

染料敏化太阳能电池  $\text{SnO}_2$  光阳极研究进展

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**摘 要:** 染料敏化太阳能电池(DSSCs)由于其成本低、原材料丰富、光电转化效率高等优点, 成为新能源开发利用领域研究的热点。光阳极是 DSSC 的重要组成部分, 对提高 DSSC 的光电转化效率具有重要意义。基于此, 首先介绍了  $\text{SnO}_2$  DSSC 的工作原理, 并分析了效率的影响因素, 接着重点讨论了  $\text{SnO}_2$  光阳极的结构设计, 在此基础上阐述了光阳极改进(表面包覆或复合、元素掺杂)的研究现状, 最后总结规律并对未来的发展趋势和前景进行展望。

**关键词:** 染料敏化太阳能电池; 光阳极; 二氧化锡

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太阳能电池因能直接将光能转化为电能, 可有效解决能源与环境方面的诸多问题而备受关注。当前, 硅基太阳能电池的光电转化效率虽已高达 25%, 但对原料硅的纯度要求苛刻, 且生产成本相对较高。自 1991 年 O'regan 等<sup>[1]</sup>报道了光电转化效率为 7.1% 的染料敏化  $\text{TiO}_2$  纳米太阳能电池以来, 该类型电池因制造成本低、制作工艺较简单、光电转化效率高等优点<sup>[2]</sup>, 引起众多国内外化学工作者的极大兴趣, 成为近年来研究的热点。通常情况下, 电池为取得高的光电转化效率应具备足够的染料吸附量、较快的电荷传输速率、在电解液中离子的快速扩散以及有效的还原对电极反应介质的特点。目前, 基于  $\text{TiO}_2$  的染料敏化太阳能电池(DSSC)的光电转化效率已达到 13%<sup>[3]</sup>, 但  $\text{TiO}_2$  存在电子扩散慢、电子迁移率小等缺点<sup>[4]</sup>, 并且  $\text{TiO}_2$  颗粒之间存在大量的晶体缺陷, 导致出现大量载流子在各个界面进行不同程度复合的现象, 极大阻碍了其光电转化效率的进一步提高。与  $\text{TiO}_2$  相比,  $\text{SnO}_2$  拥有 2 个突出的优点: 1)  $\text{SnO}_2$  具有较大的电子迁移率(约为  $125 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ), 明显高于  $\text{TiO}_2$  (小于  $1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ )<sup>[5]</sup>, 电荷传输过程中的复合损失大大降低; 2) 由于  $\text{SnO}_2$  具有更大的禁带宽度(3.5 eV)<sup>[6]</sup>, 氧化空穴的数量相

对较少, 因而 DSSC 的光稳定性大大提高。但是,  $\text{SnO}_2$  染料敏化电池仍面临 2 个主要的挑战: 1) 较低的开路电压( $V_{\text{oc}}$ ), 相比于  $\text{TiO}_2$ ,  $\text{SnO}_2$  的导带边缘正向位移高达 300 mV, 导致导带电位和电解液的氧化还原电位的差值降低, 此外  $\text{SnO}_2$  导带的正位移还会加速表面电子复合<sup>[7]</sup>, 导致较低的开路电压值; 2) 较低的电流密度,  $\text{SnO}_2$  的等电子点(pH=4~5)较小<sup>[8]</sup>, 降低了  $\text{SnO}_2$  与酸性光敏染料之间的结合力, 致使染料吸附量下降, 因而从源头上限制了电流密度的提升。如何克服上述 2 个问题成为进一步提高  $\text{SnO}_2$  光电转化效率的重要突破点。本文首先对  $\text{SnO}_2$  基 DSSC 的结构、工作原理及光电转化效率影响因素进行分析, 在此基础上重点介绍了  $\text{SnO}_2$  光阳极的设计及修饰方法, 最后总结并提出展望。

1  $\text{SnO}_2$  基 DSSC 的结构与工作原理

基于  $\text{SnO}_2$  的 DSSC 具有与  $\text{TiO}_2$  基 DSSC 相同的结构<sup>[9]</sup>, 由金属氧化物光阳极、染料敏化剂、氧化还原电解质(通常为  $\text{I}^-/\text{I}_3^-$ )以及铂对电极构成(图 1)。

$\text{SnO}_2$  染料敏化太阳能电池电荷传输也与  $\text{TiO}_2$  基 DSSC 几乎完全相同, 可分为如下 7 个过程<sup>[10]</sup>, 如图 2 所示:

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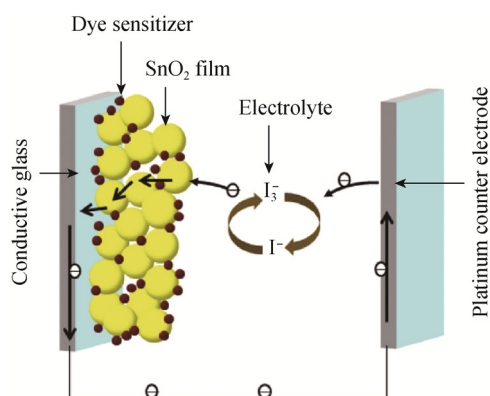
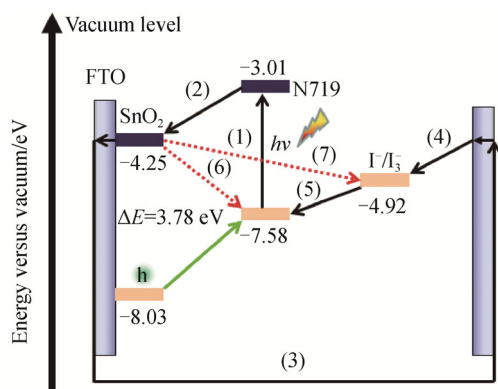
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图 1 SnO<sub>2</sub> 基 DSSC 结构示意图<sup>[9]</sup>Fig. 1 Schematic diagram of SnO<sub>2</sub>-based DSSC<sup>[9]</sup>图 2 SnO<sub>2</sub> 基 DSSC 工作原理图<sup>[10]</sup>Fig. 2 Principle of the SnO<sub>2</sub>-based DSSC<sup>[10]</sup>

1) 染料分子(S)被激发, 由基态转变为激发态(S\*);

2) 激发态染料分子将电子注入至 SnO<sub>2</sub> 导带, 形成氧化态染料(S<sup>+</sup>);

3) SnO<sub>2</sub> 导带中的电子经薄膜流入外电路;

4) 到达对电极的电子与扩散到对电极的 I<sub>3</sub><sup>-</sup> 复合, 生成 I<sup>-</sup>;

5) I<sup>-</sup> 与氧化态染料(S<sup>+</sup>)反应转化为 I<sub>3</sub><sup>-</sup>;

6) 导带中的电子与氧化态染料电荷复合, 与过程 5) 中染料的再生存在竞争(S<sup>+</sup>+e<sup>-</sup>→S);

7) SnO<sub>2</sub> 导带中的电子与电解液中 I<sub>3</sub><sup>-</sup> 发生复合反应形成 I<sup>-</sup>, 即 I<sub>3</sub><sup>-</sup>+2e<sup>-</sup>→3I<sup>-</sup>;

以上 7 个过程为电子在电池中的传输过程。

## 2 光电转化效率影响因素

器件的光电转化效率值( $\eta$ )可通过式(1)估算<sup>[11]</sup>:

$$\eta = \frac{J_{SC} V_{OC} F}{P_{in}} \quad (1)$$

其中:  $J_{SC}$  为短路电流密度(mA·cm<sup>-2</sup>);  $V_{OC}$  为开路电压(V);  $F$  为填充因子;  $P_{in}$  为入射光功率(W)。

$J_{SC}$ 、 $V_{OC}$  和  $F$  是影响 DSSC 的重要参数, 因此

提高三者的数值对提升 SnO<sub>2</sub> 基 DSSC 的光利用效率尤为重要。

$J_{SC}$  取决于电子电荷( $q$ )、入射光吸收效率( $\eta_{lh}$ )、电荷注入效率( $\eta_{inj}$ )、电荷收集效率( $\eta_{cc}$ )以及入射光强度( $I_0$ ), 通过用式(2)<sup>[11]</sup>表示:

$$J_{SC} = q \times \eta_{lh} \times \eta_{inj} \times \eta_{cc} \times I_0 \quad (2)$$

一般认为同一类染料敏化电池的  $\eta_{inj}$  是相同的;  $\eta_{lh}$  主要跟染料吸附量和光散射能力有关, 染料吸附量的增加或光散射能力的增强能有效提升  $J_{SC}$ ;  $\eta_{cc}$  则取决于所制备光阳极膜中电荷的传输性能。总之, 更高的  $J_{SC}$  依赖于更高的光散射能力、更大的染料吸附量、更快的电荷传输速度和更低的电荷再复合能力。为提高薄膜的染料吸附量, 通常要对纳米半导体氧化物的表面状态、薄膜厚度、比表面积和孔隙率等进行优化。纳米颗粒越小, 比表面积越大, 吸附的染料则越多, 但当颗粒孔隙的直径小于染料分子时则会阻碍染料分子的进入。纳米颗粒尺寸不仅影响染料的吸附, 而且也影响着光散射能力。尽管增大颗粒直径会使薄膜对光的散射增强, 但同时也会降低比表面积, 导致染料吸附量的降低, 因此需要对纳米颗粒的尺寸进行合理优化。同时, 颗粒过小、孔隙过大以及膜过厚等则会降低电子在膜内的传输速率, 电子复合的概率增大, 最终影响电池的光电转化效率。

电池  $V_{OC}$  主要受半导体氧化物性质和电解液组成的影响<sup>[12]</sup>,  $V_{OC} = |V_{fb} - V_{red}|$ , 所以  $V_{OC}$  值主要取决于半导体电极的平带电位( $V_{fb}$ )和电解液氧化还原电位( $V_{red}$ )相对大小。此外, 电荷缺陷密度也会影响导带电子的寿命, 电荷寿命或再复合时间的增加对提高  $V_{OC}$  有利<sup>[13-15]</sup>。除了半导体氧化物自身能级结构的差异外, 薄膜厚度、颗粒大小、表面处理以及掺杂等都会在不同程度上影响着半导体氧化物的能级结构, 其中薄膜厚度的增加会使半导体氧化物的平带电位正向移动, 对应半导体氧化物与电解液界面的电子转移电阻减小, 使半导体氧化物导带中的电子与电解液中 I<sub>3</sub><sup>-</sup> 更易复合, 最终导致染料敏化电池的  $V_{OC}$  降低。由于 SnO<sub>2</sub> 具有较低的导带能级, 因而 SnO<sub>2</sub> 基 DSSC 的  $V_{OC}$  通常较低。

$F$  的影响因素较为复杂, 其大小主要受电解质种类和电池系统阻抗的影响。较低的  $F$  反映了电池内部存在较高的界面内阻和严重的电子复合问题。目前, SnO<sub>2</sub> 染料敏化电池的  $F$  普遍较低, 如何优化  $F$  还需进一步研究。

### 3 $\text{SnO}_2$ 光阳极设计

由于  $\text{SnO}_2$  拥有较低的导带能级和较低的染料吸附量, 导致电池性能较差。通过对  $\text{SnO}_2$  微观形貌、结构进行合理设计, 能够有效提升其光电转化效率, 因而  $\text{SnO}_2$  光阳极材料的结构设计成为近年研究的重点。 $\text{SnO}_2$  纳米颗粒由于具有较大的比表面积且尺寸易于控制而受到研究者的极大关注, 研究者通过对合成条件加以改变从而合成尺寸不一的  $\text{SnO}_2$  纳米颗粒。Puspitasari 等<sup>[16]</sup>利用沉淀法合成  $\text{SnO}_2$  纳米颗粒, 其光电转化效率为 0.022%。Saeidi 等<sup>[17]</sup>采用溶胶-凝胶法制备了  $\text{SnO}_2$  纳米颗粒, 染料敏化电池的性能测试结果显示其光电转化效率达到了 1.43%。Ashok 等<sup>[18]</sup>采用一步热解法合成了  $\text{SnO}_2$  纳米颗粒, 其光电转化效率达到了 5.2%。Souza 等<sup>[19]</sup>利用电泳沉积法对由  $\text{SnO}_2$  纳米颗粒构成的光阳极薄膜的中颗粒的大小和孔径大小进行调控, 实现性能的优化, 最高光电转化效率达到 3.89%。Cojocar 等<sup>[20]</sup>合成的  $\text{SnO}_2$  纳米颗粒取得 3.11% 的较高的光电转化效率, 其原因是非常高的比表面积吸附了大量染料, 但经  $\text{TiCl}_4$  处理后其比表面积大幅下降而导致染料吸附量并无增加甚至下降些许, 其原因是水解产生的  $\text{TiO}_2$  堵塞了  $\text{SnO}_2$  的孔洞, 导致孔隙率下降, 最终使折射率和染料吸附同时降低。单纯  $\text{SnO}_2$  纳米颗粒无法突破其开路电压限制, 光电转化效率很难进一步突破。研究发现  $\text{SnO}_2$  纳米颗粒的光电转化效率一直不理想, 这主要是因为  $\text{SnO}_2$  纳米颗粒的光散射能力较差且电子再复合强, 电子再复合抑制了电子传输并减少电荷寿命, 而且纳米颗粒之间相互接触比较差, 再次使得电荷传输性能减弱和再复合损失增高<sup>[21–26]</sup>, 致使光电转化效率处于较低水平(图 3)。相比之下  $\text{TiO}_2$  纳米颗粒能够取得高光电转化效率<sup>[27–30]</sup>, 其主要原因是  $\text{TiO}_2$  本身的电荷传输性能较弱, 形貌对其传输性能影响较小。

为了克服  $\text{SnO}_2$  纳米颗粒的缺点, 研究者们通过使用一维纳米结构(纳米管、纳米线、纳米棒)来改善纳米颗粒较差的  $\eta_{\text{cc}}$ 。由于一维结构具有高纵横比, 能够引导电子传输和提高电荷寿命与扩散长度(图 3), 较大尺寸一维结构有助于利用光散射效应增强光染料分子的吸收。

Huo 等<sup>[31]</sup>制备了  $\text{SnO}_2$  纳米棒, 实验结果证明其比传统纳米颗粒的电子收集效率更高。Gao 等<sup>[32]</sup>也成功制备了  $\text{SnO}_2$  纳米管, 也在一定程度上提高了电池的光电转化效率。Smok 等<sup>[33]</sup>采用溶胶-凝胶

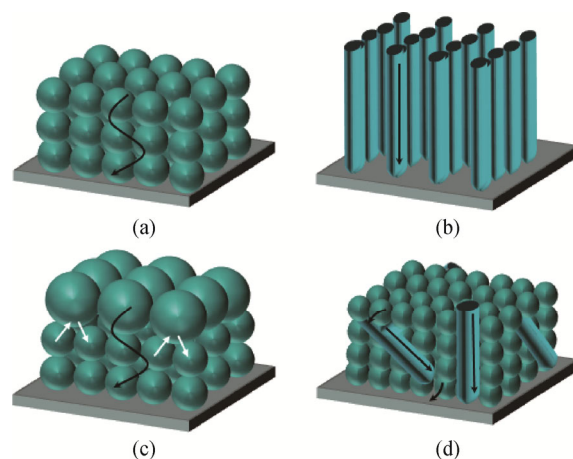


图3 电荷不同形貌电极材料中的传输路径: (a)纳米颗粒, (b)一维结构, (c)外加薄膜层的纳米颗粒和(d)纳米颗粒混合纳米棒<sup>[26]</sup>

Fig. 3 Transmission paths of the charge in different  $\text{SnO}_2$  nanostructures: (a) Nanoparticles, (b) one dimensional structure, (c) nanoparticles with thin film layer, and (d) nanoparticles with nanorods<sup>[26]</sup>

和静电纺丝混合方法制备了  $\text{SnO}_2$  纳米线, 进一步证明了纳米线结构更有利于电子传输。但是, 一维结构还存在比表面积相对较小的问题, 限制了染料吸附。当  $\text{SnO}_2$  尺寸过大而导致染料吸附量极少时, 尽管其电荷传输性能十分突出, 但光吸收能力太差, 光电转化效率依旧很低, 此时需要平衡电荷传输与比表面积之间的关系。Wang 等的研究也充分证实了此点<sup>[34]</sup>。为解决比表面积小的问题, Ashok 等<sup>[35]</sup>利用多孔结构来增加  $\text{SnO}_2$  纤维的比表面积, 其  $J_{\text{sc}}$  与  $V_{\text{oc}}$  分别达到  $5.13 \text{ mA} \cdot \text{cm}^{-2}$  与  $0.59 \text{ V}$ , 使得其光电转化效率达到 2%, 多孔  $\text{SnO}_2$  拥有较高的比表面积, 这主要是因为多孔  $\text{SnO}_2$  的内部具有较多的孔道结构。

关于  $\text{SnO}_2$  电荷传输性能, Teh 等<sup>[36]</sup>对多孔网状连接的  $\text{SnO}_2$  纳米片进行研究, 进一步证实了电荷传输路径及结构相互接触的重要性。与一维结构不同的是, 二维纳米片更容易观察其网状连接状况。Xu 等<sup>[37]</sup>对纳米颗粒、单晶纳米片以及多孔纳米片进行研究, 单晶纳米片光电转化效率(0.24%)远低于纳米颗粒(0.414%), 而多孔纳米片光电转化效率却达到 0.562%, 证实主要原因在于网状连接提供了有利的传输路径并抑制再复合而非单晶纳米片结构影响。

一维结构能够快速地收集电子, 但大多一维结构的薄膜不足以吸收大量的染料, 科研工作者开始寻找不仅能负载足够染料, 又能快速收集电子, 同时又能够有效的散射可见光的材料和方法。三维结构通过亚微米聚合物组成来增加光散射能力, 由此

提高  $\eta_{\text{cc}}$ 。尽管其较大尺寸使  $\text{SnO}_2$  具有较小的比表面积,但相比一维结构,三维结构也能使比表面积得到一定的增加。Kumar 等<sup>[38]</sup>利用电纺丝技术,通过调节前驱体溶液的浓度分别合成花状和纤维结构的纳米  $\text{SnO}_2$ (图 4),虽然这 2 种结构的尺寸相当,但由于聚合物的渗透作用,花状  $\text{SnO}_2$  具有更大的 Brunauer-Emmett-Teller (BET) 表面积( $40 \text{ m}^2 \cdot \text{g}^{-1}$ )。

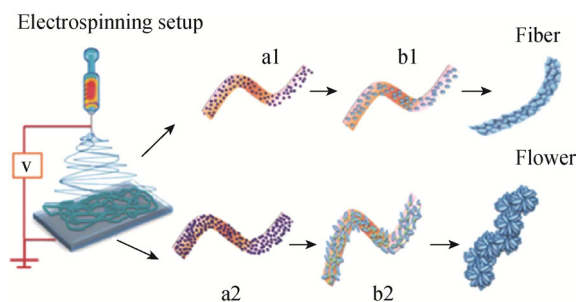


图 4 前驱体溶液浓度对电纺无机纤维结构的影响示意图<sup>[38]</sup>  
Fig. 4 Schematics showing the evolution of fiber morphology with different precursor concentrations<sup>[38]</sup>

DSSC 性能分析结果显示,花状  $\text{SnO}_2$  的电流密度 ( $\sim 7.30 \text{ mA} \cdot \text{cm}^{-2}$ ) 明显高于纤维状  $\text{SnO}_2$  ( $\sim 3.0 \text{ mA} \cdot \text{cm}^{-2}$ )。考虑到这 2 种  $\text{SnO}_2$  结构的平带电位基本相同,更高的染料吸附量( $7.8 \text{ mmol}$ )和电荷收集效率是导致花状  $\text{SnO}_2$  电流密度显著增加的主要原因。此外,花状  $\text{SnO}_2$  拥有另一个显著的优点,即拥有迄今为止已报道纯  $\text{SnO}_2$  最高的  $V_{\text{oc}}$  ( $\sim 700 \text{ mV}$ ),这主要是因为花状  $\text{SnO}_2$  具有较高的内部阻力( $R_{\text{H}} \approx 1600 \Omega$ ),从而有效地抑制电子由  $\text{SnO}_2$  向电解液的回流。相比 Ashok 等<sup>[35]</sup>合成的纳米纤维, Kumar 等<sup>[38]</sup>合成的纳米纤维拥有较长的尺寸,使电荷寿命和再复合时间增加,是其具有较大的  $V_{\text{oc}}$  的重要原因。

由于  $\text{SnO}_2$  结构对光电性能影响至关重要,而且  $\text{SnO}_2$  形貌既具有多样性又易于控制,使得工作者们对  $\text{SnO}_2$  形貌的控制进一步成为研究焦点。Birkel 等<sup>[39]</sup>通过控制沉淀剂的种类合成多种形貌的  $\text{SnO}_2$ (如图 5)。

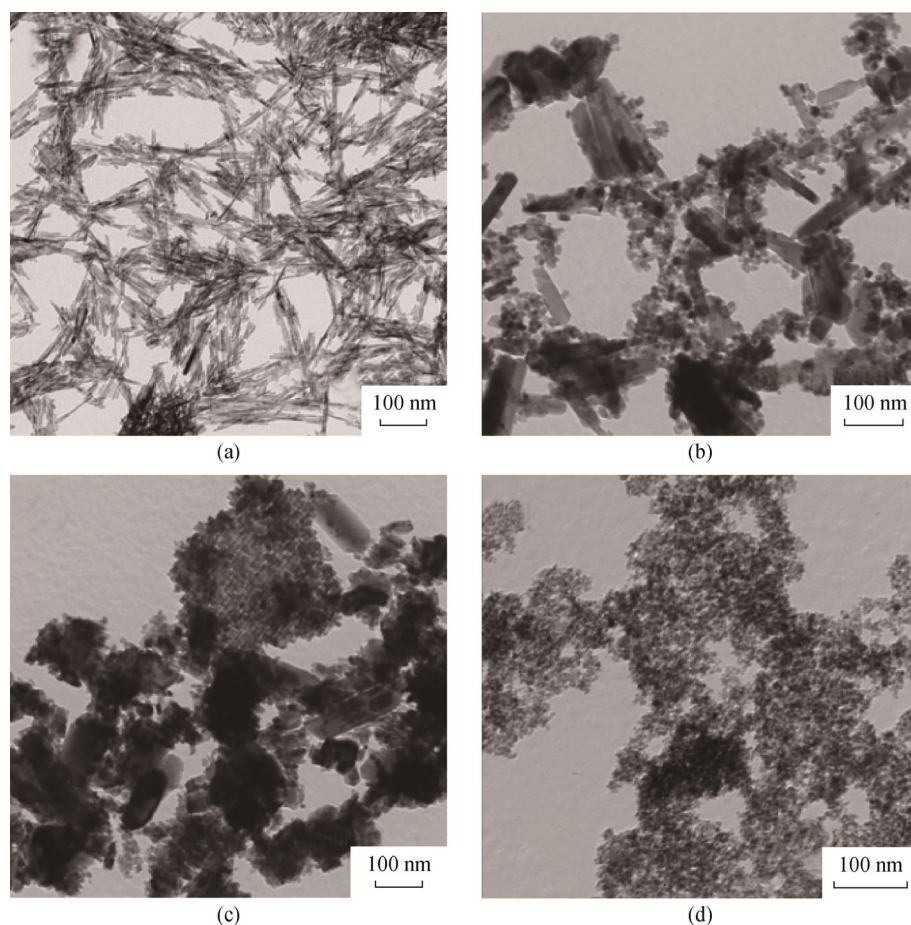


图 5 基于不同沉淀剂获得的  $\text{SnO}_2$  形貌照片: (a) NaOH, (b) KOH, (c) TMAH 以及 (d)  $\text{NH}_4\text{OH}$ <sup>[39]</sup>

Fig. 5 TEM micrographs of as-prepared  $\text{SnO}_2$  particles obtained with different precipitant: (a) NaOH, (b) KOH, (c) TMAH and (d)  $\text{NH}_4\text{OH}$ <sup>[39]</sup>

由图 5 可以明显观察到, 沉淀剂的种类对  $\text{SnO}_2$  形貌具有重要影响, 在各种结构中, 纳米棒状  $\text{SnO}_2$  拥有较高的  $V_{\text{OC}}$ , 随着棒状结构的不断弱化, 相应的  $V_{\text{OC}}$  值不断降低。除开路电压外, 电流密度也受沉淀剂种类的影响, 随着  $\text{SnO}_2$  微

观形貌的变化而变化。以上相关研究更进一步证实了  $\text{SnO}_2$  形貌对 DSSC 的影响是不可忽视的, 通过调控  $\text{SnO}_2$  形貌可以分别实现对开路电压、短路电流的优化提升, 从而有效改善电池的光电转化效率(表 1)。

表 1 基于  $\text{SnO}_2$  单一及复合结构染料敏化太阳能电池性能参数  
Table 1 Parameters of the DSSCs based on single  $\text{SnO}_2$  and  $\text{SnO}_2$  composite

| Morphologies                | $V_{\text{OC}}/\text{mV}$ | $J_{\text{SC}}/(\text{mA}\cdot\text{cm}^{-2})$ | $F/\%$ | $\eta/\%$ | Samples                                          |
|-----------------------------|---------------------------|------------------------------------------------|--------|-----------|--------------------------------------------------|
| Zero-dimensional structure  | 555                       | 5.05                                           | 51.00  | 1.43      | $\text{SnO}_2$ NPs <sup>[17]</sup>               |
|                             | 655                       | 19.60                                          | 48.90  | 5.20      | $\text{SnO}_2$ NPs <sup>[18]</sup>               |
|                             | 640                       | 14.27                                          | 42.30  | 3.89      | $\text{SnO}_2$ NCs <sup>[19]</sup>               |
|                             | 503                       | 9.87                                           | 63.70  | 3.16      | $\text{SnO}_2$ NCs <sup>[39]</sup>               |
|                             | 516                       | 2.38                                           | 40.50  | 0.50      | $\text{SnO}_2$ NPs <sup>[45]</sup>               |
|                             | 320                       | 7.37                                           | 41.00  | 1.00      | $\text{SnO}_2$ NCs <sup>[71]</sup>               |
|                             | 450                       | 5.83                                           | 56.00  | 1.48      | $\text{SnO}_2$ NPs <sup>[87]</sup>               |
|                             | 590                       | 7.00                                           | 34.40  | 1.42      | $\text{SnO}_2$ NPs <sup>[94]</sup>               |
|                             | 417                       | 7.01                                           | 37.00  | 1.10      | Meso- $\text{SnO}_2$ <sup>[97]</sup>             |
|                             | 290                       | 2.40                                           | 40.00  | 0.28      | $\text{SnO}_2$ NS <sup>[111]</sup>               |
| One-dimensional structure   | 660                       | 3.95                                           | 60.00  | 1.08      | $\text{SnO}_2$ NRs <sup>[31]</sup>               |
|                             | 930                       | 17.90                                          | 68.00  | 10.00     | $\text{SnO}_2$ nanotube <sup>[32]</sup>          |
|                             | 596                       | 5.19                                           | 64.00  | 2.00      | $\text{SnO}_2$ PNFs <sup>[35]</sup>              |
|                             | 600                       | 3.00                                           | 38.30  | 0.71      | $\text{SnO}_2$ NF <sup>[38]</sup>                |
|                             | 490                       | 7.99                                           | 27.00  | 1.06      | $\text{SnO}_2$ NTs <sup>[40]</sup>               |
|                             | 325                       | 9.49                                           | 52.90  | 1.77      | $\text{SnO}_2(\text{s})$ NRs <sup>[41]</sup>     |
|                             | 560                       | 6.72                                           | 34.19  | 1.29      | $\text{SnO}_2$ nanochannel <sup>[98]</sup>       |
|                             | 650                       | 14.00                                          | 61.00  | 5.60      | $\text{SnO}_2$ NTs <sup>[102]</sup>              |
| Two-dimensional structure   | 320                       | 5.17                                           | 39.89  | 0.62      | $\text{SnO}_2$ nanoflakes <sup>[110]</sup>       |
|                             | 300                       | 2.60                                           | 30.00  | 0.23      | $\text{SnO}_2$ Nanosheets <sup>[112]</sup>       |
| Three-dimensional structure | 560                       | 6.85                                           | 43.20  | 1.66      | Nanoporous $\text{SnO}_2$ <sup>[36]</sup>        |
|                             | 700                       | 7.30                                           | 59.60  | 3.00      | $\text{SnO}_2$ nanoflowers <sup>[38]</sup>       |
|                             | 430                       | 4.36                                           | 59.29  | 1.11      | $\text{SnO}_2$ nanoflowers <sup>[42]</sup>       |
|                             | 495                       | 8.50                                           | 35.90  | 1.51      | $\text{SnO}_2$ HNSs <sup>[54]</sup>              |
|                             | 567                       | 10.10                                          | 43.80  | 3.18      | $\text{SnO}_2$ spheres <sup>[55]</sup>           |
|                             | 692                       | 9.38                                           | 65.00  | 4.21      | $\text{SnO}_2$ microsphere <sup>[56]</sup>       |
|                             | 330                       | 4.20                                           | 31.00  | 0.42      | $\text{SnO}_2$ Sphericals <sup>[57]</sup>        |
|                             | 520                       | 3.60                                           | 56.00  | 1.04      | Coral-like porous $\text{SnO}_2$ <sup>[57]</sup> |
|                             | 383                       | 10.80                                          | 45.70  | 1.88      | $\text{SnO}_2$ MS <sup>[76]</sup>                |
|                             | 440                       | 5.44                                           | 43.48  | 1.05      | $\text{SnO}_2$ nanoflowers <sup>[78]</sup>       |
| Composite structure         | 380                       | 7.62                                           | 49.60  | 1.43      | Urchin-like $\text{SnO}_2$ <sup>[86]</sup>       |
|                             | 626                       | 18.60                                          | 44.30  | 5.16      | $\text{SnO}_2$ NP-NFs <sup>[44]</sup>            |
|                             | 525                       | 9.90                                           | 48.70  | 2.53      | $\text{SnO}_2$ NW-NPs <sup>[45]</sup>            |
|                             | 573                       | 9.66                                           | 62.50  | 3.46      | $\text{SnO}_2$ NP-SMS <sup>[46]</sup>            |
|                             | 509                       | 16.10                                          | 46.60  | 3.83      | $\text{SnO}_2$ NP/spheres <sup>[55]</sup>        |

NPs: Nanoparticles; NCs: Nanoclusters; NRs: Nanorod; SMS: reflector;  $V_{\text{OC}}$ : Open-circuit voltage;  $J_{\text{SC}}$ : Short-circuit current density;  $F$ : Filling factor;  $\eta$ : Photoelectric conversion efficiency.

此外, Desai 等<sup>[40]</sup>利用  $\text{ZnO}$  纳米线作为模板, 通过液相转换过程形成垂直对齐的  $\text{SnO}_2$  纳米管阵列, 光电转化效率达到 1.06%。Rui 等<sup>[41]</sup>在水和有相中利用热溶剂法合成长度可调的纳米棒  $\text{SnO}_2$ , 其光电转化效率达到 1.78%。Arote 等<sup>[42]</sup>采用水热法合成  $\text{SnO}_2$  纳米花结构, 最高光电转化效率达到 1.11%。Banik 等<sup>[43]</sup>利用 1 个简单的方法合成的球状  $\text{SnO}_2$ , 但其光电转化效率仅有 1.15%。

随着研究不断深入, 科研工作者采用复杂分层的  $\text{SnO}_2$  结构或者通过纳米颗粒聚合生长机制形成复杂形貌, 利用 2 种或多种结构复合, 从而获得 2 种结构的优点或弥补 1 种结构的缺点, 进而对电池性能进行优化。

Wang 等<sup>[44]</sup>合成纳米颗粒后与  $\text{SnO}_2$  纳米片结合, 使  $J_{\text{SC}}$  和  $V_{\text{OC}}$  得到一定提升, 光电转化效率高达 5.16%。Krishnamoorthy 等<sup>[45]</sup>研究与之类似, 利用  $\text{SnO}_2$  纳米线作为薄膜主体, 表面存在纳米颗粒层, 电流增大为纳米颗粒的 4 倍之多, 突显纳米线电荷传输性能的优越性。Peng 等<sup>[46]</sup>利用热溶剂法合成具有暴露面的  $\text{SnO}_2$  并添加一层薄膜反射层, 使光电转化效率达到 3.46%, 但其染料吸附量( $8.03 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2}$ )较为普通, 原因是染料浓度低于  $0.5 \text{ mmol} \cdot \text{L}^{-1}$  和比表面积相对较小, 但较高的  $F$  是需要注意的, 利用  $\text{TiCl}_4$  处理或修饰后或许会取得不错的效果。采用以上措施, 能够有效增强其光吸收和散射能力<sup>[47-51]</sup>, 并在一定程度上抑制电荷再复合, 减少电荷损失, 提高  $\eta_{\text{cc}}$ (图 3), 然而颗粒尺寸过大会导致染料吸附量大幅下降。因此优化薄膜颗粒尺寸显得尤为重要, Wang 等<sup>[52]</sup>合成表面被纳米晶体包覆的中空微球  $\text{SnO}_2$ , 性能得到一定优化。Cheng 等<sup>[53]</sup>将合成的  $\text{SnO}_2$  空心微球与 P25 颗粒(平均粒径为 25 nm 的锐钛矿晶和金红石晶混合相的  $\text{TiO}_2$ )复合, 由于增强的散射性能等原因, 其光电转化效率达到 6.77%。Chen 等<sup>[54]</sup>在无表面活性剂和模板的溶液中通过纳米颗粒聚合形成中空微球  $\text{SnO}_2$ , 区别于普通纳米颗粒, 该结构纳米颗粒之间具有紧密的接触, 其连接状态有利于电荷传输且光电转化效率达到 1.51%。Zhang 等<sup>[55]</sup>采用无表面活性剂的溶剂热法合成了由聚集的小原生纳米晶组成的单分散  $\text{SnO}_2$  微球, 这些  $\text{SnO}_2$  微球具有高的比表面积, 优异的结晶度和可调的构建单元, 光电转化效率也是远高于普通  $\text{SnO}_2$  微球。Wang 等<sup>[56]</sup>通过水热反应制备了  $\text{SnO}_2$  微球, 效率达到 4.21%。Liu 等<sup>[57]</sup>则利用球体  $\text{SnO}_2$  仿生内吞生长机制形成珊瑚多孔中空

结构, 光电转化效率达到 1.04%, 而普通球体的  $\text{SnO}_2$  的光电转化效率仅有 0.42%。

除了对  $\text{SnO}_2$  形貌进行控制,  $\text{SnO}_2$  的合成方法也尤为重要。当前比较普遍的合成方法包括水热法、溶胶-凝胶法、微波合成法、模块合成法以及气相沉积法等。Wang 等<sup>[58]</sup>通过传统水热法和微波合成法分别合成纳米片状  $\text{SnO}_2$ , 然后将结构、性能进行比较。结果发现采用微波合成的  $\text{SnO}_2$  拥有较大的比表面积和更强的光散射能力, 上述 2 个优点共同导致  $J_{\text{SC}}$  ( $11.5 \text{ mA} \cdot \text{cm}^{-2}$ )大幅度提升。相比前者, 微波法合成的  $\text{SnO}_2$  具有更长的电荷寿命和更低的电荷再复合能力。由于上述结构、性质等方面的差异, 进而对电池性能产生影响。Rashad 等<sup>[59]</sup>将共沉淀法和热溶剂法相比较, 表明在制备  $\text{SnO}_2$  性能上, 热溶剂法优于共沉淀法, 主要是因为热溶剂法合成的  $\text{SnO}_2$  电荷传输性能比较好, 电子能够迅速转移到  $\text{SnO}_2$  颗粒表面。目前, 在一维纳米结构制备技术上还存在纳米管管壁粗糙度低、管径较大和阵列堆积度低等问题, 亟待进一步优化。

## 4 $\text{SnO}_2$ 光阳极材料修饰

尽管基于  $\text{SnO}_2$  的 DSSC 取得一定的研究进展, 但是  $\text{SnO}_2$  本身的缺点极大地限制了其光电转化效率的提升。为此, 研究者尝试不同修饰方法对  $\text{SnO}_2$  进行改进, 以期大幅提升光电转化效率。

### 4.1 $\text{SnO}_2$ 表面包覆及异质复合

表面包覆是将一层导带位置更高的半导体氧化物包覆在纳米  $\text{SnO}_2$  表面, 形成阻挡层。由于包覆氧化物具有更高的等电子点和更高的导带位置, 使得  $\text{SnO}_2$  基 DSSC 具有更高的染料吸附量并且电子的再复合能力得到有效抑制, 还能够一定程度上改变  $\text{SnO}_2$  导带位置, 因此使  $J_{\text{SC}}$  和  $V_{\text{OC}}$  均能得到大幅度提升, 从而具备更高的光电转化效率, 此外, 表面包覆会给  $\text{SnO}_2$  提供一种保护层, 防止其在环境中被氧化或还原所带来的危害, 同时又可保持  $\text{SnO}_2$  本身紫外线敏感性低的特点, 提高了电池的整体稳定性<sup>[60]</sup>。

通常情况下, 阻挡层主要为绝缘体或者宽带隙氧化物<sup>[61]</sup>, 例如  $\text{ZnO}$ 、 $\text{TiO}_2$ 、 $\text{MgO}$ 、 $\text{Al}_2\text{O}_3$ 、 $\text{Y}_2\text{O}_3$  和  $\text{ZrO}_2$  等。除宽带隙氧化物外, 部分窄带隙氧化物, 如  $\text{CdO}$ <sup>[62]</sup>, 也可用作阻挡层, 这是因为  $\text{CdO}$  层厚度薄时, 同样能够满足量子限制效应。 $\text{ZrO}_2$  作为包覆物时也需要厚度足够薄, 因为  $\text{ZrO}_2$  导带边缘<sup>[63]</sup>理论上高于激发态染料, 电荷无法传输到半导体导

带中。MgO(pH=12)、Al<sub>2</sub>O<sub>3</sub>(pH=9)、Y<sub>2</sub>O<sub>3</sub>(pH=9)<sup>[64]</sup>凭借极高的等电子点和较宽带隙而被应用于修饰 SnO<sub>2</sub>。Prasittichai 等<sup>[65]</sup>利用原子层沉淀技术可控地将 Al<sub>2</sub>O<sub>3</sub> 包覆在 SnO<sub>2</sub> 表面,光电转化效率得到大幅提升。Dong 等<sup>[66–67]</sup>在此基础上通过对包覆周期加以控制,改变 Al<sub>2</sub>O<sub>3</sub> 厚度进一步探究其影响。MgO 包覆 SnO<sub>2</sub> 也被 Li 等<sup>[68]</sup>、Qureshi 等<sup>[69]</sup>和 Jayaweera 等<sup>[70]</sup>所研究,光电转化效率均取得较大提升。但是,经 MgO 和 Y<sub>2</sub>O<sub>3</sub> 包覆后会使 SnO<sub>2</sub> 光阳极的稳定性降低。ZnO 也面临着在复合电池中其化学性质不稳定的问题。KAY 等<sup>[8]</sup>分别研究了不同氧化物对 SnO<sub>2</sub> 的表面包覆行为,结果发现,不同氧化物的包覆使 SnO<sub>2</sub> 基电池的光电转化效率得到不同程度的提升。SnO<sub>2</sub> 的性能除跟包覆氧化物的种类有关外,还跟包覆层的厚度有关,O'Regan 等<sup>[1]</sup>指出最佳的包覆厚度仅为几个埃米。当包覆厚度过大时,包覆物会阻碍电荷传输并且有可能增加光阳极的电位降,造成电子注入效率降低。

为了抑制电荷的再复合作用和提高 SnO<sub>2</sub> 导带位置,金属硫化物、三元金属氧化物、聚合物都被应用于修饰 SnO<sub>2</sub> 表面并提高其光电转化效率,例如 ZnS<sup>[71]</sup>、CaCO<sub>3</sub><sup>[72]</sup>、ZnSO<sub>4</sub><sup>[73]</sup>、石墨烯<sup>[74]</sup>等均实现类似优化。除了包覆物的内在作用,包覆物的形貌也影响着电池性能。对包覆物和 SnO<sub>2</sub> 形貌进行合理设计能够有效引导电荷传输从而提高电子传输能力。Lim 等<sup>[75]</sup>研究表明 SnO<sub>2</sub> 纳米纤维与纳米片 TiO<sub>2</sub> 分层复合后增强了其光散射能力。Qureshi 等<sup>[69]</sup>指出介孔 SnO<sub>2</sub> 通过利用纳米片 MgO 复合后,不仅平带电位发生改变,而且提供了更高的比表面积。

相比其它半导体氧化物,TiO<sub>2</sub> 凭借其较高的导带位置和等电子点以及沉淀方法简单成为当前最普遍的表面包覆物,利用 TiCl<sub>4</sub> 溶液对 SnO<sub>2</sub> 薄膜进行水解处理,在 SnO<sub>2</sub> 表面形成一层 TiO<sub>2</sub>,从而对电池性能某一方面或多方面的提升改进。Wang 等<sup>[76]</sup>通过一种绿色环保的方法合成多功能 SnO<sub>2</sub> 聚集体并用 TiCl<sub>4</sub> 溶液处理,光电转化效率由原来的 1.88% 增加至 6.92%,提升幅度高达 3.5 倍之多,主要原因是 SnO<sub>2</sub> 聚集体本身就拥有很强的光散射能力,而 TiO<sub>2</sub> 修饰后使染料的吸附能力大幅提升(提升了近 3 倍)。此外,经 TiCl<sub>4</sub> 处理后所得电极的电荷再复合能力得到抑制。Abdalla 等<sup>[77]</sup>报道了 TiCl<sub>4</sub> 水解处理可提高 SnO<sub>2</sub> 基 DSSC 的电池性能,并指出 TiCl<sub>4</sub> 处理能使光阳极薄膜的染料吸附量提高。Niu 等<sup>[78]</sup>制备了纳米花状 SnO<sub>2</sub> 光阳极,经过 TiCl<sub>4</sub> 处理后,其

短路电流和开路电压值分别由 5.44 mA·cm<sup>-2</sup> 和 440 mV 增加到 12.74 mA·cm<sup>-2</sup> 和 760 mV, J<sub>SC</sub> 的提升主要得益于 TiO<sub>2</sub> 的高电子点电位,而 V<sub>OC</sub> 的提升,除了跟导带能级的改变有关外,还与 TiCl<sub>4</sub> 的处理能够使 SnO<sub>2</sub> 形成互联网状结构,增加了电子的传输速度,减少电荷因再复合而引发的表面损失有关。Mohamed 等<sup>[79]</sup>合成了 SnO<sub>2</sub>@TiO<sub>2</sub> 的材料,其性能同样得到一定程度的提升。Dong 等<sup>[80]</sup>合成具有 5 层壳的中空微球 SnO<sub>2</sub>,经 TiCl<sub>4</sub> 处理后其光电转化效率达到 7.18%,电流密度达到 17.62 mA·cm<sup>-2</sup>,其电流的增强主要是由于光散射强以及对光诱捕能力高,因为其染料吸附量仅有 0.92×10<sup>-7</sup> mol·cm<sup>-2</sup>。将 SnO<sub>2</sub> 外壳上增加小孔,其比表面积增加或许能够使电流进一步增大。Gao 等<sup>[81]</sup>合成 SnO<sub>2</sub> 网状纤维并在其表面生长出分支 TiO<sub>2</sub>,由于其网状连接,该电池具有杰出的电荷传输能力,电流达到 20.5 mA·cm<sup>-2</sup>,而染料吸附量只有 0.98×10<sup>-7</sup> mol·cm<sup>-2</sup>,F 只有 48.5%。Chen 等<sup>[54]</sup>合成的中空微球 SnO<sub>2</sub> 也具有相似的缺点,具有较低的 F,这是因为电子在表面的再复合损失多,使用石墨烯氧化物作为辅助剂或许能够进一步降低 SnO<sub>2</sub> 与 Fluorine-doped Tin Oxide (FTO)玻璃之间的接触阻力或者使用 TiCl<sub>4</sub> 水解 FTO 玻璃促进电子在表面的传输,减少电荷损失。还有许多科研工作者在表面包覆领域进行了大量研究,Wang 等<sup>[83–85]</sup>和 Thapa 等<sup>[86]</sup>合成的 SnO<sub>2</sub> 光阳极经过 TiCl<sub>4</sub> 处理后均取得较理想的光电转化效率(大于 6%),处理效果与 SnO<sub>2</sub> 微观结构有关,对于不同形貌的 SnO<sub>2</sub> 其处理效果不同,优化条件也不近相同。但是 TiCl<sub>4</sub> 水解也存在一定的不足,当纯 SnO<sub>2</sub> 本身因其结构改变能够有效抑制再复合时,TiO<sub>2</sub> 对其影响不大。依靠 TiCl<sub>4</sub> 水解而提高其 V<sub>OC</sub> 一般都能够维持在 700 mV 以上,但很难使 V<sub>OC</sub> 突破 800 mV。上述研究也证实 TiCl<sub>4</sub> 水解产生的 TiO<sub>2</sub> 其比表面积在一定程度也使 SnO<sub>2</sub> 的高表面积有一定程度下降。

除了用 TiCl<sub>4</sub> 对 SnO<sub>2</sub> 表面处理形成包覆层外,研究者还尝试利用 TiCl<sub>4</sub> 对 FTO 玻璃进行水解处理,形成一层致密氧化膜。TiO<sub>2</sub> 致密层有效地减少了 FTO 玻璃与电解液之间电荷再复合损失。而且 TiO<sub>2</sub> 层使 SnO<sub>2</sub> 与基底间的结合能力提升,对电荷传输起到一定的促进作用。Basu 等<sup>[87]</sup>利用 TiCl<sub>4</sub> 溶液对 FTO 玻璃进行预处理,并针对后处理过程中 TiCl<sub>4</sub> 浓度对 SnO<sub>2</sub> 薄膜的影响进行研究,TiCl<sub>4</sub> 预处理能够在 FTO 玻璃表面形成致密层,而 TiCl<sub>4</sub> 后处理对 SnO<sub>2</sub> 的形貌产生较大影响。具体来讲,高浓度的

$\text{TiCl}_4$  促进了  $\text{TiO}_2$  纳米粒子的集结和生长, 导致更高的分子密度, 减少了薄膜的多孔结构数量。与 Basu 等的研究相似, Cui 等<sup>[88]</sup>对  $\text{TiO}_2$  致密层和  $\text{TiO}_2$  分子厚度及包覆周期进行研究, 经过优化处理后, 使  $\text{SnO}_2$  基 DSSC 的光电转化效率达到 7.40%。Yang 等<sup>[89]</sup>同样在 FTO 基础上沉积  $\text{SnO}_2$  纳米颗粒之前先沉积了一层  $\text{TiO}_2$  致密层, 与不含致密层的电池相比,  $\text{TiO}_2$  致密层的存在使光电转化效率提升了 82.1%。

#### 4.2 离子掺杂

通过对  $\text{SnO}_2$  进行离子掺杂, 在一定程度上影响  $\text{SnO}_2$  电极材料的能带结构, 明显改变  $\text{SnO}_2$  的带隙和平带电位, 使其费米能级上移, 有效抑制电荷的再复合, 从而获得较高的开路电压。离子掺杂后会与  $\text{SnO}_2$  形成稳定的三元氧化物, 这种三元氧化物具有快速的电子传递特性, 在一定程度上改变了传统单组分光稳定性差的缺点, 这将大幅度提高整个染料敏化电池的稳定性、使用寿命及耐用度<sup>[89]</sup>。不仅如此, 金属离子掺杂在形貌、颗粒大小、BET 比表面积等方面都对  $\text{SnO}_2$  电极产生了影响。

如今, 已有很多离子被证实能够优化  $\text{SnO}_2$  其性能或抑制其不足, 例如  $\text{Ni}^{2+}$ 、 $\text{Ga}^{2+}$ 、 $\text{Mg}^{2+}$ 、 $\text{Zn}^{2+}$ 、 $\text{Al}^{3+}$  等。Dou 等<sup>[90]</sup>制备了  $\text{Zn-SnO}_2$  基 DSSCs, 并对光阳极薄膜厚度进行调控,  $\text{Zn-SnO}_2$  薄膜电池性能优于纯  $\text{SnO}_2$  薄膜电池, 并且阳极膜厚度为  $10\text{ }\mu\text{m}$  的  $\text{Zn-SnO}_2$  ( $\eta=3.00\%$ ) 优于  $8\text{ }\mu\text{m}$  的  $\text{Zn-SnO}_2$  ( $\eta=2.11\%$ ), 经  $\text{TiCl}_4$  处理后其光电转化效率更是达到 6.78%。但限制其光电转化效率进一步提升的是, 其比表面积仅有  $10\text{ cm}^2\cdot\text{g}^{-1}$ , 对其比表面积进行优化或者添加比表面积大的纳米颗粒层是提升其光电转化效率的有效手段。Li 等<sup>[91]</sup>制备被介孔球包覆的纳米片经  $\text{Zn}$  离子掺杂后, 其电荷传输能力和光吸收能力都得到增强, 这是因为  $\text{SnO}_2$  平带电位上移和等电子点增大。Li 等<sup>[92]</sup>计算出  $\text{SnO}_2$  随着  $\text{Zn}$  离子增加时的具体影响,  $\text{SnO}_2$  的平带电位由  $0.19\text{ V}$  下降到  $-0.25\text{ V}$ , 等电子点由  $\text{pH}=4.3$  增加到  $\text{pH}=5.1$ , 其再复合能力下降也得到充分的证实, 经  $\text{TiCl}_4$  处理后其光电转化效率达到 7.7%, 不仅如此, Li 等又通过在表面增加反射层, 其光电转化效率最终达到 8.23%。

$\text{Mg}$  离子掺杂后对  $\text{SnO}_2$  平带电位影响不大,  $V_{\text{OC}}$  无明显变化, 但是对  $J_{\text{SC}}$  的提升却至关重要。Yang 等<sup>[93]</sup>研究表明经  $\text{Mg}$  离子掺杂后其光电转化效率由 1.72% 提高到 4.38%, 这是因为  $\text{Mg}$  离子掺杂后改变其内部结构, 延长了电荷传输路径。相比  $\text{Mg}$  离子掺杂  $\text{SnO}_2$ ,  $\text{Ga}$  离子则对  $\text{SnO}_2$  平带电位影响十分明

显。此外, 离子的掺杂量和掺杂方式对电池性能至关重要。Teh 等<sup>[94]</sup>利用  $\text{Ga}$  离子对  $\text{SnO}_2$  进行掺杂, 发现  $\text{Ga}$  掺杂量为 3%(质量分数)的  $\text{Ga-SnO}_2$  具有最优性能(4.05%), 其  $V_{\text{OC}}$  更是达到  $740\text{ mV}$ 。经过  $\text{Ga}$  离子掺杂后,  $\text{SnO}_2$  形貌及颗粒大小均发生改变, 而且能带、费米能级、平带电位也相应发生改变。由于  $\text{SnO}_2$  导带边缘明显提高, 导致电荷的再复合能力减弱(图 6), 因此提高了  $\text{SnO}_2$  的  $V_{\text{OC}}$ 。Pannee 等<sup>[6]</sup>采用溶胶-凝胶法有效地合成了  $\text{SnO}_2$  纳米粒子和不同浓度的  $\text{Al}$  离子掺杂  $\text{SnO}_2$  纳米粒子, 其具有良好的光学、表面和电学性能, 增强了其在可能的光伏应用中的兼容性, 特别是在染料敏化太阳能电池中的应用, 当使用  $\text{Al}$  离子含有 1%(质量分数)的  $\text{Al-SnO}_2$  作为光阳极材料制造 DSSC 时, 显示出 3.51% 的光电转化效率, 远高于纯  $\text{SnO}_2$  纳米颗粒的性能(1.18%)。

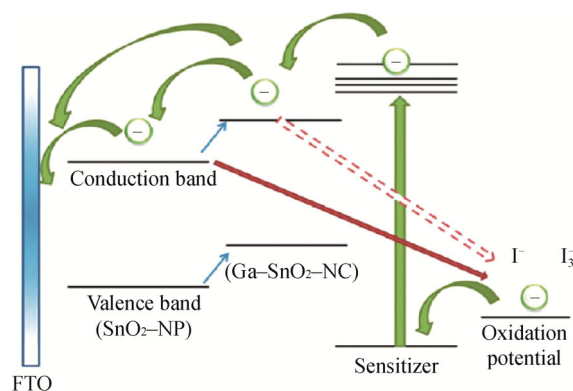


图 6  $\text{Ga}$  掺杂前后  $\text{SnO}_2$  基 DSSCs 能带结构和电子传输对比示意图<sup>[95]</sup>

Fig. 6 Illustration of band structures and electron transfers for  $\text{SnO}_2$ -based DSSCs before and after  $\text{Ga}$  doping<sup>[95]</sup>

除非贵金属掺杂外, 利用贵金属的等离子共振效应或掺杂是提升是提升  $\text{SnO}_2$  基 DSSC 的另一个重要方法。Dissanayake 等<sup>[60]</sup>将  $30\sim 35\text{ nm}$  范围内的金纳米颗粒引入  $\text{SnO}_2$  电极, 光电转化性能测试结果显示: 与不含金纳米颗粒的电极相比, 开路电压和短路电流密度分别增加了  $2.3\text{ mV}$  和  $0.23\text{ mA}\cdot\text{cm}^{-2}$ 。局部表面等离子体共振效应(LSPR)是导致上述结果的主要原因。Suriya 等<sup>[95]</sup>采用共沉积法制备出  $\text{Ag}$  掺杂  $\text{SnO}_2$  纳米颗粒, 紫外-可见光谱结果表明  $\text{Ag}$  掺杂降低了  $\text{SnO}_2$  纳米颗粒的光学带隙, 并随着有效能带隙的降低而增加了 Urbach 尾能, 光伏测量结果显示  $\text{Ag}$  掺杂  $\text{SnO}_2$  纳米颗粒具有更高的光电转化效率。上述研究成果显示贵金属掺杂的重要影响, 有效拓展了  $\text{SnO}_2$  基染料敏化太阳能电池性能的新途径(表 2)。

表 2 基于表面修饰和离子掺杂 SnO<sub>2</sub> 染料敏化太阳能电池性能参数Table 2 Parameters of DSSCs based on surface-modified and doped SnO<sub>2</sub> with different nanostructures

| Morphologies                                         | Voc/mV | J <sub>sc</sub> /(mA·cm <sup>-2</sup> ) | F/%   | η/%  | Samples                                                            |
|------------------------------------------------------|--------|-----------------------------------------|-------|------|--------------------------------------------------------------------|
| TiO <sub>2</sub> coating layer                       | 780.0  | 6.980                                   | 55.00 | 1.52 | SnO <sub>2</sub> NR–TiO <sub>2</sub> <sup>[31]</sup>               |
|                                                      | 680.0  | 9.910                                   | 49.00 | 3.47 | SnO <sub>2</sub> nanotube–TiO <sub>2</sub> <sup>[40]</sup>         |
|                                                      | 725.0  | 10.250                                  | 67.60 | 5.02 | SnO <sub>2</sub> @Air@TiO <sub>2</sub> <sup>[52]</sup>             |
|                                                      | 744.0  | 18.280                                  | 48.05 | 6.54 | SnO <sub>2</sub> HNS–TiO <sub>2</sub> <sup>[54]</sup>              |
|                                                      | 650.0  | 11.200                                  | 45.00 | 3.34 | SnO <sub>2</sub> NS–TiO <sub>2</sub> <sup>[58]</sup>               |
|                                                      | 594.0  | 19.500                                  | 59.70 | 6.92 | SnO <sub>2</sub> aggregates–TiO <sub>2</sub> <sup>[76]</sup>       |
|                                                      | 760.0  | 12.740                                  | 57.48 | 5.60 | SnO <sub>2</sub> nanoflower–TiCl <sub>4</sub> <sup>[78]</sup>      |
|                                                      | 798.0  | 4.580                                   | 62.60 | 2.29 | TiO <sub>2</sub> (5% SnO <sub>2</sub> ) NFs <sup>[79]</sup>        |
|                                                      | 720.0  | 17.620                                  | 56.60 | 7.18 | 5S–SnO <sub>2</sub> –HMS–TiCl <sub>4</sub> <sup>[80]</sup>         |
|                                                      | 763.0  | 14.390                                  | 58.30 | 6.40 | SnO <sub>2</sub> octahedra–TiO <sub>2</sub> <sup>[84]</sup>        |
|                                                      | 803.0  | 14.110                                  | 55.00 | 6.25 | SnO <sub>2</sub> microsphere–TiCl <sub>4</sub> <sup>[85]</sup>     |
|                                                      | 740.0  | 14.700                                  | 55.50 | 6.05 | Urchin-like SnO <sub>2</sub> –TiO <sub>2</sub> <sup>[86]</sup>     |
|                                                      | 450.0  | 11.400                                  | 51.00 | 2.64 | SnO <sub>2</sub> NP–TiCl <sub>4</sub> <sup>[87]</sup>              |
|                                                      | 711.0  | 10.420                                  | 51.00 | 3.80 | meso–SnO <sub>2</sub> –TiO <sub>2</sub> <sup>[97]</sup>            |
|                                                      | 330.0  | 19.650                                  | 40.00 | 2.55 | SnO <sub>2</sub> @TiO <sub>2</sub> <sup>[106]</sup>                |
|                                                      | 780.0  | 16.670                                  | 66.00 | 8.70 | D–TiO <sub>2</sub> +TS3 <sup>[107]</sup>                           |
| ZnO/MgO/Al <sub>2</sub> O <sub>3</sub> coating layer | 510.0  | 10.900                                  | 65.00 | 3.70 | SnO <sub>2</sub> NP–Al <sub>2</sub> O <sub>3</sub> <sup>[65]</sup> |
|                                                      | 341.0  | 10.870                                  | 54.00 | 2.01 | SnO <sub>2</sub> NP–Al <sub>2</sub> O <sub>3</sub> <sup>[66]</sup> |
|                                                      | 597.0  | 18.280                                  | 63.00 | 6.83 | SnO <sub>2</sub> NP–MgO <sup>[68]</sup>                            |
|                                                      | 550.0  | 9.210                                   | 49.00 | 2.48 | Mesoporous SnO <sub>2</sub> –Mg <sup>[69]</sup>                    |
|                                                      | 523.0  | 3.600                                   | 70.00 | 1.33 | SnO <sub>2</sub> –MgO <sup>[70]</sup>                              |
|                                                      | 430.0  | 9.500                                   | 42.00 | 1.77 | SnO <sub>2</sub> –MgO <sup>[71]</sup>                              |
|                                                      | 656.0  | 16.300                                  | 59.00 | 6.31 | SnO <sub>2</sub> NP–ZnO <sup>[96]</sup>                            |
|                                                      | 650.0  | 15.930                                  | 47.00 | 4.72 | SnO <sub>2</sub> NB–ZnO <sup>[103]</sup>                           |
|                                                      | 630.0  | 8.630                                   | 66.00 | 3.68 | SnO <sub>2</sub> @ZnO <sup>[103]</sup>                             |
|                                                      | 687.0  | 15.000                                  | 69.00 | 7.17 | SnO <sub>2</sub> –ZnO <sup>[105]</sup>                             |
|                                                      | 447.0  | 8.810                                   | 52.00 | 2.03 | SnO <sub>2</sub> @MgO <sup>[106]</sup>                             |
|                                                      | 665.0  | 10.450                                  | 41.80 | 2.90 | SnO <sub>2</sub> –ZnO (50%) <sup>[109]</sup>                       |
| Other oxide coating layer                            | 540.0  | 10.130                                  | 59.00 | 3.23 | SnO <sub>2</sub> NP–CdO <sup>[62]</sup>                            |
|                                                      | 454.0  | 8.840                                   | 45.80 | 1.84 | SnO <sub>2</sub> –CaO <sup>[70]</sup>                              |
|                                                      | 610.0  | 9.470                                   | 51.00 | 3.00 | SnO <sub>2</sub> NC–ZnS <sup>[71]</sup>                            |
|                                                      | 591.0  | 11.300                                  | 76.40 | 5.10 | SnO <sub>2</sub> NP–CaCO <sub>3</sub> <sup>[72]</sup>              |
|                                                      | 590.0  | 10.980                                  | 73.00 | 4.72 | SnO <sub>2</sub> –HMS–ZnSO <sub>4</sub> <sup>[104]</sup>           |
|                                                      | 570.0  | 7.220                                   | 74.00 | 3.05 | SnO <sub>2</sub> microsphere–ZnSO <sub>4</sub> <sup>[104]</sup>    |
|                                                      | 475.0  | 0.870                                   | 70.00 | 0.29 | SnO <sub>2</sub> @CuO <sup>[106]</sup>                             |
|                                                      | 598.0  | 3.910                                   | 52.00 | 1.21 | SnO <sub>2</sub> @NiO <sup>[106]</sup>                             |
|                                                      | 643.0  | 15.700                                  | 52.52 | 5.31 | RGO/SnO <sub>2</sub> <sup>[108]</sup>                              |
| Ion doping                                           | 780.0  | 6.060                                   | 62.10 | 3.00 | Zn–SnO <sub>2</sub> <sup>[90]</sup>                                |
|                                                      | 590.0  | 9.220                                   | 74.00 | 4.15 | Zn–SnO <sub>2</sub> <sup>[91]</sup>                                |
|                                                      | 560.0  | 13.480                                  | 55.40 | 4.18 | Zn–SnO <sub>2</sub> <sup>[92]</sup>                                |
|                                                      | 673.0  | 16.860                                  | 67.80 | 7.70 | Zn–SnO <sub>2</sub> –TiCl <sub>4</sub> <sup>[92]</sup>             |
|                                                      | 780.0  | 10.760                                  | 51.88 | 4.38 | Mg–SnO <sub>2</sub> <sup>[93]</sup>                                |
|                                                      | 740.0  | 7.410                                   | 73.70 | 4.05 | Ga–SnO <sub>2</sub> <sup>[94]</sup>                                |
|                                                      | 986.0  | 5.020                                   | 71.00 | 3.51 | Al–SnO <sub>2</sub> <sup>[6]</sup>                                 |
|                                                      | 454.5  | 6.070                                   | 55.22 | 1.64 | Au–SnO <sub>2</sub> <sup>[60]</sup>                                |
|                                                      | 698.0  | 1.903                                   | 51.70 | 2.79 | Ag–SnO <sub>2</sub> <sup>[95]</sup>                                |
|                                                      | 730.0  | 20.430                                  | 66.00 | 6.93 | Ag–SnO <sub>2</sub> /TiO <sub>2</sub> <sup>[101]</sup>             |

## 5 结论及展望

$\text{SnO}_2$  染料敏化太阳能电池因杰出的电荷传输能力和稳定的光学性具有替代  $\text{TiO}_2$  染料敏化太阳能电池的潜力, 但其较低的导带位置致使纯  $\text{SnO}_2$  的  $V_{\text{OC}}$  很难突破到 500 mV。同时, 较低的等电子点也限制了染料吸附, 在源头上降低了  $J_{\text{SC}}$ 。面对  $\text{SnO}_2$  纳米颗粒较差的性能, 可以改变其结构形貌, 进行表面包覆及离子掺杂来强化电荷传输和抑制电荷再复合, 通过以上措施, 使  $\text{SnO}_2$  电池的光电转化效率有了大幅提升。

目前为止基于纯  $\text{SnO}_2$  修饰电池的光电转化效率已达 8.74%, 而  $\text{SnO}_2\text{-TiO}_2$  复合电池的光电转化效率也已达到 9.53%。虽已取得巨大突破, 但离  $\text{TiO}_2$  电池(13%)还有一定的差距。不难看出, 由于  $\text{SnO}_2$  良好的传输性能,  $\text{SnO}_2$  电流密度已经能够达到较高水平(大于  $20 \text{ mA}\cdot\text{cm}^{-2}$ ), 与  $\text{TiO}_2$  的相当, 但其开路电压和填充因子还有一些差距。

今后的研究重点可以着手于以下 5 个方面:

1) DSSC 内部对于电子产生、电子传输、电子损失和电子收集已有很深了解, 但也存在很多问题亟待解决, 例如: 光生电子与  $\text{I}_3^-$  的复合机理还不清楚; 由于内部发生的电子传输

过程复杂, 至今为止还没有模型能够完全解释一定扰动光强下产生光生电流与光生电压 (IMPS/IMVS) 过程, 理论模型仍需更详细的研究; 电子从半导体薄膜导入 FTO 界面的过程有很多可能: 热发射和隧穿等, 目前还没合适的理论来描述这个界面, 需进一步研究。

2) 形貌结构对光电转化效率影响至关重要并且研究大多朝着聚集体与多种形貌并存的方向发展, 使其具有多种优良性能。在此基础上可以改变共聚物或添加辅助剂、造孔剂等进一步改进其性能, 也可以完善制备工艺及实现创新制备方法, 以获得更高的比表面积和散射能力。

3) 当前利用  $\text{TiCl}_4$  处理  $\text{SnO}_2$  面临的巨大难题是  $\text{SnO}_2$  比表面积下降而导致染料吸附量增加不大。为解决此难题, 首先可以向形貌的多孔结构方向进行改进, 以期获得更高的染料吸附量; 随后进一步研究  $\text{TiCl}_4$  含量对多种形貌  $\text{SnO}_2$  性能影响以及水解优化条件, 为  $\text{TiCl}_4$  水解各种  $\text{SnO}_2$  提供理论支撑, 以期得到最佳的水解浓度。

4) 进一步使用与  $\text{Sn}^{4+}$  半径相似的过渡金属 ( $\text{Ti}^{4+}$ 、 $\text{W}^{4+}$ 、 $\text{In}^{3+}$ ) 或者利用共掺杂金属的协同作用,

针对性提高  $\text{SnO}_2$  多种性能。

5) 为使  $\text{SnO}_2$  光电转化效率进一步突破, 必须从微观角度研究 DSSCs 的工作过程, 并且要对其各个部分进行优化, 从而找出限制电子传输的过程、提高电子产率、改善电子传输过程、降低电子损失、以期获得最佳光电转化效率。

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## Development on SnO<sub>2</sub> Photoanodes for Dye-sensitized Solar Cells

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### Extended Abstract

In the increasing severe energy crisis, the use of solar energy to replace traditional fossil fuels becomes a consensus in worldwide due to the non-renewable nature of fossil fuels and the inability of new energy sources such as hydrogen, wind, and nuclear energy. Among the forms of solar energy utilization, dye-sensitized solar cells (DSSCs) are a research hotspot in energy development and utilization due to their low cost, abundant raw materials, high efficiency, and long service life. The photoanode is an important component of DSSCs and plays a significant role in improving the photoelectric conversion efficiency of DSSCs. In recent years, various materials and modification methods for dye-sensitized solar cells are applied to design the photoanodes for the improvement of their photoelectric conversion efficiency. Among various photoanode materials, SnO<sub>2</sub> is an ideal candidate due to its higher electron mobility (*i.e.*, about 125 cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup>) and larger bandgap width (*i.e.*, 3.5 eV). However, SnO<sub>2</sub>-based dye-sensitized cells still have two main challenges, *i.e.*, the lower open-circuit voltage (*V*<sub>OC</sub>) (Compared to TiO<sub>2</sub>, the conduction band edge of SnO<sub>2</sub> shifts positively by up to 300 mV, resulting in a reduced difference between the conduction band potential and the redox potential of the electrolyte); and the lower current density (The isoelectric point of SnO<sub>2</sub> is smaller, which reduces the binding force between SnO<sub>2</sub> and acidic photosensitive dyes, leading to a decrease in dye adsorption and thus limiting the increase in current density from the source).

This review represented recent research progress on tin SnO<sub>2</sub> photoanodes in DSSCs, emphasizing the potential application of SnO<sub>2</sub> in DSSCs and the challenges. This review introduced the structure and working principle of SnO<sub>2</sub>-based DSSCs, and analyzed the key factors affecting the photoelectric conversion efficiency, including short-circuit current density (*J*<sub>SC</sub>), *V*<sub>OC</sub>, and fill factor (FF). This review discussed the factors influencing these parameters and focused on the current state of research on improving SnO<sub>2</sub> photoanodes, with the methods including surface coating, composite construction, ion doping, and metal doping. Although various modification methods are developed to improve the performance of SnO<sub>2</sub> photoanodes, the overall photoelectric conversion efficiency is still lower, restricting its widespread application in a large scale. Therefore, developing more advanced modification techniques is a necessity to further enhance the performance of SnO<sub>2</sub> (*i.e.*, its stability and recyclability), and facilitate its wide application in the energy field, thus providing an effective solution to alleviate the energy crisis.

**Summary and prospects** SnO<sub>2</sub>-based DSSCs have a potential to replace TiO<sub>2</sub> DSSCs due to their outstanding charge transport capabilities and stable optical properties. However, a lower conduction band position of pure SnO<sub>2</sub> makes it difficult to achieve an *V*<sub>OC</sub> beyond 500 mV. Also, the lower isoelectric point limits dye adsorption, inherently reducing the *J*<sub>SC</sub>. To address the poor performance of SnO<sub>2</sub> nanoparticles, modifications such as changing their structural morphology, surface coating, and ion doping can be employed to enhance charge transport and suppress charge recombination, significantly improving the photoelectric conversion efficiency of SnO<sub>2</sub> cells. To date, the photoelectric conversion efficiency of cells based on pure SnO<sub>2</sub> is 8.74%, while that of SnO<sub>2</sub>-TiO<sub>2</sub> composite cells is 9.53%. Although these are significant breakthroughs, there is still a gap, compared to TiO<sub>2</sub> cells (*i.e.*, 13%). It is evident that the current density of SnO<sub>2</sub> is able to reach a high level (*i.e.*, greater than 20 mA·cm<sup>-2</sup>) due to the good transport performance of SnO<sub>2</sub>, compared to that of TiO<sub>2</sub>, but there is still some gaps in open-circuit voltage and fill factor.

Future research aspects are as follows:

1) There is a great need for a deep understanding of electron generation, transport, loss, and collection within DSSCs, but many issues remain to be resolved. For instance, the recombination mechanism of photo-generated electrons with I<sub>3</sub><sup>-</sup> is still unclear. The complex internal electron transport process has yet to be fully explained by any model, especially under certain light intensity disturbances affecting photo-generated current and voltage (IMPS/IMVS), necessitating further detailed theoretical studies. There are many possibilities for the process of electron injection from the semiconductor film to the FTO interface, such as thermal emission and tunneling, and there is currently no suitable theory to describe this interface, requiring a further research.

2) The further use of transition metals with radii that are similar to Sn<sup>4+</sup> (such as Ti<sup>4+</sup>, W<sup>4+</sup>, and In<sup>3+</sup>) or the synergistic effect of co-doping metals can be explored to specifically improve various properties of SnO<sub>2</sub>.

3) To further break through the photoelectric conversion efficiency of SnO<sub>2</sub>, it is necessary to investigate the working process of DSSCs from a microscopic perspective and optimize each part to identify the processes limiting electron transport, improve electron yield, enhance electron transport processes, and reduce electron loss, aiming to achieve the optimum photoelectric conversion efficiency.

**Keywords:** dye-sensitized solar cells; photoanode; stannic oxide