PHOTOELECTROCHEMICAL SOLAR CELLS BASED ON DYE-SENSITIZATION OF NANOCRYSTALLINE TIO₂

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ABSTRACT

Dye-sensitized solar cells (DSCs) have attracted considerable interest as low-cost alternatives to conventional inorganic photovoltaic devices. With low-cost raw materials and relatively low-cost manufacturing technology and processes, deposited thin films have the potential to provide more than a 50 percent reduction in cost relative to traditional crystalline cell modules. Hence, we investigated the photoelectrochemical properties of mesoporous colloidal anatase films in connection with their potential application in liquid junction photovoltaic cells. A respectable light to electric energy conversion efficiency of about 9.5% in 9 mW/cm² (~ 1/10 Sun) was obtained. In comparison (a $I_{sc} =$ 2.2 mA/cm^2 and an $V_{oc} = 600 mV$ under a white light illumination of 9 mW/cm²), we obtained $I_{sc} =$ 15 mA/cm² and $V_{\infty} = 760$ mV at a light intensity of mW/cm² (direct Sun). We achieved 85 extraordinary efficiency for the conversion of incident photons to converted electrons exceeding 80% within the wavelength range of the absorption band from RuL2(NCS)2 : 2 TBA sensitizer.

Keywords: Solar Cells; Dye sensitized nc-TiO₂; and Photoelectrochemistry.

INTRODUCTION

Current commercial photovoltaie cells are dominantly based on crystalline silicon technologies, with efficiencies of about 12% for the best available devices. More than 85% of the solar cells in use today are made of crystalline silicon (c-Si). The cost of solar electricity is of the order of \$0.4/kWh, roughly ten times higher than electricity from natural gas. Although the evolution of the solar energy market since the early 1980's shows a \sim 23% reduction in the cost of solar panels with each doubling eumulative installed capacity, new photovoltaic concepts and materials are still required to make solar technologies competitive on the energy market and to foster their deployment at a large scale. Therefore, the interest in regenerative photoelectrochemical solar cells hased OT photosensitization of nanocrystalline TiO2 are regarded as high semiconductor stability, a potential light weight and low-cost alternative to conventional solid-state devices since the 1991 report [1]. Dye-sensitized nanocrystalline TiO_2 solar cells (nc-DSCs) are based on a fundamentally different working principle than solar cells based conventional semiconductors. Because, on conventional solid-state solar cells convert light into electricity by exploiting the photovoltaic effect that exists at the semiconductor junctions. In this case, the semiconductor performs two processes simultaneously: absorption of light, and separation of the electric charges (electrons and holes), which are formed as a consequence of that absorption.

In contrast to conventional silicon photovoltaic devices, the nc-DSC converts light energy to electricity on molecular level, similar to natural photosynthesis, whereby the process of light absorption and charge separation is differentiated. Since we have here a majority-carrier device with the electron injection into an n-type semiconductor, the recombination loss process well known in solid-state devices is nonexistent in this case. Figure 1 presents a schematic cross-section of liquid nanoporous-DSC (a) and the energy levels diagram of the materials used in nanoporous-DSC (b). Dye-sensitized nanocrystalline TiO_2 solar cells are based on a wide bandgap inorganic semiconductor, usually TiO_2 , which is sensitized for visible light by a monolayer of adsorbed dye. The most frequently used dye is, cis-(NCS)₂bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II). The carboxylate groups results in strong binding of this dye to the TiO_2 surface,

strong binding of this dye to the TiO_2 surface, while the NCS groups enhance the visible absorption of the dye. The photoelectrode in such a device consists of a nanoporous TiO_2 film (approximately 10 µm thick) deposited on a layer of transparent conducting oxide (TCO) on a glass {see Fig. 1(a)}. The counter electrode also consists of fluorine-doped tin oxide ($SnO_2:F$) glass on which a small amount of platinum (5-10 µg cm⁻²) is

deposited in order to catalyze the reduction of mediator. In a complete cell, photo- and counter electrodes are clamped together and the space between the electrodes and voids between the TiO_2 nanoparticles (i.e the pores of anatase network) are filled with an electrolyte. This liquid electrolyte consists of an organic solvent containing a redox couple, usually iodide/tri-iodide (I/I_3) used as a hole transport layer. This type of solar cell is based on the mechanism of a regenerative photoelectrochemical process.

The most fundamental property that should be considered during the design of such nc-DSCs is the relative energies at the semiconductor/ dye/electrolyte interface (see Fig. 1(b)). The dye excited state oxidation potentials has to be more negative than the semiconductor conduction band potential to enable the electron injection, and the oxidation potential of the dye must be more positive than the redox couple in the electrolyte solution to provide the driving force for the hole transfer [2]. Within these limits, the cell performance is affected by the exact position of the relative potentials.

To obtain reasonable efficiencies comparable to established solar cell technologies, in the *nc*-DSC the surface area is enlarged by a factor of 1000 compared to a flat surface, by using nanoparticles of TiO₂ with a diameter of approximately 10-20 nm and for 8-12 μ m thick films [3]. This greatly enhanced surface area opens new ways in various fields, such as dye-sensitized solar cell, where a ruthenium based dye converts the incoming light into charge pairs with quantum efficiency 100%.

The working principle of the *nc*-DSC is based on excitation of the dye followed by fast electron injection into the conduction band of the TiO_2 , leaving an oxidized dye molecule on the TiO_2 surface. The ultrafast rate of electron injection is critical both for high-energy conversion efficiencies obtained with this sensitizer dye, and for excellent long-term stability of this dye in photoelectrochemical solar cells. Injected electrons percolate through the nanoporous TiO_2 layer network via diffusion [2] due to electron scattering to the conductive support and are fed into the external circuit to the counter electrode. At the counter electrode, tri-iodide is reduced to iodide by metallic platinum under uptake of electrons from the external circuit. Iodide is transported through the electrolyte towards the photoclectrode, where it reduces the oxidized dye. The dye molecule is then ready to the next excitation/oxidation/reduction cycle. The total reaction of the iodide/tri-iodide

Journal of EEA, Vol. 25, 2008

redox electrolyte is a two-electron reaction and the device operates in a regenerative mode.

The solar-to-electrical energy conversion efficiencies as high as 10% - 11% at AM1.5 standard solar spectrum (i.e. 1000 W/m²) for areas < 0.2 cm² have been reported [3-5], whereas common low-cost commercial panels operate between 7 and 15%. The rate of electron transport is a major determinant of the overall efficiency of dye-sensitized nanocrystalline TiO₂ solar cells. To achieve high efficiency, much research has been directed toward improving the photocurrent and photovoltage by, for example, developing new sensitizers [6-20], increasing the light scattering properties of the film [21,22], suppressing the charge recombination [3,23], improving the interfacial energetics [23], and altering the particle morphology [4,25,26]. According to the university of Notre Dame and NASA demonstrations, the carbon nanotubes could help to make nanoparticlebased solar cells more efficient and practical. The present attained of 10% -11% energy conversion efficiency of DSC bears favorable comparison with the efficiency obtained with conventional solidstate solar cells. In this work we present the miero porous photoelectrochemical structure and properties of anatase nc-TiO2 films onto SnO2:F conducting glass, which are influenced by sintering temperature, film thickness, particle size, particle morphology, and dye-adsorption. The currentvoltage characteristics and solar energy efficiency are given.





(b)

Figure 1 Schematic description of liquid nanoporous-DSC (a) and the energy levels diagram of the materials used in nanoporous-DSC (b). CB and VB is conduction and valence band of the TiO₂; S^0 , S^+ , and S^* is the ground, oxidized form, and excited state potentials of the ruthenium dye versus (vs.) standard reference electrodes (SCE, NHE), respectively. The solid line represents the work function level of SnO₂:F versus (vs.) vacuum level; the dotted lines are I /I₃ redox potential and Pt oxidation potential versus (vs.) normal hydrogen electrode (NHE) and saturated calomel electrode (SCE). The electrolyte has contact with the individual nanocrystallites. Illumination produces an electron-hole pair in one crystallite. The hole transfers to the electrolyte and the electron transverses several crystallites before reaching the conducting substrates.

EXPERIMENTAL

All devices were produced on 2.5 cm by 1.5 cm on a transparent conducting oxide (TCO) glass substrates (i.e. SnO_2 :F glass substrates) with an active area of 0.5 cm². Cells were prepared according to methods described in literature [3]. Figure 2 shows the device configuration of the dyesensitized photoelectrochemical solar cells and the molecular structures of the material used. Commercially available TiO_2 paste (Ti-Nanoxide T, colloidal anatase particle size about 13 nm) from Solaronix, Aubonne, Switzerland was used as a

basis for the nanoporous TiO₂ laver. Nanostructured TiO_2 film was prepared by means of doctor blading technique from TiO_2 colloidal paste on SnO_2 : F conducting glass, having a surface resistivity of 8 ohm/square (Libbey Owens Ford, Toledo, USA) masked by Scotch tape. A slow drying step of the solvent and a progressive heating is necessary to ensure optimal adhesion of the TiO_2 layer onto the TCO. After drying step, the nanostructured TiO₂ film was fired to 450 °C at the rate of 5 °C/min in oven and left at 450 °C for 30 min to burn out the organic additives and to insure electrical contact between various TiO₂ colloids and between the colloids and the conducting substrates. The resulting nanostructure TiO₂ layer was 9 µm thick as monitored by Detach and optically transparent. The RuL₂ (NCS) 2: 2 TBA dye, where L stands 4,4'-dicarboxylato-2,2'bipyridyl having two protons and two tetrabutyl ammonium units attached on the carboxylic acid (Ruthenium 535-bisTBA, Solaronix Co.) was used as sensitizer for the sintered TiO₂ film layers. The transparent TiO_2 layers were immersed for 2 days in a solution of ruthenium dye, RuL₂ (NCS) 2: 2 TBA (10 mg in 50 ml ethanol). The dye-coated nanocrystalline TiO_2 films were then rinsed with absolute ethanol and dried under nitrogen flow at room conditions and used as photoanode electrodes. Subsequently, the platinized conducting SnO2:F glass as counter electrode was deposited facing the photoanode and separated by a thin spacer. Laser cut strips of Surlyn 1702 foils (Dupont, Wilmington, USA) is laminated between the glass plates to seal the cells. For comparative study, the Amosil 4 sealant (a portion made of 45% in weight of hardner and 55% in weight of resin) supplied from Solaronix was used for sealing purposes. The electrolyte used consists of polyethylene containing 0.5 M potassium iodide and 50 mM iodine, thus forming 50 mM of the triiodide (I_3) . This electrolyte has a boiling point ca. 250 °C. Filling of the cells with electrolyte was done in a rough vacuum, and the filling holes were plugged with a Surlyn 1702 pad or with an Amosil 4 epoxy.



Figure 2 Schematic diagram of the device configuration and molecular structure of the material used.

All cells were produced under ambient conditions. No actions were taken to remove possibly adsorbed oxygen from the cells. Optical absorption was recorded with a Hitachi spectrophotometer. The current-voltage (I-V) characteristics were measured using a Keithley SMU 2400 Source Meter measurement unit under illumination through the front (i.e. photoanode) side of the nc-DSC by white light lamp, direct sun and monochromatic light (a defocused Ar⁺ laser beam 488 nm), typically by averaging 80 at measurements for one point. The light intensities were measured using a calibrated Si - Photodiode. Spectrally resolved measurement of ne-DSC has been studied by Xe-arc white light lamp and a Czerny-Turner single pass monochromator, at intensity of 1 mW/cm² at each wavelength in the range of 400 to 700 nm. The surface network morphology of these film layers was examined with an atomic force microscope in contact mode (AFM: Nanoscope IIIa from digital instruments version 4.42r4).

RESULTS AND DISCUSSION

All *nc*-DSCs were produced here in the sandwich geometry between the SnO_2 : *F* conducting glass as a photo-anode and the platinized conducting SnO_2 : *F* glass counter clectrode as a cathode. Upon illumination, the electrons injected by the sensitizer

Journal of EEA, Vol. 25, 2008

into the TiO_2 conduction band travel across the nanorystalline film to the SnO_2 :F conducting glass substrate serving as photocurrent collector, while the oxidized ions diffuse toward the back electrode where they are rereduced. Under open circuit condition, the photovoltage of the *nc*-DSC represents the difference between the Fermi level of TiO_2 under illumination and the redox potential of the electrolyte. The overall energy conversion efficiency, η_e of the photovoltaic cell has been performed using the equation

$$\eta_e = (V_{oc}[V] * I_{sc}[A/cm^2] * FF)/P_{inc}[W/cm^2]$$

under different intensities, where V_{oc} , I_{sc} , FF and P_{inc} are the open circuit potential, short circuit current, fill factor and incident light power, respectively. I_{sc} is the current that is recorded when the voltage is zero. V_{oc} is the potential when the current is zero. We determine the value of the fill factor of the device, FF, by calculating the area of the maximum power rectangular area under the I-V curve in the 4th quadrant. Therefore, the filling factor is given by

$$FF = (V_{\max} + I_{\max}) / (V_{oc} + I_{sc}),$$

where V_{max} and I_{max} are voltage and current at the point of maximum power output of the rectangle with the intersection of the I-V curve.

Figure 3 shows that the I-V characteristics of RuL₂ (NCS) 2: 2 TBA-sensitized anatase nanocrystalline TiO_2 electrodes improving with annealing temperature. Upon illumination at light intensity of 9 mW/cm², the I_{sc} , V_{oc} and FF increases from 0.545 mA/cm^2 , 420 mV, and 0.5 to about 2.2 mA/cm^2 , 600 mV, and 0.6 with the annealing temperature ofthe film increases from 100 °C to 450 °C, respectively. The increase of short-circuit photocurrent of the dye-sensitzed anatase nc-TiO₂ electrodes with annealing temperature correlates with an increased concentration of adsorbed dye and improved light scattering properties of the film associated with the growth of anatase nanoparticles. Furthermore, the dependence of absorbed dye concentration on annealing temperature for Ru [LL'(NCS) 2]-sensitized nanocrystalline rutile TiO2 electrodes had been shown in [27]. An increase of V_{oc} and FF with annealing temperature is possible in our experiment because of very low recombination rate.



Figure 3 I-V curves of RuL₂ (NCS) ₂: 2 TBAsensitized nanocrystalline anatasc *TiO*₂ electrodes. The *TiO*₂ films were annealed at 100 °C (solid diamond), 225 °C (solid circles), and 450 °C (solid squares). The radiant power was 9 mW/cm² (1/10 Sun)

Figure 4 illustrates the influence of annealing temperature on the nc-TiO₂ film layers surface morphology at a temperature of (a) 100 °C and (b) 450 °C by atomic force microscope in the contact mode on a conducting glass support. According to an AFM images, the nanostructured TiO_2 electrodes in Fig. 4 are composed of interconnected and nanometersized TiO2 particles and micropores. The average pore size increased from 10 nm at a temperature of 100 °C to 30 nm at a 450 °C. It has been observed that the pore size distribution influenced by the sintering temperature. The size and shape of the colloids from which the electrodes are made determine the porosity and the surface area-to-thickness ratio of the clectrode [4]. Furthermore, the charge carrier transport can be controlled by an optimal nanoparticles interconnection and a pore-size, which guarantees an efficient electrolyte penetration (see the results in Fig. 3). Therefore, the presence of small pores slows the diffusion kinetics in the electrolyte and, thus, affects the photovoltaic response of the solar cell, especially under high illumination. Of course, other parameters, such as the viscosity of the electrolyte solvent and the concentration of iodine, will affect the transport kinetics.



0 10.0 рм

Figure 4 AFM images of the nc- TiO_2 film layers at a temperature of (a) 100 °C and (b) 450 °C. Thicknesses of the TiO_2 films were 9 µm.

(b)

Comparative studies of the current-voltage characteristics of the *nc*-DSCs with different film thickness at the same annealing temperature (450 °C) and illuminated conditions (1/10 Sun) are presented in Figure 5. As the thickness of anatase *nc*-*TiO*₂ films increased from 3 to 9 μ m, I_{sc} and V_{oc} increased from 0.8 mA/cm² to 2.4 mA/cm² and 580 mV to 650 mV, respectively. Typical fill factors of these devices were in the range of 0.5 to 0.6. This experimental evidence clearly shows that the maximum photocurrent of *nc*-DSC depends on the thickness of the porous *TiO*₂ films. This means, the

sensitized dye coverage on TiO_2 nanoparticles can be optimized by tuning the nc-TiO₂ layer thickness to an optimum value and the current that is produced by the *nc*-DSC is directly linked to the number of dye molecules that are adsorbed on the *nc*-TiO₂ electrode.



Figure 5 Photocurrent-voltage characteristics of the *nc*-DSCs with different film thickness (solid squares: 3 μm; solid circles: 9 μm), at the same annealing temperature (450 °C), and under white light illumination 9 mW/cm² (1/10 Sun).

The overall energy conversion efficiency, η_e for the nc-DSC was calculated to be approximately 9.5% at a light intensity of 9 mW/cm² (1/10 Sun). In comparison with the result in Fig. 3, we obtained I_{sc} = 15 mA/cm², V_{oc} = 760 mV and FF < 0.3 at a light intensity of 85 mW/cm² (direct sun). The I_{sc} and $V_{oc}\xspace$ values are comparable with the results from Grätzel's group [1,3]. However, the FF is low in our experiment, while Nazeeruddin et al. [3] reported a FF of 0.63 at a simulated solar light (870 W/m^2) using surface treated dye coated TiO₂ electrode with 4-tert-butylpridine and Γ/Γ_3 electrolyte in an acetonitrile solvent. The fill factor depends on the series resistances in the solar cell. We suggested that the fill factor in the cells used in this work affected by the choice of the solvent for the electrolyte with higher light intensity. R. Knödler et. al. [28] reported similar effects using propylene carbonate as a solvent with the same redox couple concentrations and simulated (1000 W/m²) solar light.

The photovoltaic external quantum efficiency or the spectrally resolved incident photon to converted electron efficiency IPCE (η_c) is defined as the

Journal of EEA, Vol. 25, 2008

number of electrons flowing through an external circuit under short circuit conditions per incident photon and is calculated from the spectrally resolved short-circuit current,

$$\eta_c[\%] = 1240/\lambda[nm] * I_{sc}[\mu A/cm^2]/I_{inc}[W/m^2],$$

where I_{inc} is the intensity of the incident light. Figure 6 shows a comparison between the spectral resolved photon to electron conversion efficiency, IPCE plotted at the right axis and the optical density at the left axis of a dye-sensitized nc-TiO₂ solar cell. One can sec very clearly, that the two curves have the same onset and spectrally resolved maxima at 536 nm. The maximum value of the photon to electron conversion efficiency of a dvesensitized nc-TiO₂ solar cell was calculated to be about 80% at 536 nm, which is comparable to carlier report [3]. The data were not corrected for the absorption and scattering of incident light, which was reported in [3] to 10-15% by the glass. Furthermore, the decline of the IPCE above 600 nm toward the red caused by the decrease in the extinction coefficient of RuL₂ (NCS)₂ and the drop of the IPCE 500 and 400 nm due to the filtering of light by the I_3 anions reported by Nazeeruddin et. al. [3].



Figure 6 Spectral resolved photon to electron conversion efficiency, IPCE (solid circles) of a dye-sensitized nanocrystalline TiO_2 solar cell (plotted on the right axis) through illumination from TiO_2 side by xenon arc lamp and optical absorption (open circles) for nanocrystalline TiO_2 film coated with RuL₂ (NCS) ₂: 2 TBA dye, where L stands 4,4'-dicarboxylato-2,2'-bipyridyl (plotted on the left axis). The dependence of the short circuit current and open circuit voltage on the incident light intensity was shown in Fig. 7(a) and (b), respectively. The short circuit current of the nc-DSC increases with the increasing light intensity and is proportional to I^{α}_{inc} ($I_{sc} \sim I^{\alpha}_{inc}$), where α is the power factor (the scaling exponent) and Iinc is the incident light. Thus, the plot of log of I_{sc} versus log of I^{α}_{inc} yields a straight line with a fitted scaling exponent $\alpha = 0.99$ between 0.1 mW/cm² and 10 mW/cm². At higher intensities I_{sc} is limited either by recombination or saturation behavior. Scaling exponents close to 1 are expected for devices, where both electron and hole transport are comparably efficient. The dependence of the open circuit voltage of the nc-DSC was plotted as a function of incident light intensity in Fig. 7(b). The open circuit voltage increases rapidly at lower intensities and begins to saturate at higher intensities. This is a phenomena similar to that seen in other organic semiconductor photoelectrode systems and is that expected for Schottky junction solar cells [29], according to the following relationship:

$$V_{oc} = nkT/q \ln(I_{ph}/I_0 + 1)$$

= nkT/q ln(I_{ph}/I_0) for I_{ph} > I_{0},

where *n* is an empirical coefficient arising from non-idealities in the junctions (n = 1 for an ideal Schottky barrier), *T* is the absolute temperature, k is the Boltzmann constant, q is the electronic charge, I_{pk} is the light generated current, and I_0 is the reverse saturation current. As can be seen from the relationship, V_{oc} increases logarithmically with the light intensity, because I_{ph} is linearly proportional to the incident light intensity. The V_{oc} increases by 82 mV per decade of light intensity. This is almost comparable to the $kT/q \cong 59$ mV per decade expected from a solar cell built using an inorganic semiconductor material, in which bulkgenerated carriers are separated by an internal electric field [30].



Figure 7 Dependence of the short circuit current (a) and open circuit voltage (b) versus incident monochromatic light intensities $(Ar^+ \text{ laser at } 488 \text{ nm})$ for illumination through the front contact of dycsensitized nanocrystalline TiO₂ solar cells. The nc-TiO₂ film thickness was 9 µm. Line is fits to a power law in Fig. 7(a), whereas the inset shows the variation of V_{oc} versus log I_{ine} in Fig.7(b).

CONCLUSIONS AND RECOMMENDATIONS

In conclusion, the sintering conditions influence the film porosity, pore-size distribution, light scattering and electron percolation across nanoporous network and consequently affect the *nc*-DSCs efficiency. The enhancement of the I_{sc} of the dye-sensitized anatase $nc-TiO_2$ electrodes indicating that the absorbed dye concentration increases with annealing temperature over the range of 100 - 450 °C due to an increase of the porous TiO_2 film thickness. Thus this can be achieved by use a small TiO_2 particles with a high internal surface area and by tuning the TiO₂ layer thickness. The increase of Voc with annealing temperature at a given I_{sc} is due to an increased light-harvesting efficiency and very low recombination rate. Furthermore, a high current density requires maximizing light absorption by the dye.

The overall energy conversion efficiency, η_e , of these solar cells presented here is calculated to be around 9.5% in 9 mW/cm² (1/10 Sun) and an IPCE of 80%. We have observed that a major limiting factor for the energy conversion efficiency of dyesensitized nanocrystalline TiO2 solar cells at higher light intensity is the low FF. We suggested that decreasing the viscosity of the solvent increase both the FF and I_{sc} , due to better diffusion of the redox couple. This means, the output of these solar cells is significantly affected by the electrolyte. Thus, a solvent with a relatively lower viscosity, such as acetonitrile is important in order to achieve high efficiencies (increased liquid viscosity leads to mass transfer limitations of the redox couple) compared polyethylene. to Using AFM spectroscopy investigations we have directly demonstrated the relationship between film morphology and photovoltaic performance.

In contrast to crystallinc silicon PV modules, the DSC is particularly suited to target markets in temperate and tropical climates, because of its good temperature stability and its excellent performance under indirect radiation, during cloudy conditions. The DSC is also particularly suited to indoor applications that require stability of voltage and power output over a wide range of low light conditions. A key market for low power cells is in a consumer- and professional battery charging particularly where the light levels may vary significantly. Although its lifetime and power conversion efficiency is less than the silicon-based system solar cell, the DSC has the following advantages:

Journal of EEA, Vol. 25, 2008

- Much less sensitive to angle of incidence of radiation, good in refracted and reflected light;
- Performs over a much wider range of light conditions due to the high internal surface of Titanium ("light sponge") - can be designed for operation at very low light;
- Can be designed to operate optimally over a wide range of temperatures;
- Much less sensitive to a partial shadowing;
- Option for transparent modules so can be used for day lighting, roof lighting, and displays;
- DSC production needs only commonly available non vacuum processing equipment, making it vastly cheaper to set up facilities; and
- DSC has significantly lower embodied energy than all other forms of solar cell.

Therefore, dye-sensitized solar cells have attracted considerable interest as low-cost alternatives and remarkable advantages to conventional inorganic photovoltaic devices.

ACKNOWLEDGEMENTS

This work was performed within the Christian Doppler Foundation's dedicated Laboratory for Plastic Solar Cells funded by the Austrian Ministry of Economic Affairs and Quantum Solar Energy Linz Ges.m.b.H. Financial supports from Austrian Foundation for Advancement of Science (FWF P12680 CHE) and from the European Commission JOULE III Programme (JOR3-CT98-0206) are gratefully acknowledged.

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72