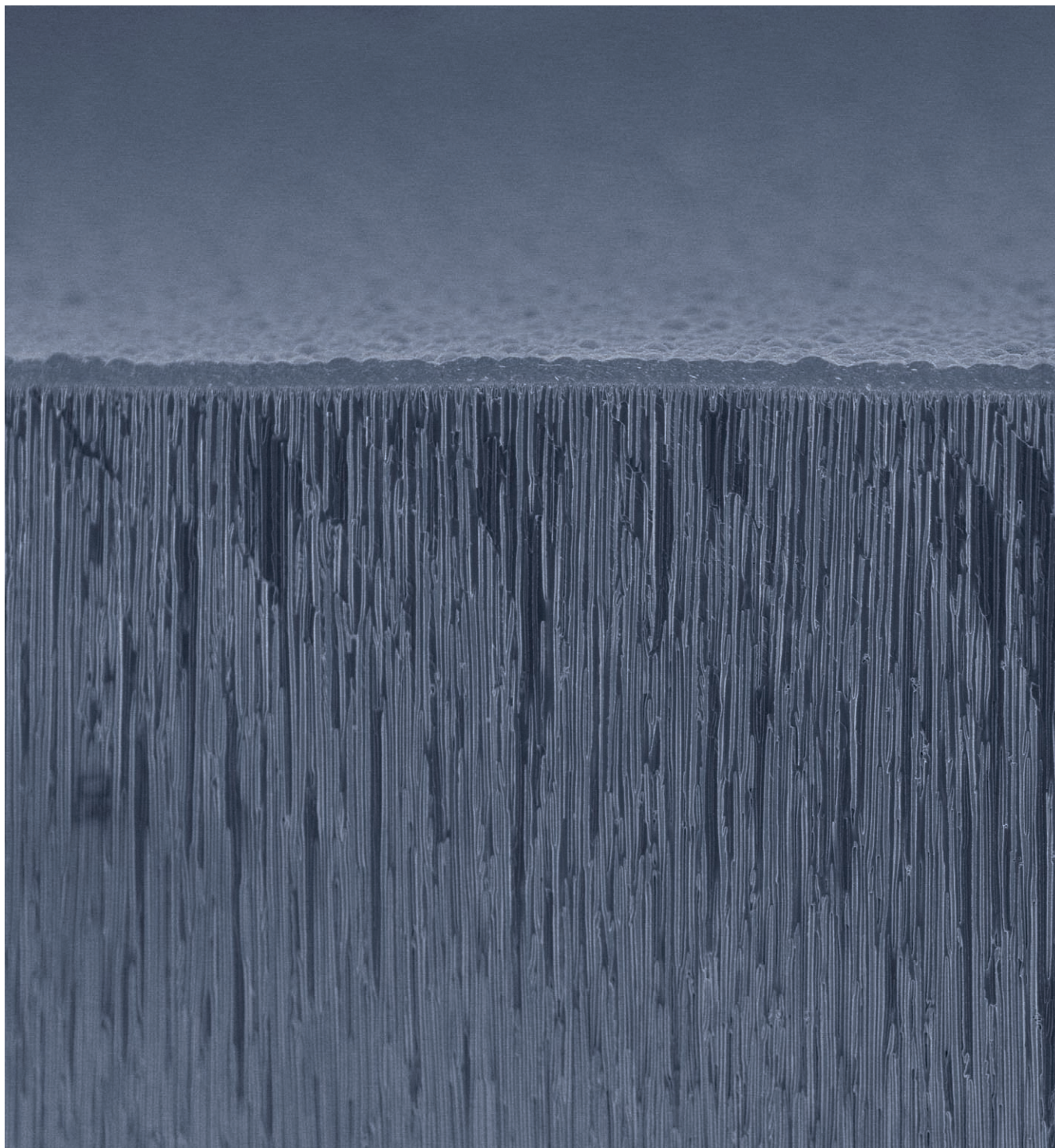


New Architectures for Dye-Sensitized Solar Cells

Alex B. F. Martinson,^[a, b] Thomas W. Hamann,^[a] Michael J. Pellin,^[b] and
Joseph T. Hupp^{*[a]}



Abstract: Modern dye-sensitized solar cell (DSSC) technology was built upon nanoparticle wide bandgap semiconductor photoanodes. While versatile and robust, the sintered nanoparticle architecture exhibits exceedingly slow electron transport that ultimately restricts the diversity of feasible redox mediators. The small collection of suitable mediators limits both our understanding of an intriguing heterogeneous system and the performance of these promising devices. Recently, a number of pseudo-1D photoanodes that exhibit accelerated charge transport and greater materials flexibility were fabricated. The potential of these alternative photoanode architectures for advancing, both directly and indirectly, the performance of DSSCs is explored.

Keywords: atomic layer • charge dynamics • dyes/pigments • nanoparticles • photovoltaic

Introduction

The massive flux of photons incident on the earth from the sun comprises an inexhaustible and plentiful energy source for the foreseeable future. In contrast to other renewable resources whose globally extractable power is less than 5 TW, the solar constant on the Earth's surface is 120 000 TW.^[1] The abundant supply and environmental friendliness of solar energy make the efficient conversion of solar radiation into electricity a compelling scientific and economic goal. While the efficiency of numerous classes of photovoltaic technology has been steadily climbing, one class—dye-sensitized solar cells (DSSCs)—has notably plateaued. After the original report of a 7% efficient DSSC in 1991, Grätzel and co-workers quickly pushed the efficiency to 10% by 1993.^[2,3] Despite the relatively incremental improvements in efficiency since then, reaching the current record of 11.2%, a sea of relevant literature has emerged to raise our basic science understanding at this intriguing confluence of electrochemistry, photophysics, and materials chemistry.^[4–7]

Like organic photovoltaics, DSSCs rely upon an interface to efficiently split excitons, the tightly bound electron-hole pairs generated by the absorption of light. In the most common and most efficient devices to date, light is absorbed

by a ruthenium complex, such as $(\text{Bu}_4\text{N})_2[\text{Ru}(4,4'\text{-dicarboxy-2,2'-bipyridine})_2(\text{NCS})_2]$,^[8] that is bound to a metal oxide photoanode via carboxylate moieties. The photoanode, usually TiO_2 , is composed of 10–20 nm diameter nanocrystals that have been spread on a transparent, conducting oxide (TCO) substrate and sintered to form a $\approx 16 \mu\text{m}$ thick film. Following light absorption, the exciton is split across the dye/nanoparticle interface in femtoseconds to picoseconds. The injected electron diffuses through the sintered particle network to be collected at the TCO, while the oxidized dye is reduced by a redox shuttle, I^-/I_3^- , dissolved in a solution that both permeates the porous photoelectrode and contacts the circuit-completing dark electrode (typically, platinized TCO). Diffusion of the oxidized form of the shuttle to the counter electrode (dark electrode) completes the circuit. The slow, random walk of electrons through the nanoparticle film limits the collection of charges to the millisecond timescale. Considering the close proximity at which opposing charges traverse the microns-thick device, the successful operation of DSSCs is a small wonder.

Charge Dynamics

In order to understand and advance DSSC technology, the kinetics and dynamics of charge movement have been examined in detail by many researchers, both experimentally and via computational modeling. The transfer of electrons and holes across several, often non-ideal and ill-defined, heterogeneous interfaces is exceptionally complex. As such, the kinetics are sensitive to many subtle factors such as excitation wavelength and dye loading conditions.^[9,10] Since the kinetics are complicated and don't always conform to a simple rate law, rate constants aren't strictly meaningful. Herein we will follow the convention of reporting half-life times (see Table S1 in Supporting Information), in order to appreciate the different time scales of the relevant processes that span nine orders of magnitude such as depicted in Figure 1.

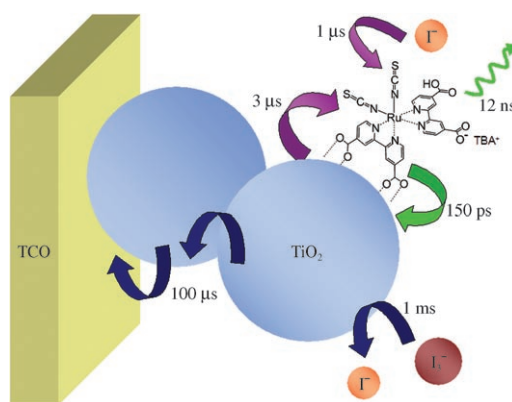


Figure 1. Kinetic processes in DSSCs. Processes in kinetic competition have similar colors.

[a] A. B. F. Martinson, Dr. T. W. Hamann, Prof. J. T. Hupp
Department of Chemistry, Northwestern University
2145 Sheridan Rd., Evanston IL 60208 (USA)
Fax: (+1) 847-467-1425
E-mail: j-hupp@northwestern.edu

[b] A. B. F. Martinson, Dr. M. J. Pellin
Materials Science Department
Argonne National Laboratory, 9700 S. Cass Avenue
Argonne, IL 60439 (USA)

Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.

For each time constant, the value shown is the most current literature datum measured on a standard cell under operating conditions, preferably at the maximum power point (≈ 700 mV).^[11–15] A standard cell is taken to be a complete device with configuration similar to the most efficient DSSC to date.^[16] Processes refer to electron dynamics unless otherwise noted and rates in direct kinetic competition are shown with the same color.

In order to relate these processes to PV performance, the charge dynamics are best viewed on a modified energy level diagram in Figure 2. Potentials are taken from literature reports, Table S2 in Supporting Information.

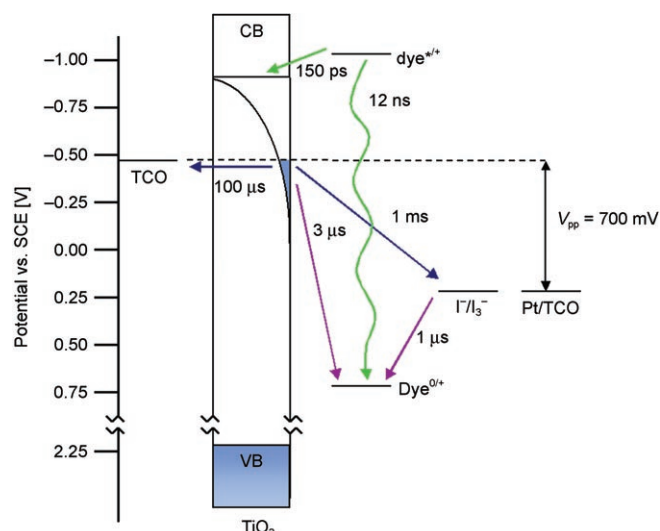


Figure 2. Kinetic processes in DSSCs on a modified energy level diagram.

The convenience of reporting half times of reaction rates may result in the misconception that there is considerable room for improvement by minimizing kinetic redundancy. For example, it appears that charge injection is almost 100 times faster than the competing process, relaxation of the excited state. If this were the case, then V_{OC} could be substantially enhanced by shifting the conduction band edge of TiO_2 negative without loss of charge collection efficiency. That this is *not* the case (or at least not entirely) is due to the dispersive kinetics of charge injection. In fact, studies of competing processes have shown that in its most efficient configuration a DSSC has comparatively little kinetic redundancy.^[11,17] This point may be visualized in Figure 3, in which order-of-magnitude estimates of area normalized rates at the maximum power point are taken from literature and presented as gaussian curves on a logarithmic time scale.^[11–15]

As state-of-the-art DSSCs have been optimized for maximum voltage while retaining near unity absorbed photon-to-current efficiency, dramatically new versions of the key components are warranted to advance the field. These could include new super chromophores that can collect light 10 to 100 times more efficiently than existing chromophores, new shuttles that can regenerate dyes at low driving force yet exhibit slow interception of injected charges, or new photo-

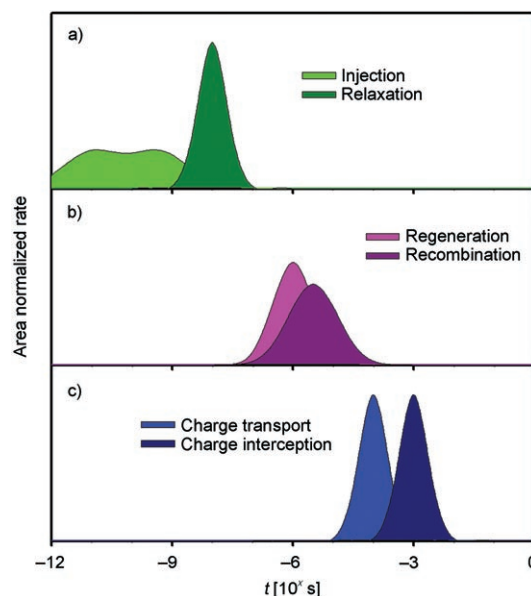


Figure 3. Area normalized rates from literature show charge dynamics in direct kinetic competition at the maximum power point.

electrode architectures. Below we consider the third idea: replacing the foundation of modern DSSC technology, the nanoparticle film, with new photoanodes.

Photoanode Requirements

By combining optical transparency with a large surface for dye loading, the introduction of a sintered titania nanoparticle (NP) film was paramount to the early success of DSSCs.^[2] The NP film exhibits remarkably slow electron diffusion matched only by the exceedingly slow charge interception by adjacent I_3^- . Even sixteen years after its inception, a complete understanding of the competition between transport of the electron through the TiO_2 -NP membrane versus interception by I_3^- —which is the key to the efficient operation of existing DSSCs—remains elusive.^[6,13] While the NP film is still present in the most efficient DSSCs to date, new materials and nanoscale architectures are attracting attention. Below we consider several alternative photoanode architectures and their potential for improving the efficiency and our understanding of DSSCs.

The demands on a DSSC photoanode are many-fold. These demands are best illustrated by examining a mathematical model that describes a photoanode's primary task, quantitative charge transport of injected electrons to the TCO. The continuity equation, introduced for DSSCs by Lindquist and popularized by Peter, describes electron generation, diffusion, and interception, respectively.^[6,18]

$$\frac{\partial n}{\partial t} = \eta_{inj} I_0 \alpha e^{-\alpha x} + D_n \frac{\partial^2 n}{\partial x^2} - \frac{n(x)}{\tau_n} = 0 \quad (1)$$

with boundary conditions:

$$n(0) = n^0 e^{\frac{qU}{k_B T}} \quad (2)$$

$$\frac{dn(x)}{dx} = 0 \quad (3)$$

Here the electron concentration, charge injection efficiency, incident photon flux, absorption coefficient, and apparent diffusion coefficient, are represented by n , η_{inj} , I_0 , α , and D_n , respectively. The effective (trap-limited) lifetime of electrons, τ_n , describes the rate of interception of electrons in the photoanode by I_3^- through the film thickness, d . The variables n^0 , q , U , k_B , and T represent equilibrium (dark) electron density, the elementary charge, voltage, Boltzmann's constant, and temperature. This steady-state equation may be solved numerically throughout the thickness, x , of the film or solved exactly at the TCO in order to generate current-voltage plots.^[18]

$$j(U) = q\eta_{inj}I_0L\alpha \frac{-L\alpha \cosh\left(\frac{d}{L}\right) + \sinh\left(\frac{d}{L}\right) + L\alpha e^{-d\alpha}}{(1-L^2\alpha^2)\cosh\left(\frac{d}{L}\right)} - qD_n n^0 \frac{\sinh\left(\frac{d}{L}\right)}{L\cosh\left(\frac{d}{L}\right)} \left(e^{\frac{qU}{k_B T}} - 1\right) \quad (4)$$

where the electron diffusion distance, L , is related to D_n and τ_n by

$$L = \frac{1}{\sqrt{D_n \tau_n}} \quad (5)$$

The kinetic competition between charge injection and excited state decay (Figure 3a) is parameterized by η_{inj} . The competition between dye regeneration and recombination to the dye⁺ (Figure 3b) is notably absent, although it has been incorporated in more detailed models.^[19] The primary duty of this model is to predict the distribution of electrons throughout the photoanode and the current-voltage characteristics for a given competition between τ_n and charge transport (τ_d), which is inversely proportional to D_n (Figure 3c). A good photoanode will maximize the number of electrons generated, the rate at which they are collected, and their lifetime by maximizing each independent variable listed above. Briefly, η_{inj} is maximized by having a large density of unpopulated states in the photoanode positive of the dye^{*/0} potential, preferably at optimal exoergicity. Maximizing the photon flux to the dye is dependent upon the transparency of the unsensitized semiconductor framework. The absorption coefficient is directly proportional to the effective molar concentration of the dye, which is determined by the roughness of the framework. D_n goes as the mobility of the semiconductor according to the Einstein relation [Eq. (6)],

$$D = \frac{\mu k_B T}{q} \quad (6)$$

but is often determined by trap controlled hopping between low energy states.^[20,21] Finally, τ_n is related to the quasi-Fermi level of electrons in the film, and also shows trap density dependence.^[22,23] All else being equal, a photoanode that increases one of these independent variables will increase efficiency, with the exception of D_n , which offers diminishing returns in the limit of kinetic redundancy (Figure 3c).

Nanoparticle Thin Films

As a transparent, high surface area framework, a metal oxide NP film was an excellent starting point for DSSCs. The ease of fabrication, minimal cost, and control over light scattering have ensured these structures provide the basis for the most efficient DSSCs to date (11.2%). Optimized films employ 10–20 nm spherical particles to form a high surface area, 12 μm thick transparent film (Figure 4). The

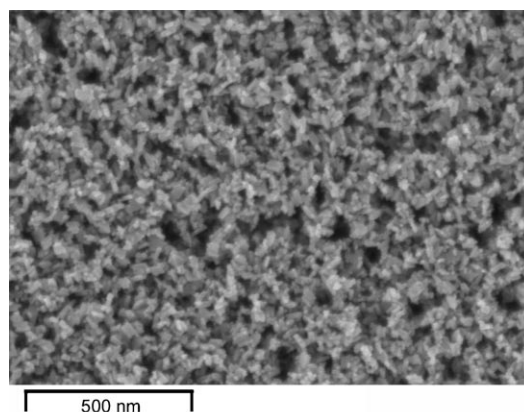


Figure 4. Conventional TiO_2 nanoparticle film.

surface area enhancement is described by the roughness factor, defined as the ratio of actual surface area to the projected surface area, with NP films exhibiting roughness factors in excess of 1000. A $\approx 4 \mu\text{m}$ thick film of much larger ($\approx 400 \text{ nm}$) particle diameter is subsequently deposited in order to scatter red and near-IR photons back into the transparent film.^[16] (The dyes employed in the most efficient cells typically absorb poorly in the red and near-IR region, so they can collect more photons in this region if a scattering layer is present.)

Despite the adequate performance of nanoparticle films in conventional DSSCs, this photoanode geometry has several disadvantages. These include low porosity, lack of materials generality, and tedious particle synthesis. But the primary weakness of the NP photoanode is the extraordinarily small apparent diffusion coefficient, D_n . Electron transport to the TCO is often modeled as the trapping and thermal release

of electrons from a distribution of sub-bandedge states. This process is highly dependent on the Fermi level, with TiO_2 nanoparticle films showing D_n of order $10^{-4} \text{ cm}^2 \text{ s}^{-1}$ when the electron concentration is similar to that at the power point.^[15,24] Using the Einstein relation along with measured mobilities (μ) of $13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for single crystal anatase TiO_2 ,^[25] photoanodes with D_n of order $10^{-1} \text{ cm}^2 \text{ s}^{-1}$ (i.e., a thousand times that in NP films) could be envisaged.

Nanorod Arrays

A DSSC photoanode based on an array of aligned nanorods was introduced in 2005.^[26] The photoanode is prepared on a conducting glass substrate on which a layer of ZnO particles has been deposited to seed nanorod growth. Preferential growth of the [0001] crystal face from solution affords moderately high aspect ratio single crystal rods perpendicular to the TCO (Figure 5). In order to further enhance anisotropic growth poly(ethyleneimine) is included in the growth solution, enabling rods with aspect ratios in excess of 125.^[27]

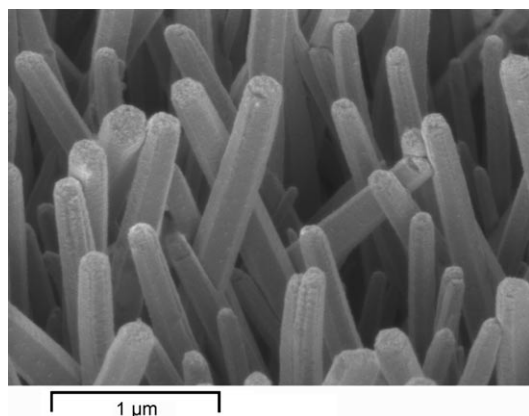


Figure 5. ZnO nanorod film grown from Zn salt solution onto F/SnO₂.

Compared to nanoparticle films (roughness factors >1000) the arrays are most notably lacking in roughness (<200), significantly decreasing J_{SC} and therefore limiting η to 1.5%.^[26] In addition, the solution growth of rods has been restricted primarily to ZnO. This is unfortunate, as ZnO photoanodes show consistently lower performance than similar TiO_2 devices, owing primarily to the instability of ZnO in acidic dye solution.^[28] Despite their modest success in DSSCs to date, nanorod photoanodes possess several attractive features including low cost, scalability, and accelerated electron transport.^[29,30]

Nanotube Arrays

To overcome the apparent limitations on nanorod array roughness, a second route to low dimensionality DSSC photoanodes has been established in the form of nanotubes. In

contrast to solution-phase nanorod growth, the electrochemical anodization of select metal films affords an array of metal oxide nanotubes with tunable roughness over 1000. When a suitable metal such as Ti is employed, the membranes may be employed directly as photoanodes with conversion efficiency approaching 7%.^[31,32]

Our group has made the fabrication of nanotubes materials-general by conformably coating anodic aluminum oxide (AAO) membranes via atomic layer deposition (ALD).^[33,34] In this technique, alternate exposures to reactive gas precursors are separated by inert gas purging to deposit films of metal oxides, sulfides, or nitrides. The self-limiting nature of the layer-by-layer growth technique makes ALD uniquely suited to high aspect ratio nanofabrication applications. The result is a transparent array of polycrystalline tubes, the wall thickness of which may be controlled with angstrom resolution (Figure 6). An optimal ZnO tube thickness grown within and upon commercially available AAO affords DSSCs with 1.6% efficiency, limited primarily by the modest roughness factor of commercial membranes (<450). The fill factor (FF) and V_{OC} of ZnO nanotube devices exceed those of any other ZnO photoanode reported to date.

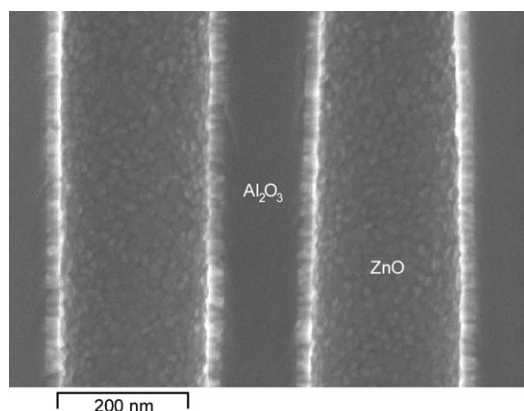


Figure 6. ZnO tubes grown by ALD on commercial AAO.

The most obvious advantage of the templated photoanodes grown by ALD is the diversity of metal oxides that may now be employed in the study of DSSCs. The hydrothermal growth of nanorod arrays has been reported for only a small subset of metal oxides. Likewise, fabricating high surface area NP photoelectrodes of different metal oxides is a technical challenge that has yet to be overcome for several oxides of interest (e.g. NiO).^[35] In contrast, the ALD of a long list of transition metal oxides may yield high surface area anodes. ALD also opens wide the possibility of mixed metal oxide devices to be employed in DSSCs. Due to the high reproducibility of the template, this approach is also especially well suited to precisely comparing metal oxides independent of photoanode geometry and roughness.

A large effective surface area, which enables significant light absorption from moderate extinction dyes, is a prereq-

uisite for efficient DSSCs. While nanorods can in principle have large roughness factors, they have not yet been developed. Similar to NP systems, the AAO templates allow for large and controllable surface areas. Unlike NPs, however, AAO templates allow for independent control of the porosity, with 50 % porous membranes feasible.^[36] The large porosities may enable thick membranes to handle large current densities by overcoming the mass-transport limitations of thick NP films. In addition, the alternative architectures are one dimensional, or pseudo-one dimensional, which should result in faster electron transport than in three-dimensional NP films. Finally, both hydrothermal growth and ALD are expected to yield more pristine semiconductors with larger polycrystalline domains compared to NP films, resulting in fewer surface trap states and grain boundaries or particle-particle junctions. The advantages of the accelerated transport and lower defect densities are considered below.

Architecture-Enabled Strategies for Improving Photovoltage: Replacing I^-/I_3^-

The novel architectures and deposition methods outlined above should stimulate the field of DSSC-based energy conversion by enabling innovative routes to improved device performance. Strategies for improving the photovoltage at open circuit (V_{OC}) in DSSCs may be divided into two categories. The first strategy is to reduce the dark current (interception current) at a given photoanode Fermi level. The second is to push the counter electrode potential more positive by changing the redox couple to which its Fermi level is pinned, Figure 2. To further complicate matters, the two strategies are enmeshed, as (all else being equal) dark currents are anticipated to depend to some extent on the redox couple's potential. In any case, the photovoltage is the difference of the Fermi level for the counter electrode (fixed at the redox shuttle potential, $E_{\text{F,redox}}$, if concentration polarization can be neglected) and the photoelectrode, ${}_nE_{\text{F}}$.

$$q U_{\text{photo}} = {}_nE_{\text{F}} - E_{\text{F,redox}} \quad (7)$$

The V_{OC} of the most efficient DSSC to date is 850 mV.^[16] In the absence of hot carrier injection, ${}_nE_{\text{F}}$ may not exceed the dye excited-state potential, thus limiting the V_{OC} to ≈ 1.3 V in traditional I^-/I_3^- DSSCs (Figure 2). Clearly, even with I^-/I_3^- there is room for improvement based on the strategy of reducing dark current.

Further improvement of V_{OC} requires an alternative redox couple with a more positive potential, approaching the dye^{0/+} potential (strategy 2). The optical gap of the Ru dye in the most efficient DSSC to date is ≈ 1.8 eV, but the dye^{0/+} potential differs from the I^-/I_3^- potential by ≈ 500 mV.^[3,37] The potential difference is necessary to drive regeneration at an acceptable rate and is a consequence of the unusually large reorganization energy for I^-/I_3^- . While detrimental to regeneration, the large reorganization energy paradoxically is *beneficial* in terms of dark current minimization.

All reports of efficient ($>4\%$ at 1 sun illumination) DSSCs to date have utilized the I^-/I_3^- couple as a dye regenerator and redox mediator. The uniquely good performance of I^-/I_3^- in these cells can be attributed to slow back electron transfer from TiO_2 to the mediator, maximizing V_{OC} in accordance with the diode equation. The I_3^-/I^- couple, however, has a number of disadvantages, including the corrosive nature of the oxidized species toward a traditional silver current collection mesh, which inhibits the low cost commercialization of DSSCs. Further, the complex kinetics precludes a general understanding of the heterogeneous electron transfer reactions in these photoelectrochemical systems. Additionally, the redox potential of I^-/I_3^- limits the maximum possible V_{OC} of the best DSSCs to 1.3 V owing to the roughly 500 mV of overpotential required for reduction of the oxidized dye as described above (see Figure 2). Attempts to increase the voltage by making the solution potential more positive require increasing the concentration of I_3^- , which simultaneously increases the rate of electron interception (lowers ${}_nE_{\text{F}}$), thereby preventing an overall V_{OC} improvement. Thus, in order to extract all the voltage available in a DSSC, alternative redox couples with potentials more closely matched to the dye oxidation potential need to be identified.

In general, one-electron, outer-sphere redox reagents such as ferrocenes have not been useful mediators in DSSCs.^[38] Although such species often rapidly reduce the oxidized dye, these systems also have substantial dark reactivity, due to facile reduction of their oxidized form by electrons in the conduction band of the TiO_2 . This rapid interception of electrons in the photoanode creates two distinct problems in the operation of a DSSC: loss of V_{OC} and diminished charge collection efficiency. The most well recognized detriment is the reduction in the V_{OC} in accordance with the diode equation. Unlike charge collection losses due to competing kinetic processes (Figure 3), slowing competing processes cannot circumvent this loss of V_{OC} . Since the light-generated current and dark current must be equal (and opposite) at open circuit, compensating for a dark-current induced loss of V_{OC} requires increasing the number of charges injected per unit time. In contrast, the loss of photocurrent (even under short circuit conditions) due to interception of diffusing electrons on their way to the TCO is controlled by a kinetic competition, shown in Figure 3c. This competition between charge lifetime (τ_n) and charge transport time (τ_d) has been extensively studied via both frequency and time resolved techniques.^[6,15,39] The theoretical treatment, already introduced as Equation (1), is employed to understand competition in DSSCs under steady state conditions. Using this formalism, the effects of accelerating electron interception (reducing τ_n) have been modeled in Figure 7. Initially, V_{OC} monotonically decreases with progressively shorter τ_n while the current density under short circuit conditions (J_{SC}) remains constant. Given sufficiently fast transport (short τ_d) only the effects of the increased dark current are visible in the J/V curve under illumination, that is, lower V_{OC} . However, under conditions of even faster interception, or when the competi-

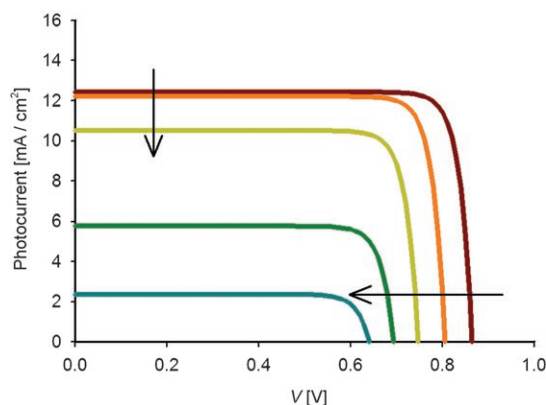


Figure 7. Current/voltage curves for DSSCs with progressively shorter charge lifetime (τ_n). Each line represents an order of magnitude faster interception. For simplicity, curves have been calculated assuming ideal behavior (diode quality factor of unity). Real DSSCs generally behave less ideally, exhibiting smaller fill factors and showing (or implying) even greater sensitivity of V_{OC} to τ_n variations.

tion in Figure 3c becomes relevant, a loss of photocurrent is predicted. As must be the case for a system in which the collection efficiency approaches unity, τ_d has been shown to be significantly smaller than τ_n in systems in which I^-/I_3^- is employed. Yet, in many other DSSCs, the kinetic competition is relevant as evidenced in numerous reports of fast interception conditions.^[38,40,41] In one particularly interesting example, DSSCs that used cobalt(III/II) tris(4,4'-di-*tert*-butyl-2,2'-bipyridyl), $[Co(tBu_2bpy)_3]^{3+/2+}$, as a redox mediator exhibited excellent efficiencies, while cobalt(III/II) tris(4,4'-dimethyl-2,2'-bipyridyl), $[Co(Me_2bpy)_3]^{3+/2+}$, systems showed poor performance.^[42] If the *tert*-butyl group acts as a spacer group to slow electron interception, the performance difference could be due to τ_n being slightly larger than τ_d for $[Co(Me_2bpy)_3]^{3+/2+}$, but τ_n being slightly smaller than τ_d for $[Co(tBu_2bpy)_3]^{3+/2+}$.^[43]

Reducing charge collection losses at low applied potentials requires a photoanode that exhibits faster charge diffusion according to:

$$D_n = \frac{d^2}{4 \cdot \tau_d} \quad (8)$$

As previously discussed, D_n is surprisingly slow in NP thin films and dependent upon nE_F effects most readily explained by the activation energy of trapping/de-trapping required to facilitate charge hopping. The result is a potential dependence of both τ_n and τ_d (or equivalently, a light-flux dependence). In contrast, hydrothermally grown ZnO photoanodes show considerably faster charge transport under short-circuit conditions (Figure 8).^[29,30] The faster transport is not surprising, given the superior crystallinity and reduced dimensionality of ZnO nanorod arrays compared to nanoparticle films.^[26] Although to a lesser degree, we find that the polycrystalline ZnO photoanodes deposited on the pseudo-one-dimensional templates described above also exhibit superior charge transport.

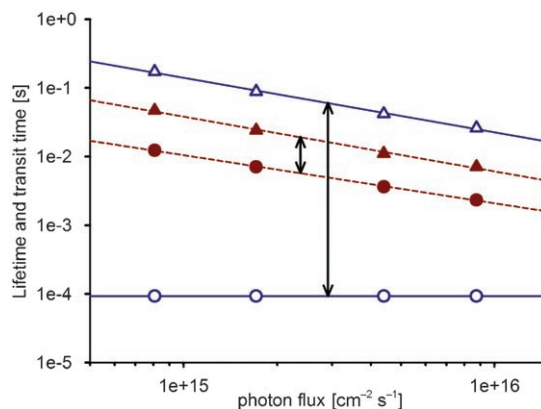


Figure 8. Charge transport (circles) and interception (triangle) lifetimes for nanocrystalline (filled, red) and nanorod (open, blue) ZnO photoanodes of similar thickness ($\approx 4 \mu m$).^[29] Importantly, the faster transport rates for the nanorod array architecture are not compensated by faster interception kinetics.

A related idea is to employ sensitizers with significantly larger extinction since this would allow equal light harvesting efficiency within a thinner photoanode. According to Equation (8), a 10-fold reduction in photoanode thickness will reduce τ_d by 100-fold. Reducing the charge collection time in this manner has the same advantages as increasing D_n . Furthermore, a reduction in dark current is expected to accompany any decrease in surface area.

Building DSSCs with significantly faster charge transport kinetics should allow devices with a wider variety of redox mediators to be used. To date, successful experiments with only the very slowest of redox shuttles have been carried out. Studies of faster shuttles, notably ferrocene, have been characterized by almost complete device failure due to poor charge collection.^[38] Alternative photoanodes should overcome this loss, as shown modeled in Figure 9, allowing for the further exploration of redox mediators including commercially attractive solid-state hole conductors.^[44,45] Furthermore, redox shuttles with more positive potentials may be studied, creating the possibility of voltages exceeding 1.0 V.

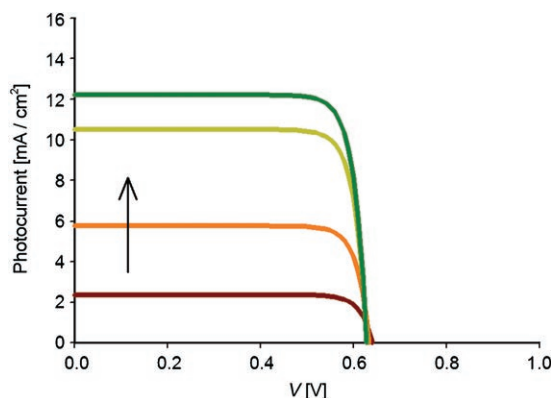


Figure 9. In devices with relatively short charge lifetimes (the shortest shown in Figure 7), charge collection at low applied potentials may be improved by increasing the diffusion rate. Each line represents an order of magnitude larger apparent electron diffusion coefficient (D_n).

Architecture-Enabled Strategies for Improving Photovoltage: Reducing the Dark Current

In the most efficient DSSCs, the primary recombination/interception pathway at open circuit is from electrons in the NP film to I_3^- in solution. In order to reduce the dark current at a given nE_F , inorganic barrier layers, alkyl chain additions to the Ru dye, and co-absorbents have been utilized with moderate success.^[12,14,46,47] These physical barriers between semiconductors and redox shuttle comprise tunneling barriers, which attenuate the rate of electron transfer from the semiconductor to the shuttle.

A related notion centers on the reaction order for the electron interception process. For triiodide as the interceptor, the mechanism of this potentially multi-electron process is complex and controversial. In particular, the reaction order with respect to electrons is debated;^[23,48] nevertheless it is clear that the interception rate increases with increasing concentration of electrons in the photoanode. This implies that photoanodes with a lower density of states at a given nE_F will exhibit slower interception, all else being equal. This effect has been illustrated nicely by Haque et al. where the electrolyte composition was varied in order to shift the density of states which controlled the rate of electron interception.^[11] The effect of reducing dark current on photovoltage may be modeled for an ideal photoanode using Equation (4). The result is an ≈ 60 mV increase in V_{OC} with each order of magnitude reduction in dark current (Figure 10). In semiconductor electrodes with larger diode quality factor, the change is even more dramatic.

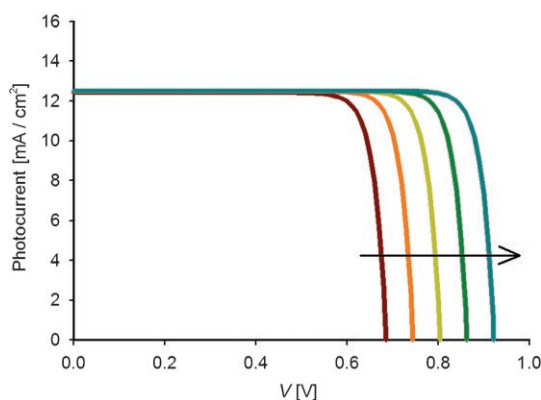


Figure 10. In ideal photoanodes, decreasing the dark current density increases the voltage at open circuit and at the power point. Each line represents an order of magnitude lower dark current density.

In nanostructured photoelectrodes, the relevant states likely comprise both conduction band states and trap states. Electron traps in TiO_2 arise mainly from “incorrectly” coordinated titanium ions found at intrinsic defect sites and surface sites, and near intercalated species. Both hydrothermal growth and ALD are expected to yield more pristine semiconductors with larger polycrystalline domains than found

in NP films, thus reducing the number of trap states. It may be possible to further reduce the number of electron traps near the semiconductor surface by atomic layer deposition of a second material. For example, ultra-thin layers of insulators such as ZrO_2 are expected to react with and bury or “correct” the coordination of these sites while at the same time presenting a tunneling barrier to electron interception. Thus, fabrication of higher quality semiconductors and/or controlling the surface chemistry with ALD^[47,49] may lead to lower dark currents at a given nE_F .

Novel electrode architectures may also influence the rate at which oxidizing redox equivalents interact with the semiconductor surface by altering the packing of chromophores. Like inorganic blocking layers, the dye itself acts to reduce the effective surface area of semiconductor exposed to the redox mediator.^[12,50] The extent of dark current reduction is dependent upon the size of the redox mediator and the porosity of the chromophoric monolayer. On flat surfaces, it has been shown that construction of chromophoric monolayers capable of blocking molecular species (while passing smaller ionic species, for example, Li^+) is feasible.^[51] As the length of chromophores is comparable to the pore size of high area photoelectrodes in many DSSCs, the curvature of the photoanode is likely to influence porosity. The convex interior surface of a tube is more likely to block entry of oxidizing equivalents compared to the convex surfaces of particles and rods (Figure 11).

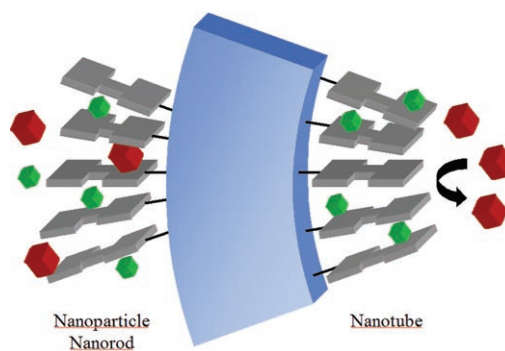


Figure 11. Idealized dyes bound to convex and concave surfaces may sieve different size species in solution, for example lithium ions (small, light green blocks) versus molecular redox shuttles (large, dark red blocks).

Novel photoelectrode architectures also should accommodate higher extinction chromophores. The porphyrin oligomer shown in Figure 12^[52] comprises one example of a potentially strongly absorbing and broadly absorbing chromophore suitable for an advanced DSSC. This next generation of chromophores, with lengths in excess of 5 nm, will have difficulty permeating typical nanoparticle photoanodes. These new “super-chromophores” have the potential to significantly reduce dark currents in DSSCs by allowing an order of magnitude lower surface area photoanode to be used without loss of light harvesting efficiency.

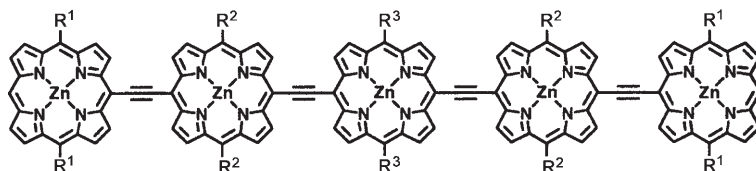


Figure 12. Porphyrin oligomers have greater extinction than traditional inorganic DSSC dyes. Incorporation of these larger chromophores will require a more porous photoanode.

J_{sc} , pushing DSSCs performance closer to the still-distant thermodynamic limit.

Conclusion

By making feasible the use of faster redox shuttles and by (potentially) enabling new ap-

Architecture-Enabled Strategies for Improving J_{sc}

The possibility of employing alternative redox mediators in DSSCs creates a cascade of new opportunities. The most exciting prospect is the ability to rapidly reduce an oxidized dye with smaller optical gap using minimal driving force. Since incident photon-to-current efficiencies already approach unity from 350–650 nm in the most efficient DSSCs, increasing the photocurrent requires extending dye absorption into the infrared. Under ideal conditions, a single junction solar cell with optical gap of ≈ 1.4 eV (corresponding to 900 nm light) has the potential to generate 33 mA cm^{-2} . Comparison of this with the highest current reported to date for a DSSC (which employs the “black dye” Ru complex) of 21 mA cm^{-2} indicates that there is much room for improvement if alternate redox couples can be utilized.^[53]

There are two approaches to narrowing the dye’s optical gap in order to collect a greater portion of the AM1.5 spectrum. Shifting the dye^{*/+} potential less negative is one possibility, but the overpotential required for electron injection into the metal oxide at a rate sufficient to compete with radiative and nonradiative decay is already essentially optimized for a given photoanode material (Figure 3a). The second approach is to push the dye⁺⁰ level more negative; however this approach is subject to a combination of problems that have thus far limited its implementation. A more negative (less positive) dye⁺⁰ potential is expected to engender slower regeneration kinetics due, at least in part, to the lower driving force of the reaction. Further compounding the problem, recombination to oxidized ruthenium and osmium dyes has been shown (at least at shorter timescales) to be subject to Marcus “inverted region” kinetics.^[54,55] (At longer times recombination seems to be trap limited, so is insensitive to the dye^{0/+} potential).^[56–58] Therefore, shifting the ground state potential of the dye negative results in a lower driving force and hence faster recombination. The concomitant problems of slower regeneration and faster recombination make the successful use of dyes that extend the spectral coverage in the current system extremely challenging.

Yet faster redox shuttles (that are incompatible with nanoparticle DSSCs) have already been shown to rapidly reduce oxidized dyes with less driving force.^[38,41] Therefore, we expect the application of faster redox shuttles to allow the competitive reduction of the oxidized form of smaller bandgap dyes, when combined with alternative photoanode geometries. These smaller band gap dyes may enable greater

approaches to dark current suppression, new photoelectrode architectures and fabrication strategies are opening up the possibility for improvement of photoelectrochemical systems that have been otherwise almost completely optimized. Solution grown ZnO nanorod arrays and templated photoanodes grown by ALD are believed to have many fewer trap states. Under short circuit conditions these novel architectures may also exhibit lower electron concentrations owing to faster charge transport to the TCO. Faster charge transport will enable a wide variety of redox mediators to be studied while retaining reasonable charge collection efficiency. This may, in turn, allow dyes with greater spectral coverage to be employed in DSSCs.

Acknowledgements

The SEM work was performed in the EPIC facility of NUANCE Center at Northwestern University. NUANCE Center is supported by NSF-NSEC, NSF-MRSEC, Keck Foundation, the State of Illinois, and Northwestern University. We gratefully acknowledge the contributions of collaborators and co-workers whose work is cited herein. We also gratefully acknowledge financial support from BP Solar, Argonne National Lab (fellowship for A.B.F.M.), and the US Department of Energy, Basic Energy Sciences Program (Grant DE-FG02-87ER13808). Work at Argonne is supported by the US Department of Energy, BES-Materials Sciences under Contract W-31-109-ENG-38.

- [1] *Basic Research Needs for Solar Energy Utilization*, BES Workshop on Solar Energy Utilization, April 18–25, **2005**.
- [2] B. O'Regan, M. Grätzel, *Nature* **1991**, 353, 737–740.
- [3] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **1993**, 115, 6382–6390.
- [4] J. Bisquert, D. Cahen, G. Hodes, S. Ruhle, A. Zaban, *J. Phys. Chem. B* **2004**, 108, 8106–8118.
- [5] G. J. Meyer, *Inorg. Chem.* **2005**, 44, 6852–6864.
- [6] L. M. Peter, *J. Phys. Chem. C* **2007**, 111, 6601–6612.
- [7] M. Grätzel, *Inorg. Chem.* **2005**, 44, 6841–6851.
- [8] M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C. H. Fischer, M. Grätzel, *Inorg. Chem.* **1999**, 38, 6298–6305.
- [9] G. Benko, J. Kallioinen, J. E. I. Korppi-Tommola, A. P. Yartsev, V. Sundstrom, *J. Am. Chem. Soc.* **2002**, 124, 489–493.
- [10] B. Wenger, M. Grätzel, J. E. Moser, *J. Am. Chem. Soc.* **2005**, 127, 12150–12151.
- [11] S. A. Haque, E. Palomares, B. M. Cho, A. N. M. Green, N. Hirata, D. R. Klug, J. R. Durrant, *J. Am. Chem. Soc.* **2005**, 127, 3456–3462.
- [12] J. E. Kroeze, N. Hirata, S. Koops, M. K. Nazeeruddin, L. Schmidt-Mende, M. Grätzel, J. R. Durrant, *J. Am. Chem. Soc.* **2006**, 128, 16376–16383.

- [13] J. N. Clifford, E. Palomares, M. K. Nazeeruddin, M. Grätzel, J. R. Durrant, *J. Phys. Chem. C* **2007**, *111*, 6561–6567.
- [14] E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz, J. R. Durrant, *J. Am. Chem. Soc.* **2003**, *125*, 475–482.
- [15] B. C. O'Regan, K. Bakker, J. Kroeze, H. Smit, P. Sommeling, J. R. Durrant, *J. Phys. Chem. B* **2006**, *110*, 17155–17160.
- [16] M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. G. Grätzel, *J. Am. Chem. Soc.* **2005**, *127*, 16835–16847.
- [17] J. R. Durrant, S. A. Haque, E. Palomares, *Coord. Chem. Rev.* **2004**, *248*, 1247–1257.
- [18] S. Sodergren, A. Hagfeldt, J. Olsson, S. E. Lindquist, *J. Phys. Chem.* **1994**, *98*, 5552–5556.
- [19] J. J. Lee, G. M. Coia, N. S. Lewis, *J. Phys. Chem. B* **2004**, *108*, 5269–5281.
- [20] J. Bisquert, A. Zaban, P. Salvador, *J. Phys. Chem. B* **2002**, *106*, 8774–8782.
- [21] L. M. Peter, N. W. Duffy, R. L. Wang, K. G. U. Wijayantha, *J. Electroanal. Chem.* **2002**, *524*, 127–136.
- [22] J. Bisquert, A. Zaban, M. Greenshtein, I. Mora-Sero, *J. Am. Chem. Soc.* **2004**, *126*, 13550–13559.
- [23] P. J. Cameron, L. M. Peter, *J. Phys. Chem. B* **2005**, *109*, 7392–7398.
- [24] N. Kopidakis, K. D. Benkstein, J. van de Lagemaat, A. J. Frank, *J. Phys. Chem. B* **2003**, *107*, 11307–11315.
- [25] L. Forro, O. Chauvet, D. Emin, L. Zuppiroli, H. Berger, F. Levy, *J. Appl. Phys.* **1994**, *75*, 633–635.
- [26] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. D. Yang, *Nat. Mater.* **2005**, *4*, 455–459.
- [27] L. E. Greene, B. D. Yuhas, M. Law, D. Zitoun, P. D. Yang, *Inorg. Chem.* **2006**, *45*, 7535–7543.
- [28] K. Keis, E. Magnusson, H. Lindstrom, S. E. Lindquist, A. Hagfeldt, *Sol. Energy Mater. Sol. Cells* **2002**, *73*, 51–58.
- [29] A. B. F. Martinson, J. E. McGarrah, M. O. K. Parpia, J. T. Hupp, *Phys. Chem. Chem. Phys.* **2006**, *8*, 4655–4659.
- [30] E. Galoppini, J. Rochford, H. H. Chen, G. Saraf, Y. C. Lu, A. Hagfeldt, G. Boschloo, *J. Phys. Chem. B* **2006**, *110*, 16159–16161.
- [31] M. Paulose, K. Shankar, O. K. Varghese, G. K. Mor, C. A. Grimes, *J. Phys. D* **2006**, *39*, 2498–2503.
- [32] K. Shankar, G. K. Mor, H. E. Prakasam, S. Yoriya, M. Paulose, O. K. Varghese, C. A. Grimes, *Nanotechnology* **2007**, *18*, 065707.
- [33] A. B. F. Martinson, J. W. Elam, J. T. Hupp, M. J. Pellin, *Nano Lett.* **2007**, *7*, 2183–2187.
- [34] M. J. Pellin, J. W. Elam, J. A. Libera, A. B. Martinson, J. T. Hupp, *ECS Trans.* **2007**, *3*, 243–246.
- [35] J. J. He, H. Lindstrom, A. Hagfeldt, S. E. Lindquist, *J. Phys. Chem. B* **1999**, *103*, 8940–8943.
- [36] S. Ko, D. Lee, S. Jee, H. Park, K. Lee, W. Hwang, *Thin Solid Films* **2006**, *515*, 1932–1937.
- [37] G. Sauve, M. E. Cass, S. J. Doig, I. Lauermann, K. Pomykal, N. S. Lewis, *J. Phys. Chem. B* **2000**, *104*, 3488–3491.
- [38] B. A. Gregg, F. Pichot, S. Ferrere, C. L. Fields, *J. Phys. Chem. B* **2001**, *105*, 1422–1429.
- [39] G. Schlichthorl, N. G. Park, A. J. Frank, *J. Phys. Chem. B* **1999**, *103*, 782–791.
- [40] B. A. Gregg, *Coord. Chem. Rev.* **2004**, *248*, 1215–1224.
- [41] S. Cazzanti, S. Caramori, R. Argazzi, C. M. Elliott, C. A. Bignozzi, *J. Am. Chem. Soc.* **2006**, *128*, 9996–9997.
- [42] S. A. Sapp, C. M. Elliott, C. Contado, S. Caramori, C. A. Bignozzi, *J. Am. Chem. Soc.* **2002**, *124*, 11215–11222.
- [43] T. W. Hamann, B. S. Brunshwig, N. S. Lewis, *J. Phys. Chem. B* **2006**, *110*, 25514–25520.
- [44] M. Grätzel, *MRS Bull.* **2005**, *30*, 23–27.
- [45] P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Grätzel, *Nat. Mater.* **2003**, *2*, 402–407.
- [46] N. Kopidakis, N. R. Neale, A. J. Frank, *J. Phys. Chem. B* **2006**, *110*, 12485–12489.
- [47] T. W. Hamann, A. B. F. Martinson, J. W. Elam, M. J. Pellin, J. T. Hupp, *Prep. Pap. ACS Div. Fuel Chem.* **2007**, *52*.
- [48] K. Zhu, N. Kopidakis, N. R. Neale, J. van de Lagemaat, A. J. Frank, *J. Phys. Chem. B* **2006**, *110*, 25174–25180.
- [49] M. Law, L. E. Greene, A. Radenovic, T. Kuykendall, J. Liphardt, P. D. Yang, *J. Phys. Chem. B* **2006**, *110*, 22652–22663.
- [50] S. Handa, S. A. Haque, J. R. Durrant, *Adv. Funct. Mater.* **2007**, *17*, 2878–2883.
- [51] K. E. Splan, J. T. Hupp, *Langmuir* **2004**, *20*, 10560–10566.
- [52] P. J. Angiolillo, K. Susumu, H. T. Uyeda, V. S. Y. Lin, R. Shediach, M. J. Therien, *Synth. Met.* **2001**, *116*, 247–253.
- [53] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* **2001**, *123*, 1613–1624.
- [54] D. A. Gaal, J. T. Hupp, *J. Am. Chem. Soc.* **2000**, *122*, 10956–10963.
- [55] D. Kuciauskas, M. S. Freund, H. B. Gray, J. R. Winkler, N. S. Lewis, *J. Phys. Chem. B* **2001**, *105*, 392–403.
- [56] D. A. Gaal, J. E. McGarrah, F. Liu, J. E. Cook, J. T. Hupp, *Photochem. Photobiol. Sci.* **2004**, *3*, 240–245.
- [57] J. Nelson, S. A. Haque, D. R. Klug, J. R. Durrant, *Phys. Rev. B* **2001**, *63*, 20.
- [58] G. M. Hasselmann, G. J. Meyer, *J. Phys. Chem. B* **1999**, *103*, 7671–7675.

Published online: March 25, 2008