表面改性水热自生长SnO₂碳布电极电化学还原CO₂性能

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摘要 电化学还原CO₂是一种有效的CO₂转化及利用方法,但是由于CO₂在电解质溶液中溶解度较低,限制了其电化学还原性能.为增加电极-溶液-CO₂的三相反应界面,本文通过水热自生长的方法在碳布基底上制备SnO₂纳米片催化剂,利用三甲氧基硅烷修饰电极使其表面具有疏水性,研究了疏水电极与亲水电极的微观形貌和元素价态,对比了疏水电极与亲水电极的表面浸润性、双电层电容、塔菲尔斜率和电化学阻抗,并在不同电位下进行了电化学还原性能测试.实验结果表明,与亲水电极相比,表面改性后的疏水电极具有更低的塔菲尔斜率和传质阻力,表现出更优的电化学还原性能;在-1.8 V(vs. Ag/AgCl)电解电位下,电流密度为(28.0±0.6) mA cm⁻²,法拉第效率为77.2%±1.9%,比亲水电极的法拉第效率提高了14.7%;经12 h的电解测试后仍可维持72.6%的法拉第效率.

关键词 电化学还原, 二氧化碳, SnO₂纳米片, 表面改性, 三相反应界面

自工业革命以来,大量化石能源消耗导致全球CO₂浓度剧增,引发严重的温室效应^[1].为应对全球气候变暖和海平面上升等一系列环境问题,研究者通过生物质固碳^[2]、光催化还原^[3]、热催化还原^[4]、电化学还原^[5]等技术来实现对CO₂的减排和转化利用.其中,电化学还原技术因具有反应条件温和、转化效率高等优势成为研究热点,还可以利用不稳定的能源(如风能、太阳能、潮汐能等)实现CO₂电化学还原,从而制备具有高附加值的化学产物(如甲酸、一氧化碳等),是一种有效的CO₂减排和储能方式^[6].

研究表明, Cu^[7]、Pb^[8]、Ag^[9]、Bi^[10]、Sn^[11]等金属催化剂可以用于电化学还原CO₂,其中, Sn基催化剂因具有储量丰富、成本低廉、无毒无害和高选择性等优点而备受关注. Del Castillo等人^[12]在碳纸上通过喷涂方法制备电极并研究了Sn颗粒大小的影响,发现粒

径为150 nm的Sn颗粒法拉第效率达到70%. Fu等人^[13]采用在碳纸上沉积分层SnO微球颗粒的方法制备电极用于电化学还原CO₂,但法拉第效率仅为62%. Liu等人^[14]通过合成具有丰富量子点及晶界的2 nm SnO₂量子线,发现该催化剂在电化学还原CO₂中具有较好的性能.由于CO₂在水中的溶解度较低,有学者提出采用气体扩散电极强化CO₂气体的传输,增加电极-溶液-CO₂的三相反应界面. Prakash等人^[15]通过对比气体扩散电极和石墨电极负载Sn颗粒发现,气体扩散电极可有效强化CO₂传输、提高催化性能. Wang等人^[16]通过聚四氟乙烯(poly tetra fluoroethylene, PTFE)和炭黑制备气体扩散电极,同时负载Sn纳米颗粒,可实现73.6%的电流效率. Sen等人^[17]在流动式反应器中通过气体扩散电极研究Sn与SnO₂催化剂用于电化学还原CO₂的性能,实现了较高的法拉第效率和电流密度. Lim等人^[18]通过

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在气体扩散电极电化学沉积具有致密尖端的Sn催化剂,得到了62.5%的甲酸法拉第效率,但同时伴有严重的副反应。可见,采用气体扩散电极可强化CO₂的传输,但大多采用改进电极材料的方式来制备新型气体扩散电极,极少通过电极表面改性的方法来增强电极-溶液-CO₂的三相反应界面。研究者通过三甲氧基硅烷修饰Cu基电极来改变电极表面润湿性,发现具有疏水特性的电极可以提高电化学还原CO₂性能,抑制析氢反应^[19-21]。同时,已有研究大多采用碳纸作为气体扩散电极的基底,而碳纸的机械性能较差、容易折断,不利于反应器的放大化。

本文采用水热自生长的方法在碳布上原位生成SnO₂纳米片,通过化学液相沉积利用三甲氧基硅烷修饰电极表面使其具有疏水性,以增加三相反应界面,增强电化学还原CO₂性能。与未经过改性的亲水电极进行电化学性能对比,研究电极表面浸润性对电化学还原CO₂性能的影响。

1 材料与方法

1.1 电极制备与表征

本文采用水热自生长的方法制备SnO₂纳米片电极。首先,将尿素溶于去离子水中,加入盐酸和巯基乙酸,再加入氯化亚锡,充分搅拌形成水热反应前驱体溶液。接着,将碳布(3 cm×3 cm)(北京晶龙特碳有限公司)先后置于适量的丙酮和乙醇中超声清洗30 min,以除去表面杂质和油性物质。随后,用盐酸溶液超声清洗以除去气体杂质。最后,将碳布放入盛有前驱体溶液的反应釜中,在加热箱中加热120℃并维持6 h。待反应结束冷却至室温后,取出电极并用去离子水冲洗3次,在60℃烘箱中干燥后得到自生长SnO₂纳米片电极。

采用化学液相沉积方法对电极表面进行疏水改性处理。将电极置于三甲氧基硅烷与甲醇混合溶液(体积比为1:100)中,并于石墨加热板上在70℃下加热1 h,随后取出自然晾干。将所得的表面改性SnO₂纳米片碳布电极记为SnO₂/CC-HB电极,未改性的SnO₂纳米片碳布电极记为SnO₂/CC-HL电极。

采用场发射扫描电子显微镜(scanning electron microscope, SEM)(日立SU8020, 中科百测)对SnO₂/CC-HB电极和SnO₂/CC-HL电极的微观形貌进行表征,同时结合能谱仪(energy dispersive spectrometer, EDS)技术对两电极的微区成分进行元素分析。采用X-射线电子能

谱(X-ray photoelectron spectroscopy, XPS)(Thermo ECALAB 250Xi, 中科百测)对SnO₂/CC-HB电极和SnO₂/CC-HL电极的主要元素进行价态分析。采用接触角测量仪(XC-CAM, 上海轩轶创析工业设计公司)对SnO₂/CC-HB电极和SnO₂/CC-HL电极的接触角进行测试。采用核磁共振仪(600 MHz固体/液体核磁, 中科百测)对电化学还原CO₂的液相产物进行定性分析,确定产物种类。

1.2 实验方法与计算

本文实验均在H型电解池中采用三电极体系进行,其中所制备的电极作为工作电极,由电极夹固定并置于阴极腔室中,阳极腔室中的铂片(2 cm×2 cm)为对电极,Ag/AgCl电极为参比电极。阴阳两极腔室均有50 mL 0.5 mol/L KHCO₃通CO₂的饱和溶液(pH 7.3),并由磁力搅拌器以300 r min⁻¹搅拌。两腔室由质子交换膜(UltrexCMI-7000, Membranes International Inc. NJ USA)隔开,采用气体质量流量计(CS200, 北京七星华创)控制CO₂流量以25 SCCM(standard cubic centimeter per minute)通入阴极电解液中。采用电化学工作站(PMCP-1000, 普林斯顿)进行电化学测试,电化学阻抗谱(electrochemical impedance spectroscopy, EIS)测试电位为-1.8 V(vs. Ag/AgCl),频率为10 mHz~100 kHz,正弦波振幅为10 mV;恒电位电解测试电位为-1.8 V(vs. Ag/AgCl),电解时间为1 h。反应后的液相产物甲酸由离子色谱仪(Thermo, ICS-5000)测量,气相产物由气相色谱仪(Nexis GC-2030, 日本岛津)测试。

甲酸或气相产物的法拉第效率(Faradaic efficiency, FE)计算如下:

$$FE = \frac{znF}{Q} \times 100\%, \quad (1)$$

其中, z 为电化学还原产物的电子转移数, $n(\text{mol})$ 为产物的摩尔数, F 为法拉第常数(96485 C/mol), $Q(\text{C})$ 为电化学还原反应的电荷库仑数。

2 实验结果与分析

2.1 电极物理表征

采用场发射扫描电子显微镜测试亲水电极与疏水电极的微观形貌,并结合能谱仪对电极表面进行元素面扫描,其结果如图1所示。由SEM图可以看出,采用水热自生长法制备的两种电极,在碳布表面成功附着了

纳米片形状的催化剂, 而经过表面改性后的疏水 $\text{SnO}_2/\text{CC-HB}$ 电极, 纳米片的外围附着了一层疏水物质; EDS图谱显示, 两种电极表面元素均有Sn和O, 而且经过化学液相沉积疏水处理后的 $\text{SnO}_2/\text{CC-HB}$ 电极还含有F元素. 结果表明, 在电极表面沉积了三甲氧基硅烷, FAS修饰后的表面改性只改变了电极表面的浸润性, 而没有破坏电极的结构和催化成分^[20].

$\text{SnO}_2/\text{CC-HB}$ 电极和 $\text{SnO}_2/\text{CC-HL}$ 电极的XPS测试

结果如图2所示. 可以看出, 两种电极在 $\text{Sn } 3d_{5/2}$ (487 eV)和 $\text{Sn } 3d_{3/2}$ (496 eV)出现两个峰, 说明两者Sn的价态相同. 对比文献[22]可以发现, Sn的价态均为 Sn^{4+} , 表明通过水热自生长成功在碳布基底上附着了 SnO_2 纳米片. 此外, 通过测量 $\text{SnO}_2/\text{CC-HB}$ 与 $\text{SnO}_2/\text{CC-HL}$ 电极的接触角(图3), 发现经过表面改性的电极具有疏水性, 其接触角为 148.8° , 而未改性的电极则呈现超亲水状态, 去离子水滴在电极表面便立刻浸入电极内部.

图1 $\text{SnO}_2/\text{CC-HB}$ 电极和 $\text{SnO}_2/\text{CC-HL}$ 电极的SEM和EDS图谱. (a), (c) $\text{SnO}_2/\text{CC-HB}$ 电极; (b), (d) $\text{SnO}_2/\text{CC-HL}$ 电极

Figure 1 SEM and EDS patterns of $\text{SnO}_2/\text{CC-HB}$ electrodes and $\text{SnO}_2/\text{CC-HL}$ electrodes. (a), (c) $\text{SnO}_2/\text{CC-HB}$ electrodes; (b), (d) $\text{SnO}_2/\text{CC-HL}$ electrodes

图2 $\text{SnO}_2/\text{CC-HB}$ 电极与 $\text{SnO}_2/\text{CC-HL}$ 电极的XPS图谱. (a) Sn; (b) F

Figure 2 XPS patterns of $\text{SnO}_2/\text{CC-HB}$ and $\text{SnO}_2/\text{CC-HL}$ electrodes. (a) Sn; (b) F

图3 电极接触角. (a) $\text{SnO}_2/\text{CC-HB}$ 电极; (b) $\text{SnO}_2/\text{CC-HL}$ 电极
Figure 3 Contact angles of $\text{SnO}_2/\text{CC-HB}$ electrode (a) and $\text{SnO}_2/\text{CC-HL}$ electrode (b)

2.2 电极电化学表征

通过双电层电容法对两组电极的电化学活性面积 (electroactive surface area, ESA) 进行表征, 结果如图4(a)所示. 可以看出, $\text{SnO}_2/\text{CC-HB}$ 电极比 $\text{SnO}_2/\text{CC-HL}$ 电极的双电层电容更低, 表明疏水的 $\text{SnO}_2/\text{CC-HB}$ 电极与电解液之间的接触面积小于亲水的 $\text{SnO}_2/\text{CC-HL}$ 电极, 虽然具有更小的电化学活性面积, 但有利于反应物 CO_2 的扩散和传输, 说明经过改性的 $\text{SnO}_2/\text{CC-HB}$ 电极有利于增加电化学反应的三相反应界面^[19].

采用塔菲尔斜率测试 (Tafel curve) 对电化学反应的动力学过程进行分析, 如图4(b)所示. 可以看出, $\text{SnO}_2/\text{CC-HB}$ 电极与 $\text{SnO}_2/\text{CC-HL}$ 电极的塔菲尔斜率分别为152.2和172.7 mV dec^{-1} . 根据文献[23], 当塔菲尔斜率大于120 mV dec^{-1} 时, 电化学还原 CO_2 的速率决定步骤是 CO_2 得到一个电子形成中间体 CO_2^- 的过程, 说明 $\text{SnO}_2/\text{CC-HB}$ 电极与 $\text{SnO}_2/\text{CC-HL}$ 电极的速率决定步骤均为该步骤, 而前者具有更小的塔菲尔斜率正是由于表面改性后电极疏水, 加强了 CO_2 气体向电极的扩散和传输, 使得中间体 CO_2^- 更容易形成, 从而证明 $\text{SnO}_2/\text{CC-HB}$ 电极具有更好的电化学反应动力学性能.

通过对电极进行电化学阻抗测试, 分析电极表面浸润性对传质阻力与传荷阻力的影响, 实验结果如图4(c)中散点所示, 等效电路图中 R_1 、 R_2 、 R_3 分别表示欧姆内阻、传荷内阻和传质内阻, 拟合结果如图4(c)中曲线及表1所示. 可以看出, $\text{SnO}_2/\text{CC-HB}$ 电极的传荷阻力 (10.59 Ω) 略大于 $\text{SnO}_2/\text{CC-HL}$ 的传荷阻力 (9.07 Ω), 这是由于表面的疏水结构影响了电荷的传递. 但同时 $\text{SnO}_2/\text{CC-HB}$ 电极的传质内阻 (3.74 Ω) 小于 $\text{SnO}_2/\text{CC-HL}$ 的传质内阻 (7.34 Ω), 说明 CO_2 更容易扩散至电极表面, 从

而强化反应物传质, 提高电化学还原性能.

2.3 电化学还原 CO_2 性能

对 $\text{SnO}_2/\text{CC-HB}$ 与 $\text{SnO}_2/\text{CC-HL}$ 电极在不同电解电位下 (-1.2~2.0 V vs. Ag/AgCl) 测试电化学还原 CO_2 性能, 电解液为 CO_2 饱和的0.5 mol/L KHCO_3 溶液, 电解时间为1 h. $\text{SnO}_2/\text{CC-HB}$ 与 $\text{SnO}_2/\text{CC-HL}$ 电极在不同电位下的电流密度如图5(a)所示. 可以看出, 两种电极的电流密度均随着电位的负移而增加, 这是由于更负的电位提供了更大的反应驱动力, 而且 $\text{SnO}_2/\text{CC-HB}$ 电极的电流密度略高于 $\text{SnO}_2/\text{CC-HL}$ 电极. $\text{SnO}_2/\text{CC-HB}$ 与 $\text{CC}/\text{SnO}_2\text{-HL}$ 电极在不同电位下的电化学还原 CO_2 产甲酸的法拉第效率如图5(b)所示. 可以看出, 两者均呈现先增加后减小的趋势, 这与Sn基催化剂还原 CO_2 的中间产物 CO_2^- 有关. 在水溶液中, CO_2 得到一个电子形成 CO_2^- 的标准电位为-2.244 V (vs. Ag/AgCl)^[24], 当电解电位过低时, 难以形成中间产物 CO_2^- , 导致甲酸的产量较低; 而当电位过高时, CO_2 还原的副反应析氢反应则更容易发生, 抑制生成甲酸的反应过程. 因此, $\text{SnO}_2/\text{CC-HB}$ 与 $\text{SnO}_2/\text{CC-HL}$ 电极均在-1.8 V (vs. Ag/AgCl) 时达到最大的法拉第效率, 分别为77.2%和62.5%, 此时电流密度分别为 (28.0 ± 0.6) 与 $(25.7 \pm 1.1) \text{ mA cm}^{-2}$. 而且, 在所有电位下, $\text{SnO}_2/\text{CC-HB}$ 电极的电流效率都比 $\text{SnO}_2/\text{CC-HL}$ 电极高, 尤其是在电位较负的时候, 这可能与电极表面的浸润性有关. 电化学还原 CO_2 反应通常被认为是在电极-溶液-反应气体的三相反应界面 (图6) 上发生, 由于经过改性的 $\text{SnO}_2/\text{CC-HB}$ 电极具有疏水性, 强化了 CO_2 向电极表面传输, 使得 $\text{SnO}_2/\text{CC-HB}$ 电极的电流效率高于 $\text{SnO}_2/\text{CC-HL}$ 电极.

图4 SnO₂/CC-HB电极与SnO₂/CC-HL电极的电化学性能. (a) 电化学活性面积; (b) 塔菲尔曲线; (c) 电化学阻抗谱

Figure 4 Electrochemical performance of SnO₂/CC-HB and SnO₂/CC-HL electrodes. (a) ESA; (b) Tafel curves; (c) EIS

2.4 电极电化学还原CO₂产物分析

对SnO₂/CC-HB电极电化学还原CO₂的产物进行定性分析: 通过核磁共振检测分析发现, 其液相产物中只有甲酸, 表明该电极对液相产物具有较高的选择性; 气相色谱检测结果发现, 气相产物仅有H₂和CO, 表明其

表1 等效电路拟合结果

Table 1 Fitting results of the equivalent circuit

电极	$R_1(\Omega)$	$R_2(\Omega)$	$R_3(\Omega)$
SnO ₂ /CC-HB	6.80	10.59	3.74
SnO ₂ /CC-HL	6.76	9.07	7.34

图5 不同电位下SnO₂/CC-HB与SnO₂/CC-HL电极的电化学还原CO₂性能. (a) 电流密度; (b) 法拉第效率

Figure 5 Performance of electrochemical reduction of CO₂ with SnO₂/CC-HB and SnO₂/CC-HL electrodes under different potentials. (a) Current density; (b) Faradaic efficiency

对气体产物也有一定的选择性. 通过计算得到不同电解电位下各产物的法拉第效率, 结果如图7所示. 可以看出, 甲酸的法拉第效率与H₂和CO呈现相反的趋势, 造成这一现象的原因是电位过负时, 副反应开始加剧, 导致H₂和CO的转化量增加. 在电位-1.8 V(vs. Ag/AgCl)时, 甲酸的法拉第效率为77.2%±1.9%, 但同时也有副产物H₂和CO生成, 其法拉第效率分别为10.8%±3.6%和8.2%±2.2%.

与国内外已发表的Sn基催化剂电化学还原CO₂性

图6 SnO₂/CC-HB 电极三相界面示意图
Figure 6 Schematic diagram of three-phase boundary of SnO₂/CC-HB electrode

图7 不同电位下电化学还原CO₂的产物
Figure 7 Products of CO₂ electrochemical reduction at different potentials

能相比(表2), 本文通过水热自生长方法制备并经过化学液相沉积表面改性的SnO₂/CC-HB电极具有良好的甲酸法拉第效率和较高的电流密度。

2.5 SnO₂/CC-HB电极寿命分析

电极寿命是衡量电极性能的重要指标之一。通过长时间电解实验测试SnO₂/CC-HB电极的寿命, 其电流密度曲线如图8所示。经计算, 在12 h连续电解后, SnO₂/CC-HB电极的甲酸法拉第效率仍能维持在72.6%。同时, 通过测量电极反应前后的接触角发现, SnO₂/CC-HB电极仍具有疏水特性, 而接触角的降低可能是由于长时间浸没于电解液中, 电解液的pH和浓度发生变化导致电极的表面浸润性发生改变。同时, 从图9(b)可以

表2 Sn基催化剂的电化学还原CO₂性能对比

Table 2 Performance comparison of Sn-based catalyst for CO₂ electrochemical reduction

阴极催化剂	电解质溶液	甲酸法拉第效率(%)	电流密度(mA cm ⁻²)	文献
Sn	KHCO ₃ + KCl	70	90	[12]
SnO ₂ /GDE	KHCO ₃	63	12	[13]
SnO ₂	KHCO ₃	87.3	13.7	[14]
Sn+Nafion	NaHCO ₃	70	27	[15]
SnO ₂ /GDE	KHCO ₃	73	13.45	[16]
SnDT/Sn/CC	KHCO ₃	62.5	18.7	[18]
SnO ₂ NPs	NaHCO ₃	93.6	10.2	[22]
SnO ₂ /CC-HB	KHCO ₃	77.2	28	本文

图8 SnO₂/CC-HB电极稳定性测试(12 h)及反应前后接触角
Figure 8 Stability test of SnO₂/CC-HB electrode (12 h) and corresponding contact angles

看出, 电极表面微观形貌也发生了变化。此外, 从电极反应前后的SEM图(图9)可以发现, 电极的微观形貌仍以SnO₂纳米片电极为主, 但有少量催化剂团聚现象出现, 其原因可能在于: 一方面来自催化剂自身的老化降解; 另一方面是所处环境的变化, 即电解液pH和溶液浓度变化, 以及生成的CO和H₂气泡的析出和运动对电极的剪切作用。SnO₂/CC-HB电极反应前后的XPS图谱如图10所示, 结果表明, Sn元素的价态无变化, 说明SnO₂在电催化过程中并没有被还原。

3 结论

本文通过水热自生长的方法成功在碳布基底上附着SnO₂纳米片催化剂, 通过化学液相沉积的方法修饰

图9 $\text{SnO}_2/\text{CC-HB}$ 电极反应前后的SEM图。(a) 反应前;(b) 反应12 h后

Figure 9 SEM pictures of $\text{SnO}_2/\text{CC-HB}$ electrode before and after reaction. (a) Original SEM; (b) SEM after 12 hours of reaction

图10 $\text{SnO}_2/\text{CC-HB}$ 电极反应前后的XPS图

Figure 10 XPS patterns of $\text{SnO}_2/\text{CC-HB}$ electrode before and after reaction

电极表面的浸润性, 并与未经处理的亲水电极进行对比。通过分析电化学活性面积、塔菲尔斜率和电化学阻抗, 发现 $\text{SnO}_2/\text{CC-HB}$ 电极具有更好的电催化性能。在不同电位下对 $\text{SnO}_2/\text{CC-HB}$ 电极和 $\text{SnO}_2/\text{CC-HL}$ 电极进行电化学还原 CO_2 性能测试, 发现电位对两者的影响呈现类似的变化趋势, 在电位 -1.8 V (vs. Ag/AgCl)时达到最大的甲酸法拉第效率, 分别为77.2%和62.5%, 且在所有电位下 $\text{SnO}_2/\text{CC-HB}$ 电极的法拉第效率均优于 $\text{SnO}_2/\text{CC-HL}$ 电极。通过稳定性测试发现, 经12 h的电解, $\text{SnO}_2/\text{CC-HB}$ 电极的甲酸法拉第效率仍能维持在72.6%。总之, 经过表面改性的疏水电极强化了 CO_2 的传质, 增加了电化学反应的三相反应界面, 有效提高了电化学还原 CO_2 性能。

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Summary for “表面改性水热自生长SnO₂碳布电极电化学还原CO₂性能”

Performance of CO₂ electrochemical reduction with surface modified self-growing SnO₂ on carbon cloth electrode prepared by hydrothermal method

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Over the past 100 years, the consumption of a large amount of fossil energy has led to an increase in CO₂ in the atmosphere, triggering a serious greenhouse effect. In response to the energy crisis and global climate change, some strategies have been proposed to reduce CO₂ emissions and convert CO₂, such as biotransformation, photochemical process, thermochemical and electrochemical reduction. Among these technologies, electrocatalytic reduction of CO₂ is an effective method for the conversion and utilization of CO₂ and mitigation of greenhouse effect. Sn-based catalysts are widely used in electrocatalytic reduction of CO₂ due to its non-toxicity, abundant reserves, low cost and high selectivity. However, the low solubility of CO₂ in electrolyte solution (only 0.33 mol/L at room temperature and ordinary pressure) limits the electrochemical reduction performance.

Herein, the SnO₂ nanosheet catalyst was prepared on the carbon cloth substrate by hydrothermal self-growing method. Then, trimethoxysilane was used to modify the wettability of the electrode surface to make it hydrophobic, increasing the contact surface of the electrode-solution-CO₂ three-phase reaction. The surface modified electrode was denoted as SnO₂/CC-HB and the unmodified one was SnO₂/CC-HL.

The micromorphology and element valence states of hydrophobic and hydrophilic electrodes were studied by physical characterization. The results show that SnO₂ nanosheets grow successfully on the carbon cloth for both SnO₂/CC-HB and SnO₂/CC-HL electrodes. By measuring the contact angle, it is found that SnO₂/CC-HB electrode shows hydrophobicity while SnO₂/CC-HL electrode is completely hydrophilic. The electrochemical reduction performance of SnO₂/CC-HB and SnO₂/CC-HL electrodes, including electrochemical active surface area, Tafel slope and electrochemical impedance were measured in an H-cell with three-electrode system. The electrolyte was 0.5 mol/L potassium bicarbonate CO₂ saturated solution (pH 7.3). The results show that although the electrochemical activity of SnO₂/CC-HB electrode is lower than that of SnO₂/CC-HL electrode, the CO₂ transfer and the three-phase reaction interface are increased because of the hydrophobicity. The Tafel slope of both electrodes is greater than 120 mV/dec, indicating that the restricted process of the electrochemical reduction of CO₂ reaction is the process of CO₂ gaining electrons. Moreover, the Tafel slope of SnO₂/CC-HB electrode is smaller, indicating that SnO₂/CC-HB electrode has a better reaction kinetics. In addition, although the charge transfer resistance of SnO₂/CC-HB electrode is higher, the mass transfer resistance is lower, suggesting enhanced mass transfer for SnO₂/CC-HB electrode.

Compared with SnO₂/CC-HL electrode, SnO₂/CC-HB electrode exhibits a better electrochemical reduction performance. The current density is (28.0±0.6) mA cm⁻² and Faradaic efficiency is 77.2%±1.9% at -1.8 V (vs. Ag/AgCl) electrolytic potential, which is 14.7% higher than that of SnO₂/CC-HL electrode. After 12 hours of electrochemical reaction, the SnO₂/CC-HB electrode still shows good hydrophobicity, and the Faradaic efficiency remains 72.6%, which proves that the electrode has a good durability. In summary, tuning the wettability of the electrode can improve the mass transfer of CO₂ and effectively enhance the performance of CO₂ electrochemical reduction.

electrochemical reduction, carbon dioxide, SnO₂ nanosheets, surface modification, three-phase reaction interface

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