

染料敏化太阳能电池用过渡金属化合物对电极的研究进展

王桂强, 王德龙, 况 帅, 嵇淑萍

(山东理工大学 化工学院, 淄博 255049)

摘 要: 由于成本低、制作工艺简单、光电转换效率高, 染料敏化太阳能电池被认为是传统太阳能电池最有力的竞争者之一。染料敏化太阳能电池常用的对电极是 Pt 电极, Pt 价格高, 储量少, 因此寻找一种价格便宜且催化性能较好的材料代替 Pt 制备对电极是目前的研究热点。过渡金属化合物品种多、制备过程简单、价格低且催化性能好, 近年来受到人们的广泛关注, 是代替 Pt 制备染料敏化太阳能电池对电极最好的材料之一。本文综述了染料敏化太阳能电池过渡金属化合物对电极的研究现状, 对过渡金属化合物对电极的性能特点及今后研究的重点进行了分析。

关 键 词: 对电极; 过渡金属化合物; 染料敏化太阳能电池; 综述

中图分类号: TK513

文献标识码: A

Research Progress on Transition Metal Compound Used as Highly Efficient Counter Electrode of Dye-sensitized Solar Cells

WANG Gui-Qiang, WANG De-Long, KUANG Shuai, ZHUO Shu-Ping

(College of Chemical Engineering, Shandong University of Technology, Zibo 255049, China)

Abstract: Dye-sensitized solar cells (DSC) has been considered as one of the most promising alternatives to conventional photovoltaic device due to its low cost, simple fabrication process and high conversion efficiency. Pt-loaded conducting substrate has been widely exploited as the standard counter electrode for DSC. However, Pt is expensive and rare, so it is most desirable to seek a low-cost substitute for Pt in counter electrode of DSC. Transition metal compound has been demonstrated to be one of the most promising counter electrode materials for DSCs owing to its low cost, simple fabrication, broad variety of materials and good catalytic activity. This article provides a review of transition metal compound counter electrodes for DSC and a brief outlook on the future development of transition metal compound counter electrodes.

Key words: counter electrode; transition metal compound; dye-sensitized solar cells; review

能源危机和环境污染是二十一世纪人类面临的最为严峻的两大挑战, 因此对可再生能源特别是太阳能的开发利用成为世界各国政府可持续发展的能源战略。染料敏化太阳能电池(Dye-Sensitized Solar Cells, DSCs)制作工艺简单、材料成本低廉、稳定性好, 自 1991 年其光电转换效率取得突破以来, 一直是国际研究的热点^[1-9]。DSCs 主要由三部分组成(图 1): 染料敏化的 TiO₂ 纳晶多孔光阳极、含有氧化还原对(通常是 I⁻/I₃⁻)的电解质以及对电极。光照射到

电池上, (1)吸附在 TiO₂ 上的染料分子吸收光由基态跃迁到激发态(D*); (2)激发态电子注入到 TiO₂ 导带后; (3)通过扩散传输到外电路, 经过外电路后到达对电极; (4)失去电子的氧化态染料(D⁺)分子被电解质中的 I⁻还原, I⁻被氧化为 I₃⁻; (5)电解质中 I₃⁻通过扩散到达对电极, 在对电极接受外电路来的电子发生还原反应生成 I⁻, 从而完成一个循环。对电极的主要作用是接受外电路电子, 催化 I₃⁻还原为 I⁻。因此 DSCs 对电极应具有较好的导电性、催化活性以及稳定性。

收稿日期: 2012-12-23; 收到修改稿日期: 2013-03-06

基金项目: 国家自然科学基金 (21273137); 山东省自然科学基金 (ZR2010BM038)

National Natural Science Foundation of China (21273137); Natural Science Foundation of Shandong Province (ZR2010BM038)

作者简介: 王桂强(1969-), 男, 博士, 副教授. E-mail: wgqiang123@163.com

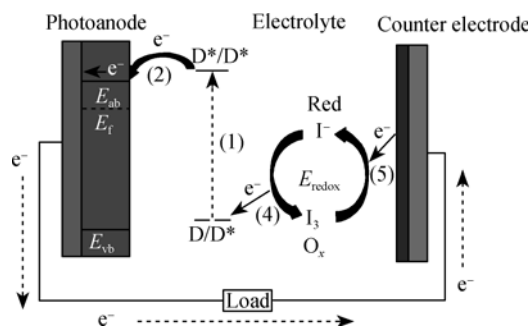


图 1 染料敏化太阳能电池结构及工作原理

Fig. 1 The structure and operation principle of dye-sensitized solar cells

目前 DSCs 常用的对电极是 Pt 电极^[10-14]。Pt 是一种稀有贵金属, 价格较高, 而且在 I^-/I_3^- 电解质体系中容易被腐蚀(生成 PtI_4 或 H_2PtI_6)^[15]。因此, 用价格便宜、稳定性好的碳材料^[16-24]、导电聚合物^[25-33]及过渡金属化合物^[34]代替 Pt 制备 DSCs 对电极引起了人们的广泛关注。与碳材料和导电聚合物相比, 过渡金属化合物种类及制备方法多样, 制备过程简单, 价格低, 而且具有较高的催化活性。因此, 近年来刊出了大量关于过渡金属化合物对电极的研究报道。本文就 DSCs 过渡金属化合物对电极进行综述, 对不同过渡金属化合物对电极的性能及制备方法进行分析比较。

1 过渡金属硫化物对电极

2009 年, Grätzel 首先采用静电沉积将纳米 CoS 粒子沉积到 ITO/聚萘二甲酸乙二醇酯薄膜(ITO/PEN)上, 制备了适用于 DSCs 的柔性对电极^[35]。电化学分析表明所制备的 CoS 电极对 I_3^- 还原反应表现出很高的催化活性, 以这种柔性 CoS 电极作为对电极, DSCs 的光电转换效率达到 6.5%。Lin 等^[36-38]用动电沉积的方法, 通过优化沉积过程制备出多孔 CoS 对电极, 用这种 CoS 对电极组装的 DSCs 光电转换效率达到 6.33%。Kung 等^[39]采用 Co_3O_4 纳米棒阵列沉积和化学浴离子交换两步法在 FTO 导电玻璃表面制备了 CoS 纳米棒阵列(图 2a)。CoS 纳米棒阵列电极的催化性能明显优于已报道的静电沉积和动电沉积法制备的 CoS 电极。以 CoS 纳米棒阵列电极作为对电极, DSCs 的效率达到 7.67%, 与相应 Pt 对电极电池效率(7.70%)一致。CoS 纳米棒阵列电极性能较好的主要原因是由于表面粗糙的一维纳米棒具有较高的比表面积和较快的电子传输能力, 从而使所组装电池具有较高的光电流密度和填充因子。

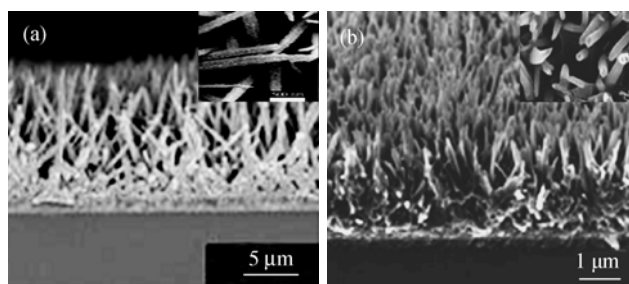


图 2 CoS 纳米棒阵列电极^[39] (a)和 NiS 纳米棒阵列电极^[43] (b)横截面 SEM 照片(插图为平面放大 SEM 照片)

Fig. 2 The cross-section SEM image of CoS acicular nanorod arrays^[39] (a) and NiS nanorod arrays electrode^[43] (b) (The inset shows a high magnification of SEM image)

Co 和 Ni 同属 VIII B 族元素, 因此 NiS 对电极也引起了人们的关注。Chi 等^[40]通过溶液热分解反应合成棒状 NiS 纳米粒子。NiS 粒子通过静电吸附在 FTO 导电玻璃表面形成稳定的膜。用这种静电自组装 NiS 电极作为对电极, DSCs 的光电转换效率达到 6.5%, 是相应 Pt 对电极电池效率(5.8%)的 1.2 倍。Sun 等^[41]采用电沉积法将 NiS 纳米粒子沉积到 FTO 玻璃表面制备 NiS 电极。以这种 NiS 电极组装 DSCs, 光电转换效率达到 6.83%, 与相应的 Pt 对电极电池效率(7.00%)相近。Ku 等^[42]采用透明的 NiS 对电极和 ET(1-乙基-1H-四氮唑-5-基硫基离子)/BET(双(1-乙基四氮唑-5-基)二硫)电解质体系, 电池的光电转换效率达到 6.25%, 比相应 Pt 电极电池效率提高 56%。Zhao 等^[43]用水热法在空白玻璃表面直接生长 NiS 单晶纳米棒阵列(图 2b)。所制备的 NiS 纳米棒阵列膜具有独特的 NiS 致密层和 NiS 纳米棒阵列层双层结构。这种特殊的双层结构使 NiS 膜兼具导电和催化双重功能, 因此可同时取代 FTO 导电层和 Pt。以 NiS 纳米棒阵列电极直接作为对电极, DSCs 的光电效率达到 7.41%, 与传统的 Pt 电极电池效率(7.55%)相近。Wu 等^[44]制备了 WS_2 和 MoS_2 对电极, 相应 DSCs 的光电转换效率分别达到 7.73%和 7.59%。

2 过渡金属氮化物对电极

除了过渡金属硫化物, 过渡金属氮化物也被用来制备 DSCs 对电极。2009 年, Jiang 等^[45]通过金属钛片阳极氧化结合氨气氮化制备了高度有序的 TiN 纳米管阵列电极(图 3(a)和(b))。TiN 纳米管阵列电极的电导性能和催化性能明显优于传统 Pt/FTO 电极。因此所组装 DSCs 的光电效率达到 7.73%, 高于相应 Pt/FTO 电极电池的光电效率(7.45%)。很明显, TiN 纳米管阵列电极电池光电转换效率较高的原因一方面是 TiN 纳米管阵列电极具有较低的欧姆内阻和较

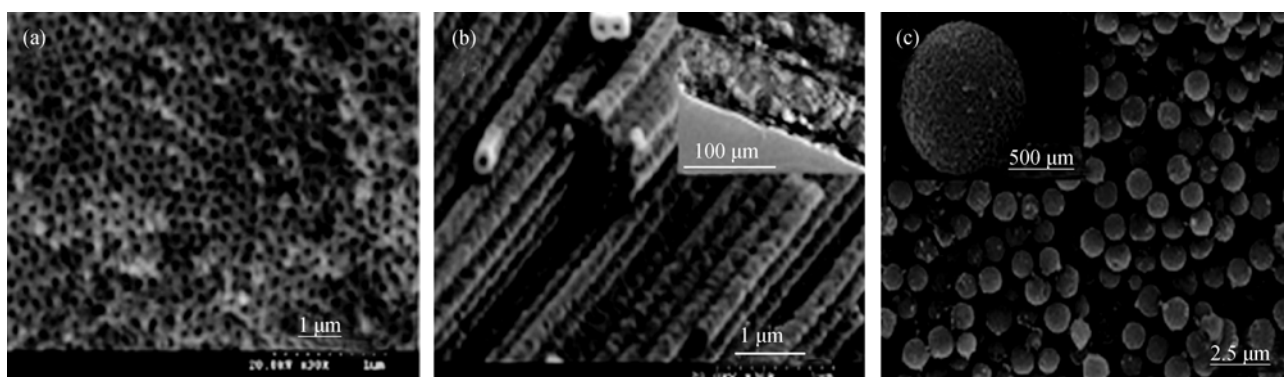


图3 TiN 纳米管阵列的表面(a)和截面(b)SEM 照片((b)中插图为 TiN 纳米管 TEM 照片)^[45]以及多级微纳结构 TiN 微球 SEM 照片(c)(插图为单个 TiN 微球 SEM 照片)^[46]

Fig. 3 SEM images of TiN nanotube arrays (a): top view, (b): cross section, the inset in (b) shows TEM image of TiN nanotube^[45] and SEM image of the hierarchical micro/nano TiN sphere(c) (the inset shows single TiN sphere)^[46]

高的催化活性,另一方面是高度有序排列的纳米管阵列结构有利于电子的传输,从而提高了电池的填充因子。因此,TiN 材料的形貌结构,对 TiN 电极的性能有较大影响。Zhang 等^[46]制备的具有多级微纳结构的 TiN 微球(图 3c)电极催化活性明显高于 TiN 平面电极和 TiN 颗粒电极。以多级微纳 TiN 微球电极组装的 DSCs 的光电转换效率达到 7.83%,比传统 Pt/FTO 电极电池的光电效率(6.04%)提高 30%。

Jiang 等^[47]用氨气分别对金属 Ni 片和 Ni 颗粒进行表面氮化,制备了双层结构的 NiN 平面电极和 NiN 颗粒电极。NiN 颗粒电极表面呈多孔结构,具有较高的比表面积,因而催化活性明显高于 NiN 平面电极。用 NiN 颗粒电极组装的 DSCs 光电效率达到 8.31%,与相应的 Pt 电极电池效率(8.41%)接近。Li 等^[48]用氨气对 MoO₂、WO₃ 及 Fe₂O₃ 进行氮化处理制备了 MoN、WN 和 Fe₂N 电极。MoN 电极对 I₃⁻ 的还原反应表现出很高的催化活性,组装的 DSCs 光电效率达到 5.57%。WN 电极的催化活性与 MoN 电极相近,但由于 WN 电极具有较大的扩散阻抗(Z_N),因此组装电池的效率高(3.67%)。Wu 等^[49]用磁控溅射法将 Mo₂N 和 W₂N 沉积到 Ti 片上,制备了柔性 Mo₂N 和 W₂N 电极。Mo₂N 和 W₂N 电极对 I₃⁻ 的还原反应表现出与 Pt 电极相似的催化活性。但 Mo₂N 和 W₂N 电极具有较大的扩散阻抗,因此所组装 DSCs 光电转换效率(Mo₂N:6.38%,W₂N:5.81%)小于 Pt 对电极电池效率(7.01%)。综合上述结果可以看出,对电极同时具备较高的催化活性和较低的扩散阻抗对于改善 DSCs 光电性能非常重要。

3 过渡金属氧化物、碳化物对电极

由于具有一些特殊的物理、化学性质及较好的催化性能和稳定性,过渡金属氧化物和碳化物代替

Pt 制备 DSCs 对电极也引起人们的关注。Wu 等^[50]将 SnO₂ 涂到 FTO 导电玻璃表面,然后在氮气气氛下对电极进行热处理制备 SnO₂ 电极。以 SnO₂ 电极作为对电极,DSCs 的光电效率达到 6.09%。Ma 所在的课题组^[51-53]通过简单的化学合成制备了 TaO、Ta₂O₅、WO₂、WO₃、H-Nb₂O₅(六方晶系)、O-Nb₂O₅(正交晶系)、M-Nb₂O₅(单斜晶系)及 NbO₂(四方晶系),然后分别将上述 8 种氧化物沉积到 FTO 导电玻璃表面,并经过热处理(N₂ 气氛)制备 DSCs 对电极。从表 1 中数据可以看出,NbO₂ 对电极性能最好,组装电池的光电转换效率达到 7.88%,高于相应 Pt 对电极电池的效率高(7.65%)。从 R_{ct}(电荷迁跃电阻)数据看,虽然 TaO、WO₂ 及 M-Nb₂O₅ 三种电极催化活性与 Pt 电极相近,但是这三种电极电池的光电转换效率都比 Pt 电极电池低。主要原因是这三种电极的扩散阻抗都明显大于 Pt 电极,因此组装的 DSCs 的短路电流密度和填充因子都小于相应 Pt 对电极电池。

WC、W₂C 和 MoC 是目前报道的三种制备 DSCs 对电极的过渡金属碳化物^[54-56]。商业化生产的 WC 和 MoC 有效催化面积和电导性都较低,因此所制备的对电极催化性能较差^[54]。Jang 等^[55]采用聚合物诱导水热法(PD)和微波辅助水热法(MW)合成了 PD-WC 和 MW-WC,其 BET 表面积分别达到 64 和 73 m²/g。以这两种碳化物制备对电极,电池的光电效率分别达到 6.61% (PD-WC)和 7.01% (MW-WC),但与 Pt 电极电池效率(8.31%)相比还偏低。

综上所述,过渡金属化合物对电极在 DSCs 中表现出与 Pt 对电极相似的催化性能。但对于不同的过渡金属化合物对电极,由于不同研究人员采用的实验条件(如电解质、光阳极等)不同,因此不能简单的通过文献报道的光电数据比较它们的性能好坏。DSCs 对电极上的催化反应发生在催化剂表面,催化剂表面的电子、能态及几何结构等因素对其催化

表 1 过渡金属氧化物对电极特性及组装染料敏化太阳能电池光电参数

Table 1 Characteristics of electrodes based on transition metal oxide and photovoltaic parameters of dye-sensitized solar cells with different counter electrodes

Electrode	Morphology	R_{ct}/Ω	Z_N/Ω	$J_{sc}/(\text{mA} \cdot \text{cm}^{-2})$	V_{oc}/V	FF	$\eta/\%$	Ref.
TaO	Porous sphere	3.82	276.00	12.59	0.77	0.67	6.48	[51]
Ta ₂ O ₅	Porous sphere	73.69	213.00	13.01	0.75	0.42	4.08	
Pt	—	7.05	9.12	13.75	0.76	0.69	7.16	
WO ₂	Nanorod	6.30	53.30	14.02	0.81	0.64	7.25	[52]
WO ₃	Block	14.6	36.20	12.30	0.79	0.48	4.67	
Pt	—	5.70	6.80	14.68	0.78	0.66	7.57	
H-Nb ₂ O ₅	Sphere	6.10	83.50	11.60	0.79	0.62	5.68	[53]
O-Nb ₂ O ₅	Prism	16.8	270.60	11.71	0.77	0.51	4.55	
M-Nb ₂ O ₅	Particles	3.80	40.90	12.12	0.78	0.61	5.82	
NbO ₂	Honeycomb	1.60	13.90	13.90	0.81	0.70	7.88	
Pt	—	2.50	7.10	14.06	0.79	0.69	7.65	

Short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (η)

活性有决定性影响。氮、氧、硫等原子与过渡金属原子结合,进入过渡金属晶界空隙生成过渡金属化合物。这些外来原子(氮、氧、硫等)与过渡金属原子间的电子迁移改变了过渡金属的电子结构和能级状态,使过渡金属化合物具有一些特殊的物理、化学性质,从而表现出与 Pt 相似的催化性能^[57-58]。但是目前还没有关于过渡金属化合物对电极在 DSCs 催化机理的详细报道。掌握过渡金属化合物对电极的催化机理,对于进一步改善其催化性能至关重要。因此深入研究过渡金属化合物对电极的催化机理是下一步研究的主要内容之一。另一方面,虽然目前过渡金属化合物对电极的催化机理尚不清楚,但是文献结果表明通过提高过渡金属化合物的比表面积和电导性能,降低其扩散阻抗,可以有效提高过渡金属化合物对电极的催化性能,从而提高 DSCs 的光电效率。

4 过渡金属化合物/碳材料复合对电极

将过渡金属化合物分散沉积到碳材料载体上,一方面可以提高过渡金属化合物的分散性和有效表面积,另一方面又能充分利用碳材料优良的电导性能,实现两种材料性能上的优势互补。因此过渡金属化合物与碳材料复合是提高过渡金属化合物对电极性能的一条有效途径。目前报道的碳材料载体主要包括石墨烯、多壁碳纳米管和介孔碳。

石墨烯是一种由单层碳原子组成的二维材料,具有优异的导电和导热能力、高的比表面积、较好的机械强度和较高的透光性,因此在微电子和光电子装置、能量转换与储存及催化等领域备受瞩目^[59-69]。近年来,将石墨烯与过渡金属化合物复合制备 DSCs 对

电极引起了广泛关注。Duo 等^[70]采用水热合成法将 Ni₂P₅ 纳米粒子沉积到石墨烯片上制备了 Ni₂P₅/石墨烯复合对电极。复合对电极的催化性能明显优于单组份电极,所组装 DSCs 的光电效率达到 5.70%,比 Ni₂P₅ 单组份电极效率提高了 45%。Das 等^[71]通过化学气相沉积结合离子吸附反应制备了 CoS/石墨烯复合电极。以 CoS/石墨烯电极为对电极, DSCs 的光电转换效率达到 3.42%,几乎达到单纯石墨烯电极的三倍。Yue 等^[72]通过球磨将 MoS 和石墨烯混合制备 MoS/石墨烯复合电极。以这种机械混合 MoS/石墨烯电极作为对电极, DSCs 的光电转换效率达到 5.98%。Liu 等^[73]用 H₂ 在 650 °C 下还原氧化石墨烯与四硫代钼酸铵混合物,使 MoS 纳米颗粒均匀地沉积在被还原的氧化石墨烯片上,从而大大提高了 MoS 的有效面积,用 MoS/石墨烯复合电极组装的 DSCs 光电转换效率达到 6.04%,比单纯 MoS 电极电池效率提高 26%。

多壁碳纳米管(MWCNT)具有较高的比表面积、优异的电导能力和机械强度、较好的稳定性,因此被广泛应用于催化剂的载体^[74-75]。另外, MWCNT 本身对 I₃⁻ 的还原反应也表现出很高的催化活性^[76-81]。将过渡金属化合物沉积到 MWCNT 上制备复合对电极,可以通过 MWCNT 和过渡金属化合物的优势互补,实现催化性能的协同效应。Tai 等^[82]将 MoS₂ 沉积到 MWCNT 上制备 MoS₂/MWCNT 复合电极(图 4(a))。由于 MWCNT 形成的导电网络和高度分散的 MoS₂ 纳米粒子的协同效应, MoS₂/MWCNT 复合电极对 I₃⁻ 还原反应的催化活性明显高于单组份 MoS₂ 电极。以 MoS₂/MWCNT 电极作为对电极, DSCs 的光电转换效率达到 6.45%,比 MoS₂ 对电极电池效率提高 28%。Song 等^[83]以羟基功能化的 MWCNT 和

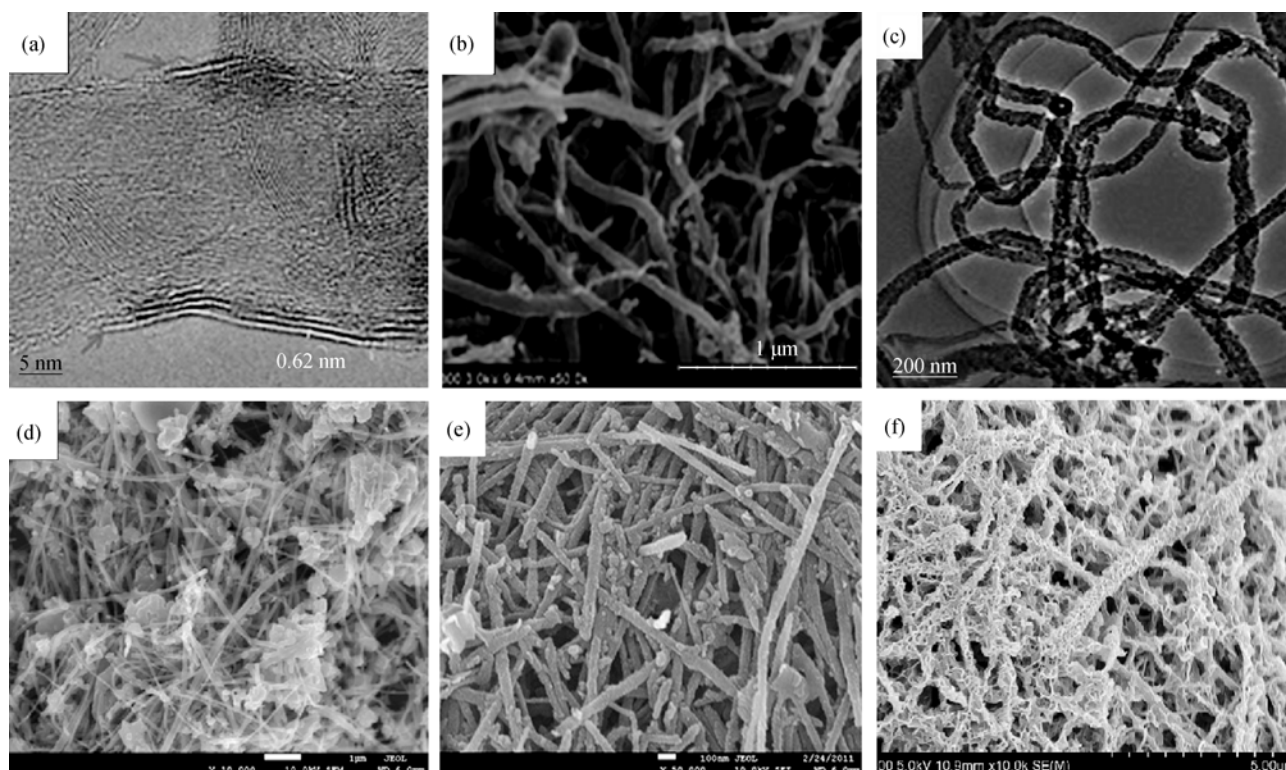


图4 MoS₂/MWCNT^[82](a)和TiN/MWCNT^[84](c)的TEM照片; MoN/MWCNT^[83](b)、WS₂/MWCNT^[85](d)、循环伏安电沉积CoS/MWCNT^[86](e)及脉冲电沉积CoS/MWCNT^[87](f)的SEM照片

Fig. 4 TEM images of MoS₂/MWCNT^[82] (a) and TiN/MWCNT^[84] (c); SEM images of MoN/MWCNT^[83] (b), WS₂/MWCNT^[85] (d), CoS/MWCNT^[86-87] CV electrodeposition (e) and Pulse electrodeposition (f)

钼酸铵为原料制备了 MoN/MWCNT 复合电极(图4(b))。MoN 分散结合在 MWCNT 表面形成的多孔结构改善了电解质中离子的扩散以及 MoN 和 MWCNT 间的电子传递。以 MoN/MWCNT 电极作为对电极, DSCs 的效率达到 6.74%, 远高于 MoN 电极电池的效率(5.57%)。Li 等^[84]通过 TiOSO₄ 在 MWCNT 表面分解后进行氨气氮化制备了 TiN/MWCNT 复合电极(图4(c))。以 TiN/MWCNT 复合电极为对电极, DSCs 的光电转换效率达到 5.41%, 远高于单组份 TiN 和 MWCNT 电极电池的效率(分别为 2.12% 和 3.13%)。Yue 等^[85]采用水热法制备的 WS₂/MWCNT 复合电极(图4(d))同时具有较高的比表面积和较好的电导特性。WS₂/MWCNT 电极对 I₃⁻ 的还原反应表现出与 Pt 电极相同的催化活性。所组装 DSCs 的光电转换效率达到 6.41%, 明显高于单纯 WS₂ 电极电池的效率(4.79%)。Lin^[86]和 Xiao^[87]等分别采用循环伏安电沉积和脉冲电沉积技术使 CoS 均匀分布在 MWCNT 表面(图4(e)和4(f))。这同时增加了 CoS 的有效催化面积和 MWCNT 与导电基底的结合力, 改善了电极的催化性能。所组装的 DSCs 光电转换效率(8.01%)明显高于相应的 Pt 电极(6.39%)和单组份 CoS 电极电池效率(7.38%)。

介孔碳(MC)具有较大的比表面积、较好的稳定

性、较高的孔隙率和电导性能, 因此介孔碳在催化剂载体、储氢材料和电极材料等方面得到广泛应用^[88-90]。与碳纳米管相似, MC 对 I₃⁻ 的还原反应同样表现出很高的催化活性^[91-95]。因此, 将 MC 与过渡金属化合物复合所制备的对电极将同时具有高比表面积和孔隙率、较好的电导性、稳定性和催化活性, 从而实现 MC 与过渡金属化合物催化性能的协同效应。Ma 等^[96-99]所在的课题组将 MoC、WC、WO₂、Ni₄P₅ 及 VC 分别沉积到 MC 表面, 制备了 MoC/MC、WC/MC、WO₂/MC、Ni₄P₅/MC 及 VC/MC 复合电极。表2中数据表明, 过渡金属化合物/MC 复合对电极的性能明显优于单一组份电极。与单一组份过渡金属化合物电极相比, 用复合对电极组装的 DSCs 光电转换效率得到显著提高。这表明将表面积和孔隙率高、电导性能好的 MC 与催化活性高的过渡金属化合物结合制备复合对电极是一种有效的提高对电极性能的方法。

在上述三类过渡金属化合物/碳材料复合电极中, 过渡金属化合物分散在石墨烯、碳纳米管和介孔碳的表面。碳材料作为载体增加过渡金属化合物催化剂的分散性, 从而提高了其有效催化面积。同时, 载体间的空隙有利于电解质中氧化还原对的扩散, 从而降低了扩散阻抗。另外, 碳材料与过渡金属

表 2 MoC/MC、WC/MC、WO₂/MC、Ni₄P₅/MC 及 VC/MC 对电极催化性能及组装的染料敏化太阳能电池光电性能
Table 2 The catalytic activity of MoC/MC, WC/MC, WO₂/MC, Ni₄P₅/MC and VC/MC electrodes and the photovoltaic parameters of dye-sensitized solar cells with different counter electrode

Counter electrode	$R_{ct}/(\Omega \cdot \text{cm}^2)$	$J_{sc}/(\text{m} \cdot \text{A} \cdot \text{cm}^2)$	V_{oc}/V	FF	$\eta/\%$	Ref.
Ni ₄ P ₅ /MC	2.2	13.85	0.780	0.69	7.54	[96]
Ni ₄ P ₅	18.9	13.84	0.770	0.54	5.71	
Pt	3.0	15.01	0.780	0.66	7.76	
MoC/MC	1.3	15.50	0.787	0.68	8.34	[97]
MoC	6.2	13.12	0.804	0.54	5.70	
WC/MC	1.5	14.59	0.804	0.70	8.18	
WC	7.0	12.66	0.807	0.52	5.35	
Pt	2.2	15.23	0.807	0.64	7.89	
WO ₂ /MC	3.6	13.55	0.808	0.71	7.76	[98]
WO ₂	3.0	12.69	0.807	0.65	6.69	
Pt	3.5	13.71	0.780	0.71	7.55	
VC/MC	2.9	13.11	0.808	0.72	7.63	[99]
VC	6.2	12.56	0.782	0.65	6.38	
Pt	4.7	14.08	0.783	0.68	7.50	

化合物紧密结合提供了外电路电子在对电极内快速传输的通道。因此，复合电极实现了碳材料载体与过渡金属化合物催化剂的优势互补。

5 总结

过渡金属化合物种类较多、制备简单、价格低而且催化活性高，可以代替昂贵的 Pt 制备高性能染料敏化太阳能电池对电极。但到现在为止，还没有关于过渡金属化合物对电极催化过程及机理的详细研究报道。因此，应加强过渡金属化合物对电极催化性能的影响因素及其催化机理的研究。

将过渡金属化合物与碳材料结合，一方面利用碳材料高的比表面积提高过渡金属化合物的分散性，从而提高其有效表面积；另一方面可以将过渡金属化合物的高催化活性与碳材料的高导电性结合起来，实现两种材料的优势互补。因此，这是一条制备高性能染料敏化太阳能电池对电极的有效途径。

对过渡金属化合物对电极的研究目前主要集中在其催化性能及组装电池的光电性能上，关于对电极的稳定性研究还偏少。在将来的研究中应加强过渡金属化合物对电极稳定性，特别是在某些特定情况下(如较高的温度、存在少量氧气或水)稳定性的研究。

参考文献:

[1] O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*, 1991, **353**(6346): 737-740.

[2] Nazerruddin M K, Kay A, Rodicio I, *et al.* Conversion of TiO₂ by Cis-x₂Bis(2,2'-bipyridine-4,4'-dicarboxylate) ruthenium (II) charge-transfer sensitized on nanocrystalline TiO₂ electrodes. *J. Am. Chem. Soc.*, 1993, **115**(14): 6382-6390.

[3] Hagfeldt A, Grätzel M. Light-induced redox reactions in nanocrystalline systems. *Chem. Rev.*, 1995, **95**(1): 49-68.

[4] Grätzel M. Photoelectrochemical cells. *Nature*, 2001, **414**(6861): 338-344.

[5] Grätzel M. Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. *J. Photochem. Photobiol. A: Chem.*, 2004, **164**(1/2/3): 3-14.

[6] Yanagida S, Yu Y, Manseki K. Iodine/iodide-free dye-sensitized solar cells. *Acc. Chem. Res.*, 2009, **42**(11): 1827-1838.

[7] Hagfeldt A, Boschloo G, Sun L, *et al.* Dye-sensitized solar cells. *Chem. Rev.*, 2010, **110**(11): 6595-6663.

[8] Vougioukalakis G, Philippopoulos A, Stergiopoulos T. Contributions to the development of ruthenium-based sensitizer for dye-sensitized solar cells. *Coord. Chem. Rev.*, 2011, **255**(21): 2602-2621.

[9] Yella A, Lee H, Tsao H, *et al.* Porphyrin-sensitized solar cell with cobalt (II/III) based redox electrolyte exceed 12% efficiency. *Science*, 2011, **334**(6056): 629-634.

[10] Papageorgiou N, Maier W F, Grätzel M. An iodine/triiodide reduction electrocatalyst for aqueous and organic media. *J. Electrochem. Soc.*, 1997, **114**(3): 876-884.

[11] Papageorgiou N. Counter-electrode function in nanocrystalline photoelectrochemical cells configurations. *Coord. Chem. Rev.*, 2004, **248**(13): 1421-1446.

[12] Wang G, Lin R, Lin Y, *et al.* A novel high-performance counter electrode for dye-sensitized solar cell. *Electrochim. Acta*, 2005, **50**(28): 5546-5552.

[13] Calogero G, Calandra P, Irrera A, *et al.* A new transparent and low-cost counter electrode based on Pt nanoparticles for dye-sensitized solar cells. *Energy Environ. Sci.*, 2011, **4**(5): 1511-1518.

- 1838–1844.
- [14] Sun K, Fan B, Ouyang J. Nanostructured films deposited by polyol reduction of a platinum precursor and their application as counter electrode of dye-sensitized solar cells. *J. Phys. Chem. C*, 2010, **114**(9): 4237–4244.
- [15] Kay A, Grätzel M. Low cost photovoltaic modules base on dye-sensitized nanocrystalline titanium dioxide and carbon powder. *Sol. Energy Mater. Sol. Cells*, 1996, **44**(1): 99–117.
- [16] Murakami T N, Ito S, Wang Q, *et al.* Highly efficient dye-sensitized solar cells based on carbon black counter electrode. *J. Electrochem. Soc.*, 2006, **153**(12): A2255–A2261.
- [17] Joshi P, Zhang L, Chen Q, *et al.* Electrospun carbon nanofibers as low-cost counter electrode for dye-sensitized solar cells. *ACS Appl. Mater. Interface*, 2010, **2**(12): 3572–3577.
- [18] Wu M, Lin X, Wang T, *et al.* Low-cost dye-sensitized solar cells based on nine kinds of carbon counter electrode. *Energy Environ. Sci.*, 2011, **4**(6): 2308–2315.
- [19] Cha S, Koo B, Lee D. Pt-free transparent counter electrode for dye-sensitized solar cells prepared from carbon nanotube micro-balls. *J. Mater. Chem.*, 2010, **20**(4): 656–662.
- [20] Zhao B, Huang H, Jiang P, *et al.* Flexible counter electrode based on mesoporous carbon aerogel for high-efficiency dye-sensitized solar cells. *J. Phys. Chem. C*, 2011, **115**(45): 22615–22621.
- [21] Wang H, Hu Y. Graphene as a counter electrode material for dye-sensitized solar cells. *Energy Environ. Sci.*, 2012, **5**(8): 8182–8188.
- [22] Trancik J, Barton S, Hone J. Transparent and catalytic carbon nanotube films. *Nano Lett.*, 2008, **8**(4): 982–987.
- [23] Li K, Luo Y, Yu Z, *et al.* Low temperature fabrication of efficient porous carbon counter electrode for dye-sensitized solar cells. *Electrochem. Commun.*, 2009, **11**(7): 1346–1349.
- [24] Jiang Q, Li G, Gao X. Highly ordered mesoporous carbon array from natural wood materials as counter electrode of dye-sensitized solar cells. *Electrochem. Commun.*, 2010, **12**(7): 924–927.
- [25] Xiao J, Chen L, Yanagida S. Application of polypyrrole as a counter electrode for a dye-sensitized solar cell. *J. Mater. Chem.*, 2011, **21**(12): 4644–4649.
- [26] Bu C, Tai Q, Guo S. A transparent and stable polypyrrole counter electrode for dye-sensitized solar cell. *J. Power Source*, 2013, **221**(1): 78–83.
- [27] Sakurai S, Jiang H, Takahashi M. Enhanced performance of a dye-sensitized solar cell with a modified poly(3,4-ethylenedioxythiophene)/TiO₂/FTO counter electrode. *Electrochim. Acta*, 2009, **54**(23): 5463–5469.
- [28] Wu L, Li Q, Fan L, *et al.* High-performance polypyrrole nanoparticles counter electrode for a dye-sensitized solar cells. *J. Power Source*, 2008, **181**(1): 172–176.
- [29] Sun H, Luo Y, Zhang Y, *et al.* In situ preparation of a flexible polyaniline/carbon composite counter electrode and its application in dye-sensitized solar cells. *J. Phys. Chem. C*, 2010, **114**(26): 11673–11679.
- [30] Tai Q, Chen B, Guo F, *et al.* In situ prepared transparent polyaniline electrode and its application in bifacial dye-sensitized solar cell. *ACS Nano*, 2011, **5**(5): 3795–3799.
- [31] Hong W, Xu Y, Shi G, *et al.* Transparent graphene/PEDOT-PSS composite films as counter electrodes for dye-sensitized solar cells. *Electrochem. Commun.*, 2008, **10**(10): 1555–1558.
- [32] Zhang J, Hreid T, Li X, *et al.* Nanostructured polyaniline counter electrode for dye-sensitized solar cells: fabrication and investigation of its electrochemical formation mechanism. *Electrochim. Acta*, 2010, **55**(11): 3664–3668.
- [33] Chen J, Li B, Zheng J, *et al.* Polyaniline/carbon film as flexible counter electrode in Pt-free dye-sensitized solar cells. *Electrochim. Acta*, 2011, **56**(12): 4624–4630.
- [34] Wu M, Ma T. Pt-free catalysts as counter electrodes in dye-sensitized solar cells. *ChemSusChem*, 2012, **5**(8): 1343–1357.
- [35] Wang M, Anghel A, Marsan B, *et al.* CoS supersedes Pt as an efficient electrocatalyst for triiodide reduction in dye-sensitized solar cells. *J. Am. Chem. Soc.*, 2009, **131**(44): 15976–15977.
- [36] Lin J, Liao J, Chou S. Cathodic electrodeposition of highly porous cobalt sulfide counter electrodes for dye-sensitized solar cells. *Electrochim. Acta*, 2011, **56**(24): 8818–8826.
- [37] Lin J, Liao J. Mesoporous electrodeposited CoS film as a counter electrode in dye-sensitized solar cells. *J. Electrochem. Soc.*, 2012, **159**(2): D65–D71.
- [38] Lin J, Liao J, Wei T. Honeycomb-like CoS counter electrodes for transparent dye-sensitized solar cells. *Electrochem. Solid-State Lett.*, 2011, **14**(4): D41–D44.
- [39] Kung C, Chen H, Lin C, *et al.* CoS Acicular nanorod arrays for the counter electrode of an efficient dye-sensitized solar cells. *ACS Nano*, 2012, **6**(8): 7016–7025.
- [40] Chi W, Han J, Yang S, *et al.* Empolying electrostatic self-assembly of tailored nickel sulfide nanoparticles for quasi-solid-state dye-sensitized solar cells with Pt-free counter electrode. *Chem. Commun.*, 2012, **48**(76): 9501–9503.
- [41] Sun H, Qin D, Huang S, *et al.* Dye-sensitized solar cells with NiS counter electrode electrodeposited by a potential reverse technique. *Energy Environ. Sci.*, 2011, **4**(8): 2630–2637.
- [42] Ku Z, Li X, Liu G, *et al.* Transparent NiS counter electrodes for thiolate/disulfide mediated dye-sensitized solar cells. *J. Mater. Chem. A*, 2013, **1**(2): 237–240.
- [43] Zhao W, Lin T, Sun S, *et al.* Oriented single-crystalline NiS nanorod arrays “two-in-one” counter electrode for dye-sensitized solar cells. *J. Mater. Chem. A*, 2013, **1**(2): 194–198.
- [44] Wu M, Wang Y, Lin X, *et al.* Economical and effective sulfide catalysts for dye-sensitized solar cells as counter electrodes. *Phys. Chem. Chem. Phys.*, 2011, **13**(43): 19298–19301.
- [45] Jiang Q, Li J, Gao X. Highly ordered TiN nanotube arrays as counter electrode of dye-sensitized solar cells. *Chem. Commun.*, 2009, **45**(44): 6720–6722.
- [46] Zhang X, Chen X, Dong S, *et al.* Hierarchical micro/nano structured titanium nitride spheres as high performance counter electrode for a dye-sensitized solar cell. *J. Mater. Chem.*, 2012, **22**(1): 6067–6071.
- [47] Jiang Q, Li G, Liu S, *et al.* Surface-nitrided nickel with bifunctional structure as low-cost counter electrode for dye-sensitized solar cells. *J. Phys. Chem. C*, 2010, **114**(31): 13397–13401.
- [48] Li G, Song J, Pan G, *et al.* Highly Pt-like electrocatalytic activity of

- transition metal nitride for dye-sensitized solar cells. *Energy Environ. Sci.*, 2011, **4**(5): 1680–1683.
- [49] Wu M, Zhang Q, Xiao J, *et al.* Two flexible counter electrode based on molybdenum and tungsten nitrides for dye-sensitized solar cells. *J. Mater. Chem.*, 2011, **21**(29): 10761–10766.
- [50] Wu M, Lin X, Guo W, *et al.* Great improvement of catalytic activity of the oxide counter electrode fabricating in N₂ atmosphere for dye-sensitized solar cells. *Chem. Commun.*, 2013, **49**(11): 1058–1060.
- [51] Yun S, Wang L, Guo W, *et al.* Non-Pt counter electrode catalysts using tantalum oxide for low-cost dye-sensitized solar cells. *Electrochem. Commun.*, 2012, **24**(1): 69–73.
- [52] Wu M, Lin X, Hagfeldt A, *et al.* A novel catalyst of WO₂ nanorod for the counter electrode of dye-sensitized solar cells. *Chem. Commun.*, 2011, **47**(15): 4535–4537.
- [53] Lin X, Wu M, Wang Y, *et al.* Novel counter electrode catalyst of niobium oxide supersede Pt for dye-sensitized solar cells. *Chem. Commun.*, 2011, **47**(41): 11489–11491.
- [54] Wu M, Lin X, Hagfeldt A, *et al.* Low cost molybdenum carbide and tungsten carbide counter electrode for dye-sensitized solar cells. *Angew. Chem. Int. Ed.*, 2011, **50**(15): 3520–3524.
- [55] Jang J, Ham D, Ramasamy E, *et al.* Platinum-free tungsten carbide as effective counter electrode for dye-sensitized solar cells. *Chem. Commun.*, 2010, **46**(45): 8600–8602.
- [56] Ko A, Oh J, Lee Y, *et al.* Characterizations of tungsten carbide as non-Pt counter electrode in dye-sensitized solar cells. *Mater. Lett.*, 2011, **65**(14): 2220–2223.
- [57] Krawiec P, De Colar P L, Glaser R, *et al.* Oxide foams for the synthesis of high-surface-area vanadium nitride catalysts. *Adv. Mater.*, 2006, **18**(4): 505–508.
- [58] Bennett L H, Cuthill J R, McAlister A J, *et al.* Electronic and catalytic properties of tungsten carbide. *Science*, 1975, **187**(4179): 858–859.
- [59] Sun Y, Wu Q, Shi G. Graphene based new energy materials. *Energy Environ. Sci.*, 2011, **4**(4): 1113–1132.
- [60] Pang S, Hernandez Y, Feng X, *et al.* Graphene as transparent electrode materials of organic electronics. *Adv. Mater.*, 2011, **23**(25): 2779–2795.
- [61] Jiang L, Lu X. Graphene application in solar cells. *J. Inorganic Mater.*, 2012, **27**(11): 1129–1137.
- [62] Kavan L, Yum J, Grätzel M, *et al.* Optically transparent cathode for dye-sensitized solar cells based on graphene nanoplatelets. *ACS Nano*, 2011, **5**(1): 165–172.
- [63] Kavan L, Yum J, Grätzel M, *et al.* Graphene nanoplatelets cathode for Co(III)/II mediated dye-sensitized solar cells. *ACS Nano*, 2011, **5**(11): 9171–9178.
- [64] Jang S, Kim Y, Kim D, *et al.* Electrostatically sprayed thin film of aqueous dispersible graphene nanosheets: highly efficient cathode for dye-sensitized solar cells. *ACS Appl. Mater. Interface*, 2012, **4**(7): 3500–3507.
- [65] Choi H, Kim H, Hwang S, *et al.* Graphene counter electrode for dye-sensitized solar cells by electrophoretic deposition. *J. Mater. Chem.*, 2011, **21**(21): 7548–7551.
- [66] Roy-Mayhew J D, Bozym D J, Punckt C, *et al.* Functionalized graphene as catalytic counter electrode in dye-sensitized solar cells. *ACS Nano*, 2010, **4**(10): 6203–6211.
- [67] Zhang H, Neo C, Mei X, *et al.* Reduced oxide graphene film fabricated by gel coating and its application as Pt-free counter electrode of highly efficient iodide/triiodide dye-sensitized solar cells. *J. Mater. Chem.*, 2012, **22**(29): 14465–14474.
- [68] Xu Y, Bai H, Li G, *et al.* Flexible graphene film via the filtration of water-soluble noncovalent functionalized graphene sheets. *J. Am. Chem. Soc.*, 2008, **130**(18): 5856–5857.
- [69] Zhang D, Li X, Li H, *et al.* Graphene based counter electrode for dye-sensitized solar cells. *Carbon*, 2011, **49**(15): 5382–5388.
- [70] Duo Y, Li G, Song J, *et al.* Nickel phosphide-embedded graphene as counter electrode of dye-sensitized solar cells. *Phys. Chem. Chem. Phys.*, 2012, **14**(4): 1339–1342.
- [71] Das S, Sudhagar P, Nagarajan S, *et al.* Synthesis of graphene-CoS electrocatalytic electrodes for dye-sensitized solar cells. *Carbon*, 2012, **50**(13): 4815–4821.
- [72] Yue G, Lin J, Tai S, *et al.* A catalytic composite film MoS₂/graphene flakes as a counter electrode for Pt-free dye-sensitized solar cells. *Electrochim. Acta*, 2012, **85**(1): 162–168.
- [73] Liu C, Tai S, Chou S, *et al.* Facile synthesis of MoS₂/graphene nanocomposite with high catalytic activity toward triiodide reduction in dye-sensitized solar cells. *J. Mater. Chem.*, 2012, **22**(39): 21057–21064.
- [74] Umeyama T, Imahori H. Carbon nanotube-modified electrodes for solar energy conversion. *Energy Environ. Sci.*, 2008, **1**(1): 120–133.
- [75] Ahmad K, Pan W. Dramatic effect of multiwalled carbon nanotube on the electrical properties of alumina ceramic nanocomposites. *Compos. Sci. Technol.*, 2009, **69**(7/8): 1016–1021.
- [76] Lee W, Ramasamy E, Lee D, *et al.* Efficient dye-sensitized solar cell with catalytic multiwalled carbon nanotube counter electrode. *ACS Appl. Mater. Interface*, 2009, **1**(6): 1145–1149.
- [77] Seo S, Kim S, Koo B, *et al.* Influence of electrolyte composition on the photovoltaic performance and stability of dye-sensitized solar cell with multiwalled carbon nanotube catalyst. *Langmuir*, 2010, **26**(12): 10341–10346.
- [78] Cho H, Kim H, Hwang S, *et al.* Dye-sensitized solar cells using graphene-based carbon nanocomposite as counter electrode. *Sol. Energy Mater. Sol. Cell*, 2011, **95**(1): 323–325.
- [79] Trancik J, Barton S, Hone J. Transparent and catalytic carbon nanotube films. *Nano Lett.*, 2008, **8**(4): 982–987.
- [80] Ramasamy E, Lee W, Lee D, *et al.* Spray coated multi-walled carbon nanotube counter electrode for triiodide reduction in dye-sensitized solar cells. *Electrochem. Commun.*, 2008, **10**(7): 1087–1089.
- [81] Suzuki K, Yamaguchi M, Kumagai M, *et al.* Application carbon nanotubes to counter electrode of dye-sensitized solar cells. *Chem. Lett.*, 2003, **32**(1): 28–29.
- [82] Tai S, Liu C, Chou S, *et al.* Few-layer MoS₂ nanosheets coated on multiwalled carbon nanotubes as low-cost highly electrocatalytic counter electrode for dye-sensitized solar cells. *J. Mater. Chem.*, 2012, **22**(47): 24753–24759.
- [83] Song J, Li G, Xiong F, *et al.* Synergistic effect of molybdenum ni-

- tride and carbon nanotube on electrocatalysis for dye-sensitized solar cells. *J. Mater. Chem.*, 2012, **22(38)**: 20580–20585.
- [84] Li J, Wang F, Jiang Q, *et al.* Carbon nanotube with titanium nitride as a low-cost counter electrode materials for dye-sensitized solar cells. *Angew. Chem. Int. Ed.*, 2010, **49(21)**: 3653–3656.
- [85] Yue G, Wu J, Lin J, *et al.* A counter electrode of multiwalled carbon nanotube decorated with tungsten sulfide used in dye-sensitized solar cells. *Carbon*, 2013, **55(1)**: 1–9.
- [86] Lin J, Liao J, Hung T. A composite counter electrode of CoS/MWCNT with highly electrocatalytic activity for dye-sensitized solar cells. *Electrochem. Commun.*, 2011, **13(9)**: 977–980.
- [87] Xiao Y, Wu J, Lin J, *et al.* Pulse electrodeposition of CoS on the MWCNT/Ti as a high performance counter electrode for the Pt-free dye-sensitized solar cells. *J. Mater. Chem. A*, 2013, **1(4)**: 1289–1295.
- [88] Ryoo R, Joo S, Kruk M, *et al.* Ordered mesoporous carbon. *Adv. Mater.*, 2001, **13(9)**: 677–681.
- [89] Lee J, Kim J, Hyeon T. Recent progress in the synthesis of porous carbon materials. *Adv. Mater.*, 2006, **18(16)**: 2073–2094.
- [90] Candelaria S, Shao Y, Zhou W, *et al.* Nanostructured carbon for energy storage and conversion. *Nano Energy*, 2012, **1(2)**: 195–220.
- [91] Ramasamy E, Chun J, Lee J. Soft-template synthesized ordered mesoporous carbon counter electrode for dye-sensitized solar cells. *Carbon*, 2010, **48(15)**: 4563–4565.
- [92] Fang B, Fan S, Kim J, *et al.* Incorporation hierarchical nanostructured carbon counter electrode into metal-free organic dye-sensitized solar cell. *Langmuir*, 2010, **26(13)**: 11238–11243.
- [93] Wang G, Xing W, Zhuo S. Application of mesoporous carbon to counter electrode for dye-sensitized solar cells. *J. Power Source*, 2009, **194(1)**: 568–573.
- [94] Ramasamy E, Lee J. Large-pore sized mesoporous carbon electrocatalyst for efficient dye-sensitized solar cells. *Chem. Commun.*, 2010, **46(12)**: 2136–2138.
- [95] Srinivasu P, Islam A, Singh S O, *et al.* Highly efficient nanoporous graphitic carbon with tunable texture properties for dye-sensitized solar cells. *J. Mater. Chem.*, 2012, **22(39)**: 20866–20869.
- [96] Wu M, Bai J, Wang Y, *et al.* Highly efficient phosphide/carbon counter electrode for both iodide and organic redox couples in dye-sensitized solar cells. *J. Mater. Chem.*, 2012, **22(22)**: 11121–11127.
- [97] Wu M, Lin X, Hagfeldt A, *et al.* Low-cost Molybdenum carbide and tungsten carbide counter electrode for dye-sensitized solar cells. *Angew. Chem. Int. Ed.*, 2011, **50(13)**: 3520–3524.
- [98] Wu M, Lin X, Wang L, *et al.* In-situ synthesized economical tungsten oxide imbedded in mesoporous carbon for dye-sensitized solar cells as counter electrode catalyst. *J. Phys. Chem. C*, 2011, **115(45)**: 22598–22602.
- [99] Wu M, Lin X, Wang Y, *et al.* Economical Pt-free catalysts for counter electrode of dye-sensitized solar cells. *J. Am. Chem. Soc.*, 2012, **134(7)**: 3419–3428.