高活性的光电催化剂提供了理论指导。在另一项工作中, 孙瀚君及其合作者^[78]开发了一种在铜纸(CP)上一步构建CAPs/Cu₂O Z型异质结的通用策略。该策略利用纳米铜在催化Glaser偶联反应时会原位氧化为Cu₂O, 实现了Z型异质结的简便制备(图8(c), (d)). 所制备的聚(2,5-二乙炔基噻吩并[3,2-b]噻吩)(pDET)/Cu₂O Z型异质结在0.3 V(vs. NHE)下的载流子分离效率达16.1%, 光电流密度达520 $\mu\text{A cm}^{-2}$, 远超纯pDET、Cu₂O以及多数已报道的无助催化剂的有机或无机/有机异质结光阴极, 为具有高催化活性的有机光电极的

设计提供了新路径。

此外, 最近的研究表明共轭聚合物还能够有效解决无机半导体催化剂中存在的严重光腐蚀和表面电子-空穴快速复合等问题。例如, 张中海课题组^[79]提出了一种原位封装策略, 使用TEB为前驱体, 通过Glaser偶联反应利用原位生成的pTEB对Cu₂O纳米线进行封装(图9)。实验结果显示, pTEB封装的Cu₂O纳米线光阴极在0 V(vs. NHE)下的光电流密度高达-12.88 mA cm^{-2} , 接近Cu₂O理论值的光电流密度, 光电转换效率达到2%。同时, 该光阴极具有较好的稳定性, 经过24 h的反应, 光电流密度仅下降7.5%。这项研究揭示了这种封装结构不仅有效保护Cu₂O免受光腐蚀, 而且pTEB和Cu₂O间的电荷转移显著提升了光电催化析氢性能, 为设计高效稳定的光电极提供了新视角。总之, 通过构建梯度同质结、p-n结、Z型异质结以及共轭聚合物封装等方式, 能有效调控载流子的转移与分离, 解决光生载流子复合和材料稳定性问题, 显著提升光电催化析氢性能。后续研究可着重探索基于共轭聚合物复合结构界面的精确调控机制, 研发适用于大规模生产的制备工艺, 以加速共轭聚合物复合结构在光电催

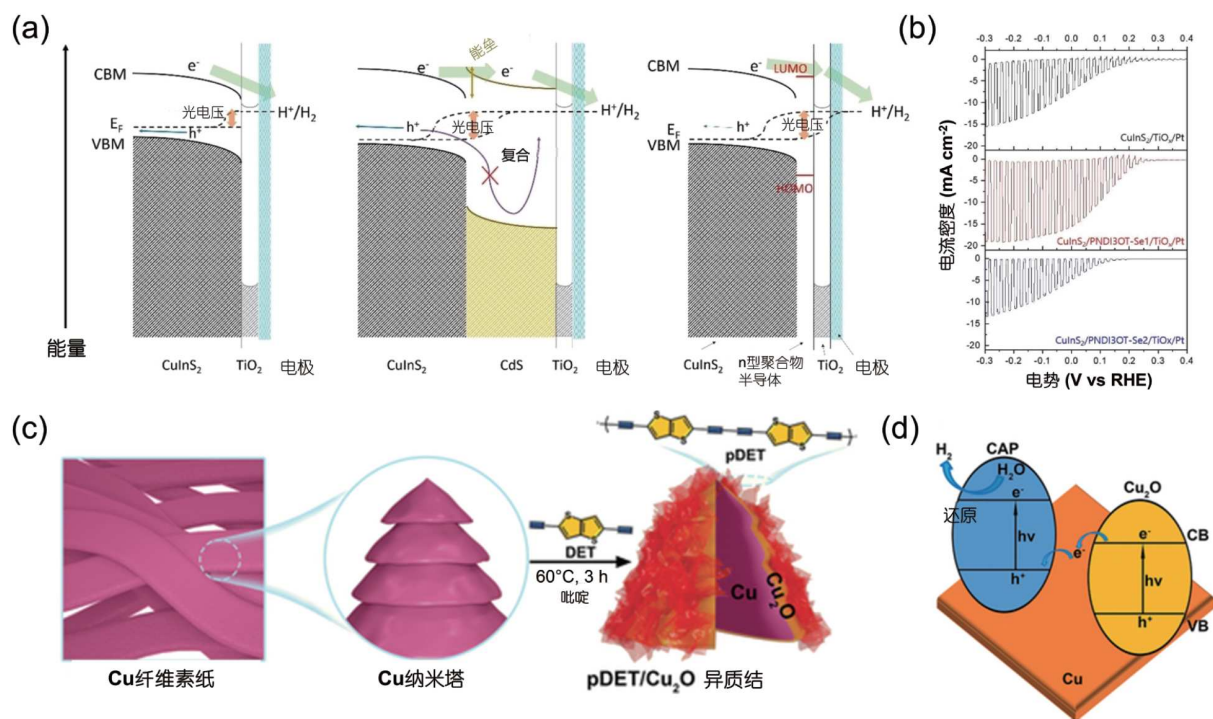


图8 (网络版彩色)无机/聚合物半导体异质结材料的构建。(a) n型异质结p-CuInS₂光电极在光照条件下析氢的电荷转移机理^[77]。(b) 不同光电极的斩光线性扫描伏安测试^[77]。Copyright © 2020, Wiley-VCH。(c) pDET/Cu CP的合成示意图^[78]。(d) CAP/Cu₂O Z型异质结中的能带排列^[78]。Copyright © 2020, Wiley-VCH

Figure 8 (Color online) Construction of inorganic/polymer semiconductor heterojunction materials. (a) Charge transfer mechanism in p-CuInS₂ photoelectrodes with n-type heterolayers for hydrogen evolution under light illumination conditions^[77]. (b) Linear sweep voltammetry under chopped light for each photoelectrode^[77]. Copyright © 2020, Wiley-VCH. (c) Schematic representation for the synthesis of pDET/Cu CP^[78]. (d) Band alignment in CAP/Cu₂O Z-scheme heterojunctions^[78]. Copyright © 2020, Wiley-VCH

化领域的实际应用进程。

3 总结与展望

在这篇综述中,我们总结了一系列共轭聚合物应用于光电催化分解制氢的研究工作并且分析了共轭聚合物在光电催化制氢领域展现出的独特优势:(1) 共轭聚合物分子水平上的结构可设计性不仅能够精确调节其能带位置和光吸收范围,还可以引入高效的催化活性位点,为光催化反应提供更多的活性中心^[80]。(2) 共轭聚合物高度离域的 π 电子系统有效促进了光生电荷的传输,通过界面工程,共轭聚合物能够与其他半导体复合形成异质结或构建梯度同质结,加快水分解反应速率^[81]。(3) 共轭聚合物所具有的高化学稳定性让其在与无机材料复合后,能够保护无机材料免受光腐蚀,同时促进载流子的分离与转移^[82]。

尽管目前共轭聚合物在光电催化析氢领域取得了长足的进步,但仍存在一些挑战亟待解决。(1) 目前大

部分共轭聚合物仍然需要依赖贵金属助催化剂,这导致了较高的应用成本。因此,如何开发低廉易得且具有更高催化性能的无助催化剂共轭聚合物半导体是一大挑战。(2) 析氢反应需在活性位点上,因此活性位点的数量、活性和选择性对于析氢性能至关重要,尽管目前通过结构设计可以在一些共轭聚合物中引入活性位点,但目前对共轭聚合物表面有效活性位点的研究报道数量仍有限。(3) 尽管目前对光电催化析氢的反应机理已经有了一定的认识,但通过不同方法获得的共轭聚合物及其复合材料的结构、活性位点与光电催化析氢性能的关系仍未完全阐明。(4) 已开发的许多共轭聚合物已表现出可观的性能和商业化潜力,但考虑到经济可行性、长时稳定性和环境可持续性等关键问题,共轭聚合物材料离实际商业化还有很长的发展之路。

为了应对一系列挑战,必须紧紧抓住共轭聚合物本身的特征优势推动其快速发展以获得具有高催化性

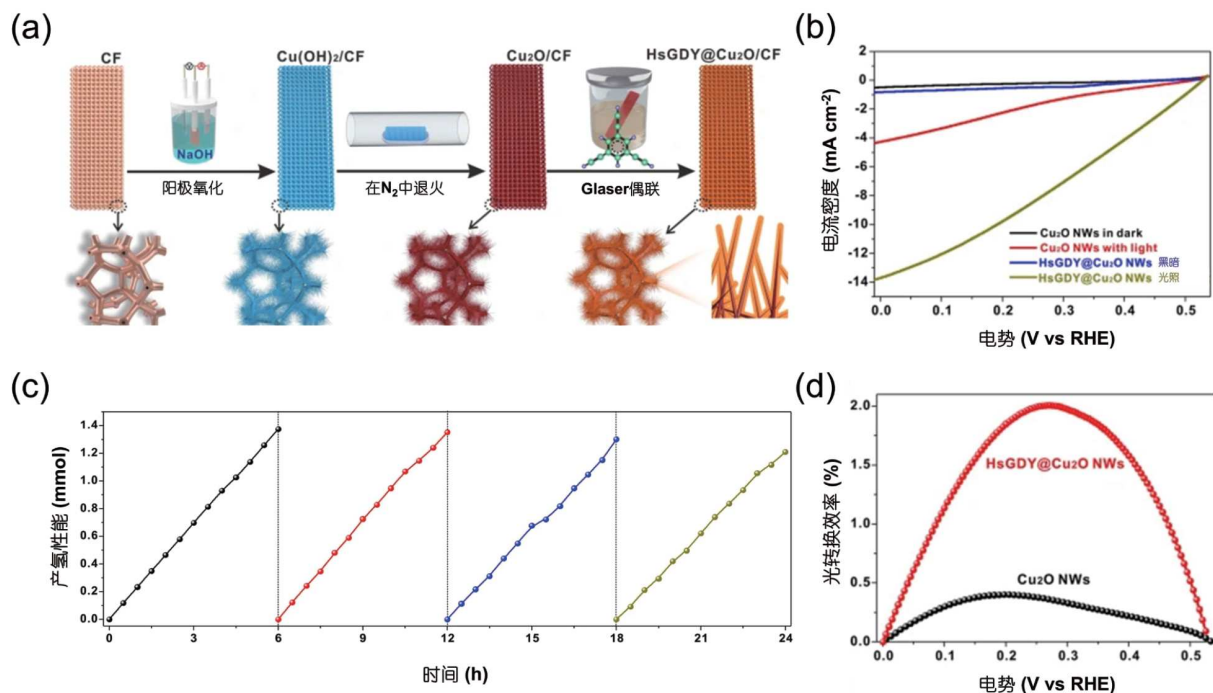


图9 (网络版彩色) 聚合物封装无机材料提升析氢性能. (a) HsGDY@Cu₂O/CF光电阴极的制备示意图. (b) Cu₂O NWs和HsGDY@Cu₂O NWs在黑暗和模拟太阳光(AM 1.5G, 100 mW cm⁻²)照射下的LSV图. (c) HsGDY@Cu₂O NWs/CF光阴极在0 V(vs. RHE)电位下产氢. (d) Cu₂O NWs和HsGDY@Cu₂O NWs的光转换效率^[79]. Copyright © 2022, Springer Nature

Figure 9 (Color online) Polymer encapsulated inorganic materials improve hydrogen evolution performance. (a) Schematic illustration of the fabrication of HsGDY@Cu₂O/CF photocathode. (b) LSV plots of Cu₂O NWs and HsGDY@Cu₂O NWs in dark and under illumination of simulated solar light (AM 1.5G, 100 mW cm⁻²). (c) Hydrogen generation on HsGDY@Cu₂O NWs/CF photocathodes at potential of 0 V (vs. RHE). (d) Photoconversion efficiency of Cu₂O NWs and HsGDY@Cu₂O NWs^[79]. Copyright © 2022, Springer Nature

能的光电催化剂. 首先, 可以开发D-A型共轭聚合物, 通过增强分子内电荷转移(ICT)效应实现宽光谱吸收(>800 nm)与低激子结合能(<0.3 eV)的兼容^[83]. 其次, 对共轭聚合物的结构进行调控, 如改变共轭链长度、引入取代基等, 可以有效地调节电荷分离与转移, 进而调节光电性质和提升催化活性^[84]. 还可以通过与其他材料的复合, 实现材料性能的协同优化, 提高光电催化析氢的效率^[85]. 此外, 对于稳定性较差的聚合物, 可以通过引入交联基团或无机保护层的方式提升其在长时光电催化过程中的稳定性. 最后, 借助光谱技术和理论计算方法, 深入理解光生电荷的转移、分离和反应过程, 为催化剂设计和性能优化提供理论指导^[86]. 除了目前已知的析氢反应途径外, 还可以探索其他可能的反应途径, 以实现高效和高选择性的光电催化析氢. 共轭聚

合物光电催化水分解制氢技术要实现从实验室研究到商业化应用的跨越还需要较长时间的发展, 通过推动跨学科深度融合, 如利用计算材料学、原位表征技术进一步探明反应机理, 结合原位电化学原子力显微镜、超快光谱技术实现电荷分离、表面反应的实时监测与解析, 未来有望突破材料性能极限, 推动低成本、高效率、长寿命光电极的规模化应用.

总之, 我们希望这篇综述能够为未来光电催化制氢的共轭聚合物半导体研究提供可行的设计思路, 从而解决共轭聚合物光生载流子快速复合和缺乏活性位点等问题. 除此之外, 我们相信随着全球碳中和目标的推进, 这一领域的研究成果不仅将为氢能产业注入新动力, 更有可能拓展到其他能源化学与材料领域, 引领下一代清洁能源技术的革新.

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Summary for “共轭聚合物光电催化析氢进展”

Research progress in conjugated polymers for photoelectrochemical hydrogen evolution reaction

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The extensive use of traditional fossil fuels has led to the twin crises of energy scarcity and environmental degradation, driving the urgent search for sustainable alternatives. Photoelectrochemical (PEC) hydrogen-production technology, which converts solar energy into chemical energy, has emerged as a promising approach to producing clean, renewable fuel. Solar energy is abundant, widely available, and environmentally friendly; however, its direct utilization and storage are challenging because of its low power density at Earth's surface. Hydrogen, by contrast, possesses a high gravimetric energy density and is therefore an ideal clean-energy carrier. PEC water splitting offers an efficient route to green-hydrogen generation by driving the thermodynamically uphill reaction under light irradiation. Continuous exploration and development of PEC materials have greatly improved hydrogen-evolution performance, yet persistent bottlenecks remain unresolved. Early work focused mainly on inorganic semiconductors. TiO₂-based catalysts, however, absorb primarily ultraviolet light, leading to poor solar spectrum utilization and suboptimal solar-to-hydrogen conversion efficiency. Other alternative inorganic candidates, such as metal oxides, sulfides, and nitrides, have demonstrated moderate catalytic activity, but their narrow spectral absorption windows, limited stability, and excessive dependence on noble metal co-catalysts hinder large-scale deployment. These limitations are particularly evident in the rapid decay of catalytic activity under prolonged operation, which stems from irreversible structural changes and surface passivation caused by harsh environments. Additional drawbacks, including high material cost, potential metal toxicity, photocorrosion, and performance degradation, further restrict their development. In recent years, organic conjugated polymers have attracted considerable attention for PEC hydrogen evolution because of their distinctive advantages. Their tunable molecular structures enable precise control of optoelectronic properties, while the continuous π -conjugated backbone facilitates efficient charge transport, and their broad spectral response, which extends into the visible and near infrared, allows more effective harvesting of solar energy. Moreover, they are generally inexpensive and chemically robust, making them promising candidates for high-performance photocatalysts. This article systematically reviews progress on organic conjugated polymers, including carbon nitride (C₃N₄), conjugated acetylenic polymers (CAPs), covalent organic frameworks (COFs), and related hybrid composites, for PEC hydrogen evolution. We focus on molecular structure design, regulation of electron distribution and transfer, mechanisms of photogenerated-carrier separation, and strategies for enhancing catalytic activity. For C₃N₄, we describe its unique structure, strengths, and limitations, along with modification methods that improve performance. The highly conjugated backbones of CAPs endow these materials with excellent light-harvesting and charge-transfer capabilities; we explore structural optimizations that introduce additional active sites. COFs possess large specific surface areas and tailorable band structures, giving them great potential, and we analyze challenges and solutions associated with their synthesis and application. For composite systems, we examine how interactions among different components facilitate charge separation and boost catalytic efficiency. Finally, we discuss outstanding problems, such as the trade-off between light absorption and charge recombination in some narrow-band-gap polymers, the high cost of materials that still rely on precious metal cocatalysts, and the limited density of active sites, as well as future research directions. Strategic priorities include advancing *in situ* characterization techniques to unravel dynamic interfacial processes and developing scalable synthesis methods to bridge the gap between laboratory prototypes and industrial applications. We anticipate that this overview will provide strong support for the exploration of other solar-driven reactions, stimulate innovation in catalyst design, and accelerate the development of clean-energy technologies. In summary, a comprehensive understanding of organic conjugated polymers for PEC hydrogen production is essential to address global energy and environmental challenges, and it is expected to open new paths toward the large-scale implementation of sustainable energy solutions.

conjugated polymers, carbon nitride, conjugated acetylenic polymers, covalent organic frameworks, photoelectrocatalysis, hydrogen evolution reaction

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