

 Open access • Journal Article • DOI:10.1021/JZ200668Q

The Grätzel Cell: Where Next? — [Source link](#)

Laurence M. Peter

Institutions: University of Bath

Published on: 13 Jul 2011 - Journal of Physical Chemistry Letters (American Chemical Society)

Related papers:

- [A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films](#)
- [Porphyrin-Sensitized Solar Cells with Cobalt \(II/III\)–Based Redox Electrolyte Exceed 12 Percent Efficiency](#)
- [Dye-Sensitized Solar Cells](#)
- [Recent advances in sensitized mesoscopic solar cells.](#)
- [Solar energy conversion by dye-sensitized photovoltaic cells](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/the-gratzel-cell-where-next-25i4jvl0cw>



Citation for published version:

Peter, LM 2011, 'The Gratzel Cell: Where Next?', *Journal of Physical Chemistry Letters*, vol. 2, no. 15, pp. 1861-1867. <https://doi.org/10.1021/jz200668q>

DOI:

[10.1021/jz200668q](https://doi.org/10.1021/jz200668q)

Publication date:

2011

Document Version

Peer reviewed version

[Link to publication](https://doi.org/10.1021/jz200668q)

This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in *Journal of Physical Chemistry Letters*, copyright © American Chemical Society after peer review. To access the final edited and published work see <http://dx.doi.org/10.1021/jz200668q>

University of Bath

Alternative formats

If you require this document in an alternative format, please contact:
openaccess@bath.ac.uk

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

The Grätzel Cell: Where next?

Laurence M Peter

Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom

l.m.peter@bath.ac.uk

RECEIVED DATE

ABSTRACT

Twenty years after O'Regan and Grätzel's seminal Nature paper entitled *A Low-Cost, High-Efficiency Solar-Cell Based On Dye-Sensitized Colloidal TiO₂ Films*, dye-sensitized solar cells (DSCs) and analogous devices have become a major topic of research, with over 1000 papers published in 2010. Although much more is now known about the physical and chemical processes taking place during operation of the DSC, the exponential increase in research effort during this period has not been matched by large increases in efficiency. This raises questions regarding the nature of the barriers that are holding back progress and whether current research is adequately addressing the key issues that are currently limiting device performance. This Perspective attempts to identify some of the factors that determine DSC performance and - as part of a selective survey of recent research highlights - presents a personal view of new approaches and research strategies that could offer ways to overcome the current efficiency stalemate.



KEYWORDS Grätzel cells, dye-sensitized solar cells, nanostructured solar cells.

The twenty years since the publication of the much-cited 1991 Nature paper entitled *A Low-Cost, High-Efficiency Solar-Cell Based On Dye-Sensitized Colloidal TiO₂ Films*’ by O’Regan and Grätzel¹ have seen the annual publication rate of papers dealing with various aspects of dye-sensitized solar cells (DSCs) rise exponentially (Fig. 1), with around a thousand papers published in 2010, the year in which Michael Grätzel was awarded the 2010 Millennium Technology Grand Prize for his work on DSCs.²

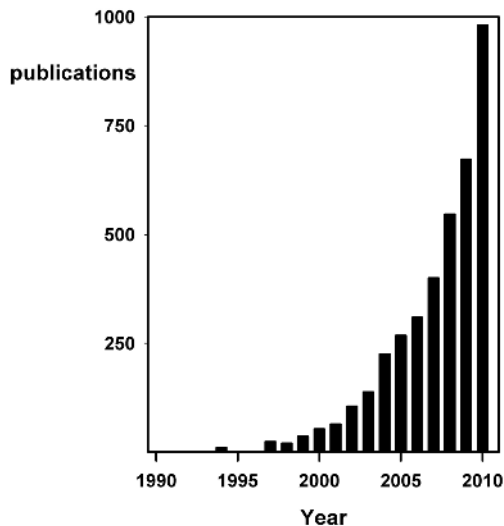


Figure 1. Annual number of publications dealing with dye-sensitized solar cells. Source ISI Web of Science: keyword “dye-sensitized”.

One might expect this increase in effort to have led to substantial improvements in the efficiency of DSCs, but in fact progress has slowed in the last few years. The latest in the series of solar cell efficiency tables collated by Green et al.³ lists the record validated AM 1.5 DSC efficiency as $10.4 \pm 0.34\%$. This value is for a 1 cm^2 cell. The record sub-module efficiency in the same table is $9.9 \pm 0.4 \%$ for a 17 cm^2 cell consisting of 8 parallel cells. Higher efficiency values have been reported for small area cells. In 2006, Chiba et al.⁴ achieved an AIST-validated efficiency of 11.1% using the so-called ‘black dye’ - a ruthenium terpyridyl⁵ complex (co-adsorbed with deoxycholic acid) and a masked area of 0.219 cm^2 . More recently, slightly higher efficiencies (up to 12.1 %) have been reported for small area (0.28 cm^2) DSCs utilizing hexyl(thiophene)-conjugated bipyridine ligands.⁶⁻⁸ It is interesting to compare these ‘champion’ efficiencies with those of competing thin film technologies. The values from the latest

efficiency table³ are: CIGS, $19.6 \pm 0.6\%$; CdTe $16.7 \pm 0.5\%$; organic bulk heterojunction, $8.3 \pm 0.3\%$. All of these values are for cells that are 1 cm^2 in area. The most remarkable of these values is the 8.3% for organic cells, which are threatening to catch up with DSCs. Clearly competition is strong, and if the DSC is to evolve into a mature and successful commercial technology, the current efficiency bottleneck needs to be addressed. However, an analysis of the around one thousand publications in 2010 shows that only a small fraction of them report real progress in terms of efficiency. In the large majority of cases, ‘improvements’ brought about, for example by changes of materials, are reported relative to arbitrary (usually low) baselines that are far removed from the performance of the state of the art cells that are fabricated in only a few laboratories. In view of this situation, it seems relevant to ask the question that is the title of this Perspective: ‘*where next?*’ Can we identify promising routes that will take us to large area ($\geq 1 \text{ cm}^2$) cell efficiencies that can compete with other thin film technologies? This Perspective examines a selection of recent work on DSCs (and their solid state analogs) that may provide pointers for the way out of the present impasse. Of course, there are other issues to be solved – stability for example – but in order to maintain a sharp focus, they are not considered here.

For the purpose of this Perspective, the DSC can be broken down into its components as well as into the processes taking place in the cell so that we can ask whether they impose (possibly fundamental) limitations on performance. At the same time, we can examine the DSC paradigm to see how far it can be extended to analogs of the DSC.

The sensitizer: limitations and opportunities

Photon absorption by the sensitizer dye (or equivalent inorganic absorber) is the first step in the sequence of processes that lead to power generation in the DSC. The efficiency of this light harvesting step depends on the optical absorption properties and coverage of the dye and on the optical path length. The well-known Shockley Queisser⁹ calculation of the thermodynamic efficiency limit (33.7%) for AM 1.5 illumination indicates that an ideal absorber should absorb all photons above a threshold energy of 1.3 - 1.4 eV (roughly 940 - 890 nm). This condition is readily met by bulk semiconductors that have a direct allowed optical transition at the appropriate band gap energy. This type of transition gives rise to

a steep absorption edge, with absorption coefficients rising rapidly to $10^4 - 10^5 \text{ cm}^{-1}$. By contrast, the molecular absorption bands of typical sensitizer dyes do not exhibit such steep onsets, and N719, the best known ruthenium bipyridine dye (*cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium)) has an absorption onset at ca. 1.65 eV (750 nm) that is significantly higher than the optimum 1.3 – 1.4 eV. The terpyridine black dye known as N749 (triisothiocyanato-(2,2':6',6''-terpyridyl-4,4',4''-tricarboxylato) ruthenium(II) tris(tetra-butylammonium)) has a better match to the Shockley Queisser optimum, but the gradual onset of absorption at low photon energies can lead to a lowering of light harvesting efficiency in the long wavelength region unless steps are taken to increase the optical path length by some form of light management, the simplest being scattering by the FTO substrate due to 'haze'⁴ or scattering by a layer of larger TiO₂ particles¹⁰.

Synthesis and characterization of new dyes have been major preoccupations in recent DSC research. The motivation for this research stems from the desire to tackle a number of problems. The first is cost. The synthesis and purification of the best performing ruthenium based dyes is expensive. The terpyridine black dye, for example, sells at around US\$3,500 a gram. Alternative metal-free dyes such as those based on the indoline structure^{11,12} have been widely investigated as alternatives, and performance figures are not far behind those obtained using ruthenium-based dyes. However, although extensive stability studies have been carried out on ruthenium-based dyes, less is known about the long term stability of the metal-free dyes. If they do prove to be sufficiently stable, they may offer a way forward in terms of lower cost. The second problem is to control the back electron transfer of electrons from the oxide to the redox system (or hole conductor). Here it is clear that that organized assembly of dye molecules and co-adsorbents at the interface can slow down electron transfer to such an extent that higher voltages can be achieved and even fast outer sphere redox systems such as ferrocinium/ferrocene¹³ can be used to replace I₃⁻/I⁻. This aspect of dye function is dealt with in the section dealing with alternative redox systems.

The design of new dyes (“panchromatic engineering”¹⁴) is also an active area of DSC research. A key question here is: how much room is there for improvement? To answer this question, we can look at a high performance DSC (11% AM 1.5 efficiency) fabricated by Ogura et al. in the Sony Corporation Laboratories¹⁵. The cell used co-sensitization by a strongly absorbing indoline dye (D131) and the ruthenium terpyridine black dye. A multilayer TiO₂ structure was used, and improved red response was achieved by incorporation of light scattering voids. Figure 2 illustrates how the combination of the two dyes improves the performance relative to the black dye on its own.

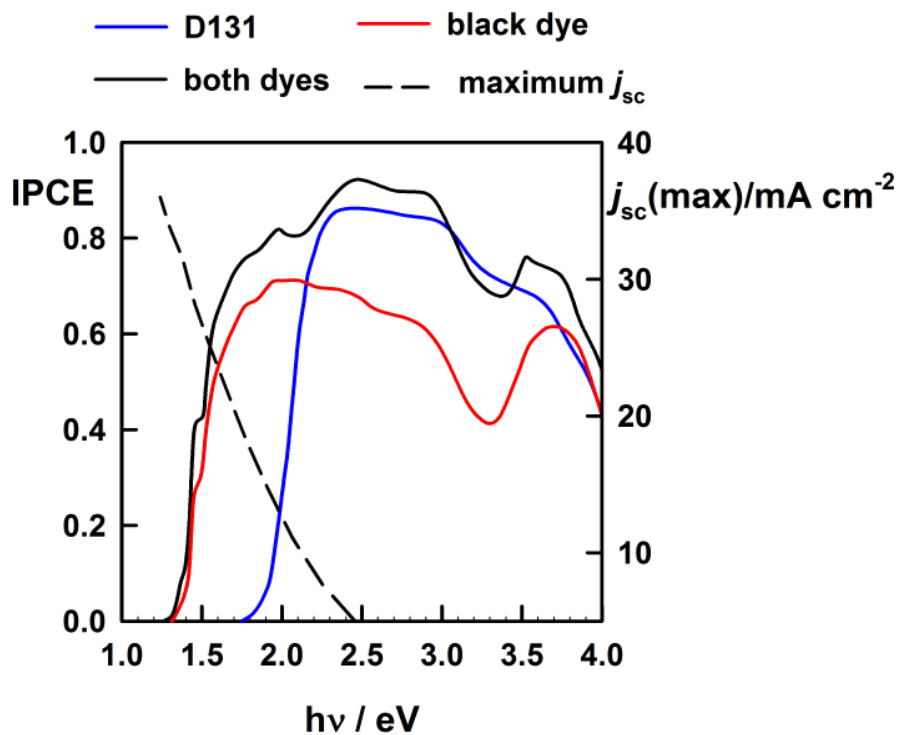


Figure 2. IPCE spectra for an 11% efficient DSC (Ogura et al, Sony Corporation¹⁵) obtained using co-sensitization with an organic dye (D131) and black ruthenium dye. IPCE data taken from reference ¹⁵.

The importance of light harvesting at photon energies below 1.5 eV (ca. 830 nm) is shown in Figure 2 by the plot of maximum attainable short circuit current density for AM 1.5 as a function of the dye ‘bandgap’. The experimental short circuit density for the cell is 22.6 mA cm⁻², which corresponds to 67% of the maximum attainable j_{sc} (broken line in Figure 2) for an abrupt onset of strong light absorption at 950 nm (33.6 mA at 1.3 eV). This calculation shows that in terms of current density, the

best cells are already operating close to the limit. Improvements in light management and reduction of reflection losses may bring some improvement, but room for progress without introducing impractical levels of complexity into the fabrication processes may be running out.

The rationale behind efforts to synthesize and evaluate new dyes requires careful thought. New dyes are often tested as a direct replacement for the 'standard' N719 in a conventional DSC. The main requirement here is to improve the response in the low energy part of the spectrum by lowering the HOMO LUMO gap of the dye without affecting the injection efficiency and regeneration rate. However, the dye may also play a role in retarding electron transfer to the redox system. This becomes particularly important if the I_3^-/I^- electrolyte is replaced by an outer sphere redox system such as ferrocinium/ferrocene (Fc^+/Fc)¹³ or by an organic hole conductor such as spiro-OMeTAD¹⁶. Since electron transfer is much faster in these systems, electrons are more likely to be lost in transit through the TiO_2 films. There are two ways in which the design of the dye can address this problem. The first is to increase the molar absorption coefficient so that thinner TiO_2 films can be used, increasing the collection efficiency for electrons. The second is to design the dye structure in such a way that it hinders the approach of redox species to the TiO_2 surface, thereby lowering the rate of back electron transfer.

Computational approaches to dye design

Synthesis and testing of new dyes is a time-consuming process. Increasingly, design strategies are being developed on the basis of first principles computational approaches¹⁷⁻¹⁹. Time-dependent density functional theory (TDDFT) calculations allow systematic exploration of the tuning of energy levels by substitution in order to identify dyes that have the desired structural, electronic and optical properties for application in DSCs. Ambitious attempts are also being made to use DFT calculations to study the interactions between different components of the DSC, for example the dye and electrolyte²⁰ and co-adsorbents^{21,22}. In its most general form, the computational approach has been used to define a protocol for selecting and combining components for new DSCs.²¹ It is often assumed that regeneration of the sensitizer dye by electron transfer from iodide ions (or an equivalent reduced species) following injection is sufficiently rapid that the back electron transfer from the oxide to the oxidized dye can be

neglected. This assumption has been called into question by recent work which shows that while back electron transfer may be negligible under short circuit conditions, it may be significant loss mechanism at the maximum power point, where the electron density is higher²³. Here too, a computational approach using molecular dynamics simulation based on DFT theory has generated new insights.²⁴

Alternatives to dyes

Clearly the use of molecular sensitizers runs into problems associated with the shape of the absorption bands. An attractive alternative is to use solid state sensitizers in the form of small semiconductor particles.²⁵ Here the question to ask is whether the absorption properties of the sensitizer really are superior to those of dyes. In order to achieve high efficiencies we still need a material that absorbs strongly for photon energies above ca. 1.3 eV. There are two ways of selecting the right material. The first is to consider the band gaps of bulk semiconductors and to choose a material with the correct band gap. On this basis, examples of suitable materials are CdTe (band gap 1.5 eV) and Bi₂S₃^{26,27} (band gap 1.25 eV). An alternative way is to select a material such as PbS with a lower band gap and then to reduce the particle size so that the band gap is tuned to the optimum energy range by quantum confinement. In the case of PbS, for example, a 4nm particle size gives an absorption onset at 1.05 eV. Figure 3 shows the energy dependence of the absorption coefficient α (cm⁻¹) of these PbS quantum dots calculated from the recent data of Moreels et al.²⁸.

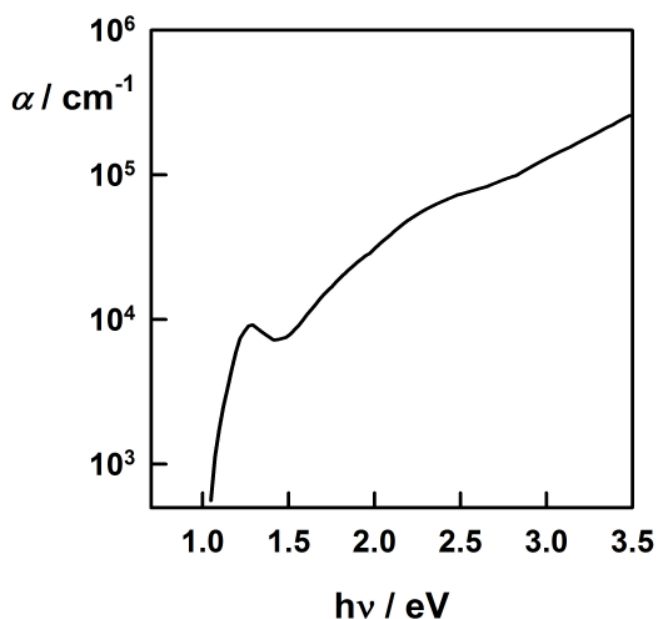


Figure 3. Photon energy dependence of the absorption coefficient of 4 nm PbS quantum dots calculated from data in ref²⁸.

These values of α were used to calculate the IPCE of a DSC based on a 10 μm thick sensitized TiO_2 film in which the TiO_2 nanocrystals (30 nm) are coated with a layer of 4nm PbS quantum dots with a particle size of 4 nm and a surface coverage of 50%. For comparison, the IPCE of the same cell sensitized by the Ru terpyridine black dye was calculated using the experimental area per molecule (0.42 nm^2), which also corresponds to a surface coverage of ca. 50%.^{29,30} The internal surface area of the film was taken as 10^3 cm^2 (based on an assembly of spheres with a packing fraction of 50%), and injection and collection efficiencies of 100% were assumed. Figure 4 compares the calculated IPCE spectra for sensitization by PbS quantum dots and the black dye. It is clear that the PbS sensitizer has the potential to outperform the ruthenium black dye for the same surface coverage. The energy dependence of α above the onset energy is similar for direct band gap semiconductors, so that we may conclude that sensitization by inorganic particles or thin films is worth pursuing. However, new organic dyes have higher molar absorption coefficients than the ‘classical’ ruthenium polypryridne dyes, so they may in turn have the potential to outperform inorganic sensitizers. When considering new sensitizers, it is worthwhile carrying out a quantitative comparison in the way outlined here.

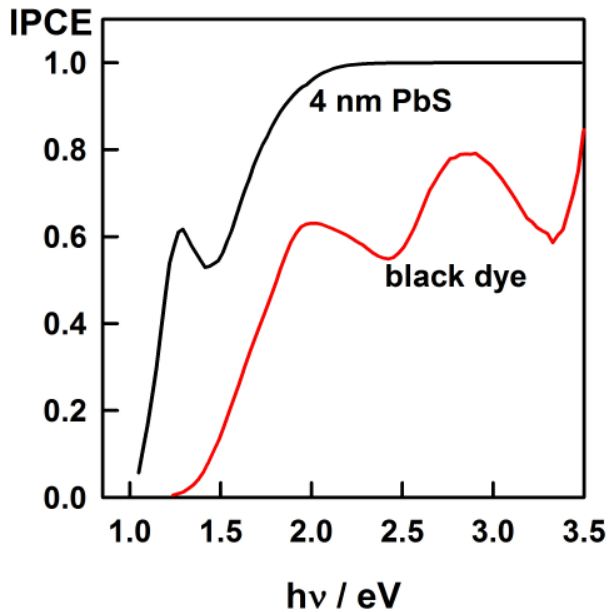


Figure 4. Comparison of IPCE spectra calculated for 50% coverage by PbS 4 nm QDs and by ruthenium black dye. TiO₂ thickness 10 μ m. TiO₂ particle size 30 nm.

So how do real semiconductor-sensitized DSCs compare with these predictions? So far the IPCE values reported for most semiconductor-sensitized DSCs are substantially lower than those predicted by this simple modeling. This may reflect low coverage or low injection efficiencies. Another problem with inorganic sensitizers is that the I₃⁻/I⁻ is not suitable since it corrodes the sensitizer. Alternative electrolytes such as polysulfide³¹ or cobalt complexes³² have been used successfully, and solid state devices based on spiro-OMeTAD have also been studied.^{33,34} Short circuit current densities in excess of 10 mA cm² have been reported for PbS-sensitized cells using a polysulfide electrolyte³¹, but the IPCE spectra suggest lower coverages than those used in the calculation above. The potential for substantial improvement is demonstrated by a recent paper that reports a remarkable 17.4 mA cm² for a DSC based on CdSe-sensitized SnO₂.³⁵ A ZnS surface passivation layer was used to reduce recombination losses. These cells show a steep rise in IPCE from the onset at around 1.6 eV to a plateau of 80%, which is similar to the calculated plot for the PbS-sensitized cell shown in Figure 4. This is consistent with the high optical density of the sensitized films, which was achieved by a multistep deposition process. If a similar approach could be used with a semiconductor such as CdTe with a lower band gap, j_{sc} values

close to - or exceeding - those of conventional DSCs should be achievable. The performance of semiconductor-sensitized cells of the type reported in ref ³⁵ is currently limited by poor open circuit voltages and fill factors. Progress in this area could make the cells serious competitors for conventional DSCs.

The mesoporous oxide – electron transport and the back reaction

The mesoporous oxide layer is one of the main distinguishing features of the DSC. Its main purpose is to optimize light harvesting by providing a high internal surface area on which the sensitizer dye is absorbed. Of course the downside of this high surface area is that it is available for the transfer of electrons to the redox system in the back reaction that determines the extent to which electrons can accumulate in the layer under illumination, generating a photovoltage. The oxide layer may also have a role in light management; for example the incorporation of scattering particles or voids increases the optical path length, improving the long wavelength response of the DSC. The oxide material of choice is still TiO₂ (anatase), although other oxides such as ZnO and SnO₂ have been investigated thoroughly. The chemical inertness of TiO₂ makes it an ideal supporting material for sensitizers that rely on carboxylate groups to attach the dye to the surface. By contrast, the pK_a of most carboxylated dyes is sufficiently low that ZnO is subject to corrosion leading to the formation of zinc carboxylate salts of the dyes that absorb light but fail to act as sensitizers. The rather high relative permittivity of anatase (~ 30 - 40) may also play a role by lowering the electrostatic interaction between injected electrons and oxidized dye molecules, reducing losses due to geminate recombination of electrons and oxidized dye molecules immediately after electron injection. It has been suggested that the lower injection efficiencies in the case of ZnO films can be traced back to formation of bound electron/oxidized dye pairs³⁶ arising from the lower relative permittivity of the oxide (~10).

It is frequently been argued that nanorods, nanotubes, nanoribbons and other nanostructures should enhance DSC performance because 1-dimensional diffusion improves collection of electrons at the anode. Two comments can be made about this assumption. The first is that the electron collection efficiency is already close to 100% in optimized cells based on mesoporous TiO₂, standard ruthenium-

based dyes and the conventional I_3^-/I^- redox electrolyte, so improvement is possible only for ‘bad’ cells. The second is that there is really little convincing experimental evidence of enhanced 1-D electron transport in these nanostructures. Considerable confusion arises in the discussion of electron ‘transport’ measurements since they usually involve some form of optical or electrical perturbation of the system that changes the occupancy of electron trapping states. It is important to realize that the response of the DSC to these perturbations does not give access to the behavior of *free* electrons. For this reason, claims to have enhanced electron transport are often based on a misconception about the nature of the dynamic current response of the DSC. In fact, the reported improvements can usually be explained in terms of changes in trap occupancy that alter the *apparent* electron diffusion coefficient³⁷. An interesting exception to this conclusion may be the case of ZnO nanorods^{38,39}, where it is possible that charge separation is enhanced by the presence of a space charge region in the highly doped oxide. In this case, the electric field component normal to the rod surface would drive injected electrons to the quasi-neutral core of the rods, where they could diffuse down to the anode contact. The lowering of electron concentration at the rod surface arising from band bending could also retard the loss of electrons by transfer to the redox system.

So should we conclude that attempts to improve electron transport in DSCs are misguided? Not necessarily. The collection efficiency is certainly high in *conventional* DSCs, but as soon as the electrolyte is changed from I_3^-/I^- to other redox systems, the collection efficiency may fall substantially due to more rapid electron transfer to redox species. The same is true in the case where the I_3^-/I^- electrolyte is replaced by a solid organic hole conductor. The average distance that electrons diffuse before undergoing electron transfer to the redox species defines the electron diffusion length, L_0 , which in the case of first order recombination kinetics is given by $(D_0 \tau_0)^{1/2}$, where D_0 is the diffusion coefficient of free electrons and τ_0 is the free electron lifetime. For efficient collection of electrons at the anode, L_0 needs to be 2 - 3 times greater than the film thickness. Of course, increasing the mobility of *free electrons* will increase the electron diffusion length, but it seems likely that D_0 is fixed by the material chosen. The mobility of electrons in TiO_2 is an order of magnitude lower than in ZnO: the

corresponding values of the electron diffusion coefficient D_0 are $0.4 \text{ cm}^2 \text{ s}^{-1}$ and $5.3 \text{ cm}^2 \text{ s}^{-1}$ for *bulk* TiO_2 ⁴⁰ and ZnO ⁴¹ respectively, so on this basis ZnO might seem the better choice. In spite of this difference, there seems little motivation to move away from TiO_2 at present.

Electrons may also be transferred from the mesoporous oxide to oxidized dye molecules. This process competes with regeneration of the dye from its oxidized state by electron transfer from the redox system²³ or solid hole conductor⁴². These processes deserve more attention since they may influence DSC performance under load conditions, particularly when the ‘standard’ components are replaced by alternative materials.

The Electrolyte: can we increase V_{oc} ? What about solid hole conductors?

V_{oc} , the open circuit voltage of the DSC is determined by the difference between the electron quasi Fermi level under illumination and the redox Fermi level⁴³. Strategies to increase V_{oc} involve retarding the rate of electron transfer to the oxidized component of the redox couple or shifting the TiO_2 conduction band energy up by adsorption of species that alter the surface dipole. Another approach is to move the redox Fermi level downwards by choosing a different redox system. Alternative redox electrolytes have been reviewed comprehensively by Hamann and Ondersam in a recent publication⁴⁴, so we will focus here on a few recent highlights. The main motivation for changing the electrolyte is to introduce more flexibility in the choice of the redox Fermi level. Alternative electrolytes that have received recent attention include cobalt polypyridine complexes^{45,46}, nickel bis(dicarbollides)⁴⁷, nitroxide radicals (TEMPO)⁴⁸, 5-mercapto-1-methyltetrazole⁴⁹ 2-mercapto-5-methyl-1,3,4-thia-diazole (MeMT)⁵⁰ and tetramethylthiourea.⁵¹ A key process in cell operation is the regeneration of the dye from its oxidized state following electron injection. This involves electron transfer from the reduced component of the redox couple. The driving force for this reaction is high (around 0.5 eV) in the conventional DSC. Ideally, we would like to move the redox level closer to the D^+/D redox level so as to increase the open circuit voltage, whilst still maintaining rapid regeneration of the dye to prevent degradation. The question ‘where next’ in this context could have a surprising answer – ‘back to where

we started'. Early work by Gregg and co-workers led to the conclusion that fast outer sphere redox couples like Fc^+/Fc are not suitable electrolytes from the DSC because the back transfer of electrons from the TiO_2 and from the substrate is facile⁵². This reduces the electron lifetime so that the electron diffusion length becomes so short that most electrons are lost in transit to the anode. In addition, V_{oc} is reduced by electron transfer from the substrate unless a blocking layer is used. In a remarkable breakthrough, Daeneke et al.¹³ have recently reported a 7.5% efficient cell based on the Fc^+/Fc couple. Elliott has aptly called this approach in which both the dye and the electrolyte are changed 'Out with both baby and bathwater'⁵³. The metal-free carbazole donor-acceptor dye (Figure 5) used in the cell not only sensitizes efficiently but when co-adsorbed with chenodeoxycholic acid it also effectively retards electron transfer to the Fc^+/Fc couple. The remarkably high open circuit voltage under AM1.5 conditions (842 mV) represents an important advance. The performance is limited by the relatively low j_{sc} (12.2 mA cm^{-2}), which may indicate that the electron diffusion length is comparable with the film thickness (overall $6.6 \mu\text{m}$). Further modification of the dye to reduce the HOMO-LUMO gap could conceivably lead to efficiencies in double figures. One potential drawback of ferrocene and other metal complexes is that their diffusion coefficients in solution are likely to be substantially lower than those of I_3^- , so that diffusion limitations could be a problem at high light intensities unless the electrode gap is reduced.

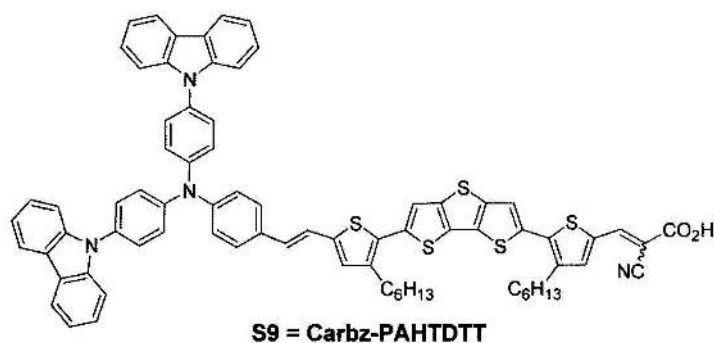


Figure 5. Carbazole dye used by Daeneke et al.¹³ in a 7.5% efficient Fc^+/Fc DSC.

We should also consider the potential of solid state hole conductors³³ as alternatives to liquid redox electrolytes. Here the competition comes from organic solar cells, which are compatible with reel

to reel processing. The current record for a solid state DSC is 6.08%¹⁶, over 2% behind the best organic cell. The solid hole conductor used in the majority of solid state DSCs is still *spiro*-OMeTAD, which was first used by Bach et al. in 1998⁵⁴, and it is not clear whether these cells will be able to compete with organic bulk heterojunction cells which are moving ahead.

The next DSC generation? Energy Transfer, tandem cells and multiple exciton generation

Clearly the efficiency of DSCs is still far from the Shockley Queisser limit for a single absorber. Several interesting approaches are being taken to try to boost efficiency – for example, enhancement of light harvesting by plasmonics⁵⁵⁻⁵⁷ and Förster resonant energy transfer (FRET)⁵⁸. Undeterred by the fact that the DSC efficiencies appear to have reached a plateau at around 12%, attempts are being made to develop tandem cells. The recent report⁵⁹ of an 11.5% tandem DSC using organic dyes to absorb different parts of the solar spectrum shows that progress is being made. However, going to a tandem cell moves the thermodynamic limit up to 42%, so there is still a long way to go.

A tantalizing possibility that is the topic of heated discussion in the literature is whether it is possible to generate more than one carrier pair by absorption of a photon if the energy is sufficiently high. The process of multiple exciton generation (MEG)⁶⁰ or carrier multiplication in quantum confined structures (quantum dots) is seen as a way of overcoming the Shockley Queisser limit. Even if the process does successfully produce multiple carrier pairs, it is still necessary to extract them into the external circuit in order to enhance efficiency. It is not clear whether this has been achieved experimentally. Sambur et al.⁶¹ have reported internal quantum efficiencies above 100% for electron injection from PbS nanocrystals into bulk TiO₂, and if this work can be substantiated and transferred to a working DSC, it will be interesting to see what currents can be achieved. However, to end on a note of caution, Nair et al.⁶² have suggested that many reports of carrier multiplication may be explained by experimental artifacts. Clearly the debate will continue, and progress (or failure) is likely to impact on the next generation of DSCs.

So where next?

This Perspective started on a slightly pessimistic note, but after considering the range of options that are open to DSC researchers, one can be optimistic that progress will be made provided that careful thought is given to the motivation for a particular research strategy. This involves more than simply thinking that something might be a good idea. Wherever possible, some quantitative consideration should be given to the potential impact on DSC performance for a well-defined system. Claims to have ‘improved’ DSC performance by (a real example) 110.7% should be firmly rejected by referees, who should insist on a meaningful baseline comparison and a proper error analysis based on data obtained with several cells. If the DSC community could refocus its efforts in this way, there is a good chance that the DSC could begin to compete with other thin film technologies. If the DSC is to progress, we do not need just more research – we need *better focused* research.

ACKNOWLEDGMENT The author thanks past and present members of his research group as well as international colleagues who have collaborated in DSC research or have discussed the topics included in this Perspective.

REFERENCES

- (1) O'Regan, B.; Grätzel, M. A Low-Cost, High-Efficiency Solar-Cell Based On Dye-Sensitized Colloidal TiO₂ Films. *Nature* **1991**, *353*, 737-740.
- (2) Meyer, G. J. The 2010 Millennium Technology Grand Prize: Dye-Sensitized Solar Cells. *Acs Nano* **2010**, *4*, 4337-4343.
- (3) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W. Solar cell efficiency tables (version 37). *Prog. Photovoltaics* **2011**, *19*, 84.
- (4) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. Komiya, R.; Koide, N.; Han, L. Y. Dye-sensitized Solar Cells with Conversion Efficiency of 11.1%. *Jpn. J. Appl. Phys.* **2006**, *45* L638-640.
- (5) Nazeeruddin, M. K.; Pechy, P.; Grätzel, M. Efficient Panchromatic Sensitization of Nanocrystalline TiO₂ Films by a Black Dye Based on a Trithiocyanato-Ruthenium Complex. *Chem. Commun.* **1997**, 1705-1706.

- (6) Cao, Y. M.; Bai, Y.; Yu, Q. J.; Cheng, Y. M.; Liu, S.; Shi, D.; Gao, F. F.; Wang, P. Dye-Sensitized Solar Cells with a High Absorptivity Ruthenium Sensitizer Featuring a 2-(Hexylthio)thiophene Conjugated Bipyridine. *J. Phys. Chem. C* **2009**, *113*, 6290-6297.
- (7) Chen, C. Y.; Wang, M. K.; Li, J. Y.; Pootrakulchote, N.; Alibabaei, L.; Ngoc-le, C. H.; Decoppet, J. D.; Tsai, J. H.; Grätzel, C.; Wu, C. G.; Zakeeruddin, S. M.; Gratzel, M. Highly Efficient Light-Harvesting Ruthenium Sensitizer for Thin-Film Dye-Sensitized Solar Cells. *Acs Nano* **2009**, *3*, 3103-3109.
- (8) Yu, Q. J.; Wang, Y. H.; Yi, Z. H.; Zu, N. N.; Zhang, J.; Zhang, M.; Wang, P. High-Efficiency Dye-Sensitized Solar Cells: The Influence of Lithium Ions on Exciton Dissociation, Charge Recombination, and Surface States. *Acs Nano* **2010**, *4*, 6032-6038.
- (9) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32*, 510-519.
- (10) Zhang, Z. P.; Ito, S.; O'Regan, B.; Kuang, D. B.; Zakeeruddin, S. M.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Pechy, P.; Humphry-Baker, R.; Koyanagi, T.; Mizuno, T.; Grätzel, M. The Electronic Role of the TiO₂ Light-Scattering Layer in Dye-Sensitized Solar Cells. *Z. Phy.Chem.* **2007**, *221*, 319-327.
- (11) Horiuchi, T.; Miura, H.; Uchida, S. Highly-Efficient Metal-Free Organic Dyes for Dye-Sensitized Solar Cells. *Chem. Commun.* **2003**, 3036-3037.
- (12) Ito, S.; Miura, H.; Uchida, S.; Takata, M.; Sumioka, K.; Liska, P.; Comte, P.; Pechy, P.; Graetzel, M. High-Conversion-Efficiency Organic Dye-Sensitized Solar Cells with a Novel Indoline Dye. *Chem. Commun.* **2008**, 5194-5196.
- (13) Daeneke, T.; Kwon, T. H.; Holmes, A. B.; Duffy, N. W.; Bach, U.; Spiccia, L. High-Efficiency Dye-Sensitized Solar Cells with Ferrocene-Based Electrolytes. *Nature Chem.* **2011**, *3*, 211-215.
- (14) Yum, J.-H.; Baranoff, E.; Wenger, S.; Nazeeruddin, M. K.; Grätzel, M. Panchromatic Engineering for Dye-Sensitized Solar Cells. *Energy Environ. Sci.* **2011**, *4*, 842-857.
- (15) Ogura, R. Y.; Nakane, S.; Morooka, M.; Orihashi, M.; Suzuki, Y.; Noda, K. High-Performance Dye-Sensitized Solar cell with a Multiple Dye System. *Appl. Phys. Lett.* **2009**, *94*, 073308-1 – 073308-3.
- (16) Cai, N.; Moon, S. J.; Cevey-Ha, L.; Moehl, T.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. An Organic D-pi-A Dye for Record Efficiency Solid-State Sensitized Heterojunction Solar Cells. *Nano Lett.* **2011**, *11*, 1452-1456.
- (17) Meng, S.; Kaxiras, E.; Nazeeruddin, M. K.; Grätzel, M. Design of Dye Acceptors for Photovoltaics from First Principles Calculations. *J. Phys. Chem. C* **2011**, *115*, 9276-9282.
- (18) De Angelis, F.; Fantacci, S.; Selloni, A.; Nazeeruddin, M. K.; Grätzel, M. First-Principles Modeling of the Adsorption Geometry and Electronic Structure of Ru(II) Dyes on Extended TiO₂ Substrates for Dye-Sensitized Solar Cell Applications *J. Phys. Chem. C* **2010**, *114*, 6054-6061.
- (19) Pastore, M.; Mosconi, E.; De Angelis, F.; Grätzel, M. A Computational Investigation of Organic Dyes for Dye-Sensitized Solar Cells: Benchmark, Strategies, and Open Issues. *J. Phys. Chem. C* **2010**, *114*, 7205-7212.
- (20) Kusama, H.; Sugihara, H.; Sayama, K. Theoretical Study on the Interactions between Black Dye and Iodide in Dye-Sensitized Solar Cells *J. Phys. Chem. C* **2011**, *115*, 9267-9275.

- (21) Le Bahers, T.; Labat, F.; Pauporte, T.; Laine, P. P.; Ciofini, I. Theoretical Procedure for Optimizing Dye-Sensitized Solar Cells: From Electronic Structure to Photovoltaic Efficiency. *J. Amer. Chem. Soc.* **2011**, *133*, 8005-8013.
- (22) Asaduzzaman, A. M.; Schreckenbach, G. Computational Studies on the Interactions Among Redox Couples, Additives and TiO₂: Implications for Dye-Sensitized Solar Cells. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14609-14618.
- (23) Anderson, A. Y.; Barnes, P. R. F.; Durrant, J. R.; O'Regan, B. C. Quantifying Regeneration in Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2011**, *115*, 2439-2447.
- (24) Schiffmann, F.; VandeVondele, J.; Hutter, J.; Urakawa, A.; Wirz, R.; Baiker, A. P. An Atomistic Picture of the Regeneration Process in Dye Sensitized Solar Cells. *Natl. Acad. Sci. USA* **2010**, *107*, 4830-4833.
- (25) Mora-Sero, I.; Bisquert, J. Breakthroughs in the Development of Semiconductor-Sensitized Solar Cells. *J. Phys. Chem. Lett.* **2010**, *1*, 3046-3052.
- (26) Peter, L. M. The Photoelectrochemical Properties of Anodic Bismuth Sulfide (Bi₂S₃) Films. *J. Electroanal. Chem.* **1979**, *98*, 49-58.
- (27) Peter, L. M.; Wijayantha, K. G. U.; Riley, D. J.; Waggett, J. P. Band-Edge Tuning in Self-Assembled Layers of Bi₂S₃ Nanoparticles used to Photosensitize Nanocrystalline TiO₂. *J. Phys. Chem. B* **2003**, *107*, 8378-8381 .
- (28) Moreels, I.; Lambert, K.; Smeets, D.; De Muynck, D.; Nollet, T.; Martins, J. C.; Vanhaecke, F.; Vantomme, A.; Delerue, C.; Allan, G.; Hens, Z. Size-Dependent Optical Properties of Colloidal PbS Quantum Dots. *Acs Nano* **2009**, *3*, 3023.
- (29) Nazeeruddin, M. K.; Pechy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. J. Engineering of Efficient Panchromatic Sensitizers for Nanocrystalline TiO₂-Based Solar Cells. *J. Amer. Chem. Soc.* **2001**, *123*, 1613-1624.
- (30) Shklover, V.; Nazeeruddin, K.; Gratzel, M.; Ovchinnikov, Y. E. Packing of Ruthenium Sensitizer Molecules on Mostly Exposed Faces of Nanocrystalline TiO₂: Crystal Structure of (NBu₄⁺)₂ Ru(H₂ tcterpy)(NCS)₃²⁻·0.5 DMSO. *Appl. Organomet. Chem.* **2002**, *16*, 635-642.
- (31) Braga, A.; Giménez, S.; Concina, I.; Vomiero, A.; Mora-Seró, I. Panchromatic Sensitized Solar Cells Based on Metal Sulfide Quantum Dots Grown Directly on Nanostructured TiO₂ Electrodes. *J. Phys. Chem. Lett.* **2011**, *2*, 454-460.
- (32) Nusbaumer, H.; Zakeeruddin, S. M.; Moser, J. E.; Grätzel, M. An alternative efficient redox couple for the dye-sensitized solar cell system. *Chem. Eur. J.* **2003**, *9*, 3756-3763.
- (33) Wang, M. K.; Liu, J. Y.; Cevey-Ha, N. L.; Moon, S. J.; Liska, P.; Humphry-Baker, R.; Moser, J. E.; Grätzel, C.; Wang, P.; Zakeeruddin, S. M.; Gratzel, M. High efficiency solid-state sensitized heterojunction photovoltaic device. *Nano Today* **2010**, *5*, 169-174.
- (34) Wang, M. K.; Moon, S. J.; Zhou, D. F.; Le Formal, F.; Cevey-Ha, N. L.; Humphry-Baker, R.; Gratzel, C.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. Enhanced-Light-Harvesting Amphiphilic Ruthenium Dye for Efficient Solid-State Dye-Sensitized Solar Cells. *Adv. Funct. Mater.* **2010**, *20*, 1821-1826.

- (35) Hossain, M. A.; Jennings, J. R.; Koh, Z. Y.; Wang, Q. Carrier Generation and Collection in CdS/CdSe-Sensitized SnO₂ Solar Cells Exhibiting Unprecedented Photocurrent Densities. *Acs Nano* **2011**, *5*, 3172-3181.
- (36) Stockwell, D.; Yang, Y.; Huang, J.; Anfuso, C.; Huang, Z. Q.; Lian, T. Q. Comparison of Electron-Transfer Dynamics from Coumarin 343 to TiO₂, SnO₂, and ZnO Nanocrystalline Thin Films: Role of Interface-Bound Charge-Separated Pairs. *J. Phys. Chem. C* **2010**, *114*, 6560-6566.
- (37) Bisquert, J.; Vikhrenko, V. S. Interpretation of the Time Constants Measured by Kinetic Techniques in Nanostructured Semiconductor Electrodes and Dye-Sensitized Solar Cells. *J. Phys. Chem. B* **2004**, *108*, 2313-2322.
- (38) Galoppini, E.; Rochford, J.; Chen, H. H.; Saraf, G.; Lu, Y. C.; Hagfeldt, A.; Boschloo, G. Fast Electron Transport in Metal Organic Vapor Deposition Grown Dye-Sensitized ZnO Nanorod Solar Cells. *J. Phys. Chem. B* **2006**, *110*, 16159.
- (39) Mora-Sero, I.; Fabregat-Santiago, F.; Denier, B.; Bisquert, J.; Tena-Zaera, R.; Elias, J.; Levy-Clement, C. Determination of Carrier Density of ZnO Nanowires by Electrochemical Techniques. *Appl. Phys. Lett.* **2006**, *89*, 203117-1 - 203117-3.
- (40) Forro, L.; Chauvet, O.; Emin, D.; Zuppiroli, L.; Berger, H.; Lévy, F. High mobility n-type Carriers in Large Single Crystals of Anatase (TiO₂). *J. Appl. Phys.* **1994**, *75*, 633-635.
- (41) Look, D. C.; Reynolds, D. C.; Sizelove, J. R.; Jones, R. L.; Litton, C. W.; Cantwell, G.; Harsch, W. C. Electrical Properties of Bulk ZnO. *Sol. Stat. Commun.* **1998**, *105*, 399-401.
- (42) Cappell, U.B.; Gibson, E.A.; Hagfeldt, A.; Boschloo, G. Dye Regeneration by Spiro-MeOTAD Solid State Dye-Sensitized Solar Cells Studied by Photoinduced Absorption Spectroscopy and Spectroelectrochemistry. *J. Phys. Chem. C* **2009** *113*, 6275-6281.
- (43) Peter, L. M. Characterization and Modeling of Dye-Sensitized Solar Cells *J. Phys. Chem. C* **2007**, *111*, 6601-6612.
- (44) Hamann, T. W. O., J.W. : Dye-Sensitized Solar Cell Redox Shuttles. *Energy Environ. Sci.* **2011**, *4*, 370-381.
- (45) Feldt, S. M.; Gibson, E. A.; Gabrielsson, E.; Sun, L.; Boschloo, G.; Hagfeldt, A. Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells. *J. Amer. Chem. Soc.* **2010**, *132*, 16714-16724.
- (46) Wang, H. X.; Nicholson, P. G.; Peter, L.; Zakeeruddin, S. M.; Grätzel, M. Transport and Interfacial Transfer of Electrons in Dye-Sensitized Solar Cells Utilizing a Co(dbbip)₂ Redox Shuttle. *J. Phys. Chem. C* **2010**, *114*, 14300-14306.
- (47) Spokoyny, A. M.; Li, T. C.; Farha, O. K.; Machan, C. W.; She, C. X.; Stern, C. L.; Marks, T. J.; Hupp, J. T.; Mirkin, C. A. Electronic Tuning of Nickel-Based Bis(dicarbollide) Redox Shuttles in Dye-Sensitized Solar Cells. *Angew. Chem. Int. Ed.* **2010**, *49*, 5339-5343.
- (48) Kato, F.; Hayashi, N.; Murakami, T.; Okumura, C.; Oyaizu, K.; Nishide, H. Nitroxide Radicals for Highly Efficient Redox Mediation in Dye-sensitized Solar Cells. *Chem. Lett.* **2010**, *39*, 464-465.
- (49) Wang, M. K.; Chamberland, N.; Breau, L.; Moser, J. E.; Humphry-Baker, R.; Marsan, B.; Zakeeruddin, S. M.; Grätzel, M. An Organic Redox Electrolyte to Rival Triiodide/iodide in Dye-sensitized Solar Cells. *Nature Chem.* **2010**, *2*, 385-389.

- (50) Tian, H. N.; Jiang, X. A.; Yu, Z.; Kloo, L.; Hagfeldt, A.; Sun, L. C. Efficient Organic-Dye-Sensitized Solar Cells Based on an Iodine-Free Electrolyte. *Angew. Chem. Int. Ed.* **2010**, *49*, 7328-7331.
- (51) Liy, Y. J., J.R.; Oarameswaran, M.; Wang, Q. An Organic Redox Mediator for Dye-Sensitized Solar Cells with Near Unity Quantum Efficiency. *Energy Environ. Sci.* **2011**, *4*, 564-571.
- (52) Gregg, B. A.; Pichot, F.; Ferrere, S.; Fields, C. L. Interfacial Recombination Processes in Dye-Sensitized Solar Cells and Methods To Passivate the Interfaces. *J. Phys. Chem. B* **2001** *105*, 1422-1429.
- (53) Elliott, C. M. Dye-Sensitized Solar Cells: Out with Both Baby and Bathwater. *Nat Chem* **2011**, *3*, 188-189.
- (54) Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. Solid-State Dye-Sensitized Mesoporous TiO₂ Solar Cells with High Photon-to-Electron Conversion Efficiencies. *Nature* **1998**, *395*, 583-585.
- (55) Brown, M. D.; Suteewong, T.; Kumar, R. S. S.; D'Innocenzo, V.; Petrozza, A.; Lee, M. M.; Wiesner, U.; Snaith, H. J. Plasmonic Dye-Sensitized Solar Cells Using Core-Shell Metal-Insulator Nanoparticles *Nano Lett.* **2010**, *11*, 438-445.
- (56) Ding, I. K.; Zhu, J.; Cai, W.; Moon, S.-J.; Cai, N.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M.; Brongersma, M. L.; Cui, Y.; McGehee, M. D. Plasmonic Dye-Sensitized Solar Cells. *Adv. Energy Mat.* **2011**, *1*, 52-57.
- (57) Atwater, H. A.; Polman, A. Plasmonics for Improved Photovoltaic Devices. *Nature Mat.* **2010**, *9*, 865-865.
- (58) Hardin, B. E.; Yum, J. H.; Hoke, E. T.; Jun, Y. C.; Pechy, P.; Torres, T.; Brongersma, M. L.; Nazeeruddin, M. K.; Grätzel, M.; McGehee, M. D. High Excitation Transfer Efficiency from Energy Relay Dyes in Dye-Sensitized Solar Cells. *Nano Lett.* **2010**, *10*, 3077-3083.
- (59) Li, L.; Hao, Y.; Yang, X.; Zhao, J.; Tian, H.; Teng, C.; Hagfeldt, A.; Sun, L. A. Double-Band Tandem Organic Dye-sensitized Solar Cell with an Efficiency of 11.5%. *ChemSusChem* **2011**, *4*, 609-612.
- (60) Nozik, A. J.; Beard, M. C.; Luther, J. M.; Law, M.; Ellingson, R. J.; Johnson, J. C. Semiconductor Quantum Dots and Quantum Dot Arrays and Applications of Multiple Exciton Generation to Third-Generation Photovoltaic Solar Cells. *Chem. Rev.* **2010**, *110*, 6873-6890.
- (61) Sambur, J. B.; Novet, T.; Parkinson, B. A. Multiple Exciton Collection in a Sensitized Photovoltaic System. *Science* **2010**, *330*, 63-66.
- (62) Nair, G.; Chang, L.-Y.; Geyer, S. M.; Bawendi, M. G. Perspective on the Prospects of a Carrier Multiplication Nanocrystal Solar Cell. *Nano Lett.* **2011**, *11*, 2145-2151.

Biography

Laurie Peter has been active in the field of photoelectrochemistry for over 30 years and has worked on different aspects of dye-sensitized solar cells since 1997. He has developed a range of experimental techniques that are now widely used for studying dye-sensitized solar cells and other photoelectrochemical systems.

Quotes

“..if the DSC is to evolve into a mature and successful commercial technology, the current efficiency bottleneck needs to be addressed.”

“Can we identify promising routes that will take us to large area ($\geq 1 \text{ cm}^2$) cell efficiencies that can compete with other thin film technologies? “

“If the DSC is to progress, we do not need just more research – we need *better focused* research.”