微纳光电转换体系中不均匀性对电荷转移的影响

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摘要 光电转换过程中的电荷转移机理研究对于理解诸如自然光合作用系统和染料敏化光伏等复杂光电转换体系中的各种光物理过程起着非常重要的作用. 由于这些物理机制通常都深藏于所研究目标材料与周围环境的各种精细的相互作用之中, 如果能把实验上观测到的各种电荷转移动力学中的普遍性总结出来, 那对光物理过程的研究来说将是非常有益和必要的. 本文将根据我们之前的相关工作, 回顾在复杂光电转换系统中与电荷转移有关的发展历史, 介绍与系统不均匀性有关的理论模型. 最后, 详细讨论动态及静态不均匀分布模型在自然光合作用体系及染料敏化体系中初始电子转移过程的应用.

关键词 电荷转移, 不均匀分布, 蛋白质动力学, 染料敏化体系, 超快光谱

电荷转移机制是研究光电转换材料中各种光物理性质的基础. 尤其是对光-电/电-光的转换过程的基本研究而言, 它不仅需要大量的实验研究, 而且还涉及更底层的理论探索. 但是在诸如自然光合作用系统、人造光伏及光催化体系中, 与初始电荷转移过程相关的微纳结构化的功能单元大都表现出非常复杂的、高度不均匀的动力学过程^[1-9], 这些动力学过程之间的竞争被认为对相应器件的光电性能有着重要影响. 通常, 要处理这些复杂的电荷转移过程, 一种较实用的方法是先基于大量简单化学反应的实验数据提出一个相对简化的理论模型, 然后再将其应用于其他复合体系中进行验证; 如果该理论与实验数据有较大偏差, 则需找到合理的解释使之可以对现有的模型进行修正. 历史上, 这种方法导致了早期Marcus电子转移理论^[10,11]的建立, 继而推动了专注于极性溶剂中电子转移过程的Kakitani-Mataga理论^[13]的发展, 以及近期针对非极性溶剂中电子转移的自由电子转移的研究^[14,15]. 由于对电子转移的研

究具有很高的价值, 任何对其更深入的理解及其更好的对复杂光电转换体系中电荷转移过程的调控都会在该领域带来新的突破. 最具代表性的就是在该领域获得了诺贝尔化学奖的研究者们: 1983年美国斯坦福大学Taube教授^[16]因在无机化学体系中氧化还原反应的电荷转移机制的开创性研究获该奖; 1992年美国加州理工学院Marcus教授^[17]由于其在电子转移过程理论方面做出的重要贡献而获得该殊荣.

另一方面, 对电荷转移机制中的电荷转移、能量转移和弛豫等过程进行实时观察在技术上具有极大挑战性, 因为这些事件都发生在从纳秒到飞秒的极短时间内. 图1给出了若干电子运动过程对应的时间尺度. 在时间分辨光谱技术出现以前, 人们对于光电转换系统中细致物理过程的研究手段极其有限. 随着飞秒超快激光技术的进步, 利用超快光谱技术在亚皮秒时间分辨能力上测量这些复杂光电转换体系中的电荷转移过程开始成为可能, 这使时间分辨光谱成为打开“黑盒子”不可替代的利器^[18-20]. 对超快

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图1 (网络版彩色)若干电子运动过程对应的时间尺度
Figure 1 (Color online) Time scales of some electron motions

光谱基本原理及若干应用的中文介绍可以参考其他综述文献[21,22]及由国内超快光谱研究领域的知名专家撰写的专业著作^[23,24]。

飞秒时间分辨光谱技术的发展赋予给了物理研究者探索更细致的有关电荷转移过程的信息的能力,但同时它也给目前的一些电子转移理论带来了更多的挑战。经典的Marcus电子转移理论满足Franck-Condon原理、能量守恒原理及电子耦合作用的基本原理,并假设每个分子态都具有明确定义的、依赖于如溶质分子本身及溶剂的核坐标等参数的势能。在这种简化条件下,其最初的表达式为^[17]

$$k = A \exp\left(\frac{-\Delta G^*}{k_B T}\right), \quad \Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda}\right)^2. \quad (1)$$

该理论认为电子转移反应的速率(k)取决于电子转移反应的本质(由参数 A 表示,通常与电子给体与受体间的距离有关)、反应自由能的变化(电子转移的驱动力, ΔG^0)以及反应物与周围溶剂的重整化能(λ)的大小。在实验检验上, Marcus理论及其后续发展的Kakitani-Mataga理论可以较好地解释在小分子溶液中的简单电子转移反应^[10-13,25-35],但是对另一些复杂体系如自然光合作用体系、人造光伏体系等观察到的呈现出非指数的衰减行为的超快电荷转移动力学则遇到了困难^[1-9,18-20,36-38]。这主要是因为复杂体系中各种不均匀分布,如分子局部结构的变化、空间分布的异质性、不均匀的相互作用分布等导致的效应都必须要考虑,否则电子转移理论与实验数据之间的差异就很难理解。

这一点从最初的Marcus表达式就可以看出,有2个可调整的变量,即驱动力(ΔG^0)和重整化能(λ),用来对更复杂的电荷转移过程进行处理。根据电荷转移前后反应物/产物与周围环境的相互作用的类型,即调整电荷转移过程中的重整化能还是驱动力,可

以将电荷转移模型分为2类:动态和静态不均匀分布模型。比如,即使仅考虑双分子电子转移,在非极性溶剂分子中发生的自由电子转移时^[14],电子从芳香族施主分子(烷烃、环烷、烷基氯化物等)转向其激发态阳离子形态,其电子转移所需时间极短(飞秒时间尺度,如图2所示)。这时施主分子的分子内动态运动,如分子键的弯曲和扭转等会主导着分子内电子密度的变化,这是由于非极性溶剂分子对重整化能的影响相对溶质分子的高频分子内振动模式来说要小得多的缘故^[15],因而,自由电子转移是一类由动态控制的电子转移,分子内动态运动就成为了这类电子转移过程的主导因素。下面,本文将通过自然光合作用反应中心中蛋白质动态结构运动及染料敏化光伏体系中静态相互作用来具体说明这两种不均匀分布对应的电荷转移理论模型,以及其在各自光电转换系统中初始电子转移的具体表现。

1 动态不均匀分布模型与光合作用反应中心的电子转移过程

在动态不均匀分布模型中,关注的是复杂的溶剂环境。这里的溶剂环境不仅包括溶剂分子本身,还将反应物(溶质)中的部分微纳结构包含进去。比如,自然光合作用的反应中心就是一类由蛋白质和色素构成的复合膜,反应中心里色素起着吸收光的作用,而周围的蛋白质环境则可以与溶剂一起看成是一类不均匀的溶剂环境,它也会随着光激发及电荷分离过程经历多个时间尺度上的弛豫^[39-41]。图3给出了蛋白质动力学的特征时间尺度及其对应的功能。

这种对重整化能的处理类似于在描述黏性溶剂中小分子之间的电子转移过程中发展起来的简化模

图2 自由电子转移中相关过程的时间尺度^[15]
Figure 2 Time range of processes relevant in free electron transfer (FET)^[15]

图3 (网络版彩色)蛋白质动力学的特征时间尺度及其对应的功能
Figure 3 (Color online) Time scale of protein dynamics and the corresponding functions

型,即将溶剂运动约化为2类^[3,39-41]:瞬时的溶剂响应(远快于电子转移)及相对慢一点的、与电子转移的时间尺度相当甚至更长的长程的溶剂重构。这样,基于反应-扩散方程^[42,43],在动态不均匀分布模型中,反应坐标位置 x 处的电子转移速率 $k(x)$ 可以表达为^[3]

$$k(x) = \frac{J^2}{h} \sqrt{\frac{\pi}{\lambda_{\text{r}} k_{\text{B}} T}} \exp \left(-\frac{(\lambda + \Delta G^0 - 2x\sqrt{\lambda_{\text{p}}})^2}{4\lambda_{\text{r}} k_{\text{B}} T} \right), \quad (2)$$

其中, J 是电子耦合矩阵元; λ 是总的重整化能,共包括了2部分:一部分是代表着比电荷分离时间尺度还快的那部分原子的弛豫,即 λ_{r} ;另一部分代表着沿着反应坐标 x 方向的,能与电荷分离过程相比拟,甚至更慢一些的溶剂弛豫,即 λ_{p} ,其典型如蛋白质的弛豫

等。由于直接从介电弛豫函数中获得时间依赖的扩散系数的难度较大,因而这也成为应用这个动态不均匀分布模型来分析电子转移动力学的主要限制因素。一种经验的方法是监控对溶剂弛豫过程敏感,如对蛋白质结构敏感的固有信号随时间的变化。下面我们以自然光合作用系统为例来进行具体说明。

在自然光合作用系统中,一个不可避免的因素就是蛋白质的运动,即蛋白质是具有活性的。这不仅意味着运动着的蛋白质是“活着”的,还表明在光合作用系统中与电子转移过程有关的能态在能量上是一直波动状态的^[39-41]。正如之前提到的,光合作用反应中心的蛋白质环境就如同一种不均匀的溶剂,在太阳能转换过程中起着非常重要的作用^[1-5,18,44]。

在光合作用细菌及绿色植物中,色素作为吸收光的天线将光能通过能量转移传递给反应中心。然后经过一系列的电子转移过程最终将光能转换成化学能存储起来。图4(a)给出了光合作用细菌及绿色植物中反应中心的特征结构及其电子转移时间。拿光合细菌*Rhodobacter sphaeroides*来说,处于激发态的电子施主 P^* (P 代表着一对细菌叶绿素)在数皮秒内将电子转移给近邻的一个细菌叶绿素 $\text{B}_{\text{A}+}$,接着转给同一侧的细菌脱镁叶绿素 H_{A} 。这里下脚标 A 和 B 表示存在2支潜在的电子转移路径,其中只有 A 分支是固有的具有活性(能够发生电子转移)的一侧,正负号分别代表失去和得到电子。在电子转移到辅酶醌 Q_{A} 之前,这个复合状态 $\text{P}^+\text{H}_{\text{A}}$ 能够存在大约200 ps^[45-47]。细菌光合作用反应中心的稳态特征吸收谱如图4(b)所示。其中,能与其他特征吸收峰较好分开的位于280 nm

图4 (网络版彩色)光合作用反应中心的功能结构、电子转移特征时间(a)及其稳态吸收谱(b)
Figure 4 (Color online) Structures, electron transfer time scales (a) and steady-state absorption spectrum (b) for a typical photosynthetic reaction center

图6 (网络版彩色)细菌光合作用反应中心在 930 nm 处的电荷分离动力学(a), (c)及对应 280 nm 处色氨酸的瞬态吸收动力学(b), (d)^[3]
Figure 6 (Color online) Charge separation dynamics probed at 930 nm (a), (c) and transient absorption dynamics probed at 280 nm (b), (d) for tryptophan in the wild-type (WT) bacterial photosynthetic reaction center and 14 mutants^[3]

图7 (网络版彩色)(a) 染料敏化太阳能电池中电荷转移过程示意图; (b) 染料C209, C213 和C215 的分子结构; (c) 具有高斯分布的局域电子注入偏移量的静态不均匀电子耦合模型示意图; (d) 各种染料敏化薄膜中归一化的电子注入动力学^[52]
Figure 7 (Color online) (a) Schematic view of the series of charge transfer processes in dye-sensitized solar cells; (b) molecular structures of C209, C213, and C215 dyes; (c) the scheme of a static inhomogeneous electronic coupling model with a Gaussian distribution (width Δ) of local offsets (D) for local injection energetics; (d) normalized electron injection dynamics for various kinds of dye-sensitized films^[52]

纳米界面处的电荷转移过程造成影响. 因为这些电荷转移过程是研究设计有利于电荷注入的纳米界面的基础, 所以测量这种发生在纳米界面的电子注入动力学就成为了被广泛研究的课题之一^[51]. 实验上, 这些观测到的动力学也是非常复杂和不均匀的. 对酞基染料来说, 部分快速的电子转移过程被认为是发生于初始激发的单线态, 而相对慢的过程则是来自于染料的三线态^[6].

那么, 在染料敏化太阳能电池中是否也存在着如同在上一节中提到的一种普遍的规则掌控着其中的电荷转移过程呢? 为了得到确切的答案, 对包含3种无金属的染料C209, C213和C215作为敏化剂的多种敏化太阳能电池进行了研究^[52]. 这3种无金属的纯有机染料都是施主- π 共轭连接体-受主型染料^[53-55], 都采用了同样的电子施主(二乙氧基取代的三苯胺)和受主(氰基丙烯酸), 但是施主与受主之间由3种不同 π 共轭连接体连接, 分别是呋喃、噻吩和硒吩, 其分子结构如图7(b)所示. 我们采用了一个包含高斯分布的注入驱动力的静态非均匀电子耦合模型来模拟这个过程(如图7(c)所示). 在这个模型中, 电子注入速率 $k(d)$ 是依赖于相对于染料或其他敏化材料的激发态的氧化物受体能量的局域偏移量 d 的. 考虑到氧化物导带底的 e 指数分布的态密度 $g(E) \propto \exp(-E/E_0)$, 其中 E_0 是实验上得到的变化的能量系数^[56-59], 这样, 这就等效于一个基于电子耦合分布的模型, 即 $k(d) = k(0)\exp(-2d/E_0)$ ^[51,60]. 假设 d 是高斯分布的, 其函数 $\rho(d_i)$ (平均值是0, 半高宽为 Δ)的表达式为^[60,61]

$$\begin{aligned}\rho(d_i) &= \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta} \exp\left[-4\ln 2\left(\frac{d_i}{\Delta}\right)^2\right] \\ &= \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta} \exp\left[-4\ln 2\left(\frac{d_i/E_0}{\Delta/E_0}\right)^2\right].\end{aligned}\quad (4)$$

将 d , $k(d)$ 和 $\rho(d_i)$ 分别取代方程(3)中的 ΔG , $k(\Delta G)$ 和 $g(\Delta G)$, 并且对所有可能的 d 值进行积分, 则由时间分辨动力学测得的在 t 时刻的激发态上与电子转移相关的能级上的电子布居数 $N_e(t)$ 为

$$\begin{aligned}N_e(t) &= N_0 \int \left\{ \exp\left(-k(0)\exp\left(\frac{2d_i}{E_0}\right)t\right) \right. \\ &\quad \times \left. \frac{2\sqrt{\ln 2}}{\sqrt{\pi}(\Delta/E_0)} \exp\left[-4\ln 2\left(\frac{d_i/E_0}{\Delta/E_0}\right)^2\right] \right\} d\left(\frac{d_i}{E_0}\right),\end{aligned}\quad (5)$$

其中, N_0 为归一化系数. 这个静态不均匀电子耦合模

型的示意图如图7(c)所示.

在式(5)中, 只要这个静态不均匀分布保持不变, 即 Δ/E_0 有一样的比值, 那么在这个模型中就只剩下电子注入速率这一个变量了. 由此, 在固定 $\Delta/E_0=1.5$ 的情况下, 我们很好地对如图7(d)所示的各类染料敏化体系中的电子注入过程进行了拟合. 对这3种无金属的纯有机染料敏化体系来说, 染料分子与 TiO_2 薄膜之间的平均电子耦合强度为 44 cm^{-1} (约合 5.4 meV), 重整化能约为 0.5 eV (如图8所示)^[52]. 这些结果都说明在各种染料敏化体系中, 尽管其自由能和动力学的变化很大, 但是其中染料与金属氧化物纳米粒子之间的电子耦合分布却是一样的, 只是在平均电子耦合强度上有所区别, 其结果表现为电子注入速率上的不同.

该静态不均匀电子耦合模型还可以推广到量子点敏化体系. 如三辛基磷包覆的 CdSe 量子点表面经过化学处理获得丁胺修饰的 CdSe 量子点, 其敏化的 TiO_2 纳米晶多孔薄膜的能力大为提高, 并且其量子点的荧光会显著发生淬灭. 对这种量子点的荧光淬灭动力学可以通过静态不均匀电子耦合模型进行处理. 图9(a), (b)给出了直径为 3.0 nm 的 CdSe 量子点敏化 TiO_2 多孔薄膜前后的稳态吸收谱和荧光谱. 由于电子会从 CdSe 量子点的激发态向 TiO_2 薄膜转移, 使得敏化薄膜上 CdSe 量子点的荧光相较于溶液状态下会发生明显的减弱. 通过静态不均匀电子耦合模型模拟给出的电子转移速率为 1.4 ns^{-1} (图9(c)), 这与

图8 (网络版彩色)3种有机染料敏化太阳能电池中电子注入速率、重整化能及驱动力之间的关系^[52]

Figure 8 (Color online) The relationship among electron injection rate, reorganization energy, and driving force in three kinds of organic dye-sensitized solar cells^[52]

图9 (网络版彩色)丁胺包覆的CdSe量子点在溶液及其敏化TiO₂薄膜中的稳态吸收谱(a)和荧光发射谱(b); (c) 归一化的CdSe量子点(直径约3 nm)敏化TiO₂薄膜中的荧光发射衰减曲线. 实线为文中模型拟合给出, 点线为仪器的响应函数^[52]; (d)丁胺包覆的CdSe量子点敏化TiO₂薄膜中电子注入速率、重整化能及驱动力之间的关系^[63]

Figure 9 (Color online) The absorption (a) and emission (b) spectra of butylamine-capped CdSe quantum dot (QD) solution and CdSe QD-sensitized TiO₂ film; (c) normalized emission decay trace for CdSe QD (3 nm) sensitized TiO₂ films. The solid line represents the kinetic fit by the model. The dotted line is the instrument response^[52]; (d) the relationship among electron injection rate, reorganization energy, and driving force in butylamine-capped CdSe QD-sensitized TiO₂ films^[63]

Konkanand等人^[62]报道的是一致的. 进一步对不同粒径的CdSe量子点敏化TiO₂薄膜中的电子转移速率的测量结果表明, 通过拟合其与驱动力之间的依赖关系, 可以得到在这种丁胺修饰的CdSe量子点与TiO₂纳米晶多孔薄膜之间的平均电子耦合强度(约为50 μ eV), 及重整化能(约为0.083 eV)(如图9(d)所示)^[63]. 这表明丁胺修饰的CdSe量子点敏化体系中的电子耦合强度较之纯有机染料C209, C213和C215敏化体系的要弱了约100倍.

3 总结

在本文中, 以2种典型的微纳光电转换体系—自

然光合作用体系和染料敏化光伏体系中的电荷转移过程为例, 详细总结了动态及静态不均匀分布在复杂光电转换系统中的影响, 并介绍了各自的理论模型. 在自然光合作用体系中应用的动态不均匀分布模型是与整个系统的重整化能的变化有关的, 由此可以看出前面提到过的自由电子转移也是其中一种极端情形(可以忽略溶剂分子对重整化能变化的贡献). 在染料敏化光伏体系中, 电子注入过程受到发生在纳米界面处的静态非均匀电子耦合模型的控制. 这主要反映着敏化体系在电子耦合强度上的静态非均匀性. 这个模型的适用范围依赖于金属氧化物受体的表面态的分布.

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Influence of inhomogeneous distributions on charge transfer in micro-nano optoelectronic conversion systems

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The mechanisms of charge transfer are of high importance for the understanding of photophysical processes in the complex photo-electron conversion systems, i.e., natural photosynthesis systems and dye-sensitized photovoltaics. Since these physical mechanisms are usually deep hidden by the subtle interactions between the subjects in study and the surrounding environments, drawing a general profile of the experimentally observed charge transfer kinetics from the universality point of view is of benefit and necessary. In this way, according to our previous works, these efforts on the aspect of charge transfer involved with both theoretical models and time-resolved experiments on the dynamical and static inhomogeneous distribution in the complex photo-electron conversion systems are summarized in this review. After a short critical survey of classic electron transfer theories, for example, the early Marcus expression, where there are two adjustable parameters, that is the driving force and reorganization energy, we focus on the recent efforts concerning the roles of inhomogeneous distributions of the static interaction (electronic coupling) and dynamical structure motions (static and dynamical inhomogeneous distribution) in these complex photo-electron conversion systems, such as protein dynamics in natural photosynthesis systems and initial electron injection in dye-sensitized systems. The details of the static and dynamical inhomogeneous distribution models are introduced at first. They are divided by the interaction types between the reactants/products and the surrounding environment in the complex photo-electron conversion systems. For the dynamical inhomogeneous distribution model in the reaction center of natural photosynthesis systems, it highlights the complex solvent environment, such as the protein environment of the reaction center. While for the static inhomogeneous distribution model in the dye-sensitized and quantum dot-sensitized solar cell systems, it considers that there are many sub-energy states, and assumes that the energy distribution of these sub-energy states meets a static Gaussian function. Thus, the change of driving force can be represented by the local shift in the energies of the oxide acceptor states relative to excited state of the dyes or quantum dots. In combination with theoretical models, this review shows that ultrafast spectroscopy as a powerful tool will continue to play an important role in the exploration of the hidden photophysical mechanisms in modern photo-electron conversion systems. Up to now, although there have been significant advances in the research of charge transfer mechanism in the complex photo-electron conversion systems, there are still many physical phenomena not fully understood, which are waiting for further investigation by ultrafast spectroscopic techniques with higher time-space resolution capabilities.

charge transfer, inhomogeneous distributions, protein dynamics, dye-sensitized systems, ultrafast spectroscopy

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