磷掺杂提升三氧化钨导带用于高效二氧化碳还原

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摘要 光电催化还原二氧化碳是一种环境友好的高效方法, 可将过量排放的 CO_2 转化为燃料与化学品, 减少温室效应并存储太阳能。本研究设计制备了新型磷掺杂的 WO_3 催化剂, 并将其用于 CO_2 和水转化为碳基化学品。通过X射线粉末衍射(XRD)、X射线光电子能谱(XPS)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)、顺磁共振(EPR)等证实了新型催化剂的成功制备; 通过紫外可见(UV-vis)、线性扫描伏安曲线(LSV)、莫特-肖特基(Mott-Schottky)和电化学交流阻抗谱(EIS)表征了其光电性能。结果表明, 随着P掺杂量的增加, 其导带位置从 WO_3 的 -0.13 V 升高到30-P样品的 -0.54 V , 增强了其对 CO_2 的还原能力; 所有样品X-P比纯 WO_3 有更高的活性, 其中15-P电极还原 CO_2 的活性最高, 其光电池的表观光量子效率为0.4%, 与植物的光合作用相当, 且导带位置越高越有利于甲酸和乙酸产物的生成, 而相对较低的导带更有利于乙醇的生成。同时, 氧空位对反应的正影响也通过设计 H_2O_2 猝灭实验进行了验证。

关键词 半导体, 三氧化钨, 能带, 掺杂, 二氧化碳还原, 光电催化

全球变暖被认为是过量二氧化碳排放引起的严重气候问题。为了降低空气中 CO_2 的浓度, 催化转化 CO_2 具有重要意义, 也是近来全球研究的热点^[1,2]。二氧化碳转化的策略包括光催化^[3~7]、电催化^[8]和光电联合催化等^[9~16]。众所周知, 半导体由于其特殊的能带结构可以将光生电子和空穴分开, 在 CO_2 还原中起着重要作用, 例如 TiO_2 ^[17,18]、 ZnO ^[19,20]和 CdS ^[21,22], 但它们在可见光范围吸收较差。将杂原子掺杂到半导体中是缩小其带隙增加吸收的有效途径^[23,24]。由于光电催化的协同效应, 外加电场可以阻止光生电子与空穴的复合从而大大提升光生电荷的利用效率, 使得光电催化二氧化碳还原成为近几年发展迅猛的研究方向; 另一方面, 光电子的高能量可以克服电催化的能垒降低反应的过电势。开发新型半导体异质结以及利用分子或

COF催化剂是光电联合催化二氧化碳还原的热点^[25~29]。

WO_3 是n型半导体, 由于其宽带隙和较低的导带位置而很少用于光催化分解水和 CO_2 还原^[30~32]。尽管有一些方法可以提升 WO_3 在光催化分解水的能力, 但效果有限。本研究目的就是要探索一种简便的方法, 提升半导体的导带位置, 从而提高其光电催化还原 CO_2 的能力。通过向 WO_3 中引入不同量的磷化物, 开发出新型的杂化半导体催化材料, 将其作为催化剂应用于光电催化 CO_2 还原。用P掺杂的 WO_3 作为光电阴极, BiVO_4 作为光电阳极, 含有1 mmol/L光敏剂曙红Y和0.1 mol/L KHCO_3 的水溶液作为电解质组装出光电催化电池, 在氙灯照射下还原 CO_2 生成甲醇、乙醇和丙酮等燃料与化学品。

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1 实验

(i) WO_3 粉末的制备. 将3 mol/L HCl 滴加到 $\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ (8 mmol)和 NaCl (16 mmol)的60 mL水溶液中, 调节pH至1. 搅拌20 min后转移至100 mL不锈钢高压釜中, 密封加热至180°C, 保持24 h. 待高压釜自然冷却后开釜, 过滤出的粉末用去离子水和乙醇分别漂洗3~5次, 70°C下真空干燥6 h, 得到白色的 WO_3 纳米颗粒.

(ii) WO_3 电极的制备. 将15 mg WO_3 粉末和10 μL Nafion溶液加入1 mL乙醇中, 混合物超声处理15 min得到浆液, 沉淀后取上清液滴在氟掺杂的二氧化锡(FTO)玻璃的导电表面上以形成均匀的膜, 电极面积为1.5 cm $\times$ 1.4 cm, 催化剂平均负载重量为4 mg. 电极片在70°C下干燥3 h备用.

(iii) 磷掺杂的 WO_3 电极的制备. 将载有 $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (10, 15, 20, 30 mg)的瓷舟置于管式炉的上游, 载有 WO_3 /FTO电极的瓷舟置于管式炉的下游, 在氩气保护下以2°C/min的速度将管式炉加热到350°C并保持2 h. 通过氩气的流动将蒸发的磷化物带到 WO_3 基材的表面对其进行掺杂改性(图1(a)), 得到的电极被分别命名为10-P、15-P、20-P和30-P.

(iv) 光电化学测量. 电化学实验线性扫描伏安曲线(LSV, 0~-1.0 V vs. SCE(饱和甘汞电极)), 扫描速率为50 mV/s)、交流阻抗谱(EIS)在电化学工作站(CHI660E)上以三电极工作模式在含有1 mmol/L曙红Y和0.1 mol/L KHCO_3 的 CO_2 饱和电解质中进行: X-P作为工作电极, 饱和甘汞电极(SCE)为参比电极; 测试Mott-Schottky曲线时以 Ag/AgCl 电极为参比电极.

(v) 光电催化二氧化碳还原实验. 用P掺杂的 WO_3 |SCE| BiVO_4 三电极系统进行光电催化 CO_2 还原实验, 电解液为50 mL 0.1 mol/L KHCO_3 水溶液, 其中含有1 mmol/L曙红Y作为敏化剂辅助吸光; 将高纯 CO_2 气体通入电解液中鼓泡30 min致饱和(pH 6.8), 调节CHI660E到适当偏压, 在300 W氙气灯(PLS-SXE300/300UV)照射下进行实验(光强度校准为200 mW/cm ^{2}). 液相产物使用 ^1H NMR(JNM-ECS 400 MHz, JOEL)进行检测. 取700 μL 的电解液, 加入35 μL 含10 mmol/L的二甲基亚砷和50 mmol/L的间苯三酚的重水; 利用水峰压制技术检测其核磁共振氢谱. 液相产物的速率由产物的积分面积和加入的二甲基亚砷及间苯三酚的积分面积进行对比得到, 积分定量时将二甲基亚砷的峰面积标定为1. 抽取反应过程中所产生的反应气体, 用色谱

柱使混合气体中的各组分分离, 以热导检测器(TCD)检测各气体组分的浓度. 根据不同气体的导热系数不同, 从而引起检测器阻值的变化. 在测量电桥的输出端立即给出相应的信号, 据此定量测出各组分的含量, 再根据标准曲线计算出产率.

$$\text{表观法拉第效率FE} = \frac{\text{产物摩尔数} \times n}{\text{电子计量摩尔数}}, \quad (1)$$

式中, n 为电子数(甲酸 $n=2$, 甲醇 $n=6$, 乙醇 $n=12$).

表观量子效率AQE

$$= \frac{\Sigma \text{产物摩尔数} \times \text{电子数} - \text{电子计量摩尔数}}{\text{光子的摩尔数}}. \quad (2)$$

2 结果与讨论

2.1 光电阴极的表征

P掺杂 WO_3 电极的X射线粉末衍射图(XRD)列于图1(b), 可以看出(100)、(001)、(200)、(111)、(201)、(220)、(202)衍射峰与六方晶系 WO_3 (JCPDS 33-1387)相比略有偏移, 反映出微小的晶格延伸. 为了确定P掺杂后 WO_3 晶格中氧空位的存在, 分别研究了4种样品的电子顺磁共振谱(EPR, 图1(c)). 可以看出, 随着P掺杂量的增加信号增强, 表明氧空位越多, 而纯 WO_3 没有信号. 样品的固体紫外-可见吸收谱如图1(e)所示, 可以看出掺杂后样品的吸收边带相比 WO_3 的420 nm都有红移, 其中15-P的吸收边带红移最大, 达到了460 nm, 对应的半导体能带示于图1(d). 对P掺杂的 WO_3 进行了电化学表征, 如图1(f)所示. 在 CO_2 氛围下, 所有P掺杂 WO_3 电极均展示了良好的光催化活性, 且随着P掺杂量的增加, 光电流逐渐增大. 扫描电子显微镜(SEM)图片可以看出其形貌为棒状结构(图1(g)); 透射电子显微镜(TEM)显示 WO_3 是高活性的(111)晶面, 晶面间距为0.267 nm(图1(h)).

2.2 光电阴极的性质

X射线光电子能谱(XPS)表明, 掺杂后的15-P可以模拟为4个去卷积峰(图2(a)), 分别对应于 W^{6+} 4f $_{7/2}$ 35.71, 4f $_{5/2}$ 37.81 eV和 W^{5+} 4f $_{7/2}$ 34.78, 4f $_{5/2}$ 37.07 eV; W^{5+} 离子与氧空位相伴相生; 由O 1s(图2(b))可见15-P样品中含有氧空位的特征峰(Vo); P 2p的XPS峰表明磷元素成功地掺杂到了 WO_3 晶体中(图2(c)). 交流阻抗谱(图2(d))表明15-P具有最小的半径即最小的电荷传输阻力,

图 1 (网络版彩色)P掺杂WO₃电极的制备以及表征. (a) 制备过程; (b) XRD; (c) EPR; (d) 能带结构; (e) UV-vis; (f) LSV. 15-P电极的SEM(g)和TEM(h)图片

Figure 1 (Color online) Preparation and characterizations of P doped WO₃ electrodes. (a) Preparation process; (b) XRD; (c) EPR; (d) band structures; (e) UV-vis; (f) LSV; SEM (g) and TEM (h) images of 15-P

表明电极和电解质之间的电子转移更高效. 这是由于P掺杂对半导体是n型掺杂, 电子注入费米能级, 从而提

升了导带电位(CB potential), 同时也增加了WO₃晶格缺陷和氧空位等, 提高了半导体的导电能力, 表现为阻抗

图2 (网络版彩色) 15-P和 WO_3 的XPS谱图(a)~(c)、 WO_3 和X-P的电化学阻抗图(d)、X-P的Mott-Schottky曲线(e)~(h)

Figure 2 (Color online) XPS spectra of WO_3 and 15-P (a)~(c), EIS spectra of WO_3 and X-P (d), Mott-Schottky curves of X-P (e)~(h)

降低。Mott-Schottky曲线(图2(e)~(h))表明P掺杂 WO_3 电极的CB带位置比 WO_3 电极本身的-0.13 V都有了明显

的提升, 且随着掺杂P元素的数量增加而增加。X-P电极的CB带从-0.13 V增加到10-P的-0.28 V, 15-P的

-0.38 V, 20-P的-0.42 V和30-P的-0.54 V(图1(d)), 表明电极对CO₂的还原能力逐步增大. 在光照或暗态条件下, P掺杂WO₃的LSV曲线(图1(f))表明, 所有条件下的电流密度均大于以纯WO₃为阴极的电池, 在光电催化(photoelectrocatalysis, PEC)条件下的电流密度大于纯电条件下的电流, 显示了材料良好的催化能力.

2.3 光电阴极的催化CO₂还原性能

在P掺杂WO₃|KHCO₃|BiVO₄的光电催化电池中研究了其有机化学品产物分布和形成速率. 图3显示了电极15-P在不同偏压下的实验结果. 可以看出, 最佳反应条件为-0.8 V偏压, 得到的液相有机化学品产物总量最多, 产物生成速率分别为甲醇20.8 $\mu\text{mol}/(\text{L h cm}^2)$ 和乙酸4.7 $\mu\text{mol}/(\text{L h cm}^2)$, 光电池效率0.4%, 与植物的光合作用相当. 在-0.6 V下, 由于从外电路电流获得的电量最少, 所以有最大的总电子效率(total electron efficiency, TEE, 图3). 由于析氢反应是CO₂还原反应的竞争反应, 在-1.0 V(vs. SCE)的条件下, 析氢反应速率过

图3 (网络版彩色)最优光电阴极15-P在不同电压下产物生成速率和总电子效率

Figure 3 (Color online) Formation rate and TEE of optimal photoelectrode 15-P at various potentials

大($41.0 \mu\text{mol}/(\text{L h cm}^2)$), 抑制了二氧化碳还原的速率. 此时, 对应的产氧速率为 $51.8 \mu\text{mol}/(\text{L h cm}^2)$. 作为对比, 未掺杂的WO₃电极在-0.6~1.0 V(vs. SCE)偏压的条

图4 (网络版彩色)氧空位淬灭和性能验证. (a) EPR随氧化时间变化谱图; (b) XPS W4f随氧化时间的变化; (c) LSV曲线随氧化时间变化; (d) 产物分布和产率随氧化时间变化

Figure 4 (Color online) Quenching and verifying experiments of oxygen vacancy. (a) EPR signal change vs. oxidation time; (b) XPS signal of W4f change; (c) LSV curve change vs. oxidation time; (d) production distribution and rate change vs. oxidation time

件下,只检测到氢气和氧气的释放而没有碳基还原产物,原因是其导带电位(-0.15 V vs. NHE)低于 CO_2 还原为有机物所需的热力学电位(如甲醇 -0.38 V),不能提供反应所需的动力(化学势)。

为进一步了解氧空位在催化反应中的重要作用,将工作电极15-P浸泡在30%的 H_2O_2 溶液中,分别在0.5、1和2 h进行氧化。电极的EPR信号随着氧化时间的增加而明显降低,2 h后EPR信号降低约90%,表明氧空位浓度逐渐降低(图4(a))。另外, W 4f的XPS能谱(图4(b))显示15-P表面的 W^{5+} 物种在30 min内被完全氧化为 W^{6+} 。15-P电极的LSV曲线表明随着氧化程度加深,其光电流明显降低(图4(c))。15-P电极的催化性能随着氧化时间的增加而降低(图4(d)),2 h后降低了50%。这充分说明了催化剂中氧空位与催化剂活性具有正相关性,且与 W^{5+} 物种相辅相成,提升了催化剂的性能。

2.4 光电催化还原二氧化碳的机理

在模拟太阳光的照射下, P掺杂 WO_3 半导体材料的

价带电子跃迁至导带并被质子捕获形成高活性氢原子^[15],立即与吸附活化的 CO_2 (P或半导体缺陷位)反应^[16],生成燃料与化学品。同时,电解液中的氢氧根负离子(OH^-)在外电压的作用下迁移到光电阳极 BiVO_4 上失去电子生成 O_2 。究其原因是外加电压的存在阻止了光生电子与空穴的复合,从而提高了催化体系对 CO_2 还原的效率。

3 结论

综上所述,本文设计制备了磷掺杂 WO_3 的新型杂化半导体材料,并将其作为高效催化剂用于光电催化 CO_2 还原制备出燃料与化学品。P掺杂的 WO_3 提高了半导体材料的导带位置,增加了氧空位和缺陷位,从而提高了其催化还原 CO_2 的活性和效率。光电池的表现光量子效率AQE达到了0.4%,与植物的光合作用相当;低电压时有利于乙醇生成,高电压时有利于甲酸和乙酸的生成。实验结果对于开发新型杂化半导体材料及其催化 CO_2 还原具有指导意义。

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Summary for “磷掺杂提升三氧化钨导带用于高效二氧化碳还原”

P-doped WO_3 semiconductor with enhanced conduction band on highly efficient photoelectrocatalytic reduction of CO_2

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Global warming is considered a serious climate problem caused by excessive emissions of carbon dioxide. Studies on catalytic conversion of CO_2 are significant in terms of reducing CO_2 concentration in the atmosphere, thus remain popular in the field. The photoelectrocatalytic (PEC) reduction of CO_2 is an environment-friendly and efficient method to convert excessive CO_2 into chemicals. With such conversion, the greenhouse effect can be alleviated through the storage and transformation of solar energy into chemical energy.

WO_3 is an n-type semiconductor with wide band gap and low conduction band position. Therefore, the use of WO_3 is rare for photocatalytic water splitting and CO_2 reduction. Although some techniques are used to improve the ability of WO_3 in photocatalytic water splitting, the light quantum efficiency (AQE) is still less than TiO_2 . In current study, a facile method is explored to enhance the conduction band position of semiconductors, thereby improving the photoelectrocatalytic reduction of CO_2 .

To the best of our knowledge, this is the first paper includes novel P-doped WO_3 catalysts being designed, prepared, and used in the reduction of CO_2 to carbon-based chemicals in water. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and electron paramagnetic resonance (EPR) experiments were applied to confirm the formation of new catalysts. The photoelectric properties of new catalysts were characterized by UV-vis, linear sweep voltammetry (LSV), Mott-Schottky, and electrochemical impedance spectroscopy (EIS) experiments.

We have developed a new type of hybrid semiconductor (P-doped WO_3) as catalytic materials by introducing the vaporized phosphide (NaH_2PO_2) onto the surface of WO_3 substrate under the flow of argon gas in a tube furnace. The PEC cell of P-doped $\text{WO}_3|\text{SCE}|\text{BiVO}_4$ was equipped with a trielectrode system and powered by a chemical workstation, in which, p-doped WO_3 was used as photocathodes in photoelectrocatalytic reduction of CO_2 . The PEC cell was fulfilled with an electrolyte containing 1 mmol/L photosensitizer Eosin Y and 0.1 mol/L KHCO_3 , and bubbled with pure CO_2 in 30 min to saturation, the experiment of CO_2 reduction in water was carried out with a proper voltage under irradiation of simulated sun light (300W Xe lamp) to generate methanol, ethanol, acetone, etc.

Our results indicates that the conduction band position of p-doped WO_3 increases from -0.13 to -0.54 V along with the increase of P-doped quantity, augmenting its ability to reduce CO_2 . It can be seen that p-doped WO_3 with oxygen vacancies has higher activity than pure WO_3 , in which, the highest activity is the catalyst 15-P, approaching to 0.4% AQE equal to natural plant, yielding methanol in a rate of $20.8 \mu\text{mol}/(\text{L h cm}^2)$ and acidic acid at a rate of $4.7 \mu\text{mol}/(\text{L h cm}^2)$. The influence of oxygen vacancies on the reaction is positive and verified by the quenching experiments of H_2O_2 . The more oxidation time, the less oxygen vacancies. The EPR signal of 15-P catalyst treated by 2 h oxidation was reduced to 10%. The catalytic activity of CO_2 reduction was decreased to 50%.

In summary, we designed and prepared a new type of p-doped WO_3 hybrid semiconductor material as efficient catalysts for photoelectrocatalytic reduction of CO_2 , resulting carbon-based chemicals. P-doped WO_3 improves the conduction band position of the semiconductors, increases oxygen vacancies and defect sites. Therefore, the activity and efficiency of catalytic reduction of CO_2 can be improved. The low voltage is favoured to ethanol production, and high voltage is favoured to acid production. The experimental results have guiding significance for the development of new hybrid semiconductor materials and their photoelectrocatalytic reduction of CO_2 .

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