

S 型 $\text{CoWO}_4/\text{ZnIn}_2\text{S}_4$ 异质结的制备及其光解水析氢性能

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摘 要: 双组分异质结是提升光解水析氢性能的一种有效方法。本研究采用水热/水浴两步法成功构筑 S 型 CoWO_4 (CWO)/ ZnIn_2S_4 (ZIS) 异质结光催化材料, 一系列先进表征技术证实 CWO 与 ZIS 形成了紧密的界面接触和完美的异质界面; 光解水析氢测试结果显示, 添加 CWO 提高了 ZIS 可见光裂解水析氢活性, 其中 CWO/3%ZIS 样品析氢速率达到 $4296.8 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, 是纯相 ZIS ($2178.2 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) 的 2 倍; 能带结构和光电子动力学分析证实 CWO/ZIS 复合体系成功构建了 S 型异质结光生载流子输运路径, 从而显著提升了光生电子/空穴对的分离效率和光生电荷传输速率, 抑制了光生电子/空穴对的复合, 最终导致 CWO/ZIS 复合体系高效地光解水产氢性能。

关键词: 钨酸钴; 硫铟化锌; S 型异质结; 光解水产氢

中图分类号: TQ174.75 文献标志码: A 文章编号: 0454-5648(2024)06-1820-12

网络出版时间: 2024-05-13



随着社会的快速发展和工业化进程的不断推进, 传统煤炭、石油等化石燃料被大量消耗, 由此引起的环境污染和能源消耗已成为人类亟待解决的 2 个核心议题。为了实现社会的可持续发展, 迫切需要优化能源结构并开发可再生清洁能源。作为一种环境友好的清洁能源, 氢能具有高能量密度、燃烧特性好、储量丰富等特点, 有望在未来获得广泛应用。然而, 当前氢源主要来自于化石燃料^[1], 制备中伴随着大量 CO_2 排放, 且化石燃料消耗大。20 世纪 70 年代, 日本科学家 Honda 教授和 Fujishima 教授发现 TiO_2 在光照下可持续分解水并产生氢气^[2], 被认为是未来最理想的氢源获取途径。然而, 传统光催化材料存在可见光响应弱、催化活性低、化学稳定性差等缺点^[3-6], 这极大地限制了光解水析氢的实际应用。

硫铟化锌(ZIS)因其良好的化学稳定性^[7]、适中的禁带宽度($2.2\sim 2.5 \text{ eV}$)^[8]、合适的导带位置(-0.79 eV)^[9]和良好的可见光吸收(吸收边约 540 nm)^[10], 被证明是一种理想的半导体光催化剂, 受到了业内学者的广泛关注。然而, ZIS 仍面临着一些需要改善

的问题, 如光生载流子复合速率高、弱的光稳定性等。国内外学者分别开发了一系列方法, 如形貌调控、元素掺杂、助催化、异质结等^[11-14], 以优化能带结构、拓展谱吸收范围、改善光电子动力学行为、提升光稳定性等。构建异质结是解决光生电子空穴对复合速率高、氧化还原能力低、光催化活性低等问题的最有效方法^[15]。近几年, 多种异质结被相继开发, 如 II 型异质结、直接 Z 型异质结、S 型异质结和 p-n 型异质结等^[16]。Ding 等^[17]采用微波水热法制备了 II 型 ZIS/g- C_3N_4 异质结, 其中 ZIS/20%g- C_3N_4 (质量分数, 下同) 表现出最佳的光催化活性, 析氢速率达到 $387 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ 。Zhang 等^[18]采用水热/沉淀两步法制备了 Z 型 CeO_2/ZIS 异质结, 发现异质结明显提升了 ZIS 光解水析氢性能, 其中, 10% CeO_2/ZIS 样品析氢速率达到 $847.42 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ 。

S 型异质结因其极好的光生载流子动力学特性和高效光解水析氢活性, 吸引了广大学者关注。而钨酸钴(CWO)作为一种典型的 p 型半导体, 带隙宽度约为 2.2 eV ^[19], 具有极好的可见光利用率, 是一

收稿日期: 2023-08-23。 修订日期: 2023-10-08。

基金项目: 国家自然科学基金青年基金(52002399); 徐州市科技计划面上项目(KC21025)

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Received date: 2023-08-23. Revised date: 2023-10-08.

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种很好的第二相材料^[20]。本工作采用水热/水浴两步法成功合成了 CWO/ZIS 复合纳米材料,通过构建 S 型异质结,利用内建电场提升光生电子/空穴的分离效率与迁移速率,并采用多种先进表征方法详细研究最终产物的物相组分、形貌结构、晶体结构、元素分布、化学态、光解水析氢性能、光生载流子分离效率、光生电荷传输速率、光生电子/空穴对复合速率等演变规律,并详细讨论了 CWO/ZIS 异质结的光催化机理。

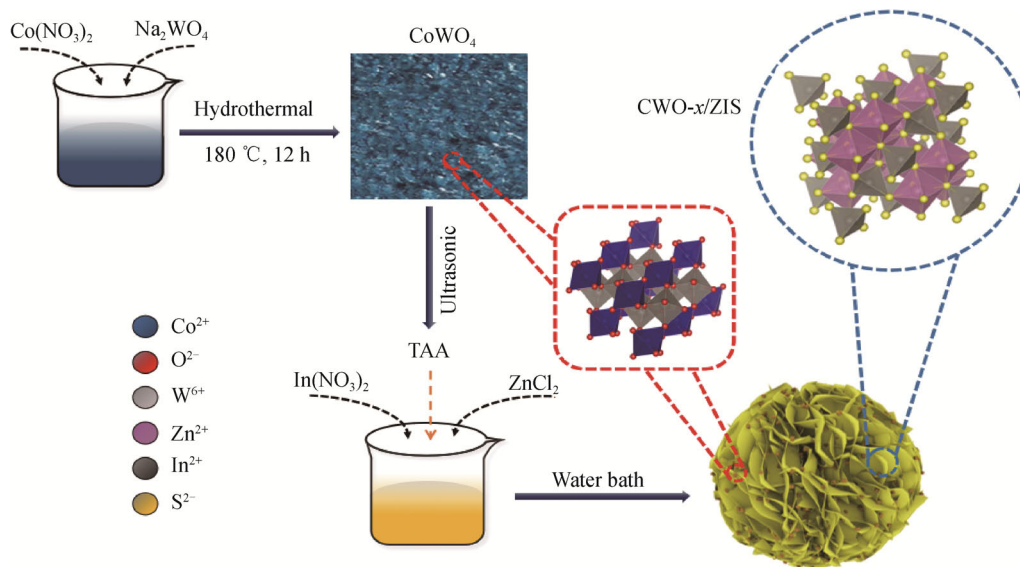


图 1 钨酸钴(CWO)及 CWO/x 硫铟化锌(ZIS)制备流程示意图

Fig. 1 Schematic preparation process of CoWO_4 (CWO) and $\text{CWO}/x\text{ZnIn}_2\text{S}_4$ (ZIS) samples

1.2 材料制备

采用水热法制备 CWO 纳米颗粒,具体流程如下:将 1.164 1 g 六水合硝酸钴加入到 40 mL 去离子水中,搅拌 15 min 直至充分溶解,标记为溶液 A;将 1.319 4 g 二水合钨酸钠加入到 40 mL 去离子水中,搅拌 15 min 至充分溶解,标记为溶液 B;随后,将 B 溶液缓慢加入到 A 溶液中,剧烈搅拌 30 min,使溶液混合均匀;将混合溶液转移至容积为 100 mL 特氟龙内衬的反应釜中,密封后在 180 °C 烘箱内反应 12 h;采用高速离心机将沉淀物离心分离并洗涤多次,产物在 60 °C 真空干燥箱内干燥,得到蓝色 CWO 纳米颗粒。

采用水浴法制备 S 型 CWO/ZIS 异质结(图 1),具体流程如下:将 CWO 粉末缓慢加入到装有 100 mL 去离子水的烧杯中,超声分散 5 min;称取 0.981 2 g 的六水合硝酸铟,加入到上述溶液中,搅拌 30 min 后,再将 0.408 9 g 的氯化锌和 0.450 8 g 的硫代乙酰胺依次加入到上述溶液,持续搅拌 30 min,将溶液转移到 80 °C 水浴锅中恒温反应 6 h。反应结

1 实验

1.1 原料与试剂

六水合硝酸钴(AR, 99%)、二水合钨酸钠(99.5%)、六水合硝酸铟(99.9%, Metals Basis)、硫代乙酰胺(ACS, $\geq 99.0\%$)上海阿拉丁生化科技股份有限公司;氯化锌(98%)、无水乙醇(分析纯, AR)、三乙醇胺(分析纯, AR)购自国药集团化学试剂有限公司。实验用水为去离子水。

束后,将沉淀物洗涤干燥,得到 CWO/ZIS 样品。根据 ZIS 的摩尔分数将复合样品命名为 CWO/xZIS (x 为 ZIS 的摩尔分数, $x = 0、1\%、2\%、3\%、4\%、5\%、6\%、10\%$)。

1.3 材料表征

采用 D8 advance 型 X 射线衍射仪(XRD, 德国 Druker 公司)表征最终样品的物相及晶体结构;采用 Sigma 500 型场发射扫描电子显微镜(FESEM, 德国 Zeiss 公司)观察样品的形貌结构,并采用配备在 MAIA3 LMH 型场发射扫描电子显微镜上的能量色散 X 射线光谱仪(EDS, 捷克 Tescan 公司)对微区成分及元素分布进行分析;采用 JEM 2100F 型透射电子显微镜(TEM, 日本电子公司)对样品的微观结构及晶格条纹进行分析;采用 ESCALAB 250Xi 型 X 射线光电子能谱仪(XPS, 美国 Thermo Fisher 公司)测定样品的元素组成及化学价态;采用 Lambda 950 型紫外-可见分光光度计(UV-vis, 美国铂金埃尔默公司)表征样品的光谱吸收性能和能带结构;采用 FS 5 型荧光分光光度计(PL)及 FLS 1000 型时间分辨

光致发光谱(TRPL, 英国爱丁堡仪器公司)对样品的光生载流子复合速率及寿命进行测试; 采用 CHI 600E 型电化学工作站对样品的瞬态光电流、电化学阻抗谱(EIS)及 Mott-Schottky 曲线进行测试(上海辰华仪器有限公司); 采用 Bruker-A300 型电子顺磁/自旋共振波谱仪(ESR, 德国布鲁克公司)对样品的活性自由基浓度和种类进行评估; 在 ThermoFischer EscaLab 250 Xi 光谱仪上进行紫外光电子能谱(UPS)以确定功函数, 使用氩 I_a 作为紫外源(光子能量为 21.22 eV)。

1.4 催化性能测试

采用 30 mL 定制光反应器和天美 GC 7900 气相色谱仪对样品光催化析氢性能进行测试, 系统采用配备 cut 420 nm 滤波片(波长范围: 420~780 nm)和全反射片的 300 W 氙灯作为可见光光源, 具体流程如下: 称取 5 mg 样品加入到含有 9 mL 去离子水和 1 mL 三乙醇胺(TEOA)的混合溶液中, 转移到 30 mL 光反应器中密封好; 将氩气充入反应器中持续 10 min, 去除反应器中的空气; 然后将反应器安装到反应平台上, 打开循环冷却水, 将反应系统温度控制在 10 °C 左右, 采用搅拌器持续搅拌; 随后打开距离反应器 10 cm 处的氙灯光源进行光照, 且每隔 30 min 从反应器中抽取 100 μ L 气体, 注入气相色谱仪中进行气体分析, 持续光照 3 h。循环实验在相同条件下多次重复上述过程。

2 结果与讨论

2.1 物相分析

图 2 是纯相 ZIS、纯相 CWO、CWO/xZIS 试样的 XRD 谱。由图 2 可见, 纯相 CWO 样品的 XRD 谱属于单斜相 CWO(JCPDS 15-0867)^[21], 位于 18.9°, 30.6°, 36.2°, 53.9° 处峰分别对应于(001), (-111), (200)和(-122)晶面, 说明已成功制备出纯相 CWO。纯相 ZIS 样品对应于六方相 ZIS(JCPDS 72-0773)^[22], 没有任何杂质峰, 说明成功制备出纯相 ZIS。而 CWO/xZIS 试样的 XRD 谱中同时出现 ZIS 与 CWO 的特征峰, 说明 CWO 与 ZIS 成功复合在一起。

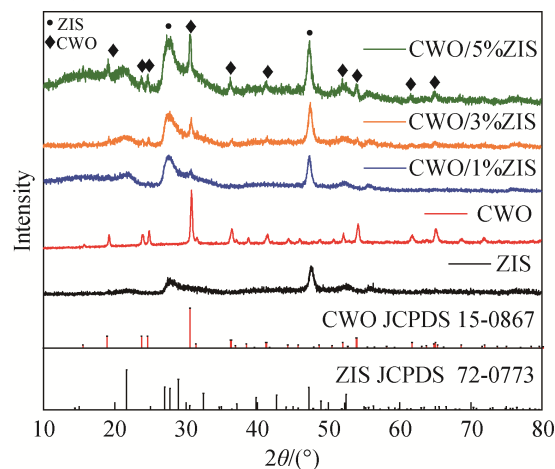


图 2 ZIS、CWO 和 CWO/xZIS 样品的 XRD 谱
Fig. 2 XRD patterns of ZIS, CWO and CWO/xZIS samples

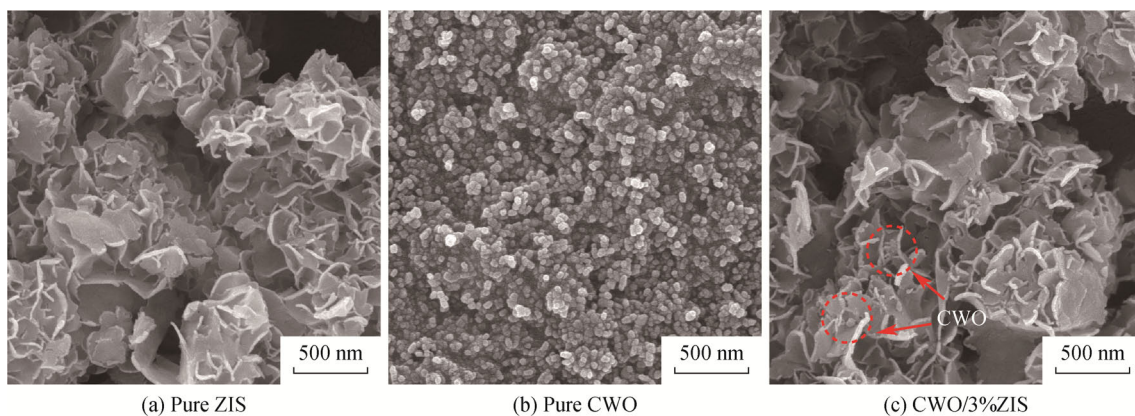


图 3 不同试样的 FESEM 照片
Fig. 3 FESEM images of different samples

2.2 微观形貌

图 3a 是纯相 ZIS 的 FESEM 照片, ZIS 是一种典型的二维纳米片结构, 且这些卷曲的纳米片团聚形成纳米花状聚集体。图 3b 显示纯相 CWO 为直径约 50 nm 的颗粒。图 3c 为 CWO/3%ZIS 样品的

FESEM 照片。由图 3c 可见, CWO 纳米颗粒附着在 ZIS 纳米片上, 进一步表明成功合成 CWO/ZIS 复合样品。从图 4 可见, CWO/3%ZIS 复合样品含有 Zn、In、S、Co、W、O 6 种元素, 且均匀分布在样品上, 说明 ZIS 与 CWO 两相分布均匀。

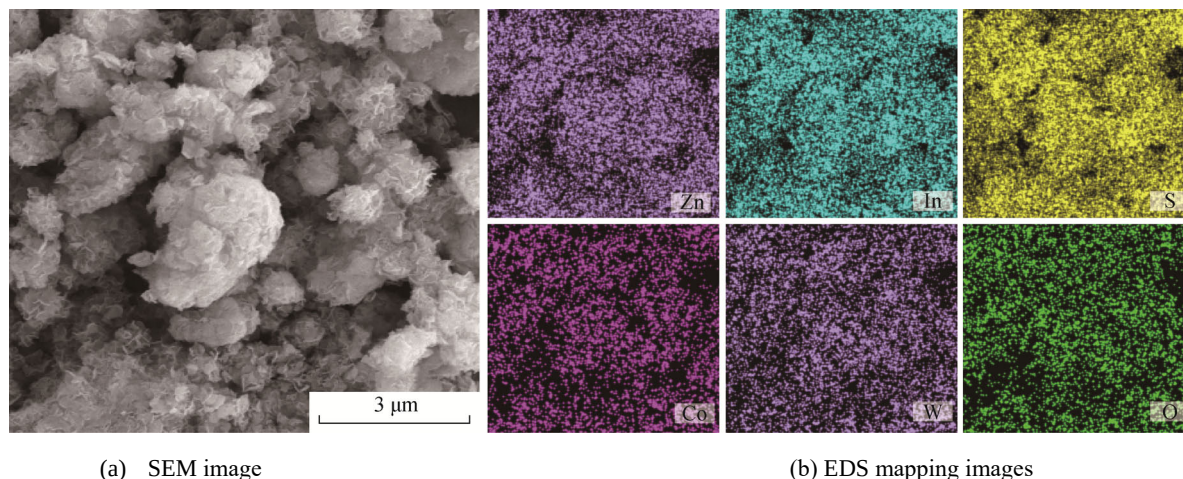


图 4 CWO/3%ZIS 样品的 SEM 照片和 EDS 面扫图
Fig. 4 SEM and EDS mapping images of CWO/3%ZIS samples

为了进一步证明 CWO/ZIS 紧密接触, 本工作采用 TEM 测试对 CWO/3%ZIS 样品进行了表征。低倍 TEM 照片可以明显看到薄片状和颗粒状的共存(图 5a), 结合 FESEM 结果, 进一步证实产物中含有 CWO 与 ZIS, 且 CWO 纳米粒子负载在 ZIS

纳米片表面。对局部区域进行放大分析, 由图 5b 可见, 产物中明显出现了 2 套不同的晶格条纹, 其中晶面间距为 0.276 nm 的晶格条纹, 对应于六方相 ZIS 的(105)晶面^[23]; 晶面间距为 0.292 nm 的晶格条纹, 对应于单斜相 CWO 的(-111)晶面^[24]。

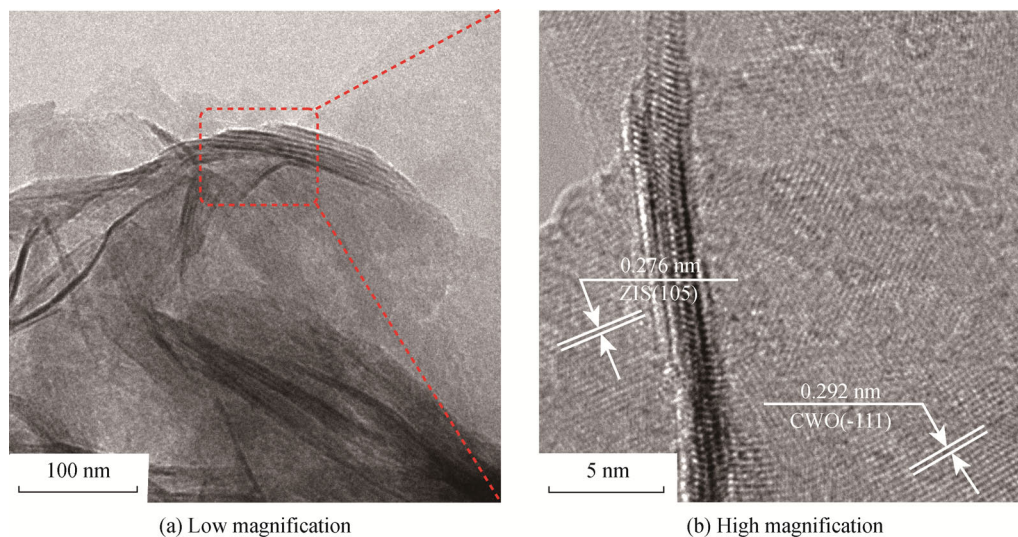


图 5 CWO/3%ZIS 样品的 TEM 照片
Fig. 5 TEM images of CWO/3%ZIS samples

2.3 XPS 分析

图 6 为纯相 ZIS、纯相 CWO 和 CWO/3%ZIS 样品的 XPS 谱。由图 6a~图 6c 可见, Zn 2p 窄扫中 1 022 eV 和 1 045 eV 处峰分别属于 Zn 2p_{3/2} 和 Zn 2p_{1/2}, 证明锌元素以 Zn²⁺形式存在^[25]; In 3d 中 444.9 eV 和 452.4 eV 处峰对应于 In 3d_{5/2} 和 In 3d_{3/2}, 证明铟元素以 In³⁺形式存在^[26]; S 2p 中 161.5 eV 和 162.7 eV 处峰对应于 S 2p_{3/2} 和 S 2p_{1/2}, 证明硫元素以 S²⁻形式存在^[27]。以上结果证实纯相 ZIS 和 CWO/3%ZIS 样品中都含有 ZIS, 进一步证实了

XRD 结果。与纯相 ZIS 相比, CWO/3%ZIS 样品中 Zn 2p, In 3d 及 S 2p 结合能均略微向更高结合能方向偏移, 表明 CWO 与 ZIS 之间发生了强烈的相互作用, 即形成了异质结。图 6d 显示了 CWO 中 Co 的化学态, 结合能 782.6 eV 和 797.2 eV 表示的是 Co 2p_{3/2} 和 Co 2p_{1/2}, 表明存在 Co²⁺^[28], 而 780.6 eV 对应的峰表示了 Co³⁺的存在^[29]。图 6e 中 CWO 的 530.3 eV 和 532.4 eV 处峰, 分别属于尖晶石结构中的晶格氧和吸附在表面和外部的的水分子^[30]。复合样品中的 O 1s 发生较大的偏移, 进一步说明 CWO 与

ZIS 之间存在强烈的交互作用。图 6f 中 W 4f 可以拟合出 35.3 eV 及 37.4 eV 2 处峰, 分别属于 W 4f_{7/2}

和 W 4f_{5/2}, 这表明 CWO 中钨元素是以 W⁶⁺ 的价态存在^[31]。

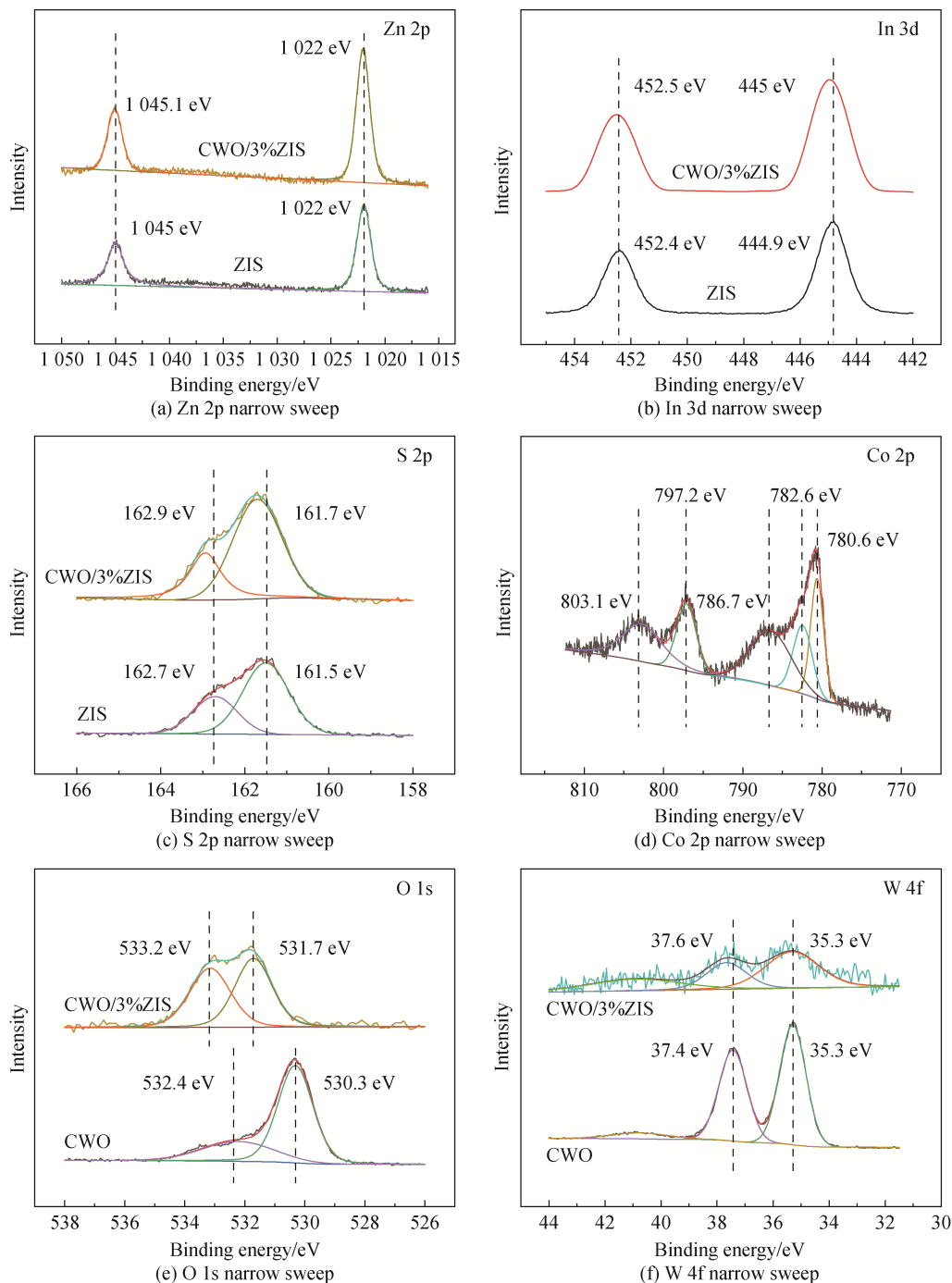


图 6 纯相 ZIS、纯相 CWO、CWO/3%ZIS 中各元素的窄扫图

Fig. 6 Narrow sweeps of each element of pure ZIS, pure CWO, and CWO/3%ZIS

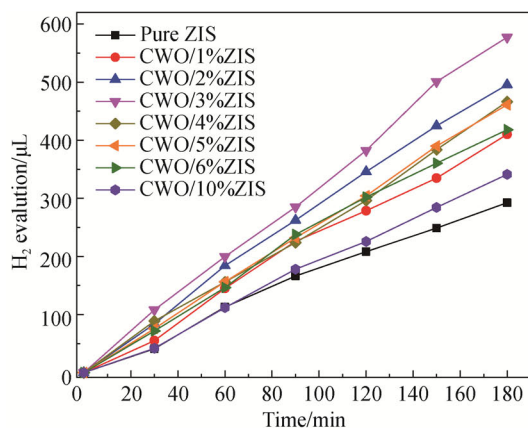
2.4 光解水产氢性能

为了证实显微结构、制备工艺与性能的关系, 对 CWO/xZIS 系列样品进行了析氢测试。图 7a 为 CWO/xZIS 系列样品光催化产氢量随光照时间变化曲线。由图 7a 可见, 在可见光照射 3 h 后, 纯相 ZIS 产氢量并不理想, 只有 103 μL 左右, 而复合样品析

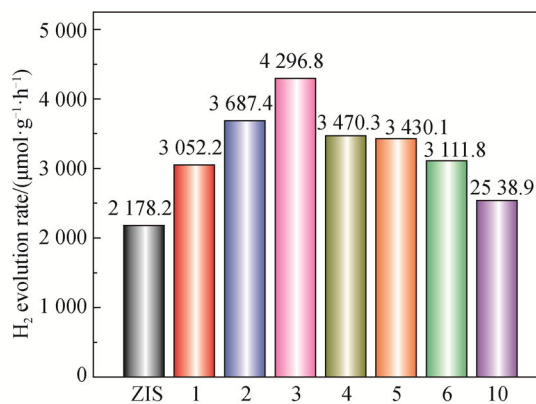
氢量出现了明显的提升, 其中 CWO/3%ZIS 的样品表现出最高的析氢活性, 产氢量达到 577.5 μL 左右。图 7b 显示的是不同试样的光催化析氢速率曲线, 随着复合比例的增大, CWO/xZIS 复合样品的析氢速率呈现出明显的正态分布, 其中 CWO/3%ZIS 试样的析氢速率最佳, 达到 4 298.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, 是纯

相 ZIS 析氢速率($2\,178.2\,\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)的 2 倍左右。图 7c 为 CWO/3%ZIS 样品的循环析氢性能曲线, CWO/3%ZIS 复合样品具有良好的稳定性, 每个循环之后加入 0.5 mL 的 TEOA, 析氢性能没有明显的

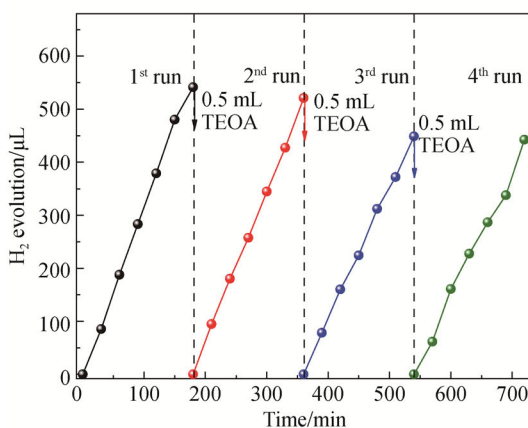
下降。而且, CWO/3%ZIS 样品的表观量子效率(AQE)相较于纯相 ZIS 从 420 nm 处的 1.0% 上升到 1.7%, 从 450 nm 处的 0.37% 上升到 0.50%, 从 475 nm 处的 0.10% 上升到 0.16%。



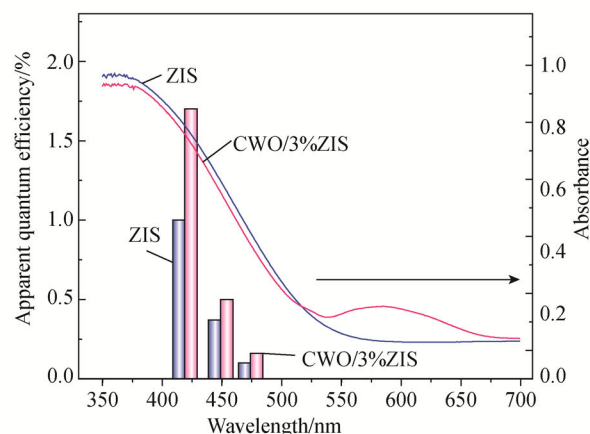
(a) Hydrogen production-time variation curve



(b) Hydrogen precipitation rate histogram



(c) Cyclic hydrogenation curve



(d) Plot of apparent quantum efficiency and absorption spectra

TEOA is triethanolamine.

图 7 CWO/xZIS 系列样品的光催化析氢测试图

Fig. 7 Photocatalytic hydrogen precipitation test chart for CWO/xZIS series samples

2.5 光谱吸收性能分析

为了探究光催化性能提升的原因, 本工作采用紫外-可见分光光度计对不同样品的光谱吸收性能进行了表征。通过实验数据计算作图得到材料吸收边和禁带宽度大小。如图 8 和表 1 所示, 复合样品带隙值与纯相差别不大, 也就是说性能的提升不是带隙宽度变化引起的。

2.6 光电性能测试

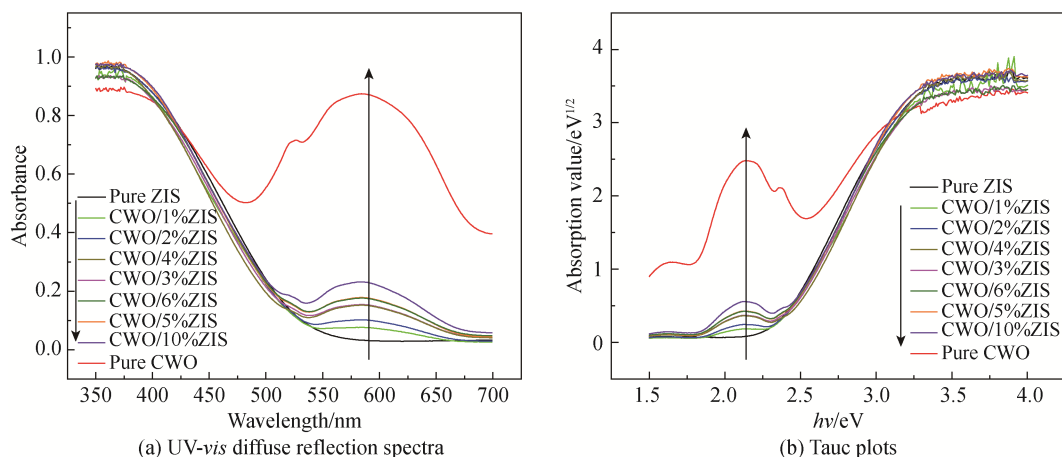
随后, 本工作对不同样品开展了电化学性能测试。图 9a 为纯相 ZIS、纯相 CWO 和 CWO/xZIS 复合样品的瞬态光电流曲线。由图 9a 可见, 相比于纯相 ZIS 和纯相 CWO, CWO/xZIS 复合样品拥有更高的光电流密度, 且 CWO/3%ZIS 样品最高, 与光解水析氢性能规律一致, 这表明

CWO/3%ZIS 样品具有最高的光生载流子分离效率^[32]。图 9b 为纯相 ZIS、纯相 CWO 和 CWO/xZIS 样品的 EIS 曲线, 相比于纯相 ZIS 和纯相 CWO, CWO/xZIS 复合样品的曲线半径更小, 且 CWO/3%ZIS 试样的最小, 说明 CWO/xZIS 复合样品的电化学阻抗最小, 拥有最快的光生载流子传输速率^[33]。

此外, 光生载流子复合也是评价催化剂的重要参数。本工作采用日立 F7000 荧光分光光度计对不同样品进行了 PL 谱进行了测试。通常, PL 光谱强度越低, 说明催化材料光生电子/空穴复合速率越小^[34]。由图 9c 可见, 相比于纯相 ZIS 和纯相 CWO, CWO/xZIS 复合样品拥有更低的强度, 且 CWO/3%ZIS 复合样品的强度最低, 说明 CWO 与

ZIS 复合之后, 显著抑制了光生电子/空穴复合。为获得更详细光生载流子动力学信息, 本工作采用

Edinburgh FLS1000 型荧光光谱仪对纯相 ZIS、纯相 CWO 以及 CWO/xZIS 复合样品的 TRPL 谱进行表征。



h : Plank constant; ν : Incident photon frequency.

图8 纯相 ZIS、纯相 CWO 及 CWO/xZIS 试样的紫外-可见漫反射光谱和 Tauc 图

Figure 8 UV-vis diffuse reflection spectra and Tauc's plots of pure ZIS, pure CWO and CWO/xZIS samples

表1 纯相 ZIS、纯相 CWO 和 CWO/xZIS 系列样品的吸收边和带隙汇总表

Table 1 Calculated absorption edges and band gaps of pure ZIS, pure CWO and CWO/xZIS samples

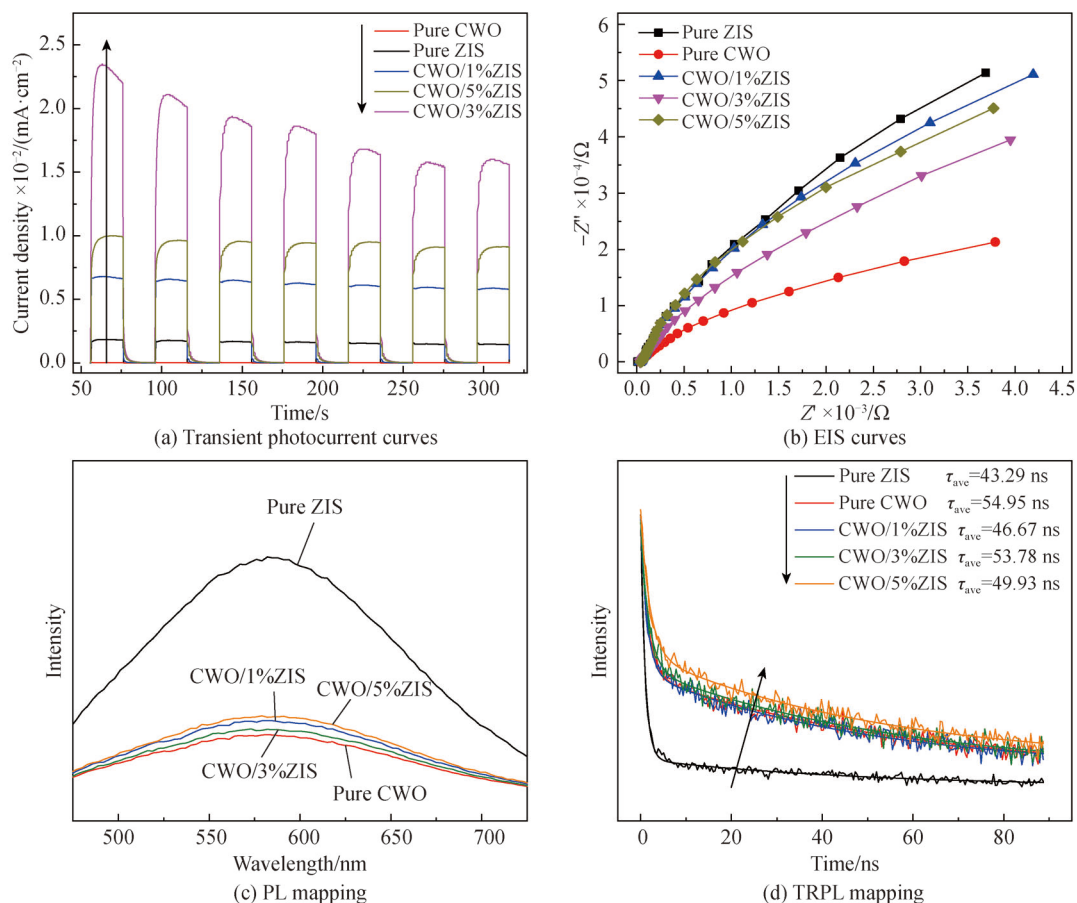
Samples	Absorption edge/nm	Band gap/eV
Pure ZIS	529.8	2.35
Pure CWO	547.2	2.27
CWO/1%ZIS	523.5	2.38
CWO/2%ZIS	526.6	2.37
CWO/3%ZIS	527.7	2.36
CWO/4%ZIS	526.5	2.36
CWO/5%ZIS	526.7	2.36
CWO/6%ZIS	527.5	2.36
CWO/10%ZIS	530.6	2.35

由图 9d 可见, 纯相 ZIS 和纯相 CWO 的平均荧光寿命分别为 43.29 ns 和 54.95 ns; CWO/1%ZIS 和 CWO/3%ZIS 复合样品分别为 46.67 ns 和 53.78 ns。由此可知, CWO 的加入使得 CWO/xZIS 复合样品的平均荧光寿命得到了增长, 进一步证实了光生载流子复合受到了明显抑制。

为了进一步解释 CWO/xZIS 异质结的光催化机理, 本工作对纯相 ZIS 和纯相 CWO 的 Mott-Schottly 和 UPS 进行了表征, 以获取 ZIS 和 CWO 半导体类型、平带电势、费米能级和能带结构。由 10a 可见, 纯相 ZIS 斜率为正, 说明 ZIS 是一种典型的 n 型半导体, 通过计算可知其平带电势相对于 RHE 为 -0.14 eV。通常, n 型半导体的导带电位(E_{CB})通常比平带电位约负 0.2 V^[35], 由此可计算出 ZIS 的 E_{CB} 为 -0.34 eV。由图 10c 可见, ZIS 的带隙(E_g) 2.35 eV, 因此

可以计算出 ZIS 的价带电位(E_{VB})为 2.01 eV。图 10b 中 CWO 斜率为负, 说明 CWO 是一种典型的 p 型半导体, 通过计算可知其平带电势为 1.92 eV。通常, p 型半导体的 E_{VB} 比平带电位约正 0.2 V^[36], 由此可计算出 CWO 的 E_{VB} 为 2.12 eV。由图 10d 可见, CWO 的 E_g 为 2.27 eV, 因此可以计算出 CWO 的 E_{CB} 位为 -0.15 eV。此外, 功函数可以反映半导体费米能级位置和载流子输运路径, 如图 10e 和图 10f, 经过测量计算后, 纯相 ZIS 和 CWO 的功函数分别为 4.72 eV 和 5.31 eV。

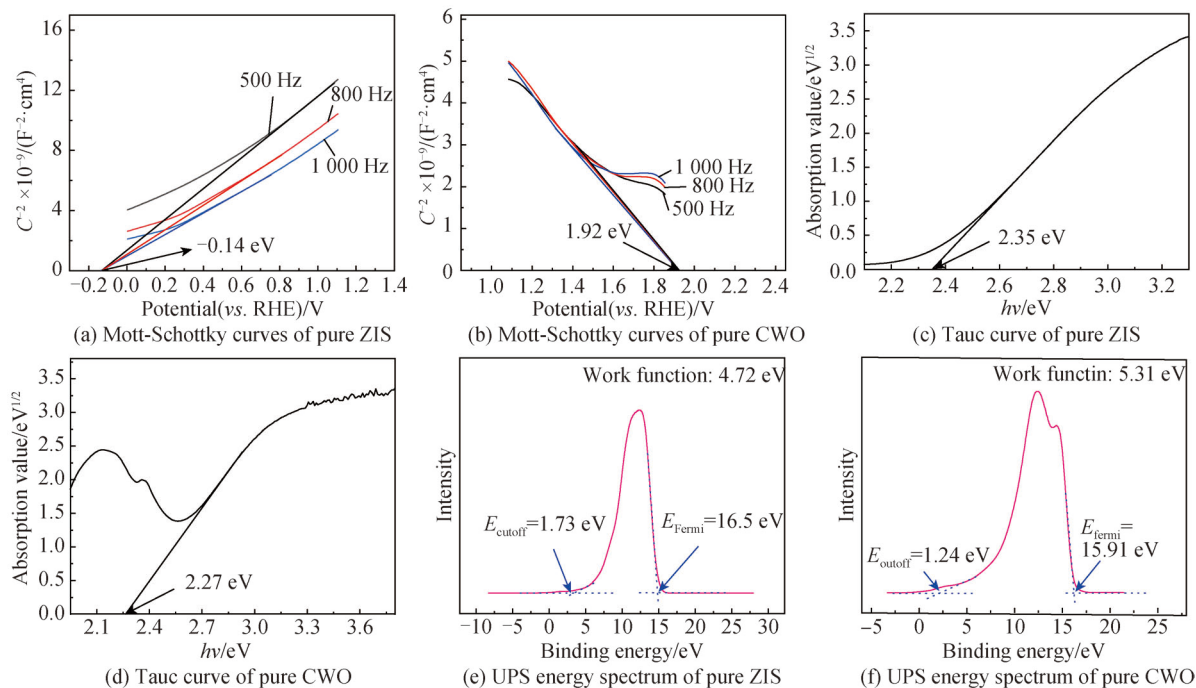
基于上述实验结果与分析, 本工作提出了 S 型 CWO/xZIS 异质结光生载流子动力学机制和光催化机理。由图 11 可见, 当 n 型半导体 ZIS 与 p 型半导体 CWO 接触后, 二者之间费米能级存在电势差, 当 CWO 纳米片生长在 ZIS 表面时, 电子会自发地重新



Z' : Resistive; Z'' : Reactance; τ_{ave} : Average carrier lifetime.

图 9 纯相 ZIS、纯相 CWO 和 CWO/xZIS 样品的光电化学测试图

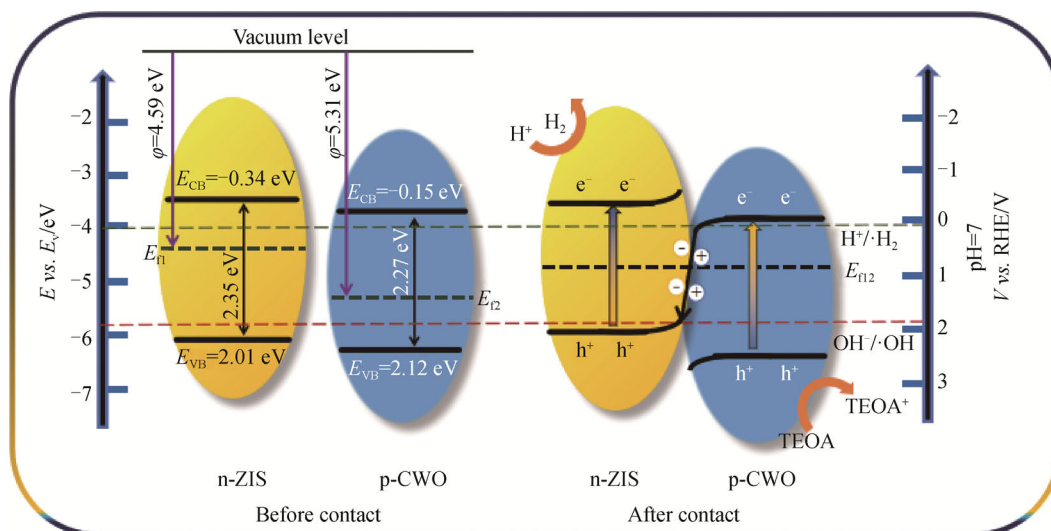
Fig. 9 Photoelectrochemical test plots of pure ZIS, pure CWO and CWO/xZIS samples



C is interfacial capacitance; E_{Fermi} : Fermi edge differential; E_{cutoff} : Secondary electron emission cutoff.

图 10 纯相 ZIS 和纯相 CWO 的 Mott-Schottky 曲线、Tauc 曲线和 UPS 能谱

Fig. 10 Mott-Schottky curves, Tauc curves and UPS energy spectra of pure ZIS and pure CWO



E_{CB} : Energy at the base of conduction band; E_{VB} : Valence has top energy; E_f : Fermi level energy; V : Electric Potential.

图 11 能带结构图及光催化机理示意图

Fig. 11 Schematic diagram of the band structure and photocatalytic mechanism

排列并从 CWO 流向 ZIS, 直到它们的费米能级达到平衡。此时, CWO 导带面积累了大量的电子, 导致能带向下弯曲并带负电, 而 ZIS 价带面失去大量电子, 导致能带向上弯曲并带正电, 最终形成一个由 CWO 指向 ZIS 的内建电场。当可见光辐照后, ZIS 和 CWO 均产生光生电子/空穴对, S 型异质结内建电场促使 CWO 导带光生电子向 ZIS 价带转移复合空穴; 结果, ZIS 导带光生电子将水中的 H^+ 还原为 H_2 , 而 CWO 价带空穴将表面吸附的牺牲剂 TEOA 消耗掉。由于 ZIS 价带光生空穴上被有效复合, 从而抑制了光生空穴对 ZIS 的腐蚀, 最终导致 CWO/xZIS 异质结体系重复性和稳定性的改善。

为了验证上述光催化机理, 本工作采用 ESR 技术研究了 CWO/xZIS 异质结光生电荷传输过程。纯

相 ZIS 及 CWO/3%ZIS 样品的 ESR 图谱如图 12 所示, 在黑暗状态下并没有检测到任何的特征峰, 但在光照条件下均可检测到明显的特征峰, 表明纯相 ZIS 及 CWO/3%ZIS 样品均可产生 $\cdot O_2^-$ 及 $\cdot OH$ 。由图 12a 可见, CWO/3%ZIS 样品的 $DMPO-\cdot O_2^-$ 特征峰信号明显高于纯相 ZIS, 表明在复合材料表面有更多的光生电子参与反应。由图 12b 可见, 与纯相 ZIS 相比, CWO/3%ZIS 样品 $DMPO-\cdot OH$ 特征峰信号强度明显提升, 表明负载 CWO 后, 表面富集更多的光生空穴。综上所述, 由于 CWO 的负载, 显著提高了光生载流子的分离效率和传输速率, 抑制了光生电子-空穴对复合, 最终显著改善了 ZIS 的光催化性能。因此, 上述结果证实了 CWO/ZIS 异质结中存在 S 型异质结的电荷迁移途径。

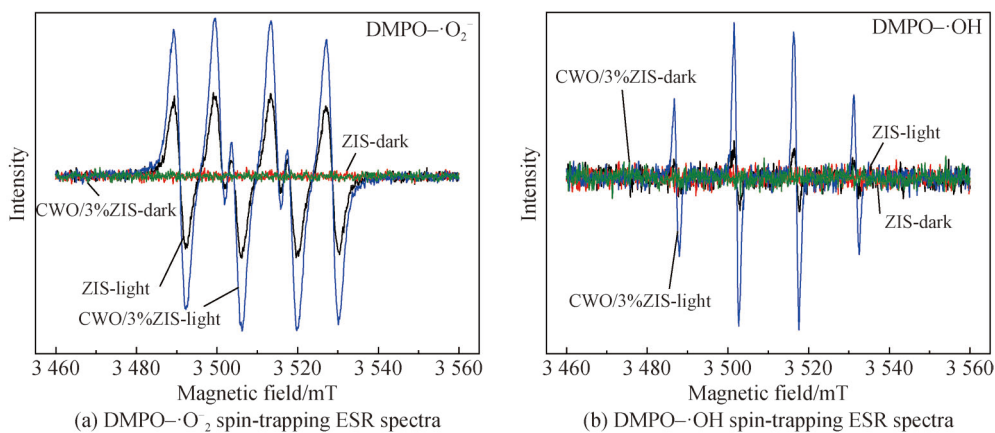


图 12 纯相 ZIS 和 CWO/3%ZIS 样品在暗、光条件下 ESR 光谱

Fig. 12 ESR spectra of pure ZIS and CWO/3%ZIS samples in dark and light conditions

3 结论

采用水热法成功合成纯相 CWO 纳米颗粒, 并通过水浴法将 CWO 纳米颗粒负载到 ZIS 纳米片上, 成功制备了 S 型 CWO/ZIS 异质结。XRD、FESEM、EDS、HRTEM、XPS 等测试结果证实 CWO 和 ZIS 间形成了紧密接触, 构建了良好的异质界面。可见光裂解水析氢测试结果显示 CWO/ x ZIS 复合样品的析氢性能相比于纯相 ZIS 有了明显的提升, 其中 CWO/3%ZIS 样品析氢速率达到 $4\,296.8\,\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, 是纯相 ZIS ($2\,178.2\,\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) 的 2 倍。UV-vis、EIS、PL、TRPL、光电流和平带测试结果表明: 由于 CWO 和 ZIS 能带结构匹配良好, 成功构建了 S 型异质结光生载流子传输通道, 使得复合样品具有更高的光生电子/空穴对的分离效率、更快的光生电荷传输速率以及更小的电子/空穴复合速率, 最终导致了 CWO/ x ZIS 异质结光解水析氢效率的提升。ESR 测试进一步证实了 S 型 CWO/ x ZIS 异质结光生载流子动力学传输机制。

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Photocatalytic Water Splitting into Hydrogen Production with S-Scheme CoWO₄/ZnIn₂S₄ Heterojunctions

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Extended Abstract

Introduction Hydrogen energy, as an environmentally friendly and clean energy source, is expected to optimize the energy structure and alleviate energy consumption due to its high energy density, good combustion characteristics and abundant reserves. Hydrogen production from photolyzed water is considered as the most ideal way to obtain hydrogen source in the future. However, the disadvantages of weak visible light response, low catalytic activity, and poor chemical stability are one of the main factors limiting the application of traditional photocatalytic materials in photolytic water hydrogenation to real life. Zinc indium sulfide (ZIS) is proved to be an ideal semiconductor photocatalyst due to its good chemical stability, moderate forbidden bandwidth (2.2–2.5 eV), suitable conduction band position (–0.79 eV), and good visible light absorption (absorption edge about 540 nm). However, ZIS suffers from a high photogenerated carrier complex rate and a weak photostability. Scholars optimized the ZIS energy band structure, expanded the spectral absorption range, improved the photoelectron dynamics behavior, and enhanced the photostability of ZIS by different approaches like morphology regulation, elemental doping, co-catalysis, and heterojunction. S-type heterojunctions have attracted recent attention due to their excellent photogenerated carrier dynamics and highly efficient photodissociation of hydrogen from water. In this paper, CWO/ZIS composite nanomaterials were synthesized by a two-step hydrothermal/water-bath method, and the photocatalytic mechanism of CWO/ZIS heterojunctions was discussed via constructing S-type heterojunctions, using the built-in electric field to enhance the photogenerated electron/hole separation efficiency and the migration rate.

Methods Cobalt tungstate (CWO) nanoparticles were firstly prepared by a hydrothermal method, and then S-type CWO/ZIS heterojunctions were prepared by a water bath method. The composite samples named as CWO/xZIS were prepared at different molar ratios of Co²⁺ to Zn²⁺ (i.e., $x = 0, 1\%, 2\%, 3\%, 4\%, 5\%, 6\%$, and 10%). The properties of the samples (i.e., physical phase components, morphology, crystal structure, elemental distribution, chemical state, photocatalytic hydrolysis performance, photogenerated carrier separation efficiency, photogenerated charge transport rate, and photogenerated electron/hole pair recombination rate) were characterized.

The photocatalytic hydrogen production performance of the samples was tested by a 30 mL customized photoreactor and a Timex GC7900 gas chromatograph. A 300 W Xenon lamp was equipped with a cut 420 nm filter (wavelength range: 420–780 nm) and an all-reflector was used as a visible light source. 5 mg of the sample was added to a mixed solution containing 9 mL of deionized water and 1 mL of triethanolamine (TEOA) and transferred to a 30 mL photoreactor sealed well. The air in the reactor was removed via charging the reactor with argon gas for 10 min. Afterwards, the reactor was mounted on the reaction platform, the circulating cooling

water was turned on, the temperature of the reaction system was controlled at $10\text{ }^\circ\text{C}$, and a stirrer was used for continuous stirring. A Xenon lamp 10 cm away from the reactor was turned on for illumination, and $100\text{ }\mu\text{L}$ of gas was extracted from the reactor for each 30 min and injected into the gas chromatograph for gas analysis for 3 h. The cyclic experiments were repeated under the same conditions for several times.

Results and discussion According to the experimental results by X-ray diffraction (XRD), pure ZIS and pure CWO samples can be prepared. The characteristic peaks of ZIS and CWO both appear in the XRD patterns of the CWO/xZIS sample, indicating that CWO and ZIS are compounded. The surface morphology and microstructure of pure ZIS, pure CWO nanomaterials and their composite samples are determined by field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM). Based on the FESEM images, pure ZIS appears a typical two-dimensional nanosheet structure, and the size of pure CWO nanoparticles is approximately 50 nm. The FESEM images of CWO/3%ZIS samples show that CWO nanoparticles are attached to ZIS nanosheets. The HRTEM images show that the coexistence of lamellar and granular forms on the CWO/3%ZIS sample occur, confirming that the product contains both CWO and ZIS. Two sets of different lattice stripes corresponding to different crystalline surfaces of pure ZIS and CWO appear in the product, which further confirms that CWO and ZIS are composited. The X-ray photoelectron spectra indicate that CWO/3%ZIS samples contain ZIS and there is a strong intense interaction between CWO and ZIS.

From the results of hydrogen production tests on CWO/xZIS samples, the samples of CWO/3%ZIS show the maximum hydrogen production activity with a photocatalytic hydrogen production rate, which is twice greater than that of pure ZIS. The reproducibility test proves that the samples of CWO/3%ZIS have a good photochemical stability. From the results of electrochemical performance tests on different samples, CWO/3%ZIS sample has the maximum photocurrent density and the minimum electrochemical impedance, thus indicating that it has the maximum photogenerated carrier separation efficiency and transport rate, which is also consistent with the photocatalytic hydrolysis to production hydrogen performance.

Conclusions Pure CWO nanoparticles were synthesized by a hydrothermal method and S-type CWO/ZIS heterojunctions were prepared via loading CWO nanoparticles onto ZIS nanosheets by a water bath method. The results of XRD, FESEM, HRTEM, and XPS confirmed the formation of a close contact between CWO and ZIS and the construction of a good heterogeneous interface. The results of visible-light water splitting hydrogen production tests showed that the hydrogen production performance of the CWO/xZIS composite samples was improved, compared with that of pure ZIS, in which the hydrogen production rate of the CWO/3%ZIS samples reached $4\,296.8\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is twice greater than that of pure ZIS (*i.e.*, $2\,178.2\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). The electrochemical performance test results showed that the S-type heterojunction photogenerated carrier transport channel was constructed due to the well-matched energy band structures of CWO and ZIS, resulting in the composite samples with a higher separation efficiency of the photogenerated electron/hole pairs, a faster photogenerated charge transport rate, and a smaller electron/hole recombination rate, thus leading to the enhancement of the photocatalytic hydrolysis into hydrogen generation efficiency of the CWO/xZIS heterojunction.

Keywords cobaltous tungstate; zinc indium sulfide; S-scheme heterojunction; photocatalytic water splitting into hydrogen production