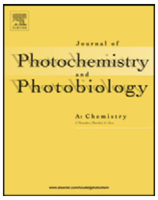
Journal of Photochemistry and Photobiology A: Chemistry 202 (2009) 159–163

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Organic chromophore-sensitized ZnO solar cells: Electrolyte-dependent dye desorption and band-edge shifts

María Quintana [a], Tannia Marinado [b], Kazuteru Nonomura [b],
Gerrit Boschloo [b,*], Anders Hagfeldt [b,1]

[a] Facultad de Ciencias, Universidad Nacional de Ingeniería, P.O. Box 31-139, Av. Tupac Amaru 210, Lima, Peru
[b] Center of Molecular Devices, Department of Chemistry, Royal Institute of Technology (KTH), Teknikringen 30, 100 44 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 16 July 2008
Received in revised form
21 November 2008
Accepted 29 November 2008
Available online 14 December 2008

Keywords:
Photoelectrochemical solar cell
Grätzel cell
Mesoporous electrode

ABSTRACT

An organic chromophore D5 (3-(5-(4-(diphenylamino)styryl)thiophene-2-yl)-2-cyanoacrylic acid) was tested as a sensitizer in photoelectrochemical mesoporous ZnO solar cells. Using thin (~3 μm) mesoporous ZnO electrodes, high incident photon-to-current conversion efficiencies of up to 70% were obtained, while power conversion efficiencies up to 2.4% were found in simulated sunlight (100 mW cm^{-2}). Long dye adsorption times (16 h) could be used without aggregation or precipitation of the dye. The composition of the iodide/triiodide-based electrolyte was found to be crucial in optimization of the ZnO-based dye-sensitized solar cell. A high concentration of Li^+ ions was found to be shift the ZnO conduction band edge to more negative potential, whereas opposite behavior is found for mesoporous TiO_2 cells. It was also found to be detrimental for solar cell performance and stability. Electrolyte-dependent and photoinduced dye desorption from the ZnO electrode was identified as a major stability problem in D5-sensitized ZnO solar cells.

1. Introduction

Dye-sensitized solar cells (DSCs) have potential to lower the cost of photovoltaic solar energy conversion. Despite intense research in the last 15 years, several aspects of the working mechanism of DSCs are still poorly understood, such as the electron transport in the mesoporous metal oxide film [1]. The large majority of investigations have been done on DSCs that are based on mesoporous TiO_2 electrodes, consisting of nanocrystals that are typically 20 nm in size. To improve understanding, several studies on alternative large bandgap metal oxide semiconductors have been initiated.

ZnO is the most popular alternative metal oxide for DSCs [2], as it has similar bandgap and conduction band position as TiO_2, while it has higher electron mobility. In a previous study, we found that the electron transport time, and thus the apparent diffusion coefficient, was the same in DSCs based on similar sized ZnO or TiO_2 nanocrystals [3]. In contrast to TiO_2-based DSCs, relatively few optimization studies have been performed for ZnO-based DSCs [4–8]. Best overall power conversion efficiencies reported on ZnO-based DSCs are around 4–5% at full sunlight intensity (100 mW cm^{-2}) [5,6,8]. A large variation of preparation procedures and a great variety of nanostructure morphologies can be obtained for ZnO with relative ease. We have, for instance, investigated the electron transport in DSCs based on aligned ZnO nanorods, which was found to be much faster than in nanocrystal-based ZnO films of similar thickness, proving that electron transport is strongly affected by grain boundaries [9].

One drawback for ZnO appears to be its chemical stability. We found that partial dissolution of ZnO in the dye bath was responsible for ineffective sensitization of mesoporous ZnO electrodes in case of the standard sensitizer $Ru(dcby)_2(NCS)_2$ [4]. Alternative sensitizers may offer an opportunity in this respect. Recently, we have developed a series of efficient organic sensitizers for TiO_2 [10–12]. In this paper, we will present results of one of these dyes, 3-(5-(4-(diphenylamino)styryl)thiophene-2-yl)-2-cyanoacrylic acid (D5) in ZnO-based DSCs. An efficiency of 2.4% under full sunlight (100 mW cm^{-2}) was obtained for a 3 μm thick ZnO film. An encouraging observation was that the dye adsorption process did not pose any problem. The overall stability of the ZnO-based DSCs was, however, still very poor in comparison with their TiO_2 counterparts. Photoinduced desorption of the dye was identified as a major degradation mechanism in the D5-sensitized ZnO solar cell.

---

[*] Corresponding author. Current address: Uppsala University, Department of Physical and Analytical Chemistry, Box 259, SE-751 05 Uppsala, Sweden.
Tel.: +46 18 471 3303.
E-mail address: Gerrit.boschloo@fki.uu.se (G. Boschloo).

[1] Current address: Uppsala University, Department of Physical and Analytical Chemistry, Box 259, SE-751 05 Uppsala, Sweden.

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.11.024

2. Experimental procedure

2.1. Preparation of ZnO films

ZnO colloids were prepared in ethanol by addition of tetramethylammonium hydroxide (25% in methanol) to a suspension of zinc acetate in ethanol previously presented by our group [13]. The resulting ZnO sol was refluxed at 80 °C for 30 min. The suspension was left to cool down and settle overnight, decanted, washed with ethanol, and finally concentrated until visibly viscous. Transparent nanostructured ZnO electrodes were obtained by depositing the paste onto conducting glass substrates (TEC8, Pilkington) by doctor blading, followed by heating in a hot-air stream at 350 °C for 30 min.

2.2. Dye sensitization and solar cell assembly

The ZnO electrodes were left overnight in the dye bath consisting of 0.5 mM D5 (available from previous studies [10,12]) in ethanol. The dyed electrode was rinsed with ethanol, dried, and assembled with a platinized conducting glass counter electrode using a 50 μm thick thermoplastic frame (Surlyn 1702). The electrolyte composition was as follows: Electrolyte **1**: 0.1 M LiI, 0.6 M tetrabutyl ammonium iodide (TBAI), 0.5 M 4-*tert*-butylpyridine (4-TBP), and 0.1 M I_2 in 3-methoxypropionitrile (MPN). Electrolyte **2**: 0.7 M TBAI, 0.001 M $LiClO_4$, 0.5 M 4-TBP, 0.1 M I_2 in MPN; Electrolyte **3**: 0.7 M TBAI, 0.5 M 4-TBP, 0.1 M I_2 in MPN. Current–voltage characteristics of the solar cells were recorded using a Newport Oriel 300 W Solar Simulator (Model 91160) and a Keithley 2400 source/meter and further techniques described elsewhere [14]. UV–vis spectra of ZnO films on TEC8 glass were recorded using an Ocean Optics HR2000 spectrometer, and were corrected for the TEC8 background.

3. Results and discussion

In previous studies we found that dye adsorption onto ZnO is a critical step for ZnO-based DSCs [4]. Specifically, when using the ruthenium-complexes N719 or N3 as sensitizer the standard immersion time for ZnO electrodes in the dye bath (∼15 h) yielded poor results due to dye aggregation on the ZnO surface, while shorter adsorption times improved solar cell performance, despite a lower dye coverage. For adsorption of the organic sensitizer D5 onto nanostructured ZnO we tested two immersion times, 4 min and 16 h. Results from the *I*–*V* characterization of D5-sensitized ZnO solar cells are summarized in Table 1. In contrast to earlier studies, long dye adsorption times did not lead to a decrease in solar cell performance, but to an improvement. The short-circuit photocurrent density J_{SC} was clearly enhanced by the longer adsorption time, due to a higher dye coverage. On the other hand, the fill factor was found to decrease by the longer dye adsorption time, which may be attributed to the increased photocurrent.

An important difference in comparison to N719 (or N3) is that dye adsorption in case of D5 appeared to stop when monolayer coverage was reached. Based on the analysis of UV–vis absorption spectra, no evidence was found for multilayer adsorption or aggregation of D5 molecules. In case of N719 (or N3) it has been found that dissolution of the ZnO leads to formation of a Zn^{2+}-N719 precipitate [4]. A similar precipitate is found by addition of zinc acetate to the dye bath. No precipitate was found, however, when zinc acetate was added to a D5 solution in ethanol. It may be expected that the carboxylic acid group of D5 will cause some dissolution of ZnO in the dye bath, but this does not lead to deposition of ineffective dye aggregates on the ZnO electrode.

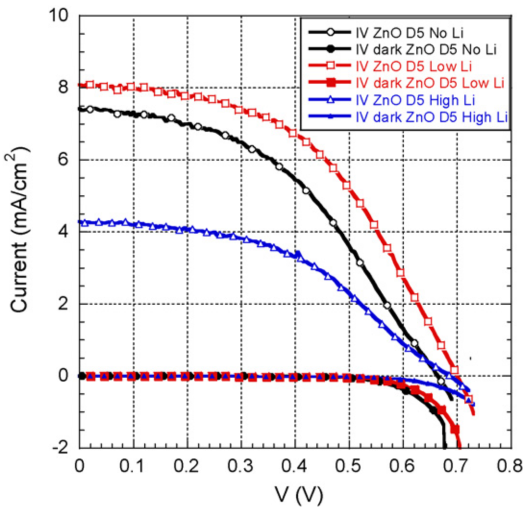


Fig. 1. Current–voltage characteristics of D5-sensitized ZnO solar cells with Electrolytes **1**–**3** under illumination (100 mW cm^{-2}, AM1.5G) and in the dark.

In an electrolyte optimization study we observed that the photovoltaic performance of D5-sensitzed ZnO solar cells was critically dependent on the concentration of lithium ions. Starting from a standard redox electrolyte used in our laboratory (Electrolyte **1**) 0.1 M LiI, 0.6 M TBAI, 0.1 M I_2 and 0.5 M 4-TBP in MPN, we found that decreasing the Li^+ concentration resulted in higher solar cell efficiencies. Excluding Li^+ altogether gave a good result, but a small concentration of 0.001 M Li^+ ions was found to be optimal yielding a power conversion efficiency of 2.4%, see Table 2, which may be compared to 3.1% obtained for a TiO_2 solar cell with similar film thickness [11]. The IV curves recorded upon illumination and in the dark are presented in Fig. 1. The dark current appears to be suppressed in the presence of a high Li^+ concentration.

Incident-photon-to-current spectra of the same solar cells showed a significantly lower photocurrent for electrolytes with a high lithium ion concentration (see Fig. 2). Normalized IPCE spectra overlap perfectly, indicating that no spectral shifts occur as function of electrolyte composition. In an optimized electrolyte, IPCE values as high as 70% were found for D5-sensitized ZnO.

In the case of TiO_2-based dye-sensitized solar cells, Li^+ ions are known to adsorb at the TiO_2 surface, affecting surface charge and lowering the energy of the conduction band edge [15–17]. The effect of Li^+ ions in ZnO-based DSC appears to be very different. While the effect of the pH of aqueous electrolytes on E_{CB} of mesoporous ZnO has been investigated [18], no studies of the effect of Li^+ ions in aprotic electrolytes on E_{CB} of ZnO are available to our knowledge. Here, we performed charge extraction measurements and electron lifetime measurements to investigate the effect of Li^+ ions on D5-sensitzed ZnO solar cells. The relation between open circuit potential and charge in the nanostructured ZnO solar cell was deter-

Table 1
Effect of dye adsorption time on *I*–*V* characteristics of D5-sensitized ZnO solar cells in simulated sunlight.[a] *Illumination conditions*: AM 1.5 G, 100 mW cm^{-2} (10 mW cm^{-2}).

Dye adsorption time	η [%]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF
4 min	1.20 (1.28)	0.72 (0.62)	2.65 (0.34)	0.64 (0.67)
16 h	1.77 (2.04)	0.75 (0.61)	4.34 (0.52)	0.55 (0.49)

[a] ZnO film thickness was ∼3 μm. Dye bath: 0.5 mM D5 in ethanol. Electrolyte **1**: 0.1 M LiI, 0.6 M TBAI, 0.5 M 4-TBP, 0.1 M I_2 in MPN. η is the power conversion efficiency, V_{OC} the open-circuit voltage, J_{SC} the short-circuit current density, and FF the fill factor.

Table 2
Effect of Li^+ content in electrolyte on *I–V* characteristics of D5-sensitized ZnO solar cells.

Electrolyte[a]	η [%]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF
1 (0.1 M Li^+)	1.82 (2.16)	0.75 (0.64)	4.52 (0.54)	0.54 (0.63)
2 (0.001 Li^+)	2.36 (2.43)	0.68 (0.56)	7.12 (0.81)	0.49 (0.54)
3 (no Li^+)	1.86 (2.43)	0.65 (0.56)	6.70 (0.81)	0.43 (0.54)

ZnO film thickness was ~3 μm. *Illumination conditions*: AM 1.5 G, 100 mW cm^{-2} (10 mW cm^{-2}).

[a] Electrolyte composition: **1** (0.1 M LiI, 0.6 M TBAI, 0.1 M 4-TBP, 0.1 M I_2 in MPN); **2** (0.001 M $LiClO_4$, 0.7 M TBAI, 0.5 M 4-TBP, 0.1 M I_2 in MPN) and **3** (0.7 TBAI, 0.5 M 4-TBP, 0.1 M I_2 in MPN).

mined at 5 different light intensities (see Fig. 3a). At a given charge, higher open circuit potentials are found for the electrolyte with a high (0.1 M) Li^+ ion concentration. This can be explained in different ways: one can assume that the trap distribution in the nanostructured ZnO, defined with respect to the conduction band edge E_{CB}, is not affected by the changes in the electrolyte. In such case, it is apparent that E_{CB} must have shifted to higher electron energy upon addition of Li^+ ions. Alternatively, one can consider that a change of electrolyte composition does lead to a change in the number of traps in ZnO. Addition of Li^+ ions to the electrolyte would then, following this argumentation, lead to a lower density of traps in the ZnO. We think that the former explanation is more plausible; it agrees well with observations on mesoporous TiO_2 solar cells that electrolyte [14,17] or surface modifications [19–21] affect E_{CB} rather than trap distribution. We will therefore use this explanation in the further discussion.

A E_{CB} shift to higher electron energy upon addition of Li^+ to the electrolyte is opposite to what is observed in TiO_2-based solar cells [15–17]. Additional measurements on D5-sensitized TiO_2 solar cells with the same electrolytes as used in this study showed that the presence of 0.1 M Li^+ was necessary to obtain high J_{SC} values, which is consistent with a shift of E_{CB} to lower energy (data not shown here). The Li^+ ion effect on D5-sensitized ZnO solar cells was, however, not straightforward. In presence of a low Li^+ concentration (1 mM), E_{CB} appeared to shift to lower electron energy compared to the situation without Li^+ ions.

The electron lifetimes in the nanostructured ZnO were determined using transient photovoltage response upon a small (<5%) square-wave modulation of the light intensity [14]. Results obtained at different light intensities are shown as function of the extracted charge in Fig. 3b. Shortest electron lifetimes were found for the highest lithium concentration (Electrolyte **1**). A small Li^+ concentration, however, appeared to be beneficial for the electron lifetime. The overall trend is that lifetimes decrease with increasing driving force.

The stability of the D5-sensitized ZnO solar cells was not very good. A significant reduction of the D5 dye load was observed when solar cells were assembled: a sandwich was made of the D5-sensitized ZnO electrode with a counter electrode, filled with redox electrolyte and left overnight. Fig. 4 shows that there was a significant reduction of the amount of adsorbed dye on the ZnO electrode after dissembling the cells. The degree of dye desorption was found to depend on the cations in the electrolyte and the exposure to light. Without exposure to light, about 20% of the D5 desorbed in Elec-

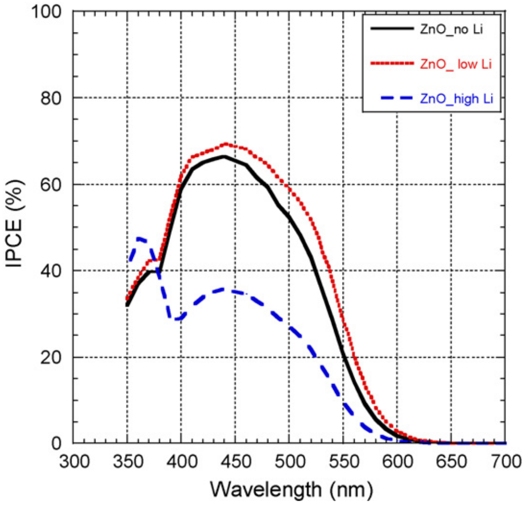


Fig. 2. Spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) D5-sensitized ZnO solar cells using Electrolytes **1**–**3**.

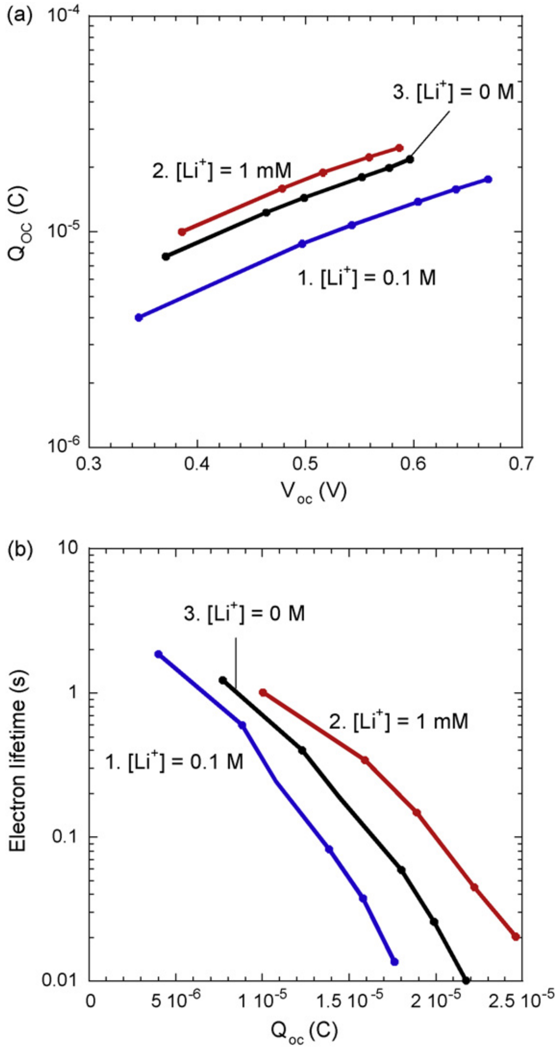


Fig. 3. (a) Extracted charge as function of open circuit potential in DSCs based on D5-sensitized ZnO, with Electrolyte **1** (blue), Electrolyte **2** (red) and Electrolyte **3** (black). (b) Electron lifetime in the same cells as function of extracted charge at different light intensities. Time constants were determined using time-resolved small modulation techniques. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

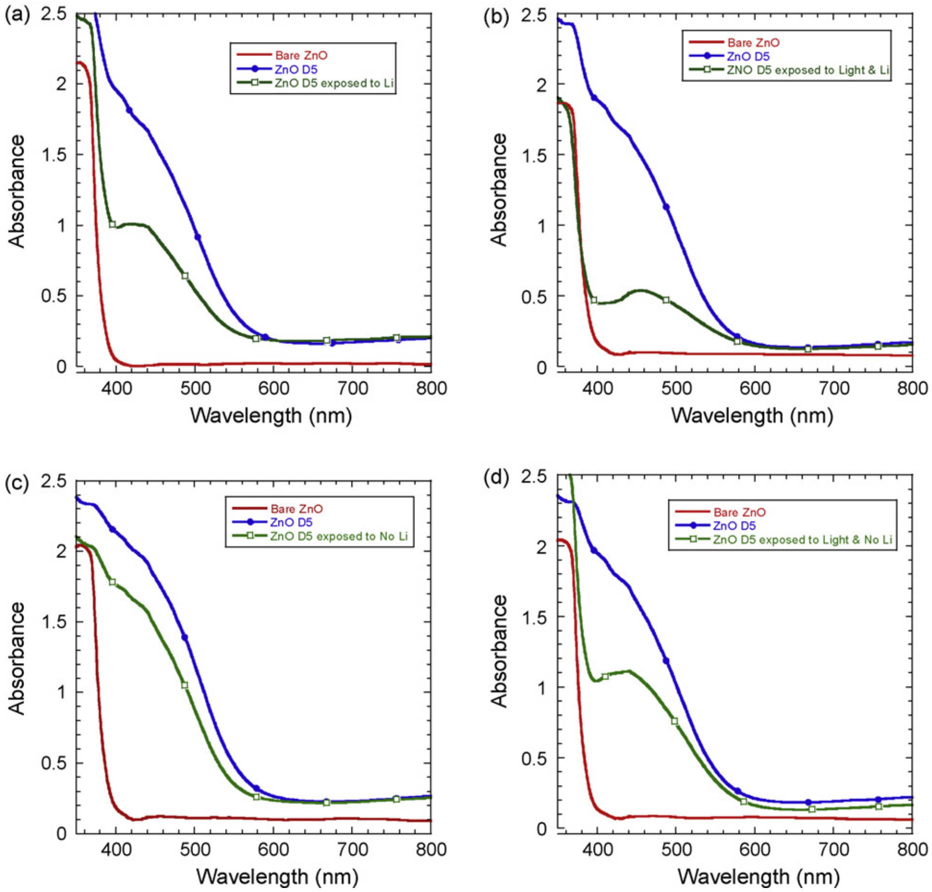


Fig. 4. Uv–vis spectra of ZnO working electrodes under different conditions. (a) Bare ZnO (red), D5-sensitized ZnO (blue) and D5-sensitized ZnO exposed to Electrolyte **1** (containing 0.1 M Li^+) in the dark (green); (b) same as (a), but the electrolyte-exposed D5-ZnO electrode was also exposed to light. (c) Bare ZnO (red), D5-sensitized ZnO (blue) and D5-sensitized ZnO exposed to Electrolyte **3** (without Li^+) (green); (d) same as (c), except that the electrolyte-exposed sensitized electrode was exposed to light. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

trolyte **3** (only TBA^+), while more than 40% desorbed in Electrolyte **1** (with 0.1 M Li^+). With light exposure (the samples where kept overnight in laboratory light, ca. 100 lx), these values were about 40% and 70%, respectively.

The underlying reasons for the dye desorption are not fully clear. Possibly there is a slow dissolution process of the ZnO surface caused by the carboxylic acid group of the D5 [22], but it is unclear how the Li^+ ions plays a role in this. As protons will be used in the dissolution process ($ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$), the surface pH of the ZnO will increase, leading to a more negative surface charge and a higher energy for E_{CB}. This is in accordance with the observed E_{CB} shift in the presence of 0.1 M Li^+. The more negative surface charge may prevent re-adsorption of the dye.

Dye desorption is strongly increased upon illumination. There are several possible explanations: Injected electrons in ZnO may reduce the binding strength of the D5 dye; oxidized dye molecules will be stronger acids causing thereby more dissolution of the ZnO surface; The UV-component in the light can cause direct excitation of the ZnO, creating holes that are known to cause dissolution of ZnO. Further investigations are needed to establish the precise mechanism of photoinduced dye desorption. Similar mechanisms may also play a role in case of dye-sensitized TiO_2 solar cells and are the subject of ongoing investigation.

In conclusion, we have investigated dye-sensitized solar cells based on mesoporous ZnO electrode modified with an organic chromophore and iodide/triiodide electrolytes. Although the dye-adsorption process appeared to be without problem, significant dye dissolution occurred after solar cell assembly. This may be attributed to slow dissolution of the ZnO surface, a process that appears to be accelerated by light. The overall stability of the solar cells was therefore poor. A way to improve stability of ZnO-based DSC is to apply a thin surface coating to make the surface more chemically resistant [23,24].

Acknowledgements

This work was financially supported by the International Science Program at Uppsala University, the Swedish Energy Agency and the Knut and Alice Wallenberg Foundation. We thank Daniel Hagberg (KTH, Organic Chemistry) for the synthesis of the D5 sensitizer.

References

[1] A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 33 (2000) 269.
[2] G. Boschloo, T. Edvinsson, A. Hagfeldt, in: T. Soga (Ed.), Nanostructured Materials for Solar Energy Conversion, Elsevier, Amsterdam, 2006, p. 227.
[3] M. Quintana, T. Edvinsson, A. Hagfeldt, G. Boschloo, J. Phys. Chem. C 111 (2007) 1035.
[4] K. Keis, J. Lindgren, S.-E. Lindquist, A. Hagfeldt, Langmuir 16 (2000) 4688.
[5] Z. Chen, Y. Tang, L. Zhang, L. Luo, Electrochim. Acta 51 (2006) 5870–5875.
[6] K. Kakiuchi, E. Hosono, S. Fujihara, J. Photochem. Photobiol. A: Chem. 179 (2006) 81.
[7] T.P. Chou, Q.F. Zhang, G.Z. Cao, J. Phys. Chem. C 111 (2007) 18804.
[8] H. Minoura, T. Yoshida, Electrochemistry 76 (2008) 109.
[9] E. Galoppini, J. Rochford, H. Chen, G. Saraf, Y. Lu, A. Hagfeldt, G. Boschloo, J. Phys. Chem. B 110 (2006) 16159.
[10] D.P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, Chem. Commun. (2006) 2245.

[11] D.P. Hagberg, T. Marinado, K.M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, J. Org. Chem. 72 (2007) 9550.
[12] D.P. Hagberg, J.-H. Yum, H. Lee, F.D. Angelis, T. Marinado, K.M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel, M.K. Nazeeruddin, J. Am. Chem. Soc. 130 (2008) 6259.
[13] C. Bauer, G. Boschloo, E. Mukhtar, A. Hagfeldt, Chem. Phys. Lett. 387 (2004) 176.
[14] G. Boschloo, L. Häggman, A. Hagfeldt, J. Phys. Chem. B 110 (2006) 13144.
[15] G. Redmond, D. Fitzmaurice, J. Phys. Chem. 97 (1993) 1426.
[16] Y. Liu, A. Hagfeldt, X.-R. Xiao, S.-E. Lindquist, Sol. Energy Mater. Sol. Cells 55 (1998) 267.
[17] K. Fredin, J. Nissfolk, G. Boschloo, A. Hagfeldt, J. Electroanal. Chem. 609 (2007) 55.
[18] G. Redmond, A. O'Keeffe, C. Burgess, C. MacHale, D. Fitzmaurice, J. Phys. Chem. 97 (1993) 11081.
[19] H. Alarcon, G. Boschloo, P. Mendoza, J.L. Solis, A. Hagfeldt, J. Phys. Chem. B (2005) 18483.
[20] B.C. O'Regan, J.R. Durrant, P.M. Sommeling, N.J. Bakker, J. Phys. Chem. C 111 (2007) 14001.
[21] Z. Zhang, N. Evans, S.M. Zakeeruddin, R. Humphry-Baker, M. Grätzel, J. Phys. Chem. C 111 (2007) 398.
[22] E.A. Meulenkamp, J. Phys. Chem. B 102 (1998) 7764.
[23] M. Law, L.E. Greene, A. Radenovic, T. Kuykendall, J. Liphardt, P. Yang, J Phys. Chem. B 110 (2006) 22652.
[24] Y.-J. Shin, J.-H. Lee, J.-H. Park, N.-G. Park, Chem. Lett. 36 (2007) 1506.