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Molecular and Material Approaches to Overcome Kinetic and Energetic Constraints in Dye-Sensitized Solar Cells

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Project Summary

Dye-sensitized solar cells (DSSCs) have attracted a lot of interest as they proffer the possibility of extremely inexpensive and efficient solar energy conversion. The excellent performance of the most efficient DSSCs relies on two main features: 1) a high surface area nanoparticle semiconductor photoanode to allow for excellent light absorption with moderate extinction molecular dyes and 2) slow recombination rates from the photoanode to I_3^- allowing good charge collection. The I_3^-/I^- couple, however, has some disadvantages, notably the redox potential limits the maximum open-circuit voltage, and the dye regeneration requires a large driving force which constrains the light harvesting ability. Thus, the design features that allow DSSCs to perform as well as they do also prevent further significant improvements in performance. As a consequence, the most efficient device configuration, and the maximum efficiency, has remained essentially unchanged over the last 16 years. Significant gains in performance are possible; however it will likely require a substantial paradigm shift.

The general goal of this project is to understand the fundamental role of dye-sensitized solar cell, DSSC, components (sensitizer, redox shuttle, and photoanode) involved in key processes in order to overcome the kinetic and energetic constraints of current generation DSSCs. For example, the key to achieving high energy conversion efficiency DSSCs is the realization of a redox shuttle which fulfills the dual requirements of 1) efficient dye regeneration with a minimal driving force and 2) efficient charge collection. In current generation DSSCs, however, only one or the other of these requirements is met. We are currently primarily interested in understanding the physical underpinnings of the regeneration and recombination reactions. Our approach is to systematically vary the components involved in reactions and interrogate them with a series of photoelectrochemical (PEC) measurements. The lessons learned will ultimately be used to develop design rules for next generation DSSCs.

Project Activities

Dye Regeneration and Recombination with Cobalt-based Redox Shuttles

Replacing I_3^-/I^- with cobalt(III/II) tris-bipyridine as a redox shuttle recently produced a new record solar energy conversion efficiency for DSSCs. This advancement is primarily due to the larger photovoltage resulting from a more positive redox potential (thus reducing the regeneration driving force). Efficient dye regeneration by such cobalt polypyridyl complexes was shown to still require a relatively large driving force of ~0.5 eV, however, which can be attributed to the large inner-sphere reorganization energy due to the transition from high spin cobalt(II) to low spin cobalt(III). We reasoned that it would be advantageous to utilize a low spin cobalt(II) complex as a redox shuttle which could further reduce the driving force required for efficient regeneration.

We compared regeneration and recombination in DSSCs with the one electron outersphere cobalt-based redox shuttles: a high spin cobalt (II) redox shuttle, $[Co(bpy)_3]^{3+/2+}$, where bpy is 2,2'-bipyridine, and a low spin cobalt (II) redox couple, $[Co(ttcn)_2]^{3+/2+}$, where ttcn is trithiacyclononane. This unique cobalt complex is low spin, stable, transparent, easy to synthesize from commercial ligands, and has attractive energetic and kinetic features for use in DSSCs. We found that $[Co(ttcn)_2]^{3+/2+}$ and $[Co(bpy)_3]^{3+/2+}$ produce comparable performance (J_{sc}, V_{oc}, ff) in DSSCs with an organic sensitizer D35cpdt under 1 sun illumination. This is surprising given the expected large differences in regeneration and recombination kinetics for these two shuttles. We therefore performed a detailed analysis of the measured incident photon to current efficiency, described by $IPCE = \eta_{LH} \times \eta_{inj} \times \eta_{reg} \times \eta_{cc}$, where η_{LH} is the light harvesting efficiency, η_{inj} is the charge injection efficiency, η_{reg} is the dye regeneration efficiency, and η_{cc} is the charge collection efficiency. The η_{LH} can be measured independently through either front (F) or back (B) illumination direction via spectrophotometry measurements. The η_{cc} is a function of the electron diffusion length, L_n, and therefore dependent on the electron diffusion distance and illumination direction. The product of η_{inj} and η_{reg} are independent of illumination direction, therefore comparisons of the IPCE from F and B illumination directions, correcting for differences in η_{LH}, produce η_{cc} and L_n. Once the η_{LHE} and η_{cc} are known, the product of η_{inj} and η_{reg} can be derived directly from fitting the IPCE. Examples of fits for $[Co(bpy)_3]^{3+/2+}$ are shown in Fig 1. This analysis indicated that L_n is 3.3 μm for $[Co(bpy)_3]^{3+/2+}$, but only 1.3 μm for $[Co(ttcn)_2]^{3+/2+}$. L_n is the square root of the product of the electron diffusion coefficient, D_n, and the electron lifetime, τ_n: $L_n = \sqrt{D_n \tau_n}$. The 3-fold difference in L_n for the two redox shuttles can be accounted for by a 10-fold lower τ_n electron lifetime for $[Co(ttcn)_2]^{3+}$ compared to $[Co(bpy)_3]^{3+}$. This result is consistent with expectations of Marcus theory since $[Co(ttcn)_2]^{3+}$ has

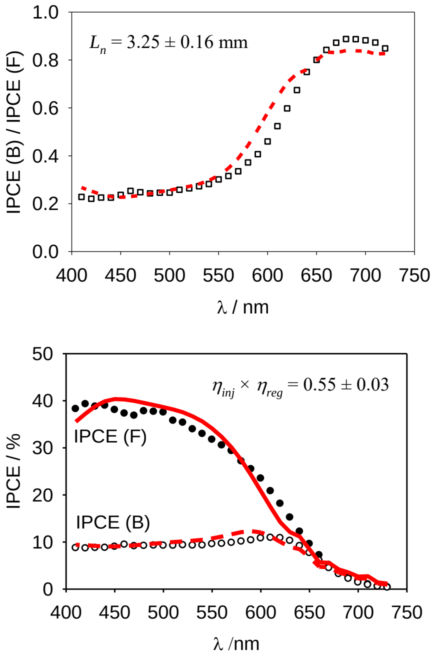

Figure 1. Fit of the B/F IPCE ratio for $[Co(bpy)_3]^{3+/2+}$ to determine the electron diffusion length and fits of the B and F IPCEs to produce the product $\eta_{inj} \times \eta_{reg}$.

a lower reorganization energy and slightly larger driving force, and was confirmed by voltage decay measurements of τ_n. The product $\eta_{inj}\times\eta_{reg}$ was found to be 0.55 for $[Co(bpy)_3]^{3+/2+}$, and 1.00 for $[Co(ttcn)_2]^{3+/2+}$. This result demonstrates that injection is quantitative and $[Co(ttcn)_2]^{2+}$ can efficiently regenerate dyes with a minimal (~200 mV) driving force. Since the same sensitizer was used in nominally identical conditions, the injection efficiency is taken to be the quantitative with $[Co(bpy)_3]^{2+}$ as well, and the regeneration efficiency is therefore only 0.55, despite the somewhat larger driving force (~300 mV). This highlights the advantage of using fast low-spin Co(II) redox shuttles. We further made comparison cells that have one Atomic Layer Deposition (ALD) cycle of alumina on the TiO_2 photoanode prior to immersing it in the sensitizer solution. Several effects of the alumina layer – which has been previously shown to improve performance for such outersphere redox shuttles – were elucidated. The regeneration efficiency increased for $[Co(bpy)_3]^{3+/2+}$, attributed to a reduced rate of recombination to the sensitizer which is in competition with regeneration. Note, this is a new interpretation and potentially impactful for future DSSC designs. The performance of DSSCs with the $[Co(ttcn)_2]^{3+/2+}$ redox shuttle likewise improved, however through an increase in the electron diffusion length. These findings demonstrate the fine balance between the regeneration and recombination reactions when outersphere redox shuttles are employed in DSSCs. Isolation of the efficiency-limiting reactions, however, allows for strategies to overcome that barrier to be identified.

Synthesis and Investigation of new Dyes

We have synthesized a suite of sensitizers based on $[Ru(dnbpy)(dcbpy)(ppy)](PF_6)$, where dnbpy = 4,4'-dinonyl-2,2'-bipyridine, dcbpy is 2,2'-bipyridine-4,4'-dicarboxylic acid, and ppy is 2-phenylpyridine. This initial series was chosen since the HOMO level (thus driving force for regeneration and recombination) can be readily tuned through modification of the ppy ligand, however the structure and coupling of the sensitizers should be nominally identical. Initial investigations performed with the $[Co(dmbpy)_3]^{2+/3+}$, dmbpy = 4,4'-dimethyl-2,2'-bipyridine, redox shuttle indicated that the nonyl groups are necessary to hinder recombination to the oxidized redox shuttle while addition of electron withdrawing fluorine substituents on the ppy ligand are necessary to lower the HOMO energy level and improve regeneration. We have recently expanded this series of sensitizers to include methyl functionalized ppy ligands to increase the HOMO energy level, introduced phosphoric acid modified bipyridine ligands to increase stability in alternative (e.g. aqueous) electrolytes, and made the first example of osmium cyclometallated analogs to further push up the HOMO energy level and increase the absorption profile. Current efforts are aimed at using this series of sensitizers to systematically

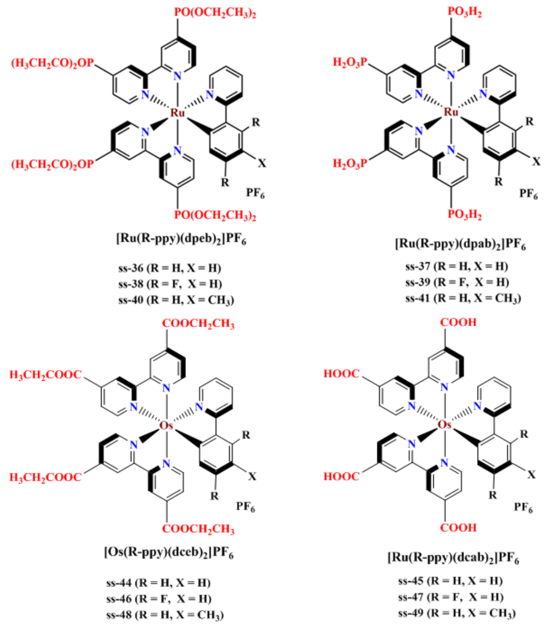

Figure 2. Structural representation of the cyclometalated sensitizers which have been synthesized and completely characterized (NMR, absorption and emission spectroscopy, electrochemistry, etc.) as part of this work.

probe the regeneration and recombination kinetics with cobalt-based redox shuttles, including the series described above. As part of this work, we are in the early stages of developing new methodologies to quantify recombination under relevant conditions (1 sun illumination, applied voltage, steady state) and dye regeneration using spectroelectrochemistry.

Spectroelectrochemical Determination of Conduction Band Edge for Nanostructured Semiconductors

The conduction band edge, **E**$_{cb,}$ is arguably the most important physical property of the photoanode that determines the injection efficiency and electron lifetime (recombination). For example, knowledge of the conduction band energy is necessary allow interpretation of recombination to outersphere redox shuttles, such as $[Co(R_2\text{-}bpy)_3]^{3+}$, as a function of driving force. The spectroelectrochemical method of measuring the conduction band energy that has generally been applied or cited, however, has several drawbacks. No other methods were known to accurately determine **E**$_{cb}$ for nanostructured semiconductors. We therefore developed new methodologies to measure **E**$_{cb}$ for NP metal oxide electrodes.

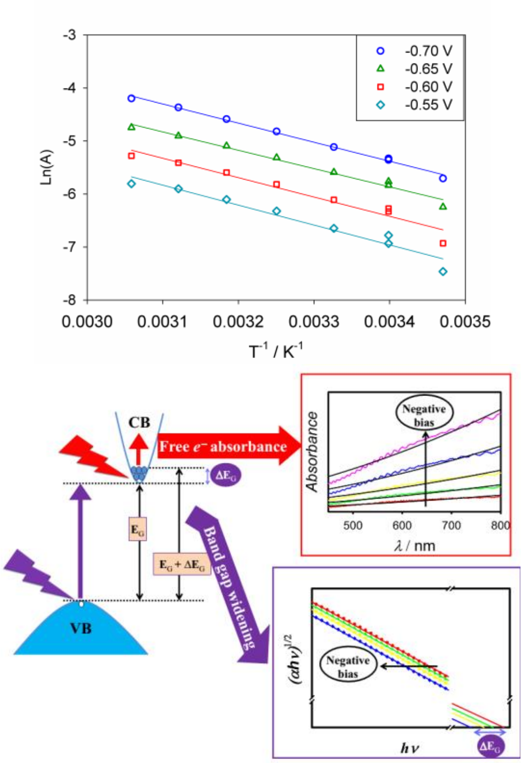

Figure 3. Top: Plot of ln(absorbance) vs. 1/T; the slope of the resultant straight line produces **E**cb and the intercept produces α. ***Bottom:*** Right top: Increase in absorbance of mesoporous TiO_2 film under negative bias. Right bottom: Blue shift of band gap due to filling of conduction band.

One method comprises temperature-dependent spectroelectrochemical measurements of conduction band electrons. These measurements consist of monitoring the absorption of near-infrared wavelengths by thin film semiconducting electrodes while varying both bias potential and temperature. The absorbance measurements were performed under steady state conditions which overcomes errors associated with a potential scan rate dependence. Another advantage of this method is that the absorptivity, α, of electrons is determined simultaneously with **E**$_{cb}$.

Since interpretation of the temperature-dependent spectroelectrochemical measurements rely on the assumption that the temperature only affects the Boltzmann population of free electrons and the density of states, we established another complementary method to determine the conduction band edge of photoanodes. This method is based on the idea that under negative potential the lower energy states in the conduction band are filled which results in an apparent blue-shift in the band gap transition, i.e. the Burstein-Moss shift. From the magnitude of this shift the free electron density in the conduction and was calculated as a function of applied potential and the position of conduction band edge determined. Additionally, the absorbance spectra of the photoanode film in the visible and near IR wavelengths were assigned to the free electrons in the conduction band and the absorption co-efficient of free electrons was also determined. These results are in excellent agreement with the temperature-dependent spectroelectrochemical results, which confirms our assignments and assumptions.

One consequence of our methods of make accurate measurements of the band positions and electron concentration, is the ability to quantify band edge unpinning which has been suggested to occur in nanostructured semiconductor photoanodes upon electron accumulation. Since this is the actual working conditions of a semiconductor in a solar energy conversion system, this understanding is critical to be able to interpret charge transfer to/from the nanostructured photoanode. The upward shift of the conduction band edge with increasing electron concentration was been explained by the presence of large density of the electrons accumulated on the surface of nanoparticles causing potential drop across the Helmholtz layer. Thus, we were also able to elucidate the trap state spatial distribution, by partitioning the trap states on the surface vs the bulk of the nanoparticles.

Publications

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