

The 2010 Millennium Technology Grand Prize: Dye-Sensitized Solar Cells

Gerald J. Meyer*

Departments of Chemistry and Materials Science & Engineering, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218

Michael Grätzel was awarded the 2010 Millennium Technology Grand Prize and the prize trophy "Peak" at the Grand Award Ceremony at the Finnish National Opera House in Helsinki for advances that have enabled practical application of dye-sensitized solar cells.¹ Professor Grätzel directs the laboratory of photonics and interfaces at the École Polytechnique de Lausanne, where he has pioneered the use of mesoscopic thin films for dye-sensitized solar cells and other energy applications. The International Selection Committee noted that Grätzel's advances are likely to "have an important role in low-cost, large-scale solutions for renewable energy".

Indeed, Grätzel's contributions have provided an entirely new paradigm for solar-energy conversion that simultaneously placed molecular and nanoscience approaches on the map with traditional photovoltaics like silicon. Prior to Grätzel's work, molecular and nanostructured solar cells were of purely academic interest; they provided opportunities to test fundamental aspects of excited states and interfacial electron transfer. The seminal 1991 *Nature* paper on dye-sensitized solar cells, which Grätzel co-authored with then graduate student Brian O'Regan, abruptly changed this mindset through the realization of an order of magnitude increase in power conversion efficiency with remarkably high stability and a potential for very low cost.² The paper demonstrated that a thin film, comprising anatase TiO₂ nanocrystallites interconnected in a mesoporous network, quantitatively collected charge from molecular excited states and vectorially transported that charge over micrometer distances. Today's dye-sensitized solar cells have confirmed efficiencies greater than 11%, and the components required to prepare them are commercially available from multiple vendors.^{3,4} The practical application is also illustrated

ABSTRACT The 2010 Millennium Technology Grand Prize was awarded to Michael Grätzel for his ground-breaking research that has led to the practical application of dye-sensitized solar cells. Although Grätzel began his research well before nanotechnology had the "buzz" that it does today, the mesoscopic thin films he has developed have paved the way for generations of scientists to exploit the nanoscale for energy conversion. In addition to practical application, his research has led to a deeper understanding of photoinitiated charge-transfer processes at semiconductor interfaces. Here, the key scientific developments that guided early progress in dye-sensitized solar cells are summarized, with emphasis on fundamental advances that have enabled practical application.

by the recent launch of industrial production by several corporations. In particular, the company G24 Innovations in Cardiff, Wales (UK), started commercial shipment of mass-produced flexible modules of dye-sensitized solar cells based on these advances on October 12, 2009. The yearly production capacity of the plant is 120 MW.⁵

Grätzel's contributions have provided an entirely new paradigm for solar-energy conversion that simultaneously placed molecular and nanoscience approaches on the map with traditional photovoltaics like silicon.

The impact of Grätzel's fundamental work on the growing community of scientists committed to solar-energy conversion is also particularly noteworthy. The ISI Web of Science index reveals that

*Address correspondence to meyer@jhu.edu.

Published online August 24, 2010.
10.1021/nn101591h

© 2010 American Chemical Society

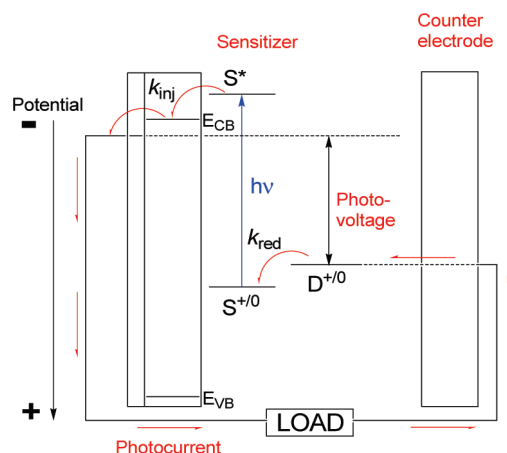


Figure 1. Simplified mechanism for light-to-electrical energy conversion in a dye-sensitized solar cell. Light absorption by a sensitizer, S , creates an excited state, S^* , that injects an electron into the semiconductor conduction band with a rate constant, k_{inj} . The now oxidized sensitizer S^+ is reduced by an electron donor, D , with a rate constant, k_{red} . The oxidized donor, D^+ , is reduced at the counter electrode, and thus the solar cell does not produce any chemical products and is termed regenerative. The photovoltage represents the energy difference between the quasi-Fermi level of the illuminated semiconductor and the counter electrode.

the 1991 *Nature* paper alone has been cited ~ 5000 times and that the number of citations grows each year.² The worldwide resonance of his work ranks him among the top 20 most cited chemists in the world. Hundreds of research groups are now actively working on a wide variety of mesoscopic thin films for energy conversion applications. One cannot attend an American Chemical Society (ACS) national meeting without hearing a multitude of talks, and even entire symposia, that are directly or indirectly inspired by Grätzel's work. While much of this research has been directed toward practical applications in energy conversion, the sensitized mesoscopic thin films afford unprecedented characterization of fundamental interfacial charge-transfer reactions that was not previously possible. The light-to-electrical energy conversion process is now understood in considerable molecular detail.

The state-of-the-art dye-sensitized solar cell has a myriad of details, most

of which go beyond what can reasonably be considered in this Nano Focus article. Rather, I include the accepted mechanism for light-to-electrical energy conversion, champion confirmed efficiencies, and give a brief history of dye-sensitized solar cells to provide perspective on the critically important fundamental advances Grätzel and his colleagues have made that led to the Millennium Grand Prize.

Dye-Sensitized Solar Cells. Dye sensitization of wide band gap metal oxide semiconductors in aqueous photoelectrochemical cells was an active area of research in the 1970s.^{6–9} Much of this work, like the celebrated studies of Fujishima and Honda,¹⁰ focused on the photosensitized splitting of water into hydrogen and oxygen gases in photoelectrosynthetic cells. Redox mediators, then called “supersensitizers”, enhanced the power conversion efficiency substantially without generation of chemical products. These photoelectrochemical cells are *regenerative* and most similar to those advanced by Grätzel. The late Heinz Gerischer identified the

mechanism for light-to-electrical energy conversion in regenerative dye-sensitized solar cells based on single-crystal semiconductor materials and provided a theoretical framework from which they could be understood.⁹ A simplified mechanism is shown in Figure 1.

The indirect 3.2 eV wide band gap of anatase TiO_2 absorbs only about 3% of the air mass 1.5 solar spectrum and is hence of limited use for solar harvesting. However, when a dye or “sensitizer”, S , is attached to the semiconductor surface, a larger spectral distribution of light can be harvested. If the excited state of the sensitizer is a sufficiently potent reductant, it may inject an electron into the TiO_2 conduction band. Excited-state injection yields an oxidized sensitizer that must be regenerated by an electron donor, D , present in an external electrolyte solution. The injected electron returns to a dark counter electrode where it reduces D^+ back to D . Hence, light is converted into electrical power without the net generation of chemical products.

Mesoscopic TiO_2 thin films sensitized to visible light with Ru(II) polypyridyl compounds have produced record efficiencies when utilized in regenerative solar cells with I^-/I_3^- redox mediators in organic solvents. Shown in Table 1 are confirmed efficiencies and characteristics of the champion dye-sensitized solar cell and submodule.¹¹ A 17 cm^2 submodule fabricated by Sony with a global efficiency of 8.5% and Sharp's single cell efficiency of 11.2% are now the highest confirmed efficiencies. They are both characterized by high short-circuit photocurrent densities and good fill factors. The open-circuit photovoltages are modest. With commercially available materials and literature procedures, it is now relatively straightforward to realize an 8% efficiency in a single cell; however, a considerable

TABLE 1. Confirmed Dye-Sensitized Solar Cell and Module Efficiencies Measured under the Global AM 1.5 Spectrum (1000 W/m²) at 25° C^a

efficiency (%)	aperture area (cm ²)	V_{oc} (V) ^b	J_{sc} (mA/cm ²) ^c	FF (%) ^d	description
11.2 ± 0.3	0.219	0.736	21.0	72.2	Sharp, single cell
8.5 ± 0.3	17.13	0.669	18.9	67.1	Sony, submodule of 8 serial cells ⁵²

^aEfficiencies certified by the Japanese National Institute of Advanced Industrial Science and Technology (AIST). ^bOpen-circuit photovoltage. ^cShort-circuit photocurrent density. ^dFill factor.

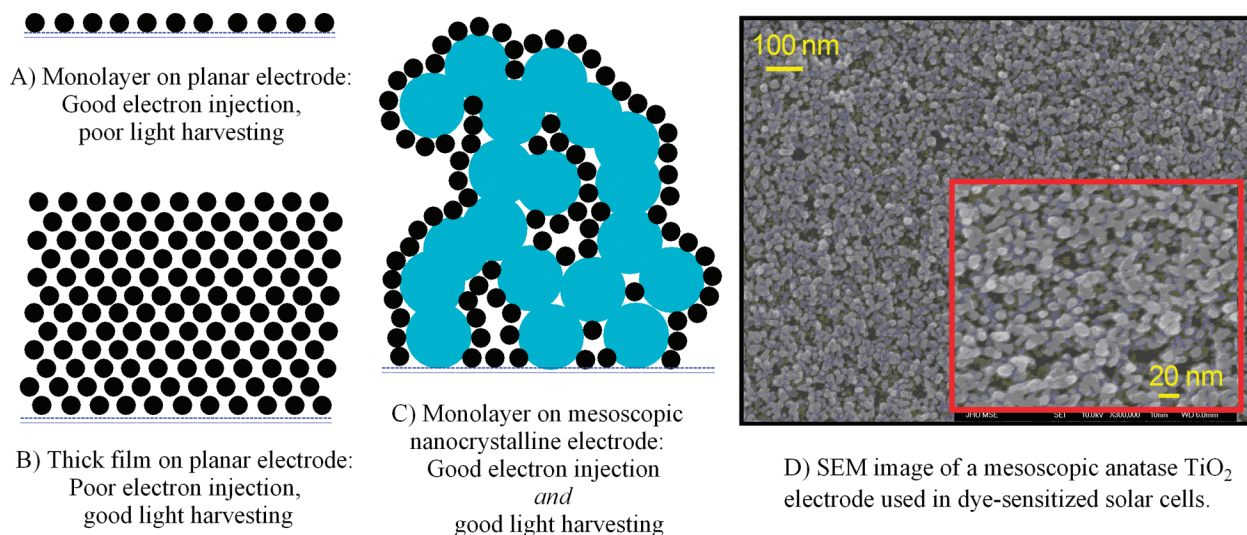


Figure 2. Development of efficient sensitized electrode materials for dye-sensitized solar cells. (A) Monolayer on dye molecules anchored to a planar electrode. Such materials showed good excited-state injection yields but poor light-harvesting characteristics. (B) Thick film of dye molecules coated on a planar electrode resulted in improved light-harvesting efficiency but poor excited-state electron injection. (C) Monolayer of dye molecules anchored to a mesoporous high-surface-area nanocrystalline electrode and (D) SEM image of a mesoscopic anatase TiO₂ electrode developed by Grätzel and colleagues that enabled practical application through good electron-injection efficiency and light harvesting.

amount of art remains in the fabrication of 10+% dye-sensitized solar cells.

Planar to Nanocrystalline Mesoscopic Thin Films. Even though the excited-state injection yields were estimated to be near unity, the early data on dye-sensitized solar cells were reported without pretense to practical application simply because a monolayer of dye molecules present on a planar surface does not harvest a significant fraction of incident photons (Figure 2A). Even with porphyrinic dyes, which have about 100 times the extinction coefficient of Ru(II) polypyridyl compounds, a monolayer on a flat surface is barely visible to the eye and transmits far more light than it absorbs.¹² Although energy transfer through an array of properly aligned multi-pigment molecules could in principle be utilized, such an approach has no experimental precedent and monolayers on flat surfaces remain impractical.¹²

The issue of poor light harvesting by a monolayer of dye molecules was recognized early on. In principle, this difficulty could be circumvented by a thick layer of dye molecules (Figure 2B). However, this too proved to be unsuccessful for practical application.¹³ A major obstacle encountered was that photons were absorbed in regions of the film where the excited state produced could not reach the

semiconductor interface. The penetration depth of light often exceeded the exciton diffusion length such that excited-state decay dominated over electron injection. A more subtle problem was that, even when excited-state injection occurred, the oxidized sensitizer was present in a low dielectric constant film that restricted ion motion and outer-sphere reorganization, behavior that often led to unwanted charge recombination. Therefore, while films of dye molecules largely solved the light-harvesting issue of molecular monolayers, poor injection yields precluded practical application. Although this film approach continues to be explored by some in organic photovoltaics, the challenge of matching film thickness with exciton diffusion length and simultaneously maintaining high light harvesting has proven to be exceedingly difficult.

The key breakthrough for practical application provided by Grätzel was to abandon completely the use of planar electrodes. Instead, he utilized high-surface-area mesoscopic materials to which a larger number of sensitizing dye molecules could be attached.^{14,15} Each dye was in intimate contact with the semiconductor and was solvated by the electrolyte, thereby providing high light harvesting, quantitative electron

injection, and negligible geminate recombination. Early work involved treating planar electrodes with titanium alkoxides that were later hydrolyzed to roughen the surface and generate fractal morphologies.¹⁴ A superior approach utilized now is to synthesize stabilized colloidal solutions that can subsequently be coated onto a conductive surface and briefly heated to promote coupling between the nanoparticles.^{2,15} Those best optimized for dye-sensitized solar cells comprise 8–20 nm anatase TiO₂ nanocrystallites interconnected in a 4–10 μm thick porous network deposited on an optically transparent electrode such as fluorine-doped tin oxide (FTO) (Figure 2D). Often, a second layer of larger anatase particles is utilized to scatter transmitted light and enhance the photocurrent response in the red portion of the visible spectrum. In addition to the obvious advantage of low cost, these nanostructured mesoscopic thin films possess many qualities ideal for solar-energy conversion and for fundamental interfacial charge separation studies:

1. A *high surface area* for sensitizer binding and efficient solar harvesting. For Ru polypyridyl sensitizers, surface coverages of $\sim 10^{-8}$ mol/cm² are typically reported, which is 500–1000 times that expected for

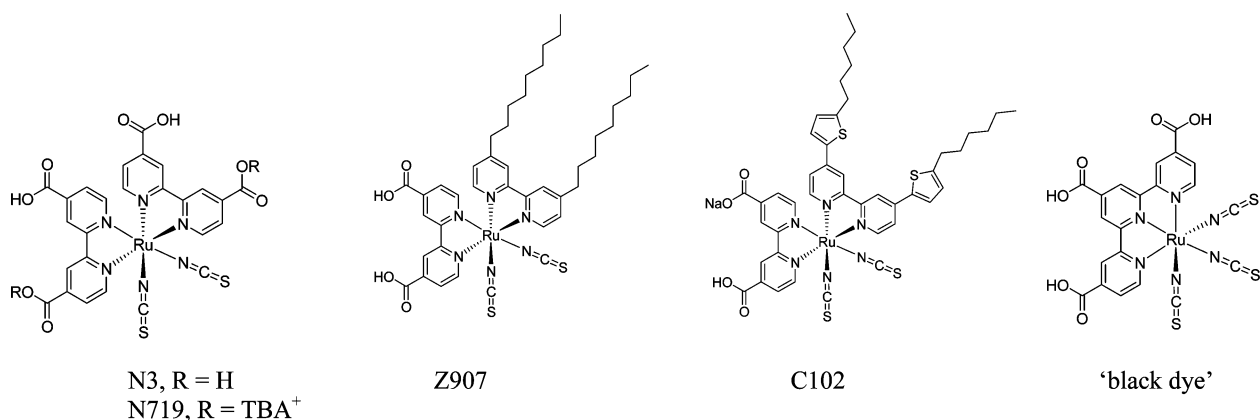


Figure 3. Chemical structures and common abbreviations of some historically successful sensitizers for practical dye-sensitized solar cells.

1. monolayer coverage on a single-crystal TiO₂ surface and corresponds roughly to about 500 sensitizers/nanocrystallite.
2. The ~50% mesoporosity for sensitizer binding and diffusion of mobile redox mediators.
3. The density of unfilled *acceptor states* can be widely tuned in energy for optimization of power conversion efficiencies and for fundamental characterization of excited states and interfacial charge separation.
4. *Injected electrons* can be efficiently collected in an external circuit. Remarkably, transport is not a problem in these materials. There is surprisingly little charge recombination at the short-circuit condition with less than 5% loss at the power point.
5. *High transparency in the visible and infrared regions* allows characterization of photoinduced electron-transfer reactions by transmission spectroscopy techniques for correlation of spectroscopic and photoelectrochemical behavior.

The key breakthrough for practical application provided by Grätzel was to abandon completely the use of planar electrodes.

These attributes are not restricted to application in dye-sensitized solar

cells and have already found applications in other areas of energy research including battery and capacitor technology. They have also been exploited in photoelectrosynthetic cells for water splitting.¹⁶ The mesoscopic material is not limited to TiO₂; in fact, the nanometer length scale is potentially ideal for photoelectrode materials like ferric oxide (Fe₂O₃) in which short hole diffusion lengths have historically limited practical application.¹⁷

Fundamental Molecular Advances. A potential drawback of the mesoscopic thin films for dye-sensitized solar cell application was that the oxidized redox mediator, D⁺, formed by sensitizer regeneration, must navigate through the mesopores to the counter electrode without first being reduced by electrons injected into TiO₂. Another key advance by Grätzel and co-workers was the identification of I⁻/I₃⁻ as a unique redox mediator that accomplishes exactly this. In 1985, graduate student Jean Desilvestro reported an incident photon-to-current efficiency (IPCE) of >40% with blue light.¹⁴ The IPCE values today are ~80% across the visible region and are near 100% when corrections are made for absorption and scattering losses by the FTO substrate. These high IPCE values correspond to confirmed current densities greater than 20 mA/cm² under AM 1.5 solar illumination. Iodide is rapidly oxidized after excited-state injection, and the I₃⁻ product is nearly quantitatively reduced at a platinum counter electrode. This aspect of dye sensitization is not as well understood as most others but is under

active investigation. Hagfeldt and Boschloo recently published an excellent review of this subject.¹⁸

Early work by Memming and others showed that Ru(II) polypyridyl coordination compounds were efficient and robust sensitizers.⁷ Goodenough later reported that carboxylic acid groups present in the 4- and 4'-positions of bipyridine, dcb is 4,4'-(COOH)₂-2,2'-bipyridine, provided strong coupling to the TiO₂ surface.⁸ These coordination compounds were, however, mainly selected for water splitting.

The development of sensitizers with appropriate redox potentials for excited-state injection and iodide oxidation that harvest large fractions of the solar spectrum was yet again advanced tremendously by Grätzel and his co-workers, particularly Dr. Md. K. Nazeeruddin. In 1994, they reported the synthesis and application of the now gold standard *cis*-Ru(dcb)₂(NCS)₂ or N3 sensitizer.¹⁹ At the time, it provided unparalleled efficiency and stability when utilized in dye-sensitized solar cells. The presence of low-lying metal-to-ligand charge transfer (MLCT) excited states resulted in broad absorption bands that harvest light throughout the visible region to ~800 nm. Since 1994, optimization of the protonation state (N719), surface orientation (Z907), extinction coefficient (C101), and spectral harvesting (black dye) have occurred, but the general Ru(NCS)_x core remains unchanged (Figure 3). Indeed, all confirmed efficiencies greater than 10% have utilized such sensitizers with I⁻/I₃⁻ redox mediators.¹¹

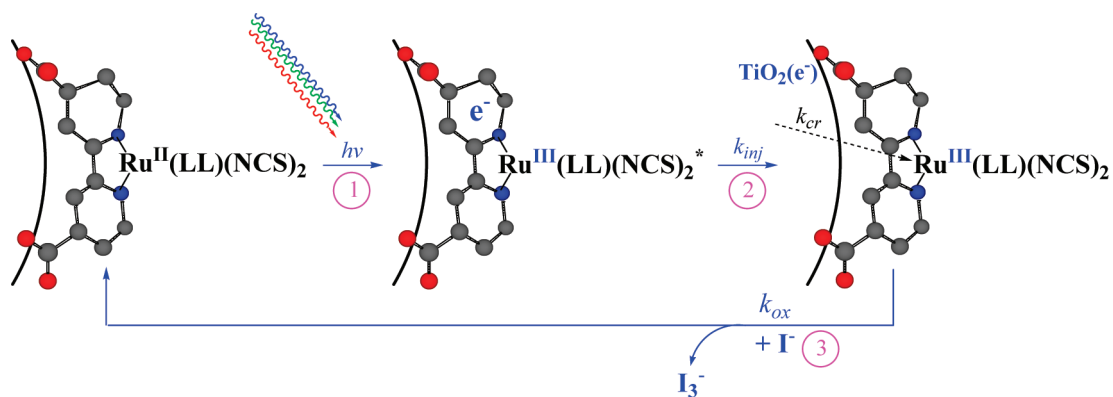


Figure 4. Light absorption, excited-state injection, and iodide oxidation termed the “sensitization cycle”. In the operational dye-sensitized solar cell, under 1 sun, AM 1.5 spectral irradiance, each sensitizer repeats this sensitization cycle roughly twice per second and is limited only by the solar flux. Also shown is unwanted charge recombination of the injected electron with the oxidized sensitizer.

Future Directions toward More Widespread Application. A useful method of viewing sensitization of TiO_2 by an N3-type compound is through the “sensitization cycle” shown in Figure 4.²⁰ Each surface-anchored sensitizer rapidly and quantitatively undergoes three consecutive charge-transfer reactions: (1) MLCT excitation, (2) excited-state electron injection into TiO_2 , and (3) reduction *via* iodide oxidation. In principle, immediately after completion of this cycle, the sensitizer is “regenerated” and could repeat the sensitization cycle of light absorption, excited-state injection, and donor oxidation. While irradiated with 1 sun of air mass 1.5 sunlight, each sensitizer repeats this cycle on average about twice per second. At the condition of maximum power generation, approximately 10 injected electrons have been estimated to reside in each TiO_2 nanocrystallite. Not shown, but necessary for energy conversion, is transport of the injected electron^{21–23} through the mesoporous thin film to the external circuit with eventual arrival at the counter electrode where it uses its remaining free energy to reduce triiodide.

The pioneering flash photolysis studies of Grätzel and co-workers first showed that MLCT excited-state injection was orders of magnitude faster than charge recombination $k_{inj}/k_{cr} > 1000$, behavior that is ideal for solar-energy conversion applications.^{14,24} If, for example, the injected electron returned to the oxidized sensitizer as rapidly as it was injected, there would be no time for iodide oxidation and no sustained photocurrent would be mea-

sured. Grätzel’s sensitization studies with short-lived excited states, such as *cis*- $\text{Ru}(\text{dcb})_2(\text{H}_2\text{O})_2^{2+}$, suggested early on that excited-state injection occurred on at least the picosecond time scale.²⁵ There now exists compelling evidence for ultrafast excited-state injection occurring on a femto- to picosecond time scale under many experimental conditions.^{26–30} The origin of the disparity in the forward and reverse electron-transfer rates is also now better understood and reflects differences in the molecular orbitals, driving forces, and mechanisms of the reactions.^{31–33} While these mechanistic studies are of interest in their own right, their relevance to the operational solar cell is doubtful,^{26–33} as the measurements were made in the absence of iodide under very different experimental conditions. *In situ* mechanistic studies are ongoing, however; as the dye-sensitized solar cell continues to evolve, the goal of working on the “true” solar cell becomes somewhat of a moving target. To build on the success of the dye-sensitized solar cell and develop low-cost architectures for solar-energy conversion and storage is just one of many motivations for understanding the interfacial sensitization cycle in precise molecular detail.

An examination of Table 1 shows that the kinetics for electron transfer in dye-sensitized solar cells are already well optimized: absorbed photons are nearly quantitatively converted to electrical current. Therefore, the only obvious means of photocurrent improvement is to harvest a larger fraction of

the solar spectrum. In this regard, the so-called “black dye”³⁴ and the novel Os(II) polypyridyl compounds developed by Bignozzi and co-workers³⁵ are of particular note as they have sensitized TiO_2 into the near-infrared region.

The kinetics are well optimized in dye-sensitized solar cells, but Table 1 reveals that the thermodynamics are not. Less than half of the free energy stored in the MLCT excited state is captured as open-circuit photovoltage, V_{oc} . The V_{oc} represents the maximum Gibbs free energy that a regenerative solar cell can produce under steady-state illumination. With the known ultrafast injection from nonrelaxed excited states, it may one day be possible to exceed the well-known Shockley–Queisser limit with dye-sensitized solar cells and realize V_{oc} values that exceed that stored in the thermally equilibrated excited state of the sensitizer.^{36,37} At a minimum, values of $V_{oc} = 1.5$ V should be obtainable and would double the efficiency of the solar cells provided that the photocurrent and fill factor remained the same. Much of the potential energy loss has been attributed to the I^-/I_3^- redox mediators,¹⁸ and considerable effort has been made to identify alternative mediators.^{38–40} Inorganic and polymeric hole conductors appear to have significant potential that may one day eliminate the need for a liquid junction.^{41,42}

The use of less expensive components and fewer processing steps may also enhance prospects for more widespread practical application. Alternative metal oxide materials and sensitizers

represent active areas of research investigations. Recently, there have been some breakthroughs using sensitizers based on organic or first-row transition metal compounds.^{43–47} The efficiency from quantum-dot sensitizers^{48,49} has also improved, and their spectral response can be tuned with size.⁵⁰ Quantum dots capable of multiple exciton generation could one day enhance power conversion efficiency above the ~30% Shockley–Queisser limit while at the same time lowering cost.⁵¹

Quantum dots capable of multiple exciton generation could one day enhance power conversion efficiency above the ~30% Shockley–Queisser limit while at the same time lowering cost.

CONCLUSION

The 2010 Millennium Technology Grand Prize was awarded to Professor Michael Grätzel for his ground-breaking research that has led to the practical application of dye-sensitized solar cells. There is every reason to believe that the cost and efficiency of dye-sensitized solar cells will continue to improve.⁵² Grätzel has dedicated much of his time and effort to this cause and has been at the forefront of every significant advance in the field. He has taken what was once an object of academic curiosity and turned it into a worldwide effort with industrial production now underway. Furthermore, he has provided a path forward with molecules interfaced to nanomaterials that chemists can exploit to provide sustainable solar energy for future generations. As the Millennium International Selection Committee correctly deduced, our community owes him a great deal for this.

Acknowledgment. A grant from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (DE-FG02–96ER14662) is gratefully acknowledged.

REFERENCES AND NOTES

1. <http://www.millenniumprize.fi/en/2010-prize/>.
2. O'Regan, B.; Grätzel, M. A. Low-Cost, High Efficiency Solar Cell Based on the Dye-Sensitized Colloidal TiO₂ Films. *Nature* **1991**, *353*, 737739.
3. Dyesol, <http://www.dyesol.com>.
4. Solaronix, <http://www.solaronix.com>.
5. G24I, <http://www.G24I.com>.
6. Spittler, M. T.; Calvin, M. Electron Transfer at Sensitized Titanium Dioxide Electrodes. *J. Chem. Phys.* **1977**, *66*, 4294–4305.
7. Gleria, M.; Memming, R. Photoelectrochemical Studies of Tris[2,2'-bipyridyl]ruthenium(II) at Semiconductor Electrodes. *Z. Phys. Chem.* **1975**, *98*, 303–316.
8. Anderson, S.; Constable, E. C.; Dare-Edwards, M. P.; Goodenough, J. B.; Hamnett, A.; Seddon, K. R.; Wright, R. D. Chemical Modification of a Titanium(IV) Oxide Electrode To Give Stable Dye Sensitization without a Supersensitizer. *Nature* **1979**, *280*, 571–573.
9. Gerischer, H. Electrochemical Techniques for the Study of Photosensitization. *Photochem. Photobiol.* **1972**, *16*, 243–260.
10. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–40.
11. Martin, A. G.; Keith, E.; Yoshihiro, H.; Wilhelm, W. Solar Cell Efficiency Tables (Version 36). *Prog. Photovoltaics Res. Appl.* **2010**, *18*, 346–352.
12. Hasselman, G. M.; Watson, D. F.; Stromberg, J.; Bocian, D. F.; Holten, D.; Lindsey, J. S.; Meyer, G. J. Theoretical Solar-to-Electrical Energy-Conversion Efficiencies of Perylene-Porphyrin Light-Harvesting Arrays. *J. Phys. Chem. B* **2006**, *110*, 25430–25440.
13. Jaeger, C. D.; Fan, F.-R. F.; Bard, A. J. Semiconductor Electrodes. 26. Spectral Sensitization of Semiconductors with Phthalocyanine. *J. Am. Chem. Soc.* **1980**, *102*, 2592–2598.
14. Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J.; Augustynski, J. Highly Efficient Sensitization of Titanium Dioxide. *J. Am. Chem. Soc.* **1985**, *107*, 2988–2990.
15. O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. Vectorial Electron Injection into Transparent Semiconductor Membranes and Electric Field Effects on the Dynamics of Light-Induced Charge Separation. *J. Phys. Chem.* **1990**, *94*, 8720–8726.
16. Youngblood, W. J.; Lee, S.-H. A.; Kobayashi, Y.; Hernandez-Pagan, E. A.; Hoertz, P. G.; Moore, T. A.; Moore, A. L.; Gust, D.; Mallouk, T. E. Photoassisted Overall Water Splitting in a Visible Light-Absorbing Dye-Sensitized Photoelectrochemical Cell. *J. Am. Chem. Soc.* **2009**, *131*, 926–927.
17. Sivula, K.; Zboril, R.; Le Formal, F.; Robert, R.; Weidenkaff, A.; Tucek, J.; Frydrych, J.; Grätzel, M. Photoelectrochemical Water Splitting with Mesoporous Hematite Prepared by a Solution-Based Colloidal Approach. *J. Am. Chem. Soc.* **2010**, *132*, 7436–7444.
18. Boschloo, G.; Hagfeldt, A. Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells. *Acc. Chem. Res.* **2009**, *42*, 1819–1826.
19. Nazeeruddin, M. K.; Kay, A.; Rodio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. Conversion of Light to Electricity by *cis*-X₂Bis(2,2'-bipyridyl)-4,4'-dicarboxylate)ruthenium(II) Charge-Transfer Sensitizers (X = Cl⁻, Br⁻, I⁻, CN⁻, and SCN⁻) on Nanocrystalline Titanium Dioxide Electrodes. *J. Am. Chem. Soc.* **1993**, *115*, 6382–6390.
20. Ardo, S.; Staniszewski, A.; Sun, Y.; Castellano, F. N.; Meyer, G. J. Stark-like Effects after Excited State Interfacial Electron Transfer at Sensitized TiO₂ Nanocrystallites. *J. Am. Chem. Soc.* **2010**, *132*, 6696–6709.
21. Peter, L. M. Characterization and Modeling of Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2007**, *111*, 6601–6612.
22. Frank, A. J.; Kopidakis, N.; van de Lagemaat, J. Electrons in Nanostructured TiO₂ Solar Cells: Transport, Recombination and Photovoltaic Properties. *Coord. Chem. Rev.* **2004**, *248*, 1165–1179.
23. Gonzalez-Vazquez, J. P.; Anta, J. A.; Bisquert, J. Determination of the Electron Diffusion Length in Dye-Sensitized Solar Cells by Random Walk Simulation: Compensation Effects and Voltage Dependence. *J. Phys. Chem. C* **2010**, *114*, 8552–8558.
24. Vlachopoulos, N.; Liska, P.; Augustynski, J.; Grätzel, M. Very Efficient Visible Light Energy Harvesting and Conversion by Spectral Sensitization of High Surface Area Polycrystalline Titanium Dioxide Films. *J. Am. Chem. Soc.* **1988**, *110*, 1216–1220.
25. Liska, P.; Vlachopoulos, N.; Nazeeruddin, M. K.; Comte, P.; Grätzel, M. *cis*-Diaquabis(2,2'-bipyridyl)-4,4'-dicarboxylate)ruthenium(II) Sensitizes Wide Band Gap Oxide Semiconductors Very Efficiently over a Broad Spectral Range in the Visible. *J. Am. Chem. Soc.* **1988**, *110*, 3686–3687.
26. Tachibana, Y.; Moser, J. E.; Grätzel, M.; Klug, D. R.; Durrant, J. Subpicosecond Interfacial Charge Separation in Dye-Sensitized Nanocrystalline Titanium Dioxide Films. *J. Phys. Chem.* **1996**, *100*, 20056–20062.
27. Heimer, T. A.; Heilweil, E. J. Direct Time-Resolved Infrared Measurement of Electron Injection in Dye-Sensitized Titanium Dioxide Films. *J. Phys. Chem. B* **1997**, *101*, 10990–10993.
28. Hannappel, T.; Burfeindt, B.; Storck, W.; Willig, F. Anchored Ru-Dye Molecules into Empty Electronic States in a Colloidal Anatase TiO₂ Film. *J. Phys. Chem. B* **1997**, *101*, 6799–6802.
29. Asbury, J. B.; Hao, E.; Wang, Y.; Lian, T.

- Bridge Length-Dependent Ultrafast Electron Transfer from Re Polypyridyl Complexes to Nanocrystalline TiO₂ Thin Films Studied by Femtosecond Infrared Spectroscopy. *J. Phys. Chem. B* **2000**, *104*, 11957–11964.
30. Benko, G.; Kallioinen, J.; Korppi-Tommola, J. E. I.; Yartsev, A. P.; Sundstrom, V. Measurement of Ultrafast Photoinduced Electron Transfer from Chemically Photoinduced Ultrafast Dye-to-Semiconductor Electron Injection from Nonthermalized and Thermalized Donor States. *J. Am. Chem. Soc.* **2002**, *124*, 489–493.
 31. Kuciauskas, D.; Freund, M. S.; Gray, H. B.; Winkler, J. R.; Lewis, N. S. Electron Transfer Dynamics in Nanocrystalline Titanium Dioxide Solar Cells Sensitized with Ruthenium or Osmium Polypyridyl Complexes. *J. Phys. Chem. B* **2001**, *105*, 392–403.
 32. Nelson, J. Continuous-Time Random-Walk Model of Electron Transport in Nanocrystalline TiO₂ Electrodes. *Phys. Rev. B* **1999**, *59*, 15374–15380.
 33. Hasslemann, G. M.; Meyer, G. J. Diffusion Limited Interfacial Electron Transfer with Large Apparent Driving Forces. *J. Phys. Chem. B* **1999**, *103*, 7671–7675.
 34. Nazeeruddin, M. K.; Pechy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphrey-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; *et al.* Engineering of Efficient Panchromatic Sensitizers for Nanocrystalline TiO₂-Based Solar Cells. *J. Am. Chem. Soc.* **2001**, *123*, 1613–1624.
 35. Altobello, S.; Argazzi, R.; Caramori, S.; Contado, C.; Da Fre, S.; Rubino, P.; Chone, C.; Larramona, G.; Bignozzi, C. A. Sensitization of Nanocrystalline TiO₂ with Black Absorbers Based on Os and Ru Polypyridine Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 15342–15343.
 36. Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p–n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32*, 510–519.
 37. Hoertz, P. G.; Staniszewski, A.; Marton, A.; Higgins, G. T.; Incarvito, C. D.; Rheingold, A. L.; Meyer, G. J. Towards Exceeding the Shockley–Queisser Limit: Photo-Induced Interfacial Charge Transfer Processes That Store Energy in Excess of the Equilibrated Excited State. *J. Am. Chem. Soc.* **2006**, *128*, 8234–8245.
 38. Oskam, G.; Bergeron, B. V.; Meyer, G. J.; Searson, P. C. Pseudo-Halogens for Dye-Sensitized TiO₂ Photoelectrochemical Cells. *J. Phys. Chem. B* **2001**, *105*, 6867–6873.
 39. Cazzanti, S.; Caramori, S.; Argazzi, R.; Elliott, C. M.; Bignozzi, C. A. Efficient Non-corrosive Electron-Transfer Mediator Mixtures for Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2006**, *128*, 9996–9997.
 40. Li, T. C.; Spokoiny, A. M.; She, C.; Farha, O. K.; Mirkin, C. A.; Marks, T. J.; Hupp, J. T. Ni(III)/(IV) Bis(dicarbollide) as a Fast, Noncorrosive Redox Shuttle for Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2010**, *132*, 4580–4582.
 41. Moon, S.-J.; Itzhaik, Y.; Yum, J.-H.; Zakeeruddin, S. M.; Hodes, G.; Grätzel, M. Sb₂S₃-Based Mesoscopic Solar Cell Using an Organic Hole Conductor. *J. Phys. Chem. Lett.* **2010**, *1*, 1524–1527.
 42. Snaith, H. J.; Grätzel, M. The Role of a “Schottky Barrier” at an Electron-Collection Electrode in Solid-State Dye-Sensitized Solar Cells. *Adv. Mater.* **2006**, *8*, 1910–1914.
 43. Wenger, S.; Bouit, P.-A.; Chen, Q.; Teuscher, J.; Di Censo, D.; Humphry-Baker, R.; Moser, J.-E.; Delgado, J. L.; Martin, N.; Zakeeruddin, S. M.; *et al.* Efficient Electron Transfer and Sensitizer Regeneration in Stable π -Extended Tetrathiafulvalene-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2010**, *132*, 5164–5169.
 44. Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Yoshihara, T.; Murai, M.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; *et al.* Novel Conjugated Organic Dyes for Efficient Dye-Sensitized Solar Cells. *Adv. Funct. Mater.* **2005**, *15*, 246–252.
 45. Hagberg, D. P.; Yum, J.-H.; Lee, H.; De Angelis, F.; Marinado, T.; Karlsson, K. M.; Humphry-Baker, R.; Sun, L.; Hagfeldt, A.; Grätzel, M. Molecular Engineering of Organic Sensitizers for Dye-Sensitized Solar Cell Applications. *J. Am. Chem. Soc.* **2008**, *130*, 6259–6266.
 46. Bessho, T.; Constable, E. C.; Grätzel, M.; Redondo, A. H.; Housecroft, C. E.; Kylberg, W.; Nazeeruddin, M. K.; Neuburger, M.; Schaffner, S. An Element of Surprise—Efficient Copper-Functionalized Dye-Sensitized Solar Cells. *Chem. Commun.* **2008**, 3717.
 47. Xai, H.-L.; Ardo, S.; Narducci Sarjeant, A. A.; Huang, S.; Meyer, G. J. Photodriven Spin Change of Fe(II) Benzimidazole Compounds Anchored to Nanocrystalline TiO₂ Thin Films. *Langmuir* **2009**, *25*, 13641–13652.
 48. Barea, E. M.; Shalom, M.; Gimenez, S.; Hod, I.; Mora-Sero, I.; Zaban, A.; Bisquert, J. Design of Injection and Recombination in Quantum Dot Sensitized Solar Cells. *J. Am. Chem. Soc.* **2010**, *132*, 6834–6839.
 49. Pattantyus-Abraham, A. G.; Kramer, I. J.; Barkhouse, A. R.; Wang, X.; Konstantatos, G.; Debnath, R.; Levina, L.; Raabe, I.; Nazeeruddin, M. K.; Grätzel, M. Depleted-Heterojunction Colloidal Quantum Dot Solar Cells. *ACS Nano* **2010**, *4*, 3374–3380.
 50. Kongkanand, A.; Tvrdy, K.; Takechi, K.; Kuno, M.; Kamat, P. V. Quantum Dot Solar Cells. Tuning Photoresponse through Size and Shape Control of CdSe–TiO₂ Architecture. *J. Am. Chem. Soc.* **2008**, *130*, 4007–4015.
 51. Nozik, A. J. Exciton Multiplication and Relaxation Dynamics in Quantum Dots: Applications to Ultrahigh-Efficiency Solar Photon Conversion. *Inorg. Chem.* **2005**, *44*, 6893–6899.
 52. While this manuscript was in revision, a new AIST-confirmed efficiency was indeed reported by Dr. Kazuhiro Noda at the European Science Foundation (ESF) Conference on Nanotechnology for Sustainable Energy in Obergurgl Austria (July 2010) for a sub-module of 16 cm² aperture area, using a nonvolatile gel type electrolyte.