

染料敏化太阳能电池敏化剂材料研究进展

陈 汉, 毕恩兵, 韩礼元

(上海交通大学 金属基复合材料国家重点实验室, 上海 200240)

摘 要: 染料敏化太阳电池(DSCs)是一种新型光伏电池,在充满前景的太阳能发电市场中,实现染料敏化太阳电池商品化的最重要的前提之一就是提高能量转换效率。介绍了染料敏化太阳电池的结构与基本原理,在影响DSCs能量转换效率的三大因素中,重点综述了通过染料敏化剂材料的设计和开发来提高电池光电流。介绍了钌多吡啶配合物、非金属有机染料、有机金属染料(酞菁锌和卟啉锌染料)的设计开发及其如何增加电池光吸收效率、降低染料分子在 TiO_2 半导体材料上的聚集及电子复合,提高电池光电流。同时介绍了现阶段通过共敏化剂方法提高DSCs的光电能量转换效率的进展。最后,对于进一步提高能量转化效率所面临的挑战,以及DSCs的商品化前景进行了展望。

关键词: 染料敏化剂材料; 太阳电池; 能量转换效率; 光电转换

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Highly Efficient Dye-Sensitized Solar Cells: Progress in Sensitizer Dyes

CHEN Han, BI Enbing, HAN Liyuan

(State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200240, China)

Abstract: Dye-sensitized solar cell (DSCs) is a new type of photovoltaic cell. High energy conversion efficiency is one of the most important keys to the commercialization of DSCs in the huge electricity generation market. The structure and the principle of DSCs are introduced. Among the three main parameters to improve the conversion efficiency of DSCs, we mainly review the development of dye to improve battery light current through the design and development of dye sensitized material, such as Ru polypyridyl complex, Metal-free organic dyes, Zn porphyrin and phthalocyanine dyes to increase the short circuit current and energy conversion efficiency. Increasing the energy conversion efficiency in DSCs with co-sensitizers is reviewed. Finally, we illustrate the challenges and outlook of how to further improve the efficiency to accelerate the progress in the commercialization of DSCs.

Key words: dye sensitizer; solar cells; energy conversion efficiency; photoelectric conversion

1 前 言

随着全球能源和环境问题的日益增加,现代社会的发展需要更多低污染、丰富可持续的能源。其中,最可行的方法之一即是利用太阳电池将太阳能直接转换成电能。目前硅基太阳电池已经商品化,相对于普通的硅基太阳电池,染料敏化太阳电池(DSCs)具有低生产成本及环保特性,从而受到越来越多的关注^[1-6]。

通常,DSCs由透明导电氧化物(TCO)电极、染料敏化纳米晶二氧化钛(TiO_2)薄膜、吸附在 TiO_2 表面的染料、铂金(Pt)对电极和电解质组成(见图1)。DSCs中主要的光电转换过程如下所述:太阳光被 TiO_2 薄膜上吸附的染料分子吸收后,染料分子中的一个电子从基态跃迁到激发态,这个电子快速注入到 TiO_2 薄膜的导带(CB)里,然后这些电子迁移至TCO前电极和外部电路中;被氧化的染料分子通过电解质中的 I^- 离子重新还原至中性状态。 I^- 会随着 I_3^- 离子在Pt对电极上的还原反应而得到再生^[7-8](见图2)。这个光电转换过程与光合成过程十分相似,所以DSCs也被称为光合成型太阳电池。

自从1991年纳米晶DSCs被报道后,为了加速未来

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第一作者: 陈汉,男,1980年生,博士

通信作者: 韩礼元,男,1956年生,教授,博士生导师

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的实际应用, 进一步提高能量转换效率的研究得到了大量开展。大量的研究集中于开发电池材料, 例如多孔性 TiO_2 膜材料、染料、电解液材料及对电极材料。至今 DSCs 的光电转换效率已经超过 11%。但是, 与硅基太阳能电池相比, 它的转换效率还有待提高^[9-10], 所以, 为了尽快实现 DSCs 的商品化与实用化, 提高 DSCs 的光电转换效率是一个关键因素之一。DSCs 的能量转换效率可以通过测量电压-电流 ($I-V$) 特性参数并由公式 1 来确定。其中, P_{in} 为太阳光照功率密度, A_{cell} 为受到光照的电池面积, I_{sc} 为短路电流, V_{oc} 为开路电压, FF 为填充系数, 见公式(1):

$$\eta = \frac{I_{\text{sc}} \cdot V_{\text{oc}} \cdot \text{FF}}{P_{\text{in}} \cdot A_{\text{cell}}} \quad (1)$$

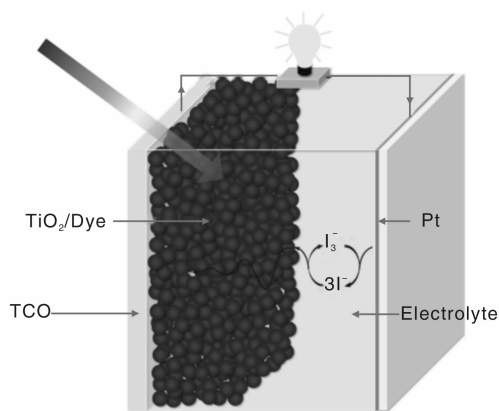


图1 染料敏化太阳能电池的结构示意图

Fig. 1 Schematic structure in dye-sensitized solar cells

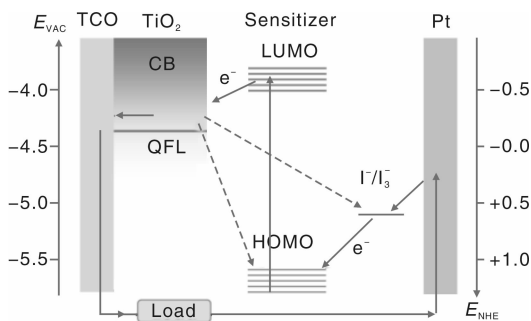


图2 染料敏化太阳能电池能量转换机理

Fig. 2 Conversion mechanism in dye-sensitized solar cells

因此, 为了达到提高 DSCs 的能量转换效率, 我们必须提高 DSCs 的 I_{sc} , V_{oc} , FF 这 3 大因素。提高这些系数的方法有很多, 比如: 提高 I_{sc} 可以通过开发新染料; V_{oc} 的高低取决于 TiO_2 的费米 (Fermi) 能级和电解液中电解质氧化还原电对的能级差, 所以很多研究致力于开发能级低的电解质; FF 主要取决于电池电路内部的电阻。在本文中, 我们选择性地论述了利用提高短路

电流 I_{sc} , 进而提高 DSCs 能量转换效率的主要进展, 其中包括如何设计开发新型敏化剂材料来提高光效应, 以及介绍如何使用 co-sensitizers 来提高光电流与光电转换效率。

高效率太阳能电池在短路条件下, 由光生成的电荷流入外电路中形成短路电流的效率接近于 1。 I_{sc} 等于光生电流 I_{ph} 与其在二极管和并联电阻中的损耗电流间的差值。如果入射光子通量为 $I_{\text{photon}}(\lambda)$, 那么外电路中的总电流应如公式(2)所示:

$$I_{\text{sc}} = q_e \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} I_{\text{photon}}(\lambda) \cdot \text{IPCE}(\lambda) d\lambda \quad (2)$$

式中, q_e 为电荷单位, $\text{IPCE}(\lambda)$ 为入射光子向电荷的转换效率, 并满足公式(3):

$$\text{IPCE}(\lambda) = \eta_{\text{LHE}} \cdot \eta_{\text{inj}} \cdot \eta_{\text{cc}} \quad (3)$$

式中, η_{LHE} 为光捕获效率, η_{inj} 表示从光激发染料到 TiO_2 的电子注入效率, η_{cc} 表示电极对光生电荷的收集效率。已有的研究已确认 η_{inj} 达到 1 的效率值需要满足以下条件, 即在 TiO_2 导带和染料最低空分子轨道 (LUMO) 之间存在约 0.2 V 的电势差 ($-\Delta G$), 为从染料至 TiO_2 的导带 (CB) 进行电子注入提供所需的驱动力^[11], 在染料最高已占分子轨道 (HOMO) 与还原氧化电势之间存在约 0.3 V 的超电势^[12-13], 为氧化染料的再生提供驱动力。在现有的效率超过 10% 的高效 DSCs 中, 我们发现 η_{inj} 和 η_{cc} 的乘积约等于 1^[5]。因此, 增加短路电流 I_{sc} 的主要方法即是提高光捕获效率 η_{LHE} , 而光捕获效率 η_{LHE} 则取决于染料的摩尔消光系数 (ϵ)、 TiO_2 薄膜上附着的染料数量以及染料敏化膜内的入射光的光程长度。

为了有效吸收更多的太阳光及获得更高的光电流, 找到在可见或近红外 (NIR) 区都具较高摩尔消光系数 (ϵ) 的染料是非常重要的。例如, 图 3 所示即为在假设 IPCE 为 100% 的条件下, 利用公式 2 计算得到的从太阳光谱紫外区至敏化剂的吸收带边区间的太阳光可以形成的光电流。如果 IPCE 谱线延伸至 800 nm, 则 I_{sc} 值等于 27.3 mA/cm²。如果 IPCE 谱线延伸至 920 nm, 光电流可达到 34.7 mA/cm²。为了获得一个较宽的光吸收光谱, 必须要减少敏化剂分子的 HOMO 与 LUMO 之间的能隙。另外, 随着 TiO_2 薄膜厚度的增加, TiO_2 薄膜中的电子与氧化还原介质之间的电荷复合将增加, 从而 V_{oc} 会降低。因此, 必须要减少 TiO_2 薄膜的厚度, 这将导致所附着的染料量也会相应地减少。因此, 要想在较薄的 TiO_2 薄膜中实现高效率的光捕获, 敏化剂分子就必须有较高的摩尔消光系数 (ϵ)。这样不仅能提高 I_{sc} , 同时还能提高 V_{oc} 。下文中, 我们综述了染料敏化剂的最新进展, 并着重讨论了分子设计及其对电池性能的

影响。

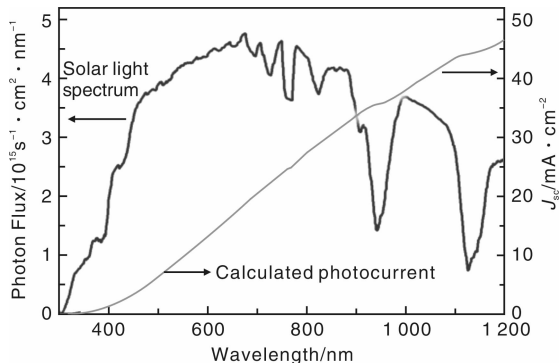


图 3 太阳光谱及在假设从 300 nm 至相应波长汇集 100% 的 IPCE 的条件下利用等式 3 计算的光电流

Fig. 3 Solar light spectrum and calculated photocurrent from equation 3 with assumed IPCE of 100% integrated from 300 nm to corresponding wavelength

2 染料敏化剂材料开发

至今为止,已开发的高效染料敏化剂包括有机金属配合物、非金属有机化合物、锌卟啉及酞菁锌等。高效敏化剂应具备一些重要结构特性,如 HOMO 与 LUMO 电子分布应具有较好的空间分布,进而稳定光激发状态、确保电子高效注入 TiO_2 电极中;以及固定基团应连接在分子的 LUMO 部分,进而实现氧化态染料的有效再生和抑制电子反向流动。

2.1 钌多吡啶配合物

在 DSCs 中,最成功的敏化剂是钌多吡啶配合物。由于其具有宽光谱吸收、与 TiO_2 /碘氧化还原电对匹配的电子能级、长的激发态电子寿命、以及优异的稳定性和结构可调性,一直以来受到广泛的关注与研究。在钌多吡啶配合物中, HOMO 主要位于钌和 NCS 配体上,而 LUMO 则主要分布在多吡啶配体上(见图 4)。这种理想的 LUMO 和 HOMO 的电子能级分布便于经由化学键向 TiO_2 进行高效的电子注入及氧化染料的再生。

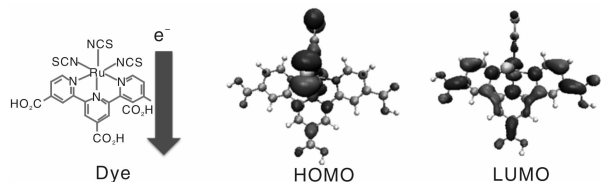


图 4 Black dye(N749)中的电子流动方向及 HOMO 和 LUMO 电子分布

Fig. 4 Electron flow and the HOMO and LUMO distributions of black dye (N749)

(NIR)区都表现出较好的光吸收能力。其中,可见-近红外(VIS-NIR)区内呈现的吸收带为钌到多吡啶配体的单线态金属到配体的电荷转移($^1\text{MLCT}$)。扩展多吡啶配体的 π -共轭可导致 LUMO 能级降低,及吸收光谱红移。例如,将 N719 中的两个 4, 4'-联羧基-2, 2'-联吡啶(dcbpy)染料^[14]转变成一个 4, 4', 4''-三羧基-2, 2': 6', 2''-三联吡啶(tctpy)配体和一个 NCS 配体,从而得到 Black dye^[15]。由于共轭度更大的 tctpy 配体及三个 NCS 配体强大的给电子能力(见图 5), $^1\text{MLCT}$ 吸收峰从 530 nm 红移至 610 nm。使得 DSCs 的 IPCE 起始点的从约 800 nm(N719)处红移至 900 nm 以上(Black dye), 如图 5 中所示。而采用更大的共轭配体 2, 2': 6', 2'': 6'', 2'''-四联吡啶(qpy)(N886)去取代多吡啶配体(N719), $^1\text{MLCT}$ 则进一步红移至 637 nm。然而,该染料分子间严重的聚集作用导致 η_{inj} 下降^[16]。

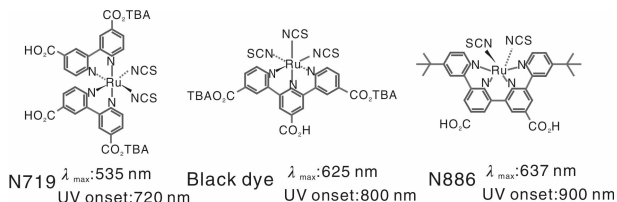


图 5 钌-NCSx-多吡啶的分子结构、吸收光谱($^1\text{MLCT}$)

Fig. 5 Molecular structures and normalized absorption spectra (by $^1\text{MLCT}$ bands) of Ru-NCSx-polypyridyl

除了通过改变配体结构来调节吸收光谱,采用不同的配位金属也是一种有效改变敏化剂的吸收特性的途径。较为成功的例子为铱 tctpy 染料,铱离子的能级移动和重原子效应将会同时增强 $^1\text{MLCT}$ 和 $^3\text{MLCT}$ 的摩尔消光系数(ϵ),使得吸收光谱可延伸至约 900 nm 处,而 IPCE 起始点将延伸至 1 000 nm 附近^[17-19]。

对于钌多吡啶染料而言,在可见-近红外区的摩尔消光系数通常低于有机染料的。例如, N719 和 Black dye 的 $^1\text{MLCT}$ 吸收峰值处的摩尔消光系数(ϵ)分别为 $14\,700$ 和 $7\,000\,\text{M}^{-1}\cdot\text{cm}^{-1}$ (而有机染料则为 $15\,000\sim 60\,000\,\text{M}^{-1}\cdot\text{cm}^{-1}$)。因此,为了能充分吸收光子,需

钌多吡啶配合物在紫外(UV)区、可见及近红外

要采用更厚 TiO_2 薄膜。然而, 增加 TiO_2 薄的厚度会降低 V_{oc} 值。因此, 增加钌多吡啶染料的摩尔消光系数 (ε) 是提高电池性能的另一重要途径。而在共配体或多吡啶配体中引入 $\pi-\pi$ 共轭基团, 能够有效地增加钌染料的摩尔消光系数。

2006 年, 文献中报道了用两个供电子的 2, 5-二甲基吡啶团置换一个 bpy 配体, 进而合成混配钌染料 N945H^[20] (见图 6a)。该染料的 ¹MLCT 带的摩尔消光系数 (ε) ($18\,900\text{ M}^{-1}\cdot\text{cm}^{-1}$) 明显高于 N719。该报道还指出 DFT 计算对高效钌多吡啶染料的分子设计具有重要的指导意义。为考察供电子取代基的影响, 引入了富电子的杂芳族化合物, 如噻吩和呋喃^[21-26]。在其他研究中, 含有噻吩衍生物和己基链(在 bpy 配体)的混配钌染料 C101^[21] 和 C106^[25] 不仅能达到 11% 以上的高转换效率, 还具有良好的稳定性能^[20,25]。在这些染料中, HOMO 能级均随着 $\pi-\pi$ 共轭基团的供电子能力的增加而提高。

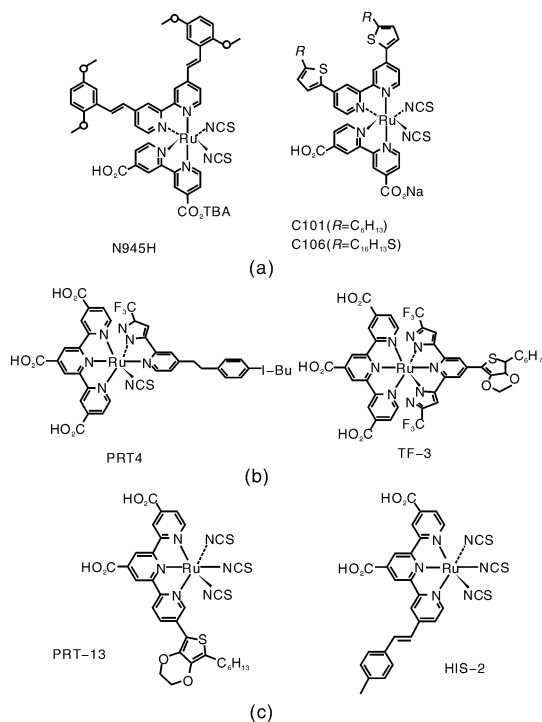


图 6 (a) 具有 π -共轭体系的钌 bpy 敏化剂的分子结构, N945H、C101 和 C106; (b) 给体取代的; (c) tpy 取代的 Black dye 类似物

Fig. 6 (a) Molecular structures of the Ru-bpy sensitizers with-conjugate system, N945H, C101, and C106, (b) donor substituted, and (c) tpy substituted black dye analogues

此外, 钌 tpy 染料的摩尔消光系数 (ε) 也较低, 所以 π -共轭扩展理念还适用于钌 tpy 配合物 (见图 6b, c)。与钌 bpy 染料相似, 采用供电子 $\pi-\pi$ 共轭配体来

取代 Black dye 中的 NCS 基团, 进而调节染料的光谱性能^[27-29]。在这些敏化剂中, ¹MLCT 的摩尔消光系数 (ε) 得到提高。但是, 由于替换配体和 NCS 配体间的 σ -给体和 π -受体的差异, 导致吸收光谱蓝移。另一方面, 一些研究将 π -共轭扩展理念应用到开发与 Black dye 类似的 tpy 配体中^[30-32]。通过 π -共轭基团取代吡啶环的 5 或 6 位的一个羧基, 成功提高了这些染料在紫外-可见光区的 ε 值。同时, 与 Black dye 相比, ¹MLCT 带的 ε 几乎没有任何改变。通过 DFT 计算发现利用己基噻吩或其它强供体代替羧化物时, 低的 LUMO 能级主要分布在 dtpy 配体上^[30-31]。最近, 我们开发出了一种含有 4 位甲基苯乙烯取代的吡啶钌染料 HIS-2^[33]。HIS-2 染料的 LUMO 能级分布在 dtpy 和苯乙烯基组上。因此, 不仅提高了 UV 区内 $n-\pi$ 和 $\pi-\pi$ 吸收的 ε 值, 还提高了 NIR 区内的 ¹MLCT 带的 ε 值。与 Black dye 相比, 在全部光谱区域内, HIS-2 的 IPCE 光谱都得到了改进。而取代基的取代位置和供电子特性不同导致了两种钌 dtpy 染料间的 LUMO 分布差异。

在光照条件下, 染料分子中 NCS 基很容易与电解质中的溶剂、氧化还原介质和/或添加剂发生消除或交换反应, 因此从分子稳定性的角度来看, 开发能取代 NCS 的多齿配体具有非常重要的意义。最先报道出的转换效率达到 10.1% 的不含 NCS 的钌染料为环金属钌配合物, YE-05^[34]。此后, 又相继开发出了各种不含 NCS 的钌 dc bpy^[34-37] 和钌 tctpy^[29-31] 敏化剂, 且转换效率均在 9% 以上。

2.2 非金属有机染料

由于不含金属的有机染料具有高摩尔消光系数、低成本、及易于分子修饰等优点, 所以受到越来越多的关注。给体- π 共轭体-受体 (D- π -A) 结构是一种基本且广泛使用的分子设计方案。通常采用强给电子的基团 (如三芳胺^[38]、呋喃^[39]、二氢吡啶^[40-43]、吩噻嗪^[44-46]、三并噻吩^[47]) 作为给体。受体则是由吸电子基团和锚定基组成。锚定基团经常采用具有吸电子能力及与 TiO_2 电极的协调性的氰基丙烯酸及其类似物^[48-49]、绕丹宁^[40-41,44,50-52] 和吡啶及其衍生物^[53-54]。而 π -共轭体则包括多烯^[55-57]、聚炔烃^[58-60]、噻吩^[61-64]、呋喃^[65-67]、吡咯^[68-70]、并噻吩^[71-74] 等。在 D- π -A 有机染料中, HOMO 主要分布在给体和富含电子的 π -共轭体上, 而 LUMO 则分布在受体和锚定基团上。总的来说, 与钌多吡啶染料相比, D- π -A 染料在可见-近红外区具有更高的摩尔吸收系数。

最近两年, 朱为宏、田禾等向共轭桥链中引入缺电

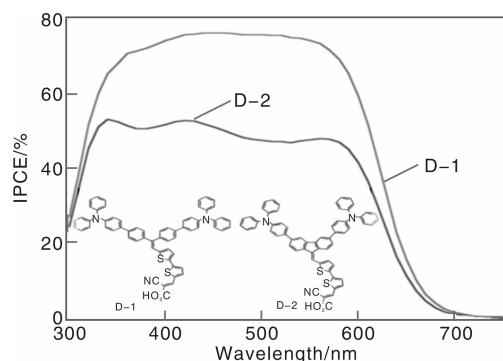


图 9 D-1 和 D-2 的分子结构和 IPCE 谱图

Fig. 9 Molecular structures and IPCE spectra of D-1 and D-2^[64]

①其宽且平面的共轭结构易于导致分子聚集，从而加重电荷复合；②HOMO 与 LUMO 轨道均分布在大环体系，导致光生载流子很难脱离大环注入到二氧化钛的导带；③酞菁锌和卟啉锌通常在 B-带和 Q-带之间的可见光区域鲜有吸收。因此，克服这些缺点将成为开发新型酞菁锌和卟啉锌类染料的关键所在。

卟啉锌染料在 450 nm 附近具有很强的 B-带吸收 ($\epsilon > 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1}$)，在 600 nm 附近表现出中等强度的 Q-带吸收 ($\epsilon > 2 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$)。卟啉环的 β -位、外围的间位以及大环体系均能够进行多样化取代，易于衍生出结构多样的卟啉锌配合物^[107-109]。近年来，科学家们开发出一系列具有不对称结构的卟啉锌染料，此类染料表现出优异的光电性能(图 10a)。例如，GD2 是一个具有推-拉结构的卟啉锌染料，其大环外围间位完全被 4-甲基苯基取代，锚定基团通过共轭 π 键连接在卟啉环的 β -位^[110]。GD2 分子的不对称性导致电子流具有方向性，电子能够从分子的 LUMO 轨道有效地注入到二氧化钛的导带，表现出较高的光电转换效率(7.1%)。将强给电子基团和强吸电子能力的锚定基团引入卟啉体系是一种使分子 LUMO 和 HOMO 轨道空间排布分离的有效方法。例如，YD2^[111](图 10a)中二苯胺具有很强的给电子能力，分子 HOMO 轨道分布在二苯胺基团上，而 LUMO 轨道离域于卟啉和锚定基团。由于卟啉环是一个很宽的平面结构，易引起分子聚集从而降低其光电转换效率，简单地引入烷基链的方法很难抑制分子间聚集，因此新的策略应运而生。比如在卟啉环的外围间位引入邻位取代的苯基^[5,112]，如图 11b 所示，基于 LD 系列染料的分子动力学计算表明，苯环上的邻位烷基链能够有效地覆盖卟啉环。LD 系列染料的 IPCE 值随着烷基链的增长而提高，带有 12-烷基链的染料 LD14 和 LD16 的 IPCE 最大值均高达 90%。

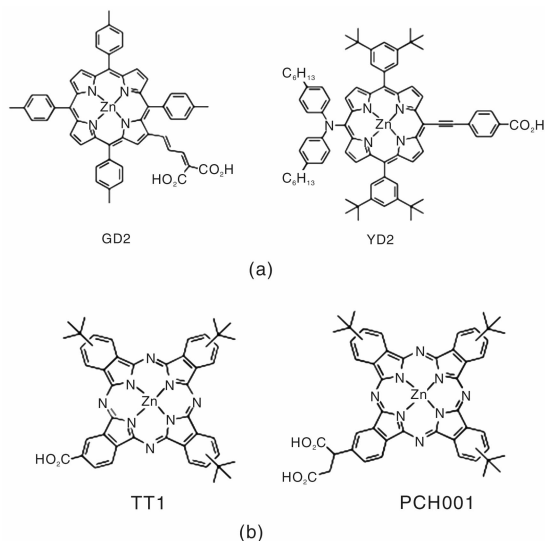


图 10 (a) 不对称 D-A 型卟啉锌的分子结构，(b) 不对称型酞菁锌分子结构

Fig. 10 (a) molecular structures of asymmetric and D-A type ZnPor dyes and (b) asymmetric ZnPc dyes

不同于结构多样的卟啉锌染料，不对称结构的酞菁锌难以合成，应用于染料敏化太阳能电池中的酞菁锌染料屈指可数。早期报道的酞菁锌染料的光电转换效率大都小于 1%^[113-116]。2007 年，研究者报道了含有 3 个叔丁基和一个锚定基团的不对称酞菁锌染料 PCH001^[117]和 TT1^[118]，它们分别表现出 3.52% 和 3.05% 的光电转换效率(图 10b)。此外，通过分子设计来抑制酞菁染料聚集的策略报道于 2010 年^[119]，含有不同位阻取代基的酞菁锌类染料 PcS2, PcS5 和 PcS6 各表现出不同程度的分子聚集。研究表明，分子聚集程度取决于取代基的分子体积大小，增大取代基空间位阻能够有效抑制染料分子聚集，从而提高不对称酞菁锌染料的光电转换效率。相比叔丁基取代的染料 PcS2，2,6-二苯基苯氧基取代的酞菁锌染料 PcS6 表现出更高的光电转换效率(4.6%)，后者的 IPCE 最大值高达 78%。到目前为止，性能优异酞菁锌染料仍然很少，因此急需更有效的策略来开发性能优异的酞菁锌染料，以应用于染料敏化太阳能电池中。

2.4 共敏化剂

理想状态下，DSCs 中的染料敏化剂在 AM1.5 照射(功率为 100 mW/cm^2)条件下应能吸收 1.3 ~ 1.4 eV (约 920 nm) 以上的所有光子^[120]。然而，实验上很难合成一种染料敏化剂能捕获覆盖 UV 区至 NIR 区的所有光子，并将光生电子高效注入 TiO_2 。因此，研究者开发了一种被称作“Dyes Cocktails”的方法，即利用具有互补吸收特性的多种染料对 TiO_2 薄膜进行协同共

敏化^[110,121-123]。

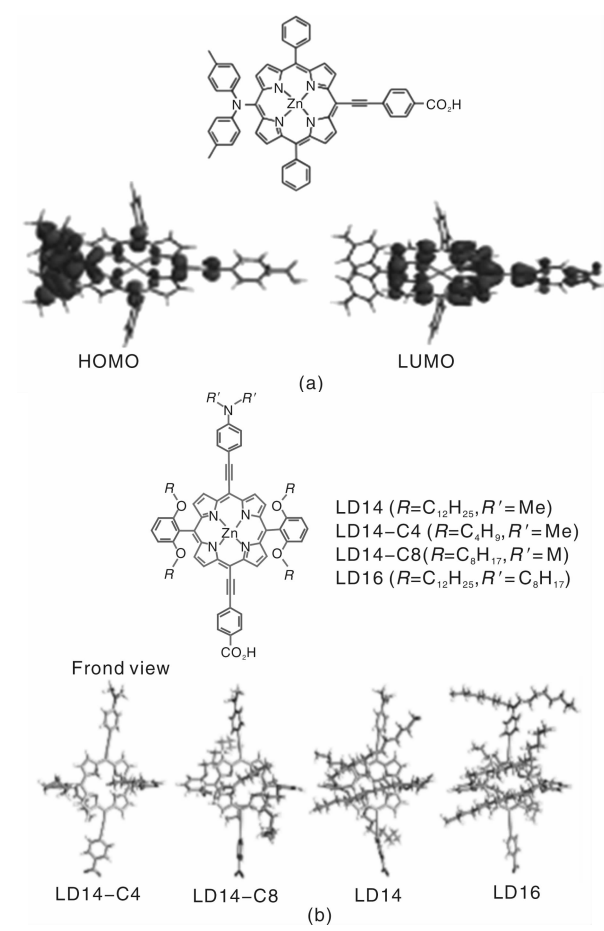


图 11 (a) D-A 型卟啉锌的 HOMO 和 LUMO 分布图, (b) 采用长烷基链(黑色部分)包埋卟核, 抑制卟啉分子间 $\pi-\pi$ 聚集的演示图

Fig. 11 (a) the HOMO and LUMO distributions of D-A type porphyrin dye and (b) inhibitions of the intermolecular $\pi-\pi$ stacking on porphyrins by the long alkylchains (black) enveloping the porphyrin core

Black dye 是高效 DSCs 中最常用的染料之一。它的 IPCE 光谱能覆盖整个可见波长区, 并扩展到 NIR

区。然而, 由于电解质中的 I_3^- 在 400 nm 区域具有强的竞争吸收, 从而导致在该区域中, 基于 Black dye 的 IPCE 中产生一个低谷。为了进一步提高效率, 我们提出了利用共敏化剂来填补该 IPCE 中低谷的方法。为了实现上述目标, 采用的共敏化剂应具有 3 个特性: ①在 400 nm 区域具有高的摩尔吸收系数; ②合理的分子结构及尺寸, 从而避免与 Black dye 发生强的竞争吸附和聚集; ③提高表面覆盖率, 抑制 TiO_2 薄膜中的电子与 I_3^- 发生再结合。基于以上设计思想, 我们开发了一种简单的有机 D- π -A 染料 Y1, 成功填补了 Black dye IPCE 光谱中 400 nm 附近的低谷, 如图 12 中所示。最终, Black dye 和 Y1 共敏化电池的 I_{sc} 和 V_{oc} 同时得到大幅提高, 使当时的转换效率提高到 11.4%^[6]。在其他报道中, 有机染料 D131 或 NKX-2553 和 Black dye 的共敏化体系中, 转换效率达到 11.0%^[124-125]。而研究者利用钌配合物 C106 和有机染料 D131 不同的分子尺寸和锚定基团, 实现了染料分子在 TiO_2 表面选择性分布, 进而增加各自染料的 I_{sc} 和 V_{oc} 值^[126]。利用吸收峰为 532 nm 的 Y123 染料与在 480 ~ 630 nm 范围内吸收较弱的卟啉染料 YD2-o-C8 共敏化, 有效的提高了 YD2-o-C8 绿光区内的 IPCE 响应^[5]。卟啉锌染料 LD12 与有机染料 CD5 结合则将 JSC 从 14.97 mA/cm^2 提高至 16.74 mA/cm^2 ^[127]。此外, 利用两种卟啉染料 (YD2-o-C8 和 YDD6) 及一种有机染料 (CD4) 共敏化的电池, 在 400 ~ 700 nm 的波长区内呈现较高的 IPCE 光谱, 同时进一步扩展至近红外区^[128]。然而, 与将钌染料或卟啉染料与不含金属的有机染料共敏化相比而言, 利用两种或以上不含金属的有机染料共敏化的高效 DSCs 方面的文献报道很少^[122,129-132]。表 1 给出的是通过公共试验中心验证的 DSCs 器件光电转换效率^[4,6,15,133-135]。与其它未经过认证的高效率 DSCs 相比, 这些经过认证的效率值均从使用“Black dye”的 DSCs 中获得。

表 1 由公证机构所测 DSCs 转换效率

Table 1 Energy conversion efficiencies of DSCs certified in public test center

Efficiency/%	Area/ cm^2	$J_{\text{sc}}/\text{mA} \cdot \text{cm}^{-2}$	V_{oc}/V	FF	Sensitizer	Test centre	Achieved by	Year
11.4	0.231 (ap)	21.34	0.7423	0.722	Black dye	AIST	NIMS6	2011
11.1	0.219 (ap)	20.9	0.736	0.722	Black dye	AIST	Sharp4	2006
10.9	0.203 (ap)	20.8	0.744	0.704	Black dye	AIST	AIST133	2008
10.4	0186 (ap)	20.5	0.721	0.704	Black dye	EPEL	EPEL14	2001
10.2	0.231 (ap)	21.3	0.692	0.690	Black dye	AIST	TUS134	2006
10.9	1.094 (ap)	22.2	0.732	0.673	Black dye	AIST	NIMS135	2012

Note: ap——aperture area

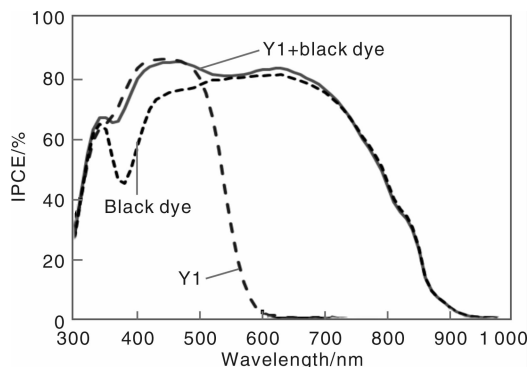


图12 基于Y1、Black dye和Y1+Black dye的DSC的IPCE光谱

Fig. 12 IPCE spectra of DSCs based on Y1, Black dye, and Y1 + Black dye

3 结 语

由于DSCs器件的光电转换效率高于10%，许多研究机构都在致力于开发大面积模块，比如日本的索尼公司报道称基于“Black dye”装配的太阳能电池模块效率可达到9.9%（组合式），夏普公司运用了集成式模块效率可达到9.2%，同时15 cm × 15 cm模块的效率为8.0%。然而，与效率可达到25%的单晶硅太阳能电池相比，DSCs的效率还相对较低。但是，在潜在发展前景面前，DSCs吸引了一些大公司（如Sharp、Fujikura、Dyesol、G24i和Solaronix）的研发兴趣，使得相关技术和生产设备的开发得到了快速发展。同时这些公司也在投入大量的资源去开发一些具有特色的新产品。作为能量转换的太阳能电池，提高能量转换效率是今后开发的一个主要研究项目，怎样开发新的红外吸收染料，提高共敏化特性，开发新的添加剂和电解质是今后的一个研究方向，解决这些问题需要更加有效的研究。预计在不远的将来，其光电转换效率与稳定性都将得到很大提高。

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碳纳米材料家族增加新成员

球状的富勒烯、筒状的碳纳米管和片状的石墨烯之后，碳纳米材料家族又有了新成员。日本研究人员开发出一种像马鞍一般弯曲的碳纳米分子，有望在电子元件和医疗等领域得到应用。

名古屋大学教授伊丹健一郎率领的研究小组在 2013 年 7 月 15 日的《自然·化学》杂志网络版上报告了这一成果，他们将这种碳纳米分子命名为“弯曲纳米石墨烯”。

研究小组以由 6 个碳原子形成的六角形分子为基本单位，利用“交叉耦合”法，使不同分子结合在一起。但如果只用六角形分子，只能形成片状的石墨烯，为此，研究人员在六角形分子之间又增加五角形和七角形的碳分子，从而形成了弯曲的结构。

这种新材料高 0.6 nm、宽 1.3 nm，呈黄色。由于碳分子之间有大量微小的空间，所以容易溶解到乙醇等有机溶剂中，很容易应用到电子基板上，有望用于制造太阳能电池和电子元件等。

如果向溶有这种新型碳纳米分子的溶液照射紫外线，这种分子能发出绿色的荧光，所以它还有望用于生物成像领域。

(From http://www.cas.ac.cn/xw/kjshm/gjdt/201307/t20130715_3899314.shtml)

我国成功制备出世界最长碳纳米管

爬上“梯子”摘星星，坐着“电梯”去月亮，这些科幻的场景，将有可能成为现实。近日，在北京市科委支持下，清华大学魏飞教授团队成功制备出单根长度达半米以上的碳纳米管，创造了新世界纪录，这也是目前所有一维纳米材料长度的最高值。相关内容近日在线发表在国际著名期刊《美国化学会纳米》上。

碳纳米管是迄今发现的力学性能最好的材料之一，其单位质量上的拉伸强度是钢铁的 276 倍，远远超过其他材料。《科学美国人》杂志曾提出“在地球与月亮之间搭建一座天梯”的诱人梦想，但跨越如此长的距离而不被自身重量拉断的材料，只有碳纳米管，并且是批量制备，具有宏观长度、理论力学性质、单根长度达到米级甚至公里级以上。

对于碳纳米管的生长而言，其高温生长过程中催化剂的失活是一个不可逆的规律，从而限制了碳纳米管的长度；并且，随着催化剂失活，长的碳纳米管密度会急剧下降。因此，尽可能地提高其催化剂活性概率是进一步提高碳纳米管长度的唯一途径。该团队充分发挥材料制备和化工技术学科交叉的优势，在制造设备、制备工艺方面进行大量改进和创新，首次将生长每毫米长度碳纳米管的催化剂活性概率提高到 99.5% 以上，最终成功制备出单根长度超过半米的碳纳米管。

魏飞称：“我们制备的碳纳米管具有完美的结构、优异的力学性能和宏观的长度，目前我们正在从事 1 m 以上碳纳米管的制备，下一步希望能够制备出公里级以上长度并具有宏观密度的碳纳米管。这些工作将为太空天梯的制备开启一线曙光。”

(来源：科技日报)