Solar Cells

DOI: 10.1002/anie.200900423

A p-Type NiO-Based Dye-Sensitized Solar Cell with an Open-Circuit Voltage of 0.35 V**

Elizabeth A. Gibson, Amanda L. Smeigh, Loïc Le Pleux, Jérôme Fortage, Gerrit Boschloo, Errol Blart, Yann Pellegrin, Fabrice Odobel, Anders Hagfeldt,* and Leif Hammarström**

In 2000, He et al. reported that the combination of a NiO-based photoactive cathode with a TiO_2-based photoanode produced a tandem device with an open-circuit voltage (V_{OC}) of 0.73 V,[1] which is the sum of the open-circuit potentials of the separate devices, where the TiO_2-based electrode contributed 0.65 V and the NiO-based electrode 0.08 V. Tandem dye-sensitized solar cells (TDSCs), such as He's, have suffered from the lack of research directed at the optimization of the photocathode, despite the potential they hold in developing higher voltage devices. Only recently have researchers begun to address issues associated with NiO-based DSCs, such as low short-circuit photocurrents (J_{SC}) and poor fill factors (FF).[2–6] We present herein a three-fold increase in V_{OC} (0.35 V), while maintaining a J_{SC} of 1.7 mA cm^{-2}, for a p-type NiO dye-sensitized solar cell (p-DSC) employing a carefully designed "dyad" sensitizer and a cobalt-based redox mediator. We have almost quadrupled the p-DSC conversion efficiency from the previous record, 0.055 %,[4] to 0.20 %. Interestingly, the improvements within the p-DSCs translate to improvements in TDSC performance, namely achieving a V_{OC} of 0.91 V, a FF of 0.62, and an efficiency of 0.55 %. The results reported herein present the most significant increase in photovoltaic efficiency of p-DSCs to date, emphasizing the importance of molecular engineering in sensitizer and redox-mediator development to achieve substantial gains in DSC performance.

A schematic representation of a TDSC is shown in Figure 1. Absorption of light by the sensitizers, in separate photo-processes, causes an electron to be injected into the conduction band (CB) of the TiO_2 at the anode and a hole to be injected into the NiO at the cathode. These charges diffuse through the respective semiconductors to the SnO_2:F charge collector. To complete the circuit, the oxidized and reduced forms of the redox mediator regenerate the dye at the cathode and anode, respectively.

Often DSCs have a counter electrode of platinized conducting glass. In p-type devices, the V_{OC} is the potential energy difference between the quasi-Fermi level close to the valence band (VB) and the Nernstian potential of the redox mediator.[7] Efforts to improve the V_{OC} of TiO_2-based n-type DSCs (n-DSCs) have involved modifications to the electrolyte[8,9] and doping of the semiconductor itself.[10,11] The various redox couples suffered from slow regeneration kinetics[12,13] or fast recombination with the semiconductor,[14] as a result the I^-/I_3^- mediator, though problematic, has prevailed as the electrolyte of choice for n-DSCs. Previously, the p-side in a TDSC contributed little to the overall tandem performance, owing to the low V_{OC}, in the presence of I^-/I_3^-, and the low photocurrent. We report herein our rational-design effort directed at improving p-DSC performance.

We present three p-DSCs composed of a cobalt mediator and three different sensitizing dyes: coumarin 343 (C343), a typical sensitizer for p-type DSCs[2–4,6,15,16], and PI and PINDI, two peryleneimide-based dyes.[5] Optimized sensitization conditions for PI and PINDI, greatly improved the adsorption of the dyes onto the NiO photocathode, compared to Ref. [5], improving light-harvesting ability. The nanostructured NiO films were up to 5 μm thick, and prepared according to Nakasa et al.[17] In a move away from the typical I^-/I_3^- electrolyte, $Co^{II/III}$ tris(4,4′-di-*tert*-butyl-2,2′-dipyridyl) perchlorate was employed as the redox mediator. The motivation for this change is two fold; first, the cobalt-based electrolyte is optically dilute, making more photons available for the sensitizer; second, the Nernstian potential of the $Co^{II/III}$ couple is more negative than that of I^-/I_3^-, which is likely to increase the V_{OC} of the p-DSC (see Supporting Information).

Incident photon-to-current efficiency (IPCE) spectra of the p-DSCs are shown in Figure 2. The PINDI p-DSC exhibits superior performance to that of the C343- and PI-sensitized devices with a peak IPCE value of 31 %, the highest reported

---

[*] L. Le Pleux, Dr. J. Fortage, Dr. E. Blart, Y. Pellegrin, Dr. F. Odobel
CEISAM, Chimie et Interdisciplinarité, Synthèse, Analyse, Modélisation, Faculté des Sciences et des Techniques
Université de Nantes, 2, rue de la Houssinière
BP 92208, 44322 NANTES Cedex 3 (France)
E-mail: Fabrice.Odobel@univ-nantes.fr

Dr. E. A. Gibson,[+] Dr. G. Boschloo, Prof. A. Hagfeldt
Department of Physical and Analytical Chemistry
Uppsala University
Box 259, SE-751 05 Uppsala (Sweden)
E-mail: Anders.Hagfeldt@fki.uu.se

Dr. A. L. Smeigh,[+] Prof. L. Hammarström
Department of Photochemistry and Molecular Science
Uppsala University
Box 523, SE-751 20 Uppsala (Sweden)
Fax: (+46) 18-471-6844
E-mail: Leif@fotomol.uu.se

Prof. A. Hagfeldt
Also at Centre of Molecular Devices, Department of Chemistry, Royal Institute of Technology
Teknikringen 30, SE-100 44 Stockholm (Sweden)

[+] These authors contributed equally to the work.

[**] This project was supported by The Knut and Alice Wallenberg Foundation, the Swedish Energy Agency, ANR (project "PhotoCumElec"), and the "Région Pays de la Loire" program PERLE.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900423.

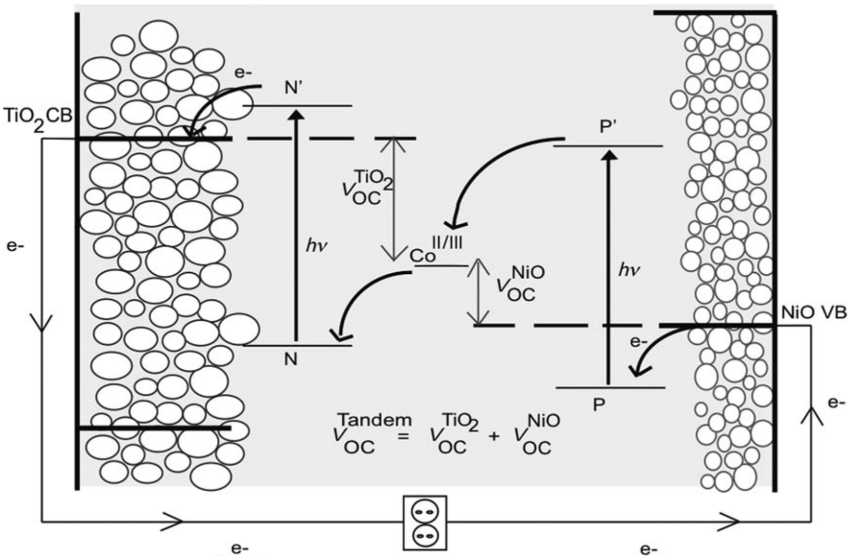

Figure 1. Schematic representation of a tandem dye-sensitized solar cell (TDSC). TiO_2 CB and NiO VB represent the Fermi level in the conduction band of TiO_2 and the valence band of the NiO, respectively; N and N′, P and P′ represent the energetics of the sensitizers; $Co^{II/III}$ represents the redox potential of the electrolyte.

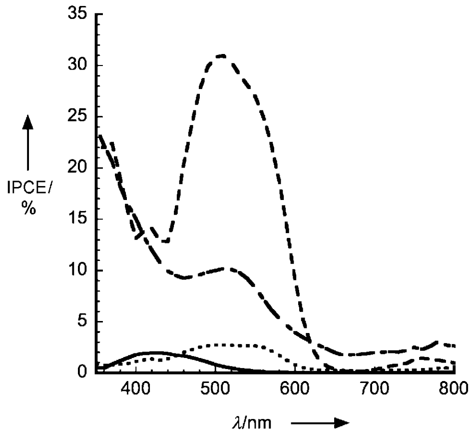

Figure 2. Incident photon-to-current conversion efficiency (IPCE) spectra of C343 (——), PI (•••••), and PINDI (-----) on NiO; N719 on TiO_2 (–•–•) in the presence of cobalt-based electrolyte. Film thickness of NiO and TiO_2 were 5 μm and 1.5 μm, respectively.

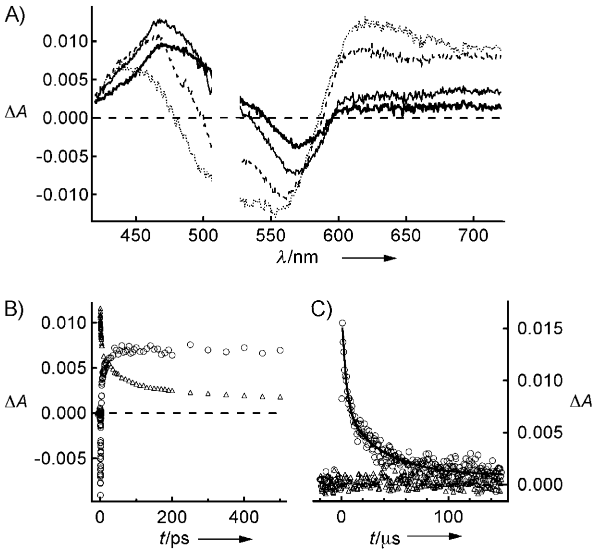

Figure 3. Time-resolved transient absorption (ΔA) measurements. A) PINDI/NiO with 0.1 M $LiClO_4$ at various time delays after excitation are shown: 0 ps (dots), 1 ps (dashes), 100 ps (thin solid line), and 1 ns (thick solid line). Kinetic traces at PI/NiO (600 nm, △) and PINDI/NiO (500 nm, ○) are shown from $t=-5$ ps to 0.5 ns (B)and $t=-2$ μs to 150 μs (C).

IPCE value for a p-DSC. The poor performance of C343- and PI-sensitized devices with the $Co^{II/III}$ redox couple is most likely due to their rapid recombination and the absence of a pre-associated complex that has been implicated in a recent study of C343-sensitized NiO in the presence of an I^-/I_3^- electrolyte.[6] PINDI, a "dyad", consists of a peryleneimide unit, similar to PI, covalently linked to a napthalenediimide (NDI) acceptor. This dyad structure has been shown to promote charge separation, there by reducing the rate of recombination and improving the efficiency of the device.[5]

Since charge-separation and recombination kinetics have been correlated to the performance of DSCs, time-resolved transient absorption experiments were carried out on PI- and PINDI-sensitized NiO films (Figure 3). The high adsorption of sensitizer PINDI onto NiO has enabled elucidation of the charge-injection mechanism for PINDI-sensitized NiO, to date it was only possible to speculate at this mechanism.[5] A broad positive peak around 605 nm indicates the formation of the perylene radical anion (PI^-) occurs within the first 0.5 ps (see Figure 3 A and Supporting Information). The PI^- signal at approximately 605 nm then decays, on an approximately 1 ps timescale, concomitantly with the rise of a band at 475 nm. This synchronized behavior is indicative of a charge-separation process, which results in the formation of the naphthalenediimide radical anion (NDI^-; growth of a feature at ca. 475 nm[5]), while the PI ground-state recovers (decay/flattening of ca. 605 nm region).

In the absence of a redox mediator, the reduced sensitizers recombine with the hole in the NiO on very different timescales. As shown in Figure 3 B,C, films sensitized with PI recombine rapidly, $\tau_1 = 100$ ps (60%), $\tau_2 = 500$ ps (30%), with a small fraction remaining at times greater than 5 ns (10%), which is in agreement with results in Ref. [5]. Figure 3 C shows, for the first time, the recombination associated with PINDI; $\tau_1 \approx 5$ μs (60%) and $\tau_2 \approx 50$ μs (40%). The slower recombination of PINDI, approximately 10^5 times slower than PI, is presumably the important factor in the improved performance of the PINDI p-DSCs with the cobalt-based electrolyte over both the PI and C343 p-DSCs.

Current-voltage (J–V) curves for the best performing p-, n-, and tandem DSCs are presented in Figure 4. The PINDI-sensitized p-DSC exhibits a V_{OC} of 0.35 V. This is a three-fold increase over the highest reported value for a NiO-based DSC (C343/NiO:I^-/I_3^-, 0.12 V).[4] We attribute this increase to the more negative redox potential of the cobalt redox couple compared with I^-/I_3^-.[13] Additionally, we show an increase in J_{SC} of approximately 0.4 mA cm^{-2} in comparison to the best p-DSC.[4]

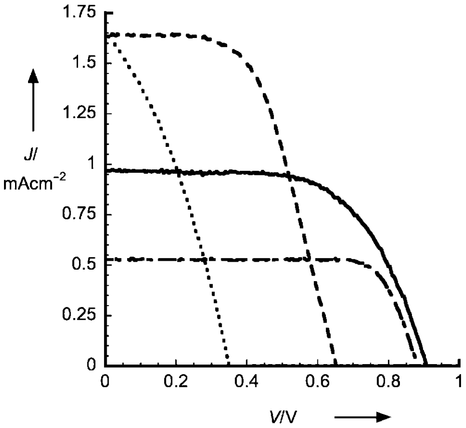

Figure 4. Current–voltage (J–V) curves for PINDI/NiO p-DSC (••••); N719/TiO_2 n-DSC (–––); TDSC, with N719/TiO_2 as the photoanode and PINDI/NiO as the photocathode, illuminated from the NiO side (–•–•) and TiO_2 side (——) in the presence of the cobalt-based electrolyte. Film thickness of NiO and TiO_2 were 5 μm and 1.5 μm, respectively.

In view of the above results, we assembled a TDSC. The highest possible V_{OC} attainable for our TDSC consisting of the $Co^{II/III}$ couple, a N719/TiO_2 (V_{OC} 0.67 V; N719 is a common Ru complex for TiO_2 DSCs) photoanode, and a PINDI/NiO (V_{OC} 0.35 V) photocathode is 1.02 V; we achieve a V_{OC} of 0.91 V. This value is better than the best-performing N719/TiO_2 n-DSC (0.86 V)[18] and is equal to the highest reported for a TDSC.[19] By exact matching of the anodic and cathodic photocurrent, using specific film thicknesses (a relatively thin TiO_2 film, 2 μm, rather than the 10–20 μm of record devices), current generation from NiO as a passive electrode is avoided. Additionally, the FF is significantly improved, 0.8 versus 0.19[1,19] and the overall conversion efficiency reaches, 0.55 %, one of the highest reported.[19]

We attribute this enhanced TDSC performance to the suitability of the $Co^{II/III}$ redox couple to both the NiO- and TiO_2-based[12,13,20,21] electrodes and the slow recombination of the PINDI sensitizer. We expect a further enhancement in the photocurrent and performance if we use sensitizers with complimentary absorption spectra, that is, one absorbing the low-energy photons while the other absorbs high-energy photons, since currently there is considerable overlap (Figure 2).

In conclusion, the improvements to the performance of NiO-based DSCs presented herein, V_{OC} 0.35 V and J_{SC} 1.7 mA cm^{-2}, have set new standards in p-DSC performance and have made it possible to construct a tandem device where the p-side contributes significantly to the photocurrent as well as increasing the V_{OC}.

Experimental Section:

p-Type photocathodes were made by following published procedures[17] to achieve film thicknesses of 5 μm. The NiO electrodes were soaked in dye a solution (0.1 mM) for 16 h; acetonitrile (Coumarin 343, Aldrich), methanol (PI, Ref. [5]), or acetone (PINDI, Ref. [5]). n-Type photoanodes were also prepared in accordance with literature methods[22,23] resulting in films of 1.5 μm. The TiO_2 electrodes were immersed in a solution of N719 (Solaronix; 0.1 mM) in ethanol for 16 h. The electrolyte was composed of $Co^{II/III}$ tris(4,4′-di-*tert*-butyl-2,2′-dipyridyl) perchlorate (0.1M/0.1M) and $LiClO_4$ (0.1M) in propylene carbonate. Specific procedures for electrode preparation, electrolyte synthesis, device assembly, and device performance are available in the Supporting Information.

NiO films were deposited on glass slides for transient absorption (TA) measurements and illuminated through the back contact (200 nJ at 520 nm). Instrumental specifics for both TA systems are reported elsewhere.[5,24]

Received: January 22, 2009
Revised: March 10, 2009

Keywords: donor–acceptor systems · dye-sensitized solar cells · electrolytes · energy conversion · sustainable chemistry

---

[1] J. He, H. Lindström, A. Hagfeldt, S.-E. Lindquist, *Sol. Energy Mater. Sol. Cells* **2000**, *62*, 265.
[2] P. Qin, H. Zhu, T. Edvinsson, G. Boschloo, A. Hagfeldt, L. Sun, *J. Am. Chem. Soc.* **2008**, *130*, 8570.
[3] A. Nattestad, M. Ferguson, R. Kerr, Y.-B. Cheng, U. Bach, *Nanotechnology* **2008**, *19*, 295304.
[4] S. Mori, S. Fukuda, S. Sumikura, Y. Takeda, Y. Tamaki, E. Suzuki, T. Abe, *J. Phys. Chem. C* **2008**, *112*, 16134.
[5] A. Morandeira, J. Fortage, T. Edvinsson, L. Le Pleux, E. Blart, G. Boschloo, A. Hagfeldt, L. Hammarström, F. Odobel, *J. Phys. Chem. C* **2008**, *112*, 1721.
[6] A. Morandeira, G. Boschloo, A. Hagfeldt, L. Hammarström, *J. Phys. Chem. C* **2008**, *112*, 9530.
[7] A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* **2000**, *33*, 269.
[8] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin, M. Grätzel, *Thin Solid Films* **2008**, *516*, 4613.
[9] J. M. Kroon, N. J. Bakker, H. J. Smit, P. Liska, K. R. Thampi, P. Wang, S. M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Würfel, R. Sastrawan, J. R. Durrant, E. Palomares, H. Pettersson, T. Gruszecki, J. Watler, K. Skupien, G. E. Tulloch, *Prog. Photovoltaics* **2007**, *15*, 1.
[10] S. Iwamoto, Y. Sazanami, M. Inoue, T. Inoue, T. Hoshi, K. Shigaki, M. Kaneko, A. Maenosono, *ChemSusChem* **2008**, *1*, 401.
[11] S. Nakade, T. Kanzaki, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Phys. Chem. B* **2005**, *109*, 3480.
[12] H. Nusbaumer, S. M. Zakeeruddin, J.-E. Moser, M. Grätzel, *Chem. Eur. J.* **2003**, *9*, 3756.
[13] S. A. Sapp, M. Elliott, C. Contado, S. Caramori, C. A. Bignozzi, *J. Am. Chem. Soc.* **2002**, *124*, 11215.
[14] Z. Zhang, P. Chen, T. N. Murakami, S. M. Zakeeruddin, M. Grätzel, *Adv. Funct. Mater.* **2008**, *18*, 341.
[15] A. Morandeira, G. Boschloo, A. Hagfeldt, L. Hammarström, *J. Phys. Chem. B* **2005**, *109*, 19403.
[16] J. He, H. Lindström, A. Hagfeldt, S.-E. Lindquist, *J. Phys. Chem. B* **1999**, *103*, 8940.

[17] A. Nakasa, E. Suzuki, H. Usami, H. Fujimatsu, *Chem. Lett.* **2005**, *34*, 428.

[18] M. Grätzel, *Inorg. Chem.* **2005**, *44*, 6841.

[19] A. Nakasa, H. Usami, S. Sumikura, S. Hasegawa, T. Koyama, E. Suzuki, *Chem. Lett.* **2005**, *34*, 500.

[20] S. Nakade, Y. Makimoto, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Phys. Chem. B* **2005**, *109*, 3488.

[21] J. J. Nelson, T. J. Amick, C. M. Elliott, *J. Phys. Chem. C* **2008**, *113*, 18255.

[22] S. Ito, P. Liska, P. Comte, R. Charvet, P. Péchy, U. Bach, L. Schmidt-Mende, S. M. Zakeeruddin, A. Kay, M. K. Nazeeruddin, M. Grätzel, *Chem. Commun.* **2005**, 4351.

[23] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.

[24] F. Chaignon, J. Torroba, E. Blart, M. Borgström, L. Hammarström, F. Odobel, *New J. Chem.* **2005**, *29*, 1272.