

Charge Transport in ZnO Nanorod Array Dye-Sensitized Solar Cells

by Alex Martinson

Among the most efficient classes of excitonic photovoltaics (PVs) today are dye-sensitized solar cell (DSSCs) pioneered by Grätzel.^{1,2} DSSCs harness high-surface-area sintered-nanoparticle networks loaded with organic dyes to achieve good light harvesting efficiency and excellent exciton dissociation. While DSSCs generally have excellent absorbed photon to current efficiencies, the long and tortuous path through sintered particle networks in state-of-the-art DSSCs results in high electron concentrations under standard solar illumination, increasing the rate of charge recombination.^{3,4} Relatively slow diffusion of electrons through the network requires that efficient cells use a slow redox couple (I/I^3) to avoid recombination with electrons in the semiconductor. Thus, a significant overpotential of the redox couple is required to accelerate the regeneration of the ground state of the dye, ultimately resulting in low photovoltages.

If one can avoid simultaneously accelerating back electron transfer from the photoelectrode to the dye or regenerator, speeding up electron transport provides opportunities for increasing performance of DSSCs in several ways. The useful thickness of a photoanode is determined by its effective electron diffusion length,

$$L_n = (D_n \tau_n)^{1/2} \quad (1)$$

where D_n is the effective diffusion coefficient for the electron within the photoelectrode and τ_n is the survival time of the electron with respect to

recombination with the oxidized dye or regenerator. In the most efficient liquid electrolyte DSSCs, L_n is already greater (at most wavelengths) than the thickness required to collect most of the incident photons. Here the value of faster transport (larger D_n) would be to make the cells tolerant to faster recombination dynamics (shorter τ_n (Eq. 1); the electron collection efficiency is a measure of the competition between transport and recombination). In principle, faster redox shuttles could then be employed. As dye regeneration by inherently faster shuttles need not be accelerated by large overpotentials, this change could directly address the problem of low photovoltage that has plagued DSSCs since their inception.

Intensity modulated photocurrent and photovoltage spectroscopy probes the rates of recombination and charge transfer in operating DSSCs.⁵⁻⁸ Figure 1 shows real and imaginary components of the photomodulated current for a nanoparticle electrode as a function of modulation frequency, $f = \omega/2\pi$. The average transport time may be estimated from the minimum angular frequency in the imaginary plot: $\tau_d = \omega_{\min}^{-1}$.

The second trace shows the results for a nanorod array electrode. The striking feature is a shift of two orders of magnitude to ward higher characteristic lag frequency, indicating the transport dynamics are two orders of magnitude faster for electrons within the nanorod array electrode.

Similar analysis of the photomodulated voltage under open

circuit conditions yields average charge lifetimes, τ_n . The charge dynamics as function of light intensity are summarized in Fig. 2. The measured ratio of recombination time to transport time for the nanorod electrode varies from 280 to 1850. If the results are extrapolated to the number of photons incident in the absorbing range of the dye under AM 1.5 illumination, the ratio becomes ~64 – or about 18 times that seen with the nanoparticle electrode geometry. Thus, nanorod array cells should be capable of sustaining efficient charge collection over much greater thicknesses than nanoparticle-based cells.

In summary, photomodulation experiments with dye-sensitized ZnO solar cells show that electron transport is tens to hundreds of times faster in nanorod array electrodes than in nanocrystalline particulate electrodes. Recombination, on the other hand, is slightly slower. Taken together, these findings support the contention that nanorod geometries are likely to provide very substantial dynamical advantages in operating dye-sensitized solar cells. ■

Acknowledgments

The material in this report was originally published in the paper, "Dynamics of Charge Transport and Recombination in ZnO Nanorod Array Dye-sensitized Solar Cells," by Alex B. F. Martinson, *et al.*, in *Phys. Chem. Chem. Phys.*, **8**, 4655 (2006).

(continued on next page)

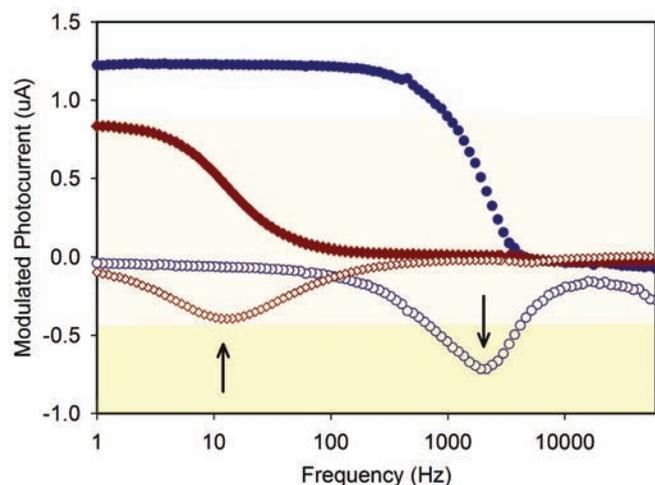


Fig. 1. Real (filled) and imaginary (open) components of the photomodulated current for a 3.8 μm thick nanoparticle electrode (red) and a 4.5 μm thick nanorod electrode (blue, corrected for RC attenuation) as a function of modulation frequency.

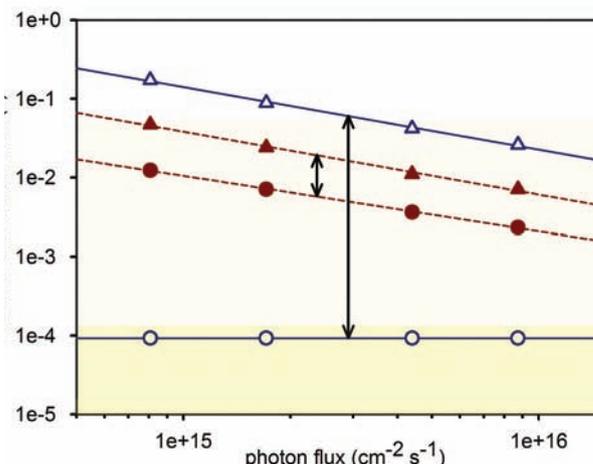


Fig. 2. Electron lifetime (triangles) and average transit time (circles) over a range of illumination intensities. Arrows highlight the difference between τ_n and τ_d for nanoparticle (filled red symbol) and nanorod (open blue symbol) devices.

The author thanks The Electrochemical Society for the Colin G. Fink Summer Fellowship and Joseph Hupp for his guidance and encouragement.

References

1. 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 and M. Grätzel, *J. Am. Chem. Soc.*, **123**, 1613 (2001).
2. M. K. Nazeeruddin, F. DeAngelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru and M. Grätzel, *J. Am. Chem. Soc.*, **127**, 16835 (2005).
3. A. C. Fisher, L. M. Peter, E. A. Ponomarev, A. B. Walker and K. G. U. Wijayantha, *J. Phys. Chem. B*, **104**, 949 (2000).
4. P. J. Cameron and L. M. Peter, *J. Phys. Chem. B*, **109**, 7392 (2005).
5. L. M. Peter and K. G. U. Wijayantha, *Electrochim. Acta*, **45**, 4543 (2000).
6. G. Schlichthorl, S. Y. Huang, J. Sprague and A. J. Frank, *J. Phys. Chem. B*, **101**, 8141 (1997).
7. F. Cao, G. Oskam, G. J. Meyer and P. C. Searson, *J. Phys. Chem. B*, **100**, 17021 (1996).
8. L. Dloczik, O. Ieperuma, L. Laueremann, L. M. Peter, E. A. Ponomarev, G. Redmond, N. J. Shaw and I. Uhlendorf, *J. Phys. Chem. B*, **101**, 10281 (1997).

About the Author

ALEX B. F. MARTINSON is a PhD candidate in the Department of Chemistry at Northwestern University under the direction of Joseph T. Hupp. He may be reached at a-martinson2@northwestern.edu.



Save the Date

211th ECS Meeting
May 6-11, 2007

Registration

Deadline for advance meeting registration is April 6, 2007.

Hotel

The Hilton Chicago is the meeting headquarters hotel. Reservations are due April 6, 2007.

Short Courses

Molecular Electronics; Fullerenes and Carbon Nanotubes: From Basics to Materials Science and Biological Activities; and Advanced Impedance Spectroscopy

ECS Transactions

Full papers presented at ECS meetings will be published in the new online publication, *ECS Transactions*. Visit the ECS website for more details.

Travel Grants

Travel grants are available for student attendees.

www.electrochem.org