



MONASH University

**‘Advancing the performance of photocathode
dye-sensitized solar cells for their application
in tandem solar cells’**

Thesis submitted for the Degree of Doctor of Philosophy

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M.Sc. (Mechanical Engineering)

B.Eng. (Production)

School of Chemistry

2013

Notice 1

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Abstract

The aim of this thesis is to improve the performance of photocathode DSCs for their use in tandem DSCs. The scale of solar photovoltaic technology application is limited because of high costs. The research in the area of solar photovoltaic is focused on low cost technologies. Dye-sensitized solar cells (DSCs) are one of the attractive technologies for its projected low manufacturing costs. These solar cells are lagging behind in conversion efficiencies compared to other technologies available in the market.

The efficiency of conventional DSCs can be improved with tandem solar cell architecture. In tandem solar cell approach, a photoanode DSC (n-DSC) is assembled with a photocathode DSC (p-DSC). Theoretically, efficiency improves due to the increase in the range of absorption spectra. However, the tandem DSC efficiencies are lagging behind the theoretical ones; because of underperforming photocathode DSCs. The p-DSC produces low photocurrents (5.4 mA/cm²) and has low efficiency (0.42 %) due to low open circuit voltages (350 mV).

During this work, the application of microball structured NiO in p-DSC improved dye loading and p-DSC short circuit photocurrent (7.0 mA/cm²). The high efficiency p-DSCs using a cobalt ethylenediamine based electrolyte are reported in this thesis. Cobalt ethylenediamine electrolyte has favorable rest potential which helped to improve the p-DSC efficiency up to 1.3 %. A p-type semiconductor with high ionization potential (CuCrO₂) improved V_{oc} of p-DSC up to 740 mV. A transparent thiolate/disulfide based electrolyte has been studied and investigated as an alternative electrolyte in p-DSCs and tandem pn-DSCs.

General Declaration

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes two original papers published in peer-reviewed journals and two submitted publications for review. The core theme of the thesis is p-type dye-sensitized solar cells. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the School of Chemistry under the supervision of Assoc. Prof. Udo Bach and Prof. Leone Spiccia.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of chapter 3, 4, 5, and 6 my contribution to the work was design and execution of experiments including all the solar cell fabrication, characterization of solar cells, optimization of device performance, data analysis; drafting and editing all publications. The p-DSC sensitizers used throughout the thesis were synthesized and provided by Günther Götz, Martin Weidelener, Amaresh Mishra, and Peter Bäuerle (Ulm University, Germany). Qiang Wu and Zheng Hu (Nanjing University, China) delivered The NiO microballs used in chapter 3. Michelle Ma synthesized $[\text{Co}(\text{en})_3](\text{BF}_4)_3$ compound used in chapter 4 and chapter 5. Rishabh Bhargava prepared the electrolyte solution and PEDOT counter electrodes used in chapter 6. Dehua Xiaong and Wei Chen synthesized CuCrO_2 NPs used in chapter 5. Intensity modulated photocurrent, Intensity modulated photovoltage-spectroscopy and charge extraction measurements in chapter 4 were carried out on equipment build and designed by Dr. Noel W. Duffy (CSIRO Australia – Clayton) with help from Torben Daeneke, they also provided guidance in the interpretation of the

results. Satoshi Makuta and Dr Torben Daeneke supported the transient absorption measurements in chapter 5. The measurements were carried out under the guidance of Dr. Yasuhiro Tachibana (RMIT University, Australia) who designed and build the instrument.

Thesis chapter	Publication title	Publication status*	Nature and extent of candidate's contribution
3	Improved photocurrents for p-type dye-sensitized solar cells using nano-structured nickel(II) oxide microballs	Published	Experimental design, all experimental measurements, interpretation of results, drafting of the Manuscript
4	Highly Efficient p-Type Dye-sensitized Solar Cells based on Tris(1,2-diaminoethane)Cobalt(II)/(III) Electrolytes	Published	Experimental design, all experimental measurements, interpretation of results, drafting of the Manuscript
5	Improved Photovoltages for p-Type Dye-sensitized Solar Cells using CuCrO ₂ nanoparticles	Submitted	Experimental design, all experimental measurements, interpretation of results, drafting of the Manuscript
6	Thiolate/disulfide Based Electrolytes for p-Type and Tandem Dye-sensitized Solar Cells	Submitted	Experimental design, all experimental measurements, interpretation of results, drafting of the Manuscript

Signed:



(Satvasheel Powar)

Date: 14th May 2013

This thesis is dedicated to my beloved family.

Acknowledgements

This thesis had been possible only because of the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study.

First my utmost gratitude to my supervisors, Associate Professor Udo Bach and Professor Leone Spiccia, they supported me throughout my PhD. Many thanks to Professor Yi-Bing Cheng for help in networking with researchers from Nanjing University and Wuhan National Laboratory for Optoelectronics.

The assistance of all the DSC research team members at Monash University is greatly appreciated. Further, I would like to specially acknowledge the assistance of Peter Chen who mentored me in the beginning of my PhD, Fuzhi Huang for assistance with BET measurements, advices on IPCE, Solar simulator. Torben Daeneke, Andrew Nattestad, Dongchuan Fu for useful discussions and insights. I want to thank Rod Mackie for assistance with XRD measurements, Scott Watkins and Akhil Gupta for assistance with AC-2 measurements, George Lee for TEM measurement

Günther Götz, Martin Weideler, Amaresh Mishra, and Peter Bäuerle (Ulm University, Germany) for the p-DSC dye supply. Qiang Wu and Zheng Hu (Nanjing University, China) for the NiO microballs synthesis. Michelle Ma for $[\text{Co}(\text{en})_3](\text{BF}_4)_3$ synthesis. Rishabh Bhargava for the electrolyte solution and PEDOT counter electrodes preparation. Dehua Xiaong and Wei Chen for synthesizing CuCrO_2 -NPs (Wuhan National Laboratory for Optoelectronics); Noel W. Duffy (CSIRO Australia – Clayton) for assistance with IMVS, IMPS and charge extraction measurements and analysis; Satoshi Makuta and Dr. Yasuhiro Tachibana (RMIT University, Australia) for their help in the transient absorption measurements and analysis. Further, I appreciate help from administrative staff of Materials Engineering department and School of Chemistry

Finally, I would like to thank my parents who encouraged me to start my PhD and my wife Amruta who supported me to go on.

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Abbreviations

ACN	Acetonitrile
APCE	Absorbed photon to charge carrier conversion efficiency
BZN	Benzonitrile
CV	Cyclic voltammetry
ΔOD	Change in optical density
DSC	Dye-sensitized solar cell
Fc/Fc ⁺	The ferrocene / ferrocenium redox couple
FF	Fill factor
FTO	Fluorine doped tin oxide
FWHM	Full width at half maximum
GDP	Gross domestic product
GuSCN	Guanidinium thiocyanide
η	Energy conversion efficiency
HOMO	Highest occupied molecular orbit
IMPS	Intensity modulated photocurrent spectroscopy
IPCE	Incident photon to charge carrier conversion efficiency
J-V	Current density-potential measurements characterization
J _{sc}	Short circuit current density
LED	Light emitting diode
LHE	Light harvesting efficiency
LiTFSI	Lithium bis(trifluoromethane)sulfonamide
LUMO	Lowest unoccupied molecular orbit
MPN	4-Methoxypropionitrile
n-DSC	n-type dye-sensitized solar cells
NHE	Normal hydrogen electrode
NiO	Nickel(II) oxide
NMR	Nuclear magnetic resonance
NP	Nanoparticles
p-DSC	p-type dye-sensitized solar cells
PEDOT	Poly(3,4-ethylenedioxythiophene)
TAS	Transient absorption spectroscopy
tBP	<i>tert</i> -butylpyridine
TCO	Transparent conducting oxide
τ_d	Mean charge transport time
τ_n	Electron lifetime
τ_{obs}	Observed half life
UV-Vis	Ultraviolet and visible light
V _{oc}	Open circuit voltage

Chapter 1

Solar Energy – A general overview

“Energy is at the heart of the quality of life.”¹ The world’s energy demand is growing rapidly with population and increasing standards of living. The global population will grow to about nine billion people by 2040. Hence, the global energy demand will rise by 30% in 2040 compared to 2010. The world will experience more than double the economic output and prosperity.² Approximately, 70% of globally used electricity is generated from fossil fuels.³ In 2006, the world’s growing demand for oil accounted to nearly 1,000 barrels a second.⁴ This demand is projected to grow to 1300 barrels a second (118 million barrels per day) by 2030 to meet the expected demand.⁵ The International Energy Agency’s (IEA) key scenarios in the World Energy Outlooks (WEO) and Energy Technology Perspectives (ETP) demonstrated that by 2050, oil demand would rise by about two-thirds; coal demand would be almost triple, and gas demand would more than double compared to its demand in 2009.⁶

It is presumed with this consumption rate, that the world will run out of conventional sources of energy within this century.⁷ Electricity generation accounts for about 40% of global green house gas emissions and these emissions are estimated to grow by 58% by 2030.³ This will seriously affect the ecological life of the Earth. Renewable energy sources such as sun, wind, and biomass will need to be utilized to overcome this impending energy crisis.⁴ Renewable energy sources will help in conserving scarce conventional sources of energy as well as minimizing green house emissions.

Among the various renewable energy producing technologies, this thesis will focus particularly on solar photovoltaic energy. The photovoltaic devices convert sunlight directly into electrical energy. Direct utilization of solar radiation to produce electricity is an ideal way to use nature's renewable energy sources. In contrast to conventional power enclosures photovoltaic power can be generated among people in decentralized manner and therefore is useful in remote areas or for mobile applications avoiding losses associated with power transmission and costs. The solar panels operate without noise, emissions, and need very little maintenance. The sun produces an enormous amount of energy as heat, and light. The earth and its atmosphere receive continuously 1.7×10^{17} W of radiation from the sun.⁸ It is believed that the present global energy requirements can be fulfilled with a small fraction of the solar energy that reaches the earth. Considering 10% efficient solar panel approximately 0.16% of the earth’s land surface is required to harvest 20 TW of electrical energy covering global energy consumption (Figure 1).⁹ The huge theoretical potential of solar electricity makes it attractive for large-scale utilization. Solar electricity is a rapidly growing energy industry (Figure 2).¹⁰ Solar cells have found markets in a variety of applications ranging from consumer electronics (e.g. calculators) to centralized megawatt scale power plants (as big as 550 MW).¹¹



Figure 1. Global map showing the land needed for 20 TW (equivalent to global electrical energy consumption) solar power generation with 10% efficient solar cells (Source: R. F. Service, *Science*, 2005, **309**, 548-551)

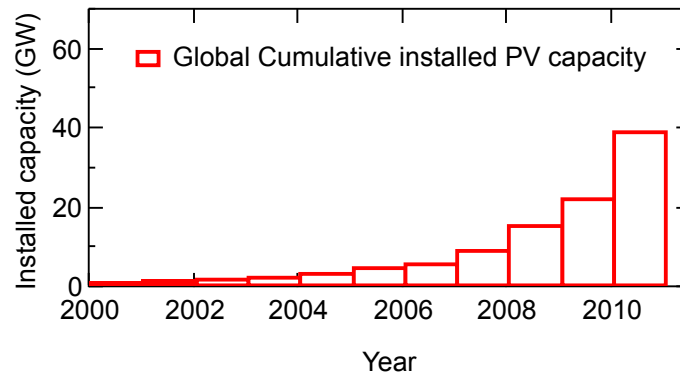


Figure 2. Year wise global cumulative installed PV capacity (Data source: the European Photovoltaic Industry Association)

Despite significant developments, the total installed global PV capacity currently only covers 0.5% of the global energy demand.¹⁰ The photovoltaic module costs and their efficiencies have been major limiting factors in the achievement of huge solar energy prospect. Another limitation of the solar photovoltaic is that it requires an energy storage device to store non-consumed energy that can be used at other times like during the night hours.

Figure 3 shows historic and present efficiency records for solar cell research published by the National Renewable Energy Laboratory, USA.¹² Martin Green has divided all solar photovoltaic technologies in three generations.¹³ The first generation includes single junction solar cells consisting of crystalline silicon pn-junctions. Presently, this generation is dominating the commercial market.¹⁴ First generation solar cells have a quite high efficiency, but highly

crystalline, pure silicon is needed. Since producing the pure silicon requires energy intensive and expensive processes, the prices for these solar cells are high.¹⁵ This generation of solar cells has matured to a stage where cost reductions are difficult to achieve. First generation solar cells are approaching the single junction solar cell's theoretical (the Shockley-Queisser) efficiency limit of 31% under one sun illumination (AM1.5G).¹⁶⁻¹⁹ The Shockley-Queisser limit (detailed balance limit) is the maximum theoretical efficiency of a solar cell using one single p-n junction.¹⁶

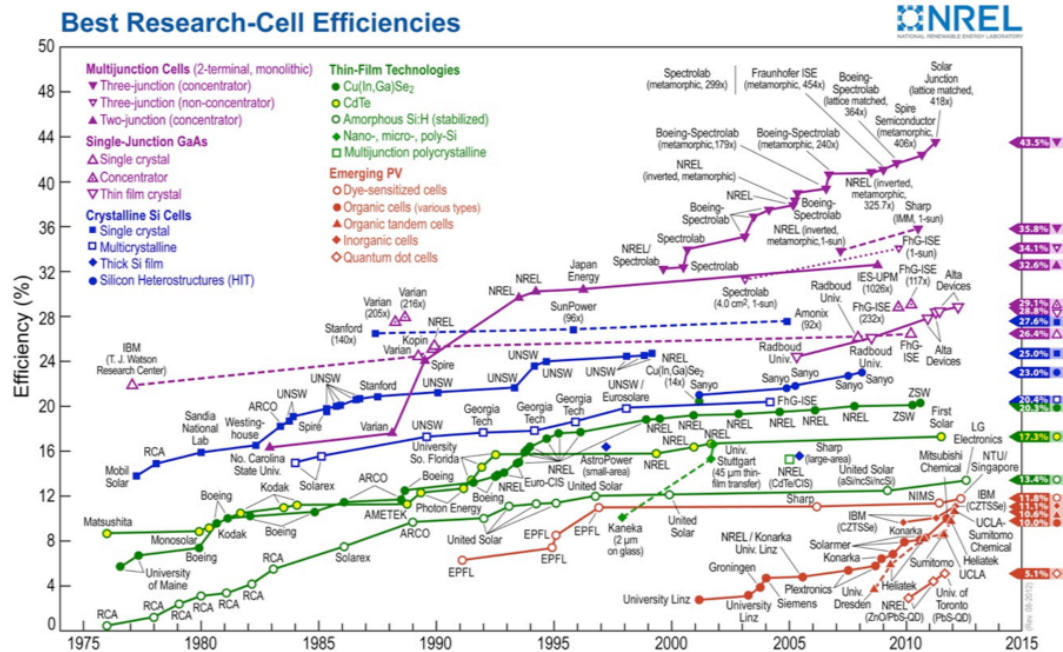


Figure 3. Historic and present record solar cell research efficiencies of the major photovoltaic technologies (Data source: National Renewable Energy Laboratory)

The second generation solar cells have been developed with low manufacturing costs and more moderate efficiencies. This generation of solar cells is also known as thin film solar cells. The second generation solar cells which have made it to market successfully include amorphous silicon (a-Si), copper indium gallium selenide (CIGS), cadmium telluride (CdTe).

Nanotechnology is a booming trend in science and technology.^{20, 21} The nanotechnology trend has recently emerged in the field of photovoltaic energy conversion. Research and development of nanoscale materials alongside its application in expected to lead to the realization of low-cost solar cells in the future.²² Dye-sensitized solar cells (DSCs) are one such application of nanotechnology. The highest reported conversion efficiency of DSCs has reached 12.3%.²³ The projected low manufacturing costs of DSCs have attracted attention as an alternative second generation solar cell technologies. Being single junction solar cells, the second generation solar

cell technologies are still constrained by the same theoretical (the Shockley-Queisser) efficiency limit of 31% as first generation technologies.^{18, 19}

To overcome the single junction theoretical limit and to reduce the Shockley-Queisser loss researchers came up with a solution by creating a multi junction solar cell. The broad solar emission spectrum is then divided into different energy ranges to convert each range with a cell of a well-matched bandgap. The theoretical limit of such a tandem solar cell with two junctions can be 43% as opposed to 31% for single junction solar cells. The maximum theoretical efficiencies with infinite junctions would be limited to 85%.^{17, 18} Martin Green has termed this type of solar cells, including a range of other architectures, which are capable of exceeding the Shockley-Queisser limit of 31%, as third generation photovoltaics.^{13, 24-26}

The third generation solar cell technique has been demonstrated in DSCs; assembling high efficiency dye-sensitized photoanodes (n-DSCs) and dye-sensitized photocathodes (p-DSCs) in series connection. According to Kirchhoff's circuit law, photovoltages are additives in this type of tandem architecture while the photocurrent is limited by the weakest performing photoelectrode. The demonstrated tandem dye-sensitized solar cells (pn-DSCs) were limited in efficiency due to its underperforming photocathodes.^{27, 28} This thesis is focused on optimizing the performance of p-DSCs for its application in pn-DSCs.

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Chapter 2

Literature review

2.1 Solar photovoltaic

A solar cell is a device that converts sunlight into electricity. Solar cells generate a current and a voltage via the absorption of photon energy from sunlight. In practice, the most common solar cell designs are based on semiconductor materials in the form of a p-n junction (Figure 1). Solar operation involves two key processes: 1) the absorption of incident photons to create electron-hole pairs and 2) the transport of these high-energy charge carriers to the external circuit to dissipate the gained power.¹ When a solar cell is illuminated with light, electron-hole pairs (excitons) are generated due to the absorption of incident photons that have an energy greater than the bandgap (E_g). These generated charge carriers are separated by the electric field that exists at the p-n junction and then diffuse to the junction. These light-generated carriers flow through the external circuit, where they dissipate the gained power.

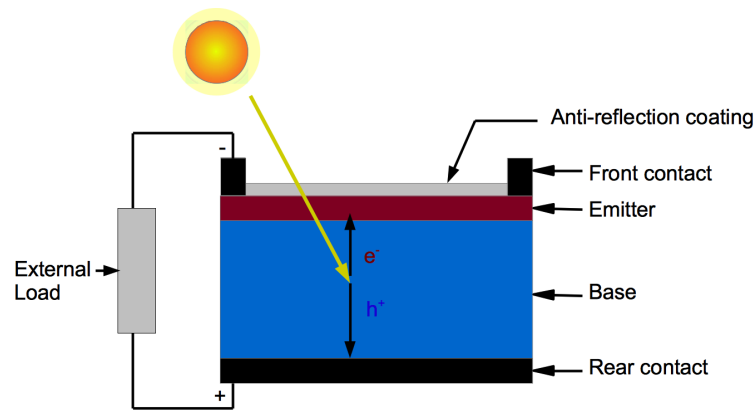


Figure 1: Cross-section of a single p-n junction solar cell. The anti-reflection coating minimizes reflection losses. The emitter (an n-type semiconductor) and base (a p-type semiconductor) are connected to an external load.

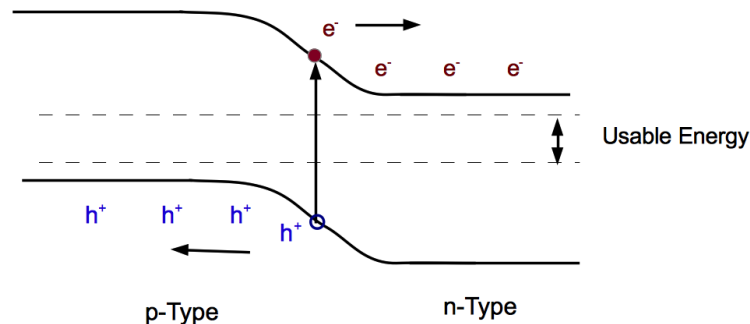


Figure 2: Band diagram of a p-n junction under light irradiance; the formed excitons are separated by the built-in potential.

Solar cell energy generation depends on the absorption spectrum (the wavelength of the harvested light), which correlates to the bandgap of the semiconductor material. The bandgap of a semiconductor corresponds to the minimum amount of energy that is required to excite an electron from the valence band to the conduction band. Photons with an energy equal to or greater than the semiconductor bandgap can be used to produce electrical energy. Hence, each semiconductor is limited to converting just a part of the solar spectrum. A wide bandgap semiconductor would absorb only the ultraviolet region of the solar spectrum, whereas a narrow bandgap semiconductor would absorb a wider range of wavelengths. However, excitons with an energy greater than the bandgap dissipate excess energy as heat and cannot be used to produce useful power.^{2,3}

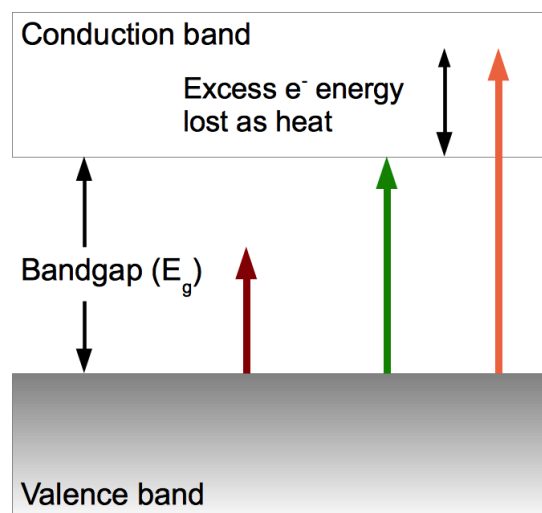


Figure 3: Photons (red) with an energy less than the bandgap of the semiconductor cannot drive an electron to the conduction band of the semiconductor. Photons (orange) with an energy greater than the bandgap of the semiconductor can excite an electron from the valence band to the conduction band, but the electron energy greater than the bandgap dissipates in the form of heat. The useful part of the photon energy for producing electrical energy equals the band gap (green).⁴

The theoretical maximum efficiency of a solar cell depends on the bandgap of the used semiconductor. William Shockley and Hans Queisser proposed a detailed balance limit (a maximum theoretical efficiency) for a single p-n junction solar cell based on the assumption that every incoming photon could create only one exciton; the excitons with an energy greater than the bandgap dissipate the excess energy as heat.⁵ The maximum theoretical efficiency of a solar cell (the Shockley–Queisser limit or the detailed balance limit) that uses a single p-n junction (with a bandgap of 1.3 eV) under one sun illumination (1000 W/m^2 , AM1.5) is 31%.⁵ Figure 4 shows the highest achieved efficiency of 28.3% (green) and the losses that are associated with it,

such as entropy-related losses (blue) and energy losses due to thermalization.⁶

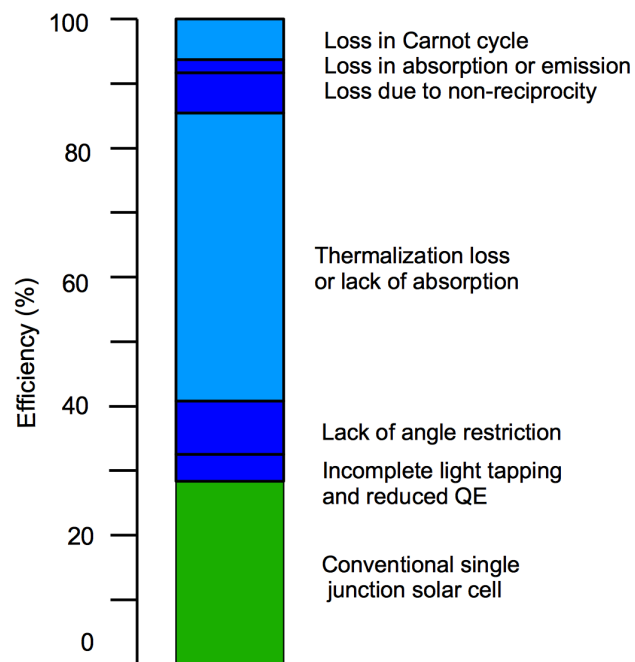


Figure 4: Maximum achieved efficiency (green) and associated losses for a single junction solar cell (blue and cyan).⁶

2.2 Dye-sensitized solar cells (DSCs)

The estimated low manufacturing costs of DSCs have attracted the attention of researchers because DSCs can be an alternative to traditional p-n junction solar cells.^{7, 8} In conventional p-n junction solar cells, the semiconductor conducts both the key processes of light absorption and charge carrying. DSCs work in a different manner, i.e., the light absorbing sensitizer is anchored to the surface of a wide bandgap semiconductor and the wide bandgap semiconductor acts as a charge collector.

The maximum reported conversion efficiencies for lab-scale test cells are up to 12.3% under one sun condition (1000 W/m^2 , AM1.5G).⁹ Sub-modules that consist of eight parallel-connected cells with an aperture area of 17 cm^2 have achieved a certified conversion efficiency of 9.9%.^{10, 11}

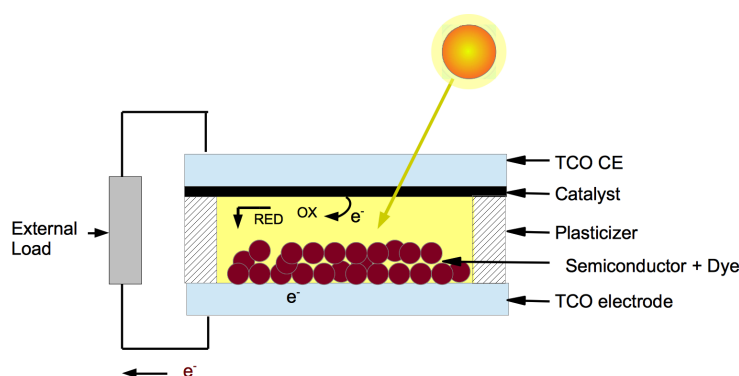


Figure 5: Cross-section of a typical dye-sensitized solar cell (DSC).

The cross-section of a DSC is shown in Figure 5. A DSC typically consists of a transparent conductive oxide (TCO) electrode that is coated with a wide bandgap mesoporous semiconductor. A monolayer of a dye is adsorbed onto the mesoporous semiconductor. A counter electrode with a catalytic coating is assembled with the working electrode (the dye-coated semiconductor electrode). An electrolyte consisting of a redox mediator, such as iodide/triiodide (I^-/I_3^-), is filled between the two electrodes.

Figure 6 shows the band energy diagram and a schematic representation of the charge transfer process in a typical DSC that is based on an n-type semiconductor (n-DSC). Light absorption is performed by the dye monolayer that is anchored to the surface of the wide bandgap semiconductor (Figure 6). Upon light absorption, an electron is excited from the dye's HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital).

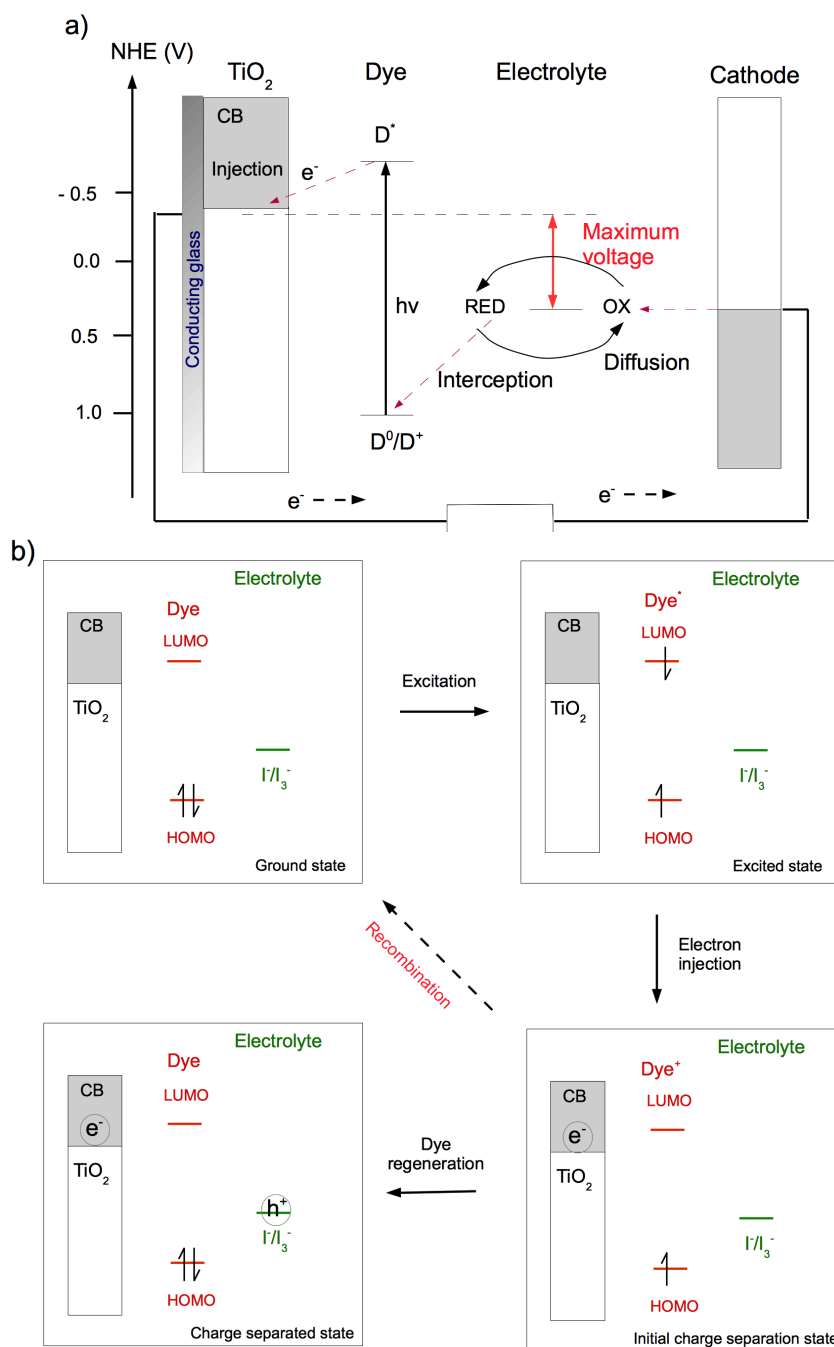


Figure 6: a) Band energy diagram and operating principle of a typical TiO_2 -based n-DSC.¹² b) Schematic representation of the charge transfer process in a typical TiO_2 -based n-DSC. The photoexcitation of the sensitizer is followed by electron injection into the conduction band of the oxide semiconductor film. The dye molecule is regenerated by the redox system, which is regenerated itself at the counter electrode by the electrons that pass through the load.

If the dye's LUMO level is more positive (vs. the vacuum scale) than the conduction band of the n-type semiconductor (typically TiO_2), the excited electron is injected into the conduction band of the semiconductor, leaving behind an oxidized dye cation (dye^+). The injected electron diffuses through the semiconductor to the TCO electrode. The dye cation is reduced (regenerated) by the

reduced species of the redox couple. The hole migrates to the counter electrode through the electrolyte. The electron migrates through the external load and completes the circuit at the counter electrode, where it reduces the triiodide to iodide.^{8, 13}

Undesirable charge recombination reactions can limit the solar cell (DSC) efficiency. The injected electron in the conduction band of the semiconductor can recombine with the dye cation. Another possible recombination is between the injected electrons and the oxidized mediator.^{14, 15}

The theoretical maximum voltages of n-DSCs correspond to the difference between the redox potential of the redox mediator and the quasi-Fermi level of the n-type semiconductor under illumination.

Generations of solar cells

Martin Green has categorized all solar photovoltaic technologies into three generations (first, second and third).¹⁶⁻²¹ The first generation includes single junction solar cells that are based on silicon wafers. Crystalline silicon solar cell technology has reached certified efficiency levels of 25% for a lab-scale cell (4 cm²) and 23% for a module (778 cm²).^{22, 23}

Second-generation solar cells (thin-film solar cells) are made from thin layers of semiconductor materials a few microns thick. The combination of using less material and lower-cost manufacturing processes makes second-generation solar cells cheaper than first-generation solar cells. However, second-generation solar cells are less efficient than first-generation ones. Recently, second-generation solar cells have made rapid progress, thus narrowing the performance gap between these cells and first-generation solar cells.¹¹ Second-generation solar cells that are based on CIGS (CuInGaSe₂) have already reached a certified efficiency of 19.9% for lab-scale solar cells (aperture area of 0.996 cm²).²⁴ Dye-sensitized solar cells belong to the second-generation family with a highest certified efficiency of 11.4% (for a cell area of 0.23 cm²). The previous recorded certified efficiency (11.1%) was based on a cell area of 1 cm².¹¹

The first two generations of solar cells are based on a single junction and are thus constrained by the same theoretical (Shockley-Queisser) efficiency limit of 31% under one sun illumination.^{5, 25, 26} With an increase in light intensity, the Fermi level increases, approaching the conduction band edge and leading to higher voltages. With an infinite concentration of direct sunlight, this efficiency limit can increase up to 40.8%.^{25, 26} The principal limiting factor for these single junction solar cells is the thermalization losses that are described in Figure 3. Using multiple semiconductors with various bandgaps, these losses can be minimized by absorbing a broader section of the solar spectrum, as shown in Figure 7. In the case of a two-junction solar cell, the first wide bandgap material can absorb high energy photons and pass on the remaining photons to the second junction. The second junction with a narrower bandgap semiconductor can absorb the remaining photons. The theoretical limit of such a two-junction solar cell design with optimized bandgap materials can increase up to 42.9% under one sun illumination (AM 1.5G) and up to 55.9% with concentrated direct sunlight.^{25, 26} Increasing the number of junctions to three, four and infinite can increase the conversion efficiency up to 49.3%, 53.3% and 68.2%, respectively, under one sun illumination. The corresponding efficiencies under concentrated sunlight would be 63.8%, 68.8% and 87.8%, respectively. To date, the highest reported (and certified) solar cell

efficiency of 43.5% was achieved using three junctions (GaInP/GaInAs/Ge) under a 418-fold sunlight concentration.^{11, 27, 28}

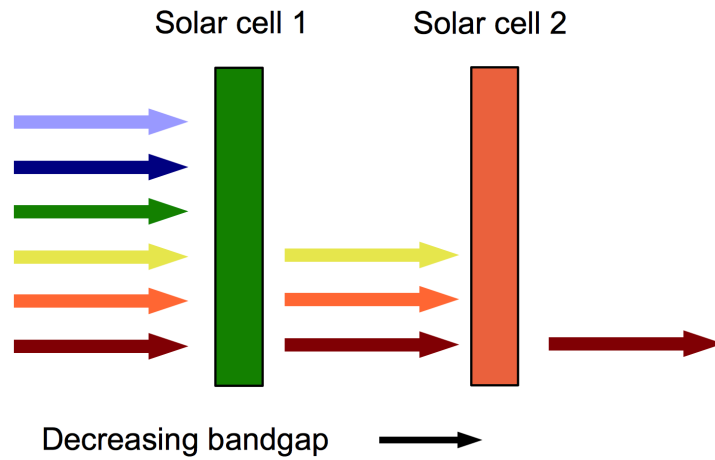


Figure 7: Schematic representation of a two-junction device; the first wide bandgap semiconductor materials can harvest high-energy photons. The unabsorbed low-energy photons are transmitted to the second semiconductor material, which can absorb lower energy photons.

Martin Green has termed this type of solar cell, including a range of other architectures that can exceed the Shockley-Queisser limit of 31%, as third-generation photovoltaics.¹⁶⁻²¹ The concept of third generation is expected to increase the efficiencies compared with those of low-cost single junction solar cells.

The other third-generation concepts include hot carrier solar cells, multiband cells and thermophotovoltaic and thermophotonic devices. Hot carrier solar cells aim to reduce collision losses. Hot carrier solar cells can extract charges without inelastic collision losses. An excited electron in the conduction band can be extracted to the conduction band edge without thermalizing. The concept of thermophotovoltaics utilizes a light from a heated body other than the sun as illumination. All of these third-generation solar cell concepts have been explained in depth by Martin Green in his book on third-generation photovoltaics.¹⁶

2.3 Tandem solar cells

The concept of tandem (or multi-junction) solar cells, which consist of several sub-cells in series or in parallel, has been developed and demonstrated in different solar cell technologies (e.g., GaInP/GaAs/GaInAs). The efficiencies of tandem solar cells have been shown to be beyond the theoretical limit of 31%.¹¹

Dye-sensitized solar cells (DSCs) have attracted the attention of researchers due to their low projected costs.^{7, 8} The highest reported conversion efficiencies for dye-sensitized photoanodes (n-DSCs) are up to 12.3% under simulated sunlight (1000 W/m², AM1.5).⁹ These record efficiencies still lag behind those of conventional silicon solar cells and of some other thin-film solar cell technologies.¹¹ Researchers have been endeavoring to improve the efficiencies of n-DSCs by altering the semiconductors, sensitizers and redox mediators. One attractive alternative approach for improving the efficiencies is to build third-generation tandem dye-sensitized solar cells (pn-DSC).

2.3.1 Stacked model tandem solar cells

a) Parallel-connected stacked tandem DSCs

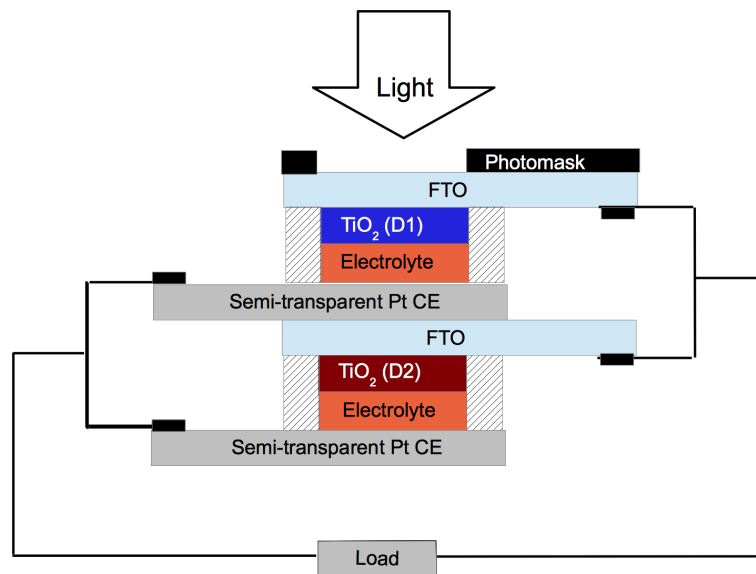


Figure 8: Schematic representation of a stacked model tandem solar cell; in a stacked model tandem, two solar cells are stacked on top of each other. The incident light passes through the first cell before reaching the second solar cell.²⁹

In 2004, Kubo *et al.* and Durr *et al.* proposed an extremely simple multi-stacked tandem DSC structure (Figure 8).^{29, 30} These tandem structures consist of two n-DSCs connected in parallel and stacked on top of one another. The incident light passes through the first cell before reaching the second solar cell. In parallel-connected tandem solar cells, the photocurrents are added, and the photovoltage is limited by the lower photovoltage-producing solar cell. Kubo *et al.* reported such tandem solar cells with efficiencies of up to 7.6% and a maximum open circuit voltage (V_{OC}) of 690 mV. Durr *et al.* reported an efficiency of 10.5% with a corresponding V_{OC} of 545 mV. This type of tandem structure could surpass the Shockley-Queisser limit if dyes with complementary absorption spectra are used. By using the near-IR absorbing SQ1 dye in the bottom cell of a parallel-connected tandem solar cell, Fan *et al.* reported an efficiency of 8.29%.³¹

Scott *et al.* reported an optically transparent cathode with a layer of cis-dichloro-bis(4,4'-dicarboxy-2,2'-bipyridine)osmium(II) for use in this type of stacked tandem structure.³² Yanagida *et al.* optimized this type of tandem structure using an N719-sensitized top cell and a near-infrared-responsive bottom cell. The authors reported lab conversion efficiencies of 11% and a certified conversion efficiency of 10.6% under one sun condition (AM 1.5, 1000 W/m²).³³ Ito *et al.* reported a V_{OC} of 1.8 V for such a tandem architecture.³⁴

b) Series-connected stacked tandem DSCs

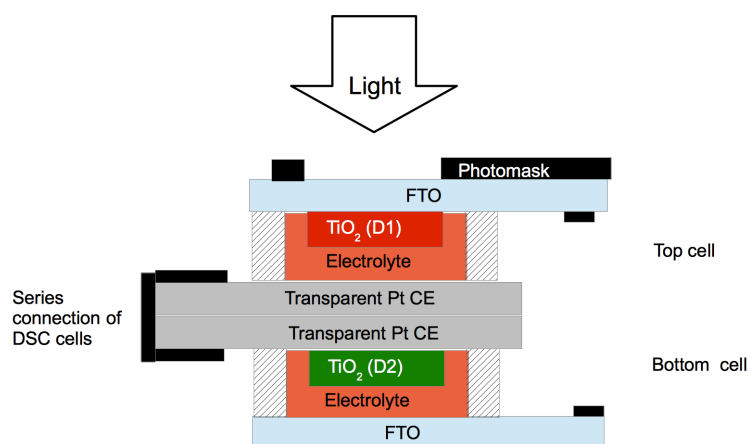


Figure 9: Schematic representation of a series-connected stacked tandem solar cell.³⁵

Yamaguchi *et al.* reported a similar tandem structure for series-connected solar cells. In series-connected tandem solar cells, the photovoltages are added, and the photocurrent is limited by the lower photovoltage-producing solar cell. The reported efficiency for this type of series-connected tandem solar cell was 8.8% with a V_{OC} of 1.3 V. The top cell was sensitized with NKX-2677, and

a black dye was used for bottom cell sensitization.³⁵ These tandem structures increase the solar cell efficiencies compared to those of the individual components, but this structure may not reduce the cost per watt for tandem solar cells because the design is based on two complete solar cells.

2.3.2 DSC tandem solar cells combined with other PV technology

a) DSC/CIGS

With a design similar to that of parallel-connected stacked tandem solar cells, DSCs have been reported that integrate other types of photovoltaic devices, such as CIGS. Liska et al. demonstrated such a solar cell using a DSC as a top cell and a copper indium gallium selenide (CIGS) thin-film solar cell as a bottom cell and reported an efficiency of ~15%.³⁶ Researchers are investigating and optimizing DSC/CIGS tandem solar cells. Recent reports also include a thorough analysis of the electronic and optical losses, as well as photocurrent optimization using various proportions of CIGS and surface treatments.^{34, 37-41}

b) DSC/a-Si

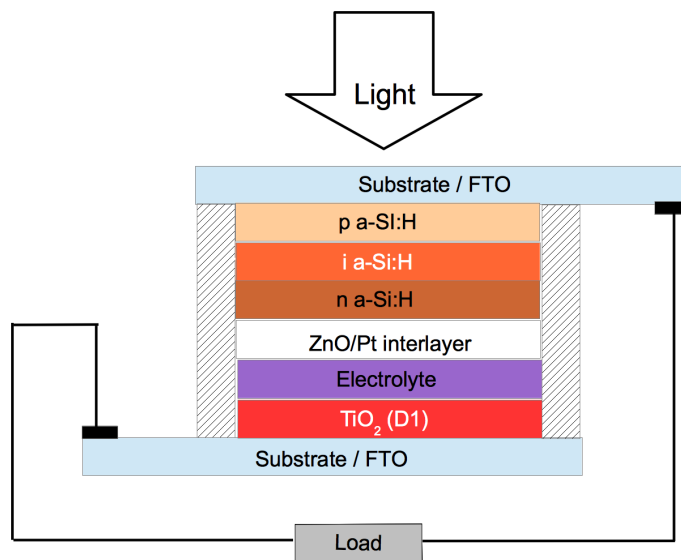


Figure 10: Schematic representation of a stacked model DSC/a-Si tandem solar cell. The light passes through the a-Si solar cell before reaching the DSC.⁴²

Hao et al. reported a DSC/a-Si solar cell that used a series-connected tandem solar cell architecture. Figure 10 shows the implemented design. This tandem solar cell design delivered

J_{SCS} of up to 10.61 mA/cm^2 and a V_{OC} of 1.45 V with an overall efficiency of 8.31% under one simulated sun (1000 W/m^2 , AM 1.5 G).⁴²

c) DSC/BHJ

Another application of the series-connected tandem solar cell architecture was demonstrated by Bruder *et al.* and combined a solid state n-DSC with a ZnPc/ C_{60} -based bulk-heterojunction (BHJ) solar cell.⁴³ The BHJ device was evaporated onto the solid-state device to form a tandem solar cell, as shown in Figure 11. DSC/BHJ tandem solar cells have been reported to attain conversion efficiencies of up to 6% and high open circuit voltages (V_{OCs}) of up to 1.36 V .

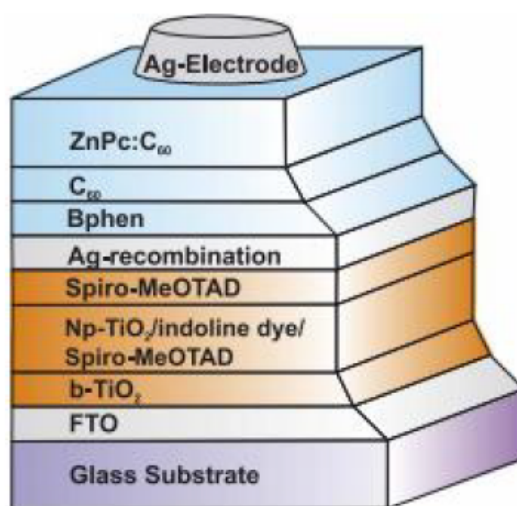


Figure 11: Schematic representation of DSC/BHJ tandem solar cells.⁴³

2.3.3 Two photoanode solar cells with a common counter electrode

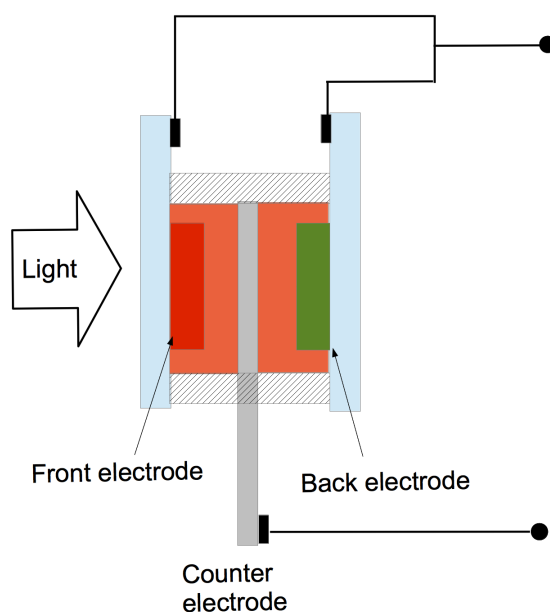


Figure 12: Schematic representation of the tandem solar cell that was proposed by Murayama and Mori using two photoanodes with a common counter electrode.^{44, 45}

Murayama and Mori proposed and demonstrated another tandem DSC architecture in which two photoanodes face each other and have a common counter electrode (a Pt mesh sheet) between them (Figure 12).^{44, 45} This architecture uses a common electrolyte for both solar cells. To optimize this architecture, different semiconductors can be used. However, V_{OC} matching for both sides of the tandem solar cell would be difficult using the same electrolyte system. The maximum reported efficiency for such an architecture is 4.7%.^{44, 45}

2.3.6 Photocathode-photoanode tandem solar cells

In n-DSCs, the photocurrent results from dye-sensitized electron injection into n-type semiconductors, such as TiO_2 , whereas in p-DSCs, electron transfer is from the valence band of the p-type semiconductor (NiO is the most commonly used to date) to the photoexcited dye.^{46, 47} These complementary responses provide an opportunity to assemble n-DSCs and p-DSCs in series to produce tandem dye-sensitized solar cells (pn-DSCs).^{47, 48}

He *et al.* proposed this alternate architecture, which combines an n-DSC with a photocathode dye-sensitized solar cell that is based on a p-type semiconductor (p-DSC).⁴⁸ This type of tandem architecture represents a simple series connection of an n-DSC and a p-DSC.

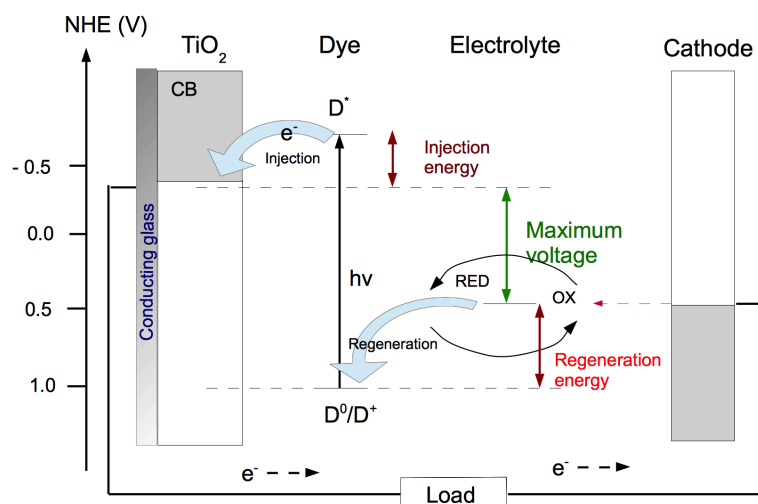


Figure 13: Schematic representation of the energy diagram of a tandem DSC device that combines a photocathode DSC with a photoanode DSC.⁴⁷

According to Kirchhoff's circuit law, the photovoltages are additive in this type of series-connected tandem architecture. However, the photocurrent that passes through the device is limited by the weakest performing photoelectrode, which is usually the photocathode.^{47, 48} In a first approximation, the theoretical V_{OC} of a pn-DSC is the potential difference between the valence band edge of the p-type semiconductor and the conduction band edge of the n-type semiconductor. In a proof of concept report, He et al. reported a V_{OC} of 733 mV with a contribution of 650 mV from the n-DSC and of 83 mV from the p-DSC, but the overall efficiency was limited to 0.39% due to the poor photocurrent density of the p-DSC.

Photoanodes have reached highest conversion efficiencies of up to 12.3% and photocurrent densities (J_{SCS}) of up to 17.66 mA/cm² under simulated sunlight (1,000 W/m², AM1.5).⁹ The highest reported pn-DSC efficiencies have reached up to 1.91%, and the photocurrents have reached up to 2.4 mA/cm².⁴⁷ The efficiency and photocurrent of this type of tandem solar cell is limited due to poor performing photocathodes. The highest reported efficiency of a photocathode is limited to 0.61% under simulated sunlight (1,000 W/m², AM1.5), and the highest reported photocurrent density is 5.48 mA/cm².⁴⁹⁻⁵¹ Theoretically, p-DSCs should be able to function as efficiently as n-DSCs.

As p-type photoactive electrodes replace the Pt counter electrodes in n-DSCs, pn-DSCs could potentially be cheaper alternatives (price per watt) to n-DSCs.

To date, there has been extremely limited research on this type of pn-DSC.^{48, 52-54} The achievement of high efficiency pn-DSCs would require the following: (i) the development of p-DSC and n-DSC sensitizers with complementary absorption spectra, (ii) new p-type semiconductors with higher ionization potentials and/or alternative n-type semiconductors with lower conduction band edges to improve the V_{OC} and (iii) optically transparent electrolytes.

2.4 p-Type DSCs

In n-DSCs, the photocurrent results from dye-sensitized electron injection into n-type semiconductors, such as TiO_2 .⁸ Photocurrent generation in p-DSCs results from electron transfer from the valence band of the p-type semiconductor to the photoexcited dye.^{46, 47} Figure 14 shows the band energy diagram and a schematic representation of the charge transfer process of a typical p-DSC. In the following terms HOMO and LUMO corresponds to the according molecular orbitals of the dye in its ground state. Light absorption is performed by a monolayer of a dye that is anchored to the surface of a wide bandgap p-type semiconductor, similar to an n-DSC. Upon light absorption, an electron is excited from the dye's HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital). From this stage, the process in p-DSCs differs from that in n-DSCs. Fast electron transfer follows the dye excitation from the valence band of the p-type semiconductor to the low energy SOMO level of the excited dye. This process is also known as dye-sensitized hole injection into the valence band of the semiconductor. Subsequently, the photoreduced dye can transfer an electron to the oxidized species in the electrolyte (I_3^- in the case of an iodide-based redox electrolyte). The hole in the valence band of the p-type semiconductor diffuses to the back contact. The reduced species in the electrolyte are converted to the oxidized form at the counter electrode.

Similar to an n-DSC, charge recombination reactions can limit the solar cell (DSC) efficiency. The electron from the LUMO level of the photoreduced dye can recombine with an injected hole in the valence band of the p-type semiconductor. In a second recombination mechanism, the reduced form of the redox mediator recombines with the hole in the valence band of NiO. The back electron transfer from the reduced dye to the p-type semiconductor is a major cause of efficiency losses. Donor-acceptor dyes with long linker chains can significantly reduce these losses because the charge recombination rate decreases with increasing bridge length, i.e., increasing distance between the acceptor and the NiO surface.⁴⁷

The theoretical (maximum) open circuit voltages of p-DSCs correspond to the difference between the redox potential of the redox mediator and the quasi-Fermi level of the p-type semiconductor valence band.

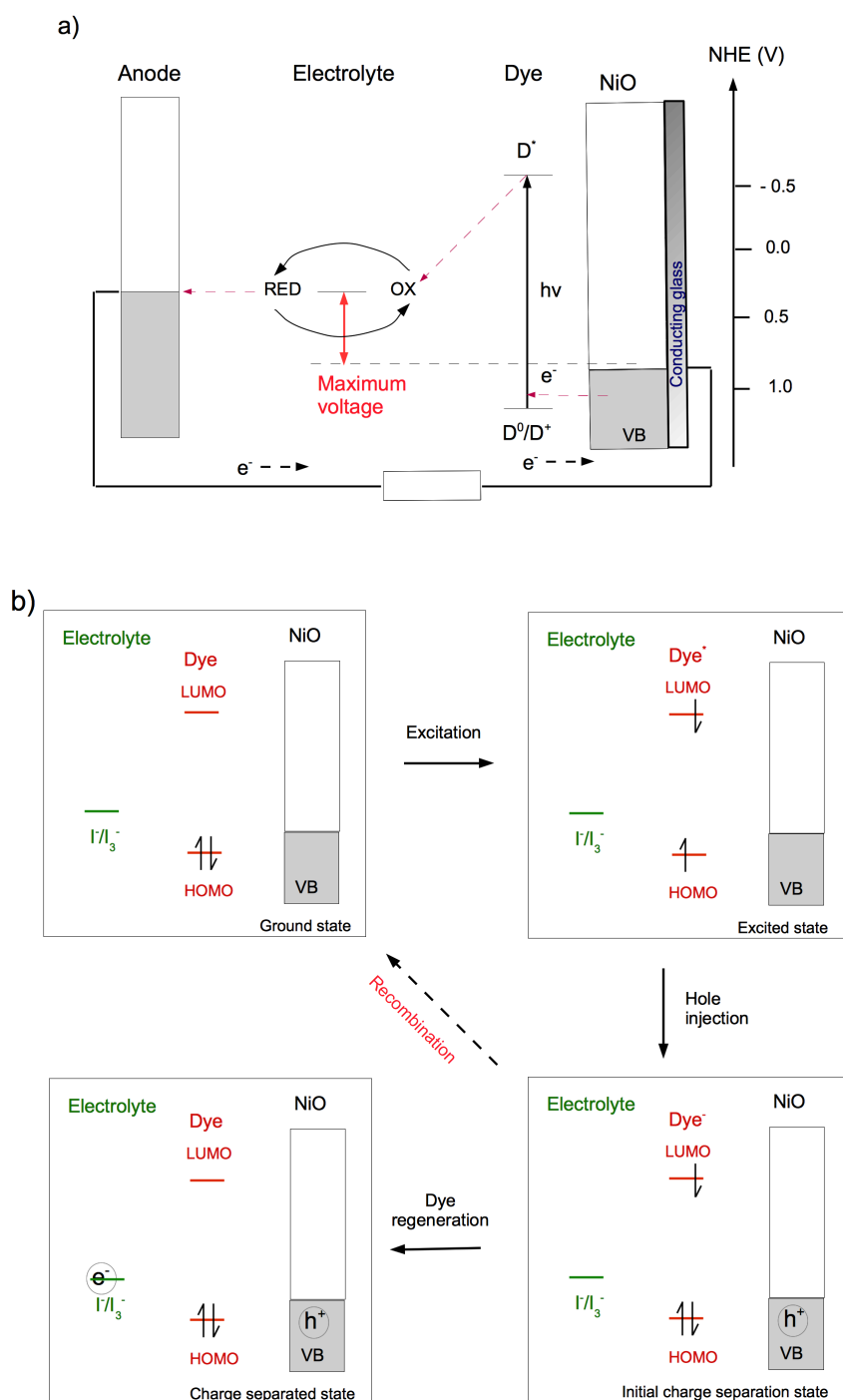


Figure 14: a) Band energy diagram and operating principle of a typical NiO-based p-DSC. b) Schematic representation of the charge transfer process in a typical NiO-based p-DSC.

p-DSCs are an underexplored field compared with their counterpart, n-DSCs, and are the subject of less than 50 publications (as of mid-2012). Figure 15 shows the efficiencies that have been reported in the literature versus the reported year.⁴⁶⁻⁷⁹ The maximum reported efficiency to date is 0.61% with a V_{OC} of 294 mV and a J_{SC} of 5.11 mA/cm².⁵¹ The progress in p-DSC development has been very slow from their first demonstration in 1999 until 2008. Because research attention

to p-DSCs has increased since 2008, the efficiency improved from 0.057% to 0.61% in mid-2012.^{51, 56} The reported efficiencies, associated problems and potential solutions will be discussed in more detail in the next section on the components of DSCs.

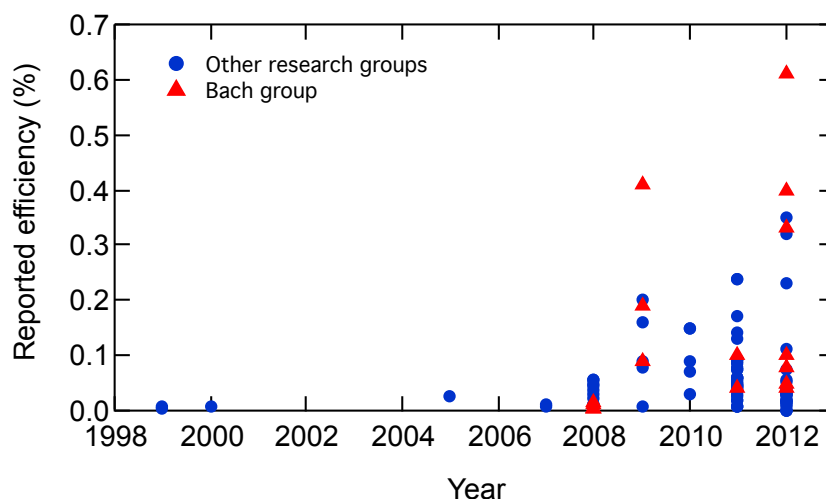


Figure 15: The reported photocathodic efficiencies from the literature. Red triangles represent the efficiencies that were reported by the Bach group, and blue dots represent the efficiencies that were reported by other research groups.⁴⁶⁻⁷⁹

2.5 Components of DSCs

2.5.1 Substrate material

Transparent conducting oxide (TCO) coated glass is the most commonly used substrate material for thin-film semiconductor photoelectrodes. FTO (F:SnO₂) and ITO (In:SnO₂) are common TCOs that are used in DSCs; FTO is more thermally stable than ITO and is therefore preferred.^{80, 81} The conductivity of ITO decreases with increasing annealing temperature. For flexible substrate applications, ITO/PEN, i.e., ITO-coated poly(ethylene naphthalate), and ITO-coated poly(ethylene terephthalate) (ITO/PET) are preferred due to their ease of manufacturing on polymer substrates.⁸²⁻⁸⁷ Other reported TCO materials include conductive polymers, such as polyaniline (PANI) and polyethylenedioxythiophene^{88, 89}, aluminum-doped zinc oxide⁹⁰⁻⁹³ and carbon nanotubes.⁹⁴ Chemical and thermal stability along with superior conductivity are prerequisites for TCOs that are used in solar cells. A Ti foil substrate material has been used in flexible, commercial DSC modules.^{95, 96} The use of Ti foil as a working electrode substrate for n-DSCs requires a transparent counter electrode material because light needs to shine through the counter electrode and the electrolyte.

2.5.2 Semiconductor material

In conventional p-n junction solar cells, the semiconductor performs both the key processes of photoelectron generation and providing an electric field to separate charges. The p-n junction solar cells are formed, by joining n-type and p-type semiconductor materials. The n-type region has a high electron concentration and the p-type a high hole concentration. The electrons diffuse from the n-type side to the p-type side and similarly, holes diffuse from the p-type side to the n-type.

In DSCs, the absorption and electron transport processes are decoupled. The dye adsorbed on the semiconductor accomplishes light absorption and injects an electron into the conduction band of the n-type semiconductor (hole injection in the case of a p-type semiconductor). The primary function of the semiconductor is in the charge transport process of the DSC. The semiconductor

should have a larger surface area for sufficient dye loading. Other prerequisites include mechanical stability, high conductivity, low absorption and minimum recombination between the semiconductor and the redox mediator.

In DSCs charge recombination is an interfacial process. It is therefore slow and can be tuned by controlling the semiconductor/dye/electrolyte interface. In silicon pn-junction solar cells majority and minority charge carriers co-exist in the same phase, making it particularly vulnerable towards charge recombination at defect sites within the semiconductor. This explains the requirement for extremely pure, high-cost crystalline materials for high-efficiency silicon solar cells, which is in contrast to DSCs where requirements in respect to material purity are much less stringent.

n-DSCs

In n-DSCs, for efficient charge injection from the excited state dye into the conduction band of the semiconductor, there must be an adequate driving force between the LUMO of the dye and the conduction band edge of the semiconductor. Additionally, the potential difference between the conduction band edge of the n-type semiconductor and the redox potential of the electrolyte determines the V_{OC} of the n-DSCs. The replacement of TiO_2 with an n-type semiconductor that has a more negative conduction band potential (vs. NHE) than TiO_2 can improve the V_{OC} of an n-DSC.

The most commonly used n-type semiconductor is TiO_2 in the anatase phase with a nominal particle size of ~ 20 nm.⁹⁷⁻⁹⁹ Rutile phase TiO_2 nanoparticles have been reported to generate an open circuit voltage (V_{OC}) similar to that of anatase phase nanoparticles. However, rutile phase nanoparticles generate lower short circuit current (J_{SC}) values than anatase phase nanoparticles.¹⁰⁰ If scattering layers are needed, larger particles (particle size of 300-400 nm) are used for a scattering layer on top of a transparent layer with 20 nm particles. The larger particles scatter the unabsorbed light back to the smaller particles upon illumination.¹⁰¹

Other reported n-type semiconductors include ZnO ,^{102, 103} SnO_2 ,¹⁰⁴ WO_3 ,¹⁰⁵ Nb_2O_5 ,^{106, 107} $SrTiO_3$ ¹⁰⁷ and Zn_2SnO_4 .¹⁰⁸ ZnO -coated SnO_2 has achieved conversion efficiencies of 6.3%.¹⁰⁹ Mixed oxide combination systems consisting of these semiconductor materials have also been studied. One such combination of tin and zinc oxides was reported with an efficiency of 8%.¹¹⁰

p-DSCs

In p-DSCs, for efficient hole injection from the HOMO level of the dye into the valence band of the p-type semiconductor, there must be an adequate driving force between the HOMO level of the dye and the valence band edge of the semiconductor. Additionally, the potential difference between the valence band edge of the p-type semiconductor and the redox potential of the electrolyte determines the V_{OC} of the p-DSCs. The replacement of NiO with a semiconductor that has a higher ionization potential than NiO can improve the V_{OC} of p-DSCs.

NiO is the most commonly used semiconductor in p-DSCs.^{111, 112} NiO is abundant and has a bandgap of ~3.5-4 eV.¹¹³⁻¹¹⁶ NiO has a rock salt structure with lattice parameters 4.195 Å and 4.261 Å. NiO has a melting point of 1998 °C, which is higher than that of TiO₂ (1825 °C).^{117, 118} NiO also has a higher charge carrier density than TiO₂.⁴ NiO has been used in other applications, such as catalysts,¹¹⁹⁻¹²¹ super-capacitors,¹²²⁻¹²⁴ gas sensors,¹²⁵ magnetic materials¹²⁶ and electrochromic devices.¹²⁷⁻¹³⁰

Mesoporous NiO photocathodes have been produced using different methods, such as nanocasting,⁷⁸ electrodeposition,¹³¹ hydrothermal synthesis,^{56, 132} spray pyrolysis¹³³ and sol-gel synthesis.^{50, 59, 134}

Other reported dye-sensitized p-type semiconductors include CuO,¹³⁵ boron-doped diamond,¹³⁶ CuAlO₂,⁶⁶ CuCrO₂,⁷⁶ CuGaO₂,^{75, 77} CuCNS¹³⁷ and GaP¹³⁸. p-type semiconductors have also been used in n-DSCs to increase the hole collection efficiency. The p-type semiconductors that were used in n-DSCs for hole collection include NiO,¹³⁹⁻¹⁴² CuO,^{143, 144} CuSCN,^{145, 146} CuI,¹⁴⁷ CuAlO₂¹⁴⁰ and CuBr.¹⁴⁸ The hole collecting semiconductors (p-type semiconductors) that have been used in bulk-heterojunction solar cells contained NiO,¹⁴⁹ MoO₃,¹⁵⁰⁻¹⁵³ V₂O₅¹⁵⁴⁻¹⁵⁶ and WO₃.^{157, 158}

Although NiO is a commonly used p-type semiconductor in p-DSCs, NiO is not the best p-type semiconductor for p-DSCs due to the following drawbacks. 1) NiO is used to make super capacitors.¹⁵⁹⁻¹⁶¹ The hole diffusion coefficients of NiO (10^{-8} to 10^{-7} cm²/s depending on the preparation method) are two orders of magnitude smaller than the electron diffusion coefficient of TiO₂.^{50, 111, 162} The high capacitive nature of NiO combined with inefficient transport interferes with charge extraction. 2) NiO absorbs approximately 30-40% of the overall incident light when

used in p-DSCs.⁴⁷ 3) The maximum V_{OC} is limited to 350 mV when NiO is used in conjunction with I^-/I_3^- -based electrolytes.⁶⁹

In summary, for high performance p-DSCs, there is a need to develop new p-type semiconductors or to modify the available ones. An ideal p-type semiconductor would have a wide bandgap, a large surface area, high hole mobility, and a suitable valence band potential for efficient hole injection from highly efficient p-type dyes (preferably with higher ionization potentials than NiO).

2.5.3 Sensitizer (Dye)

In DSCs, the dye that is anchored to the semiconductor surface is responsible for light absorption and charge injection into the conduction band of the n-type semiconductor (the valence band in the case of a p-type semiconductor). An ideal sensitizer would absorb across a broad range of the solar spectrum to harvest a large number of photons. The dyes should be photochemically and electrochemically stable.

n-DSCs

For efficient charge injection from the excited state dye into the conduction band of the semiconductor, the dye should have a lower (more negative vs. NHE) LUMO level than the conduction band of the n-type semiconductor. The HOMO level of the dye should be more positive (vs. NHE) than the redox potential of the redox mediator (vs. NHE) to provide the requisite driving force for efficient dye regeneration. Because the dye is primarily responsible for light absorption, a dye with a broad absorption spectra is useful in DSCs. Dyes with a high molar extinction coefficient offer flexibility for use in thinner semiconductor films, which, in turn, help to reduce the charge diffusion pathway.

Since 1991, a huge number of dyes have been tested in DSCs. The most commonly used and commercially available dyes are based on ruthenium complexes such as N719, Z907 and black dye (N749).^{163, 164} Ruthenium is a rare material on earth; hence, the supply of ruthenium is limited and expensive. Researchers have tried to replace Ru with other metals. Zinc porphyrins are a promising replacement and their application in DSCs, including DSCs with the highest conversion efficiency solar cells, has been demonstrated.^{9, 165-169} The highest reported overall efficiency of 12.3% under one sun illumination (AM 1.5G) was achieved by co-sensitizing DSC with YD2-o-C8 and Y123 dye.⁹ Metal-free organic dyes have also been synthesized and applied to DSCs. Organic dyes have higher extinction coefficients than ruthenium dyes and can be a cheaper alternative.¹⁷⁰ The best efficiency for n-DSCs that use metal free organic dyes has exceeded 10 %.¹⁷¹

Organic sensitizers for DSCs generally consist of an electron donor that is connected to an acceptor with a conjugated spacer (a donor- π -acceptor system). The donors are from the family of electron-rich amines, and the π -conjugated bridge frequently contains thiophene units, which have excellent transport properties.¹⁷² The anchoring group is attached to the acceptor and is

closer to the semiconductor surface. The donor part is kept away from the semiconductor surface to reduce charge recombination.¹⁷³

The above-mentioned dyes only absorb visible light and UV; to improve the efficiency, the near-IR and IR spectra should also be absorbed and utilized. Studied infrared dyes include squaraine dyes (e.g., the SQ2 dye) that are commercially available¹⁷⁴⁻¹⁷⁷ and cyanine dyes.^{173, 175} Some dyes require a co-adsorbing additive, such as chenodeoxycholic acid.

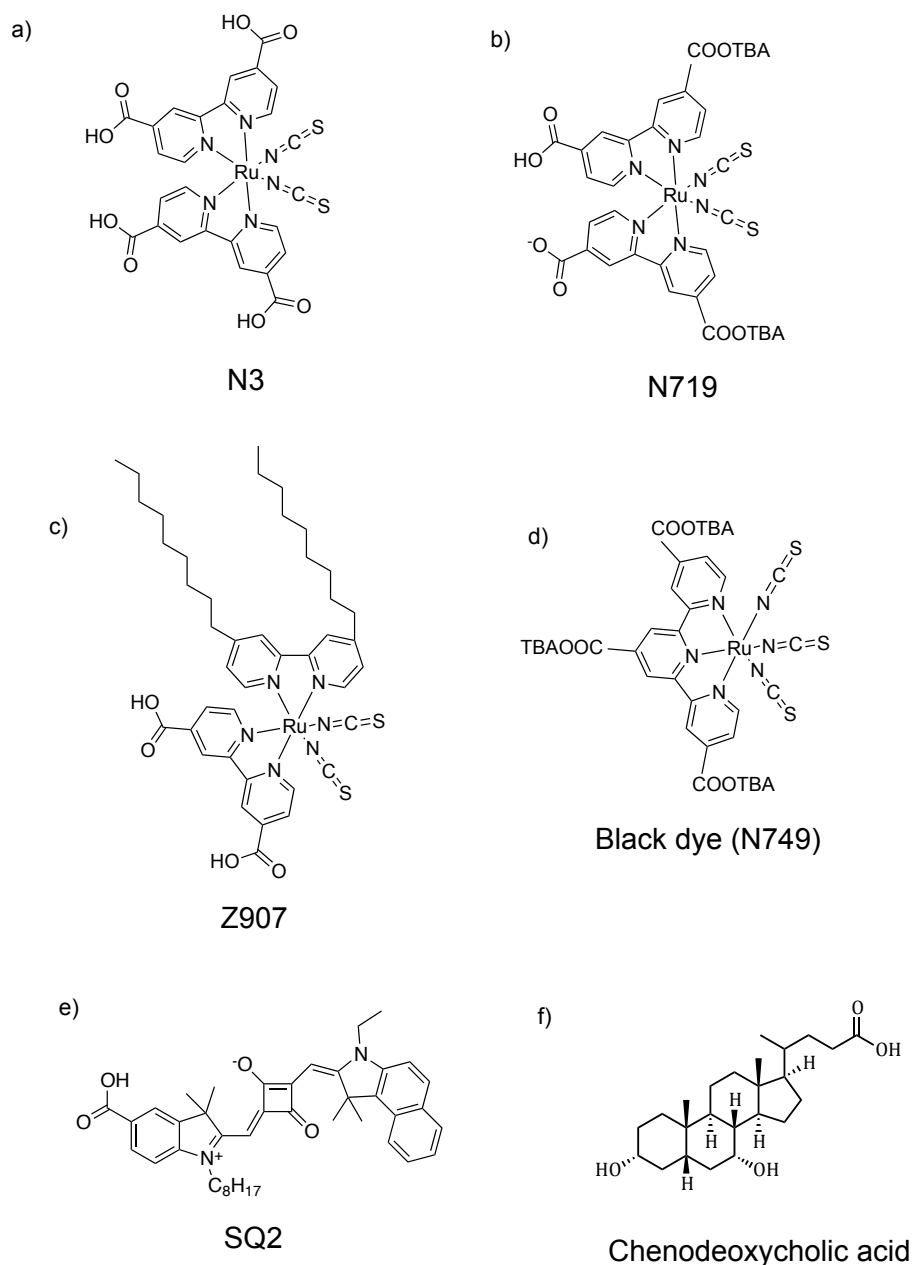


Figure 16: Chemical structures of commonly used sensitizers in n-DSCs: a) N3 dye, b) N719 dye, c) Z907 dye, d) black dye (N749), e) SQ2 dye and f) chenodeoxycholic acid.

p-DSCs

In p-DSCs, for efficient charge injection from the dye into the valence band of the semiconductor, the dye should have a higher (more positive vs. NHE) HOMO level than the valence band of the p-type semiconductor. The LUMO level of the dye should be lower (more negative vs. NHE) than the redox potential of the redox mediator to provide the requisite driving force for efficient electron injection. Dyes with high molar extinction coefficients would be advantageous because NiO absorbs approximately 30-40% of incident light for a film thickness of $\sim 2 \mu\text{m}$.⁴⁷

He *et al.* used erythrosin B and the porphyrin-based TPPC sensitizers for a NiO-based p-DSC demonstration.^{46, 48} Following the p-DSC demonstration, researchers attempted to produce p-DSCs using dyes similar to those that were used for n-DSCs such as N719.⁵⁴ Despite the favorable HOMO and LUMO levels, most of the dyes that were used in n-DSCs were not suitable for use in p-DSCs.⁵⁴ The other dyes that were used in the early stage of p-DSC research include C343, eosin B, erythrosin J, fast green, NK-2612, NK-2684, NK-3628, NKX-2311, rhodamine 101 and rhodamine 110. Of these dyes, C343, a commercially available dye, had the highest reported efficiency (0.057%) with a V_{OC} of 113 mV.^{46, 48, 53-57, 61, 67} The chemical structures of these early stage research dyes are shown in Figure 17, and the J-V characterization data are shown in Table 1.

Table 1: Sensitizers studied in the early stage of research on p-DSCs with their corresponding J-V performance parameters.

Sensitizer	V_{OC} (mV)	J_{SC} (mA/Cm ²)	η (%)	Reference
Erythrosin B	82.8	0.269	0.0071	⁴⁶
	83	0.27	0.0071	⁴⁸
	120	1.05	0.045	⁶¹
TPPC	98.5	0.079	0.003	⁴⁶
C343	113	1.61	0.057	⁵⁶
	101	0.86	0.031	⁵⁷
	95	0.87	0.03	⁶⁷
	93	1	0.027	⁵³
	98	0.55	0.016	⁵⁴
C337	80	0.3	0.01	⁵⁵
	75	0.2	0.006	⁵⁵
	77	0.14	0.0032	⁵⁴
Eosin B	77	0.14	0.0032	⁵⁴
Erythrosin J	122	0.36	0.011	⁵⁴
Fast Green	93	1.44	0.043	⁵⁷
NK-2612	73	0.45	0.013	⁵⁷
NK-2684	123	1.3	0.055	⁵⁷

NK-2684	85	1.3	0.038	59
NK-3628	77	0.43	0.011	57
NKX2311	100	0.66	0.022	59
Rhodamine 101	69	0.12	0.0022	54
Rhodamine 110	80	0.15	0.0031	54

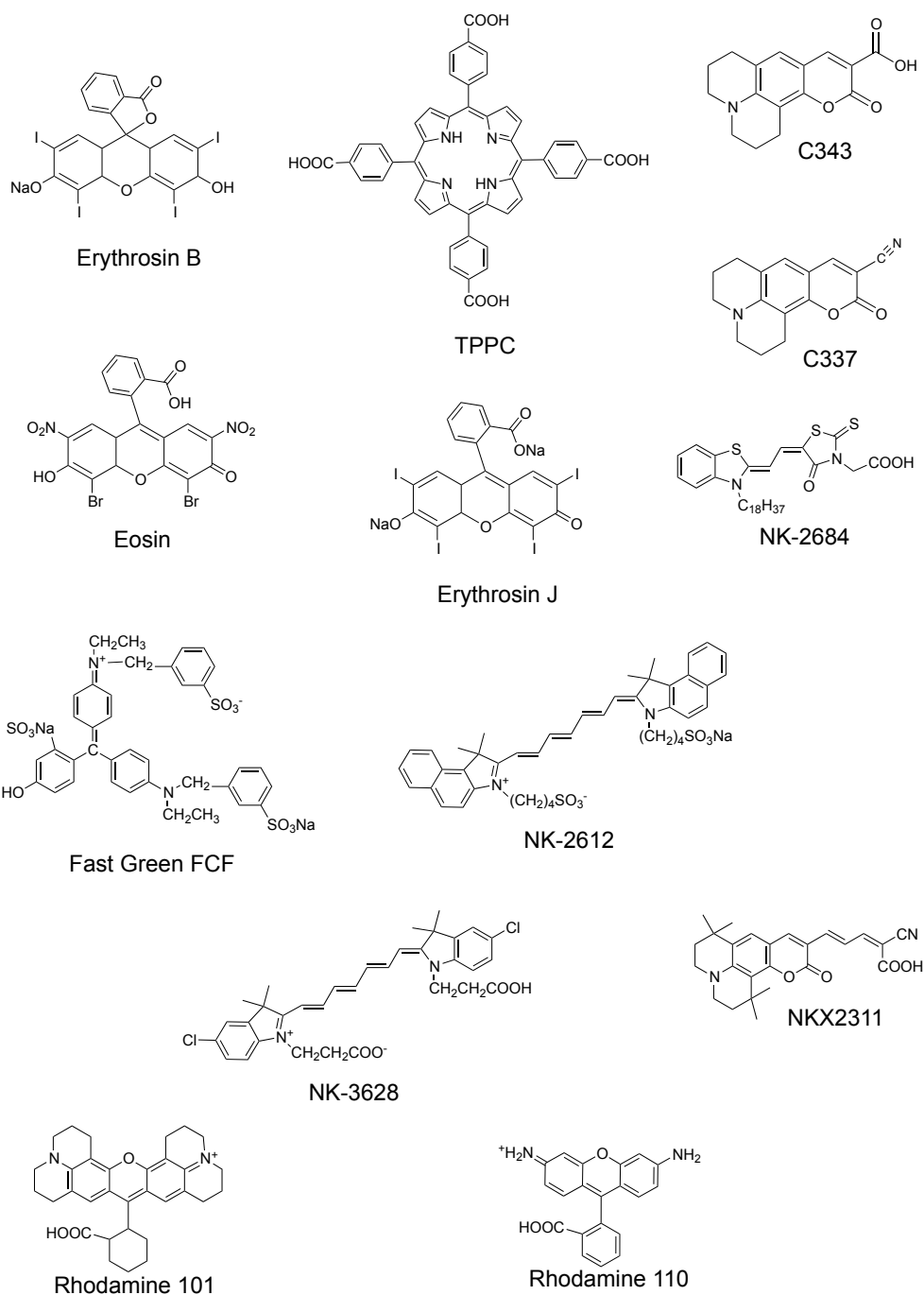


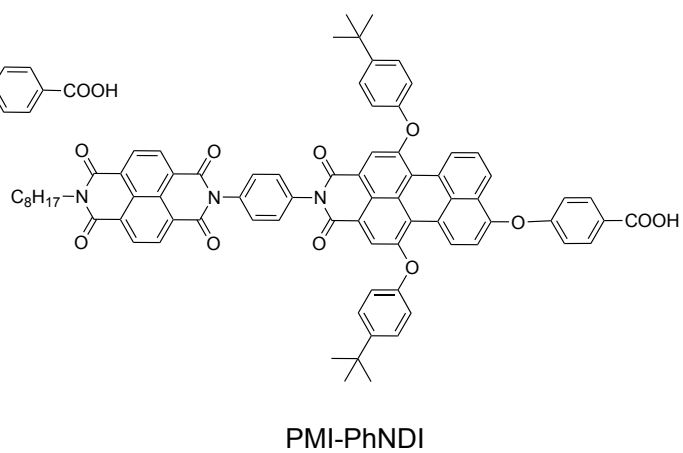
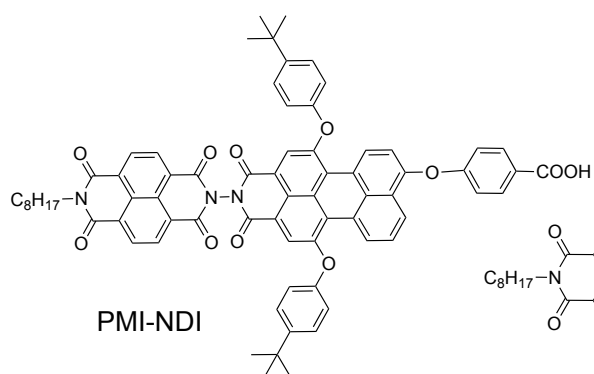
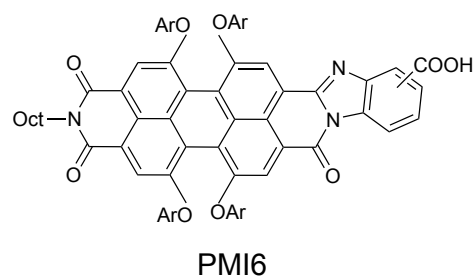
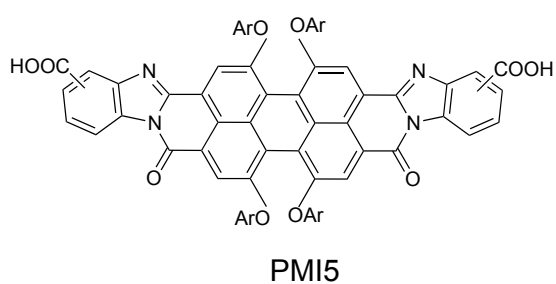
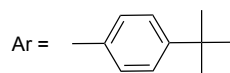
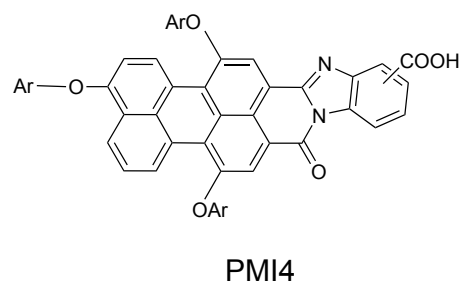
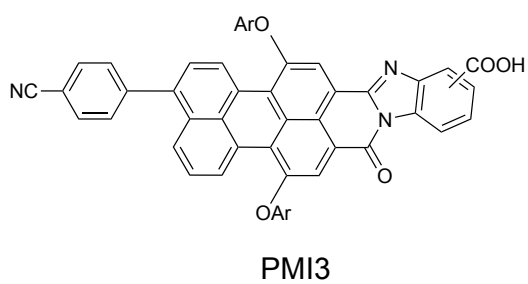
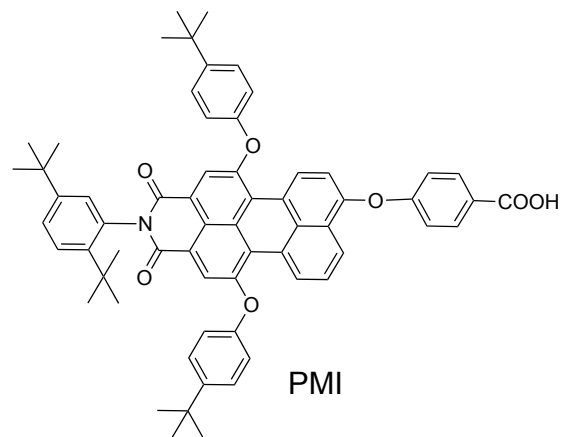
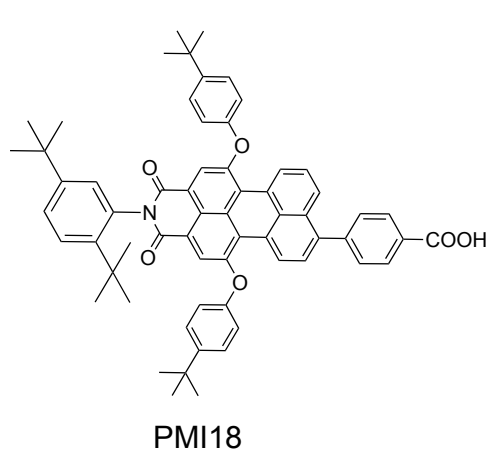
Figure 17: Chemical structures of the sensitizers studied in the early stage of research on p-DSCs. The J-V performance parameters are shown in Table 1.

Morandeira *et al.* introduced sensitizer-acceptor dyads as sensitizers that could reach an absorbed photon-to-charge carrier conversion efficiency (APCE) of 45%.¹⁷⁸ Using a similar concept, a series of dyads was studied in p-DSCs. A PMI-NDI dyad in conjunction with a cobalt-based electrolyte could reach efficiencies up to 0.24%.⁶² The studied dyads are shown in Figure 18, and their corresponding J-V performances are shown in Table 2.

Table 2: Sensitizing dyads studied in p-DSCs with their corresponding J-V performance parameters.

Sensitizer	V _{OC} (mV)	J _{SC} (mA/Cm ²)	η (%)	Reference
PMI 18	85 [a]	0.342	0.007	65
	100	1.418	0.043	65
	85	1.42	0.04	71
PMI	80	0.26	0.006	52
	85 [a]	0.25	0.006	65
	110	1.316	0.046	65
	70	1.41	0.03	71
	45	0.01	0.0001	75
	95 [b]	0.014	0.0003	75
				71
PMI3	85	1.41	0.04	71
PMI4	80	1.07	0.03	71
PMI5	70	0.94	0.02	71
PMI6	75	0.54	0.01	71
PMI-NDI	350 [a]	1.66	0.2	52
	370 [a]	1.3	0.16	132
	160	1.05	0.04	62
	200 [a]	1.45	0.09	62
	240 [a]	1.61	0.13	62
	340 [a]	2	0.24	62
	125 [a]	2.32	0.08	62
	200 [a]	2.42	0.17	62
	275 [a]	2.65	0.24	62
	285 [a]	1.2	0.141	65
	120	1.76	0.073	65
	187	0.29	0.23	75
	375 [a, b]	0.12	0.0149	75
				65
PMI-PhNDI	210 [a]	0.78	0.048	65
PMI-PhNDI	130	1.64	0.074	65
PMI-PhC60	180	0.58	0.04	65
PMI-PhC60	95	1.88	0.058	65
WSI-NDI [b]	77 [b]	0.025	0.0005	70

The sensitizers that have been used in conjunction with alternative electrolytes [a] and/or an alternative semiconductor [b]



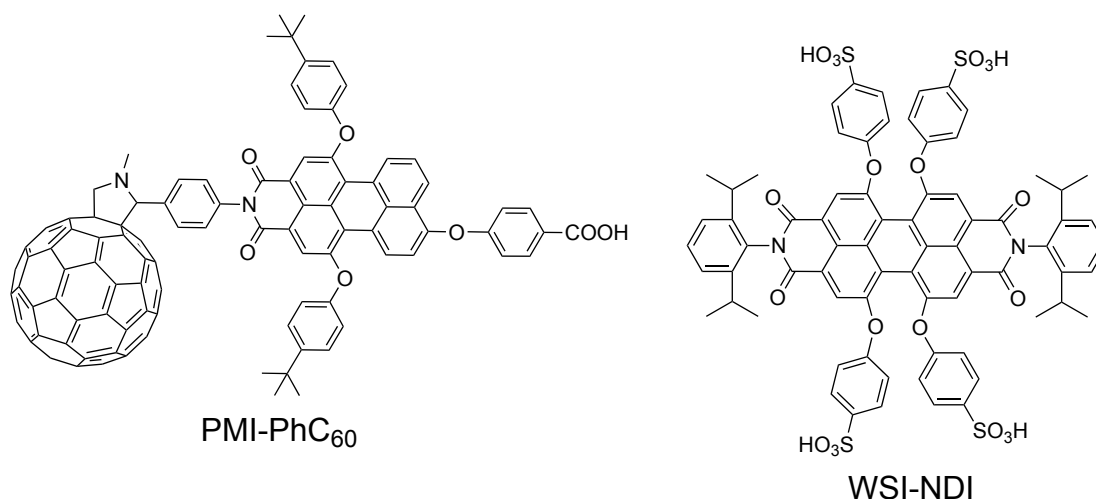


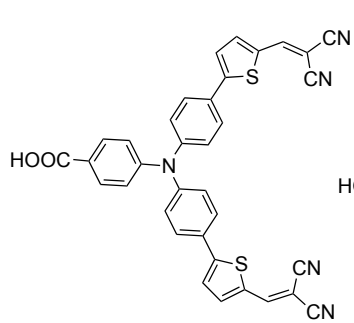
Figure 18: Chemical structures of the sensitizing dyads studied in p-DSCs. The J-V performance parameters are shown in Table 2.

The donor-acceptor dyes were designed and applied in n-DSCs. In such a configuration, an acceptor group was attached to an anchoring group, closer to n-type semiconductor. The donor-acceptor dye designs of n-DSCs were applied to p-DSCs. However, the same design did not work for p-DSCs, as the acceptors were closer to the p-type semiconductor surface increasing recombination. Following the dyad design, Qin et al. introduced the donor-acceptor type organic chromophore P1 as a p-DSC sensitizer with a conversion efficiency of 0.05%.⁵⁸ In p-DSC sensitizers, the anchoring group is attached to the donor and is closer to the semiconductor surface. Nattestad *et al.* reported the highest p-DSC conversion efficiency (0.41%) with a donor-acceptor type dye that was based on PMI as an acceptor and TPA as a donor. The authors also showed that, if the acceptor part is kept away from the semiconductor surface, charge recombination is reduced.⁴⁷ Because this donor-acceptor configuration improves the efficiency, researchers are focusing on this type of dye structure to further improve the efficiencies. Figure 19 shows the different donor-acceptor sensitizers that were used in p-DSCs, and Table 3 summarizes the corresponding J-V performances.

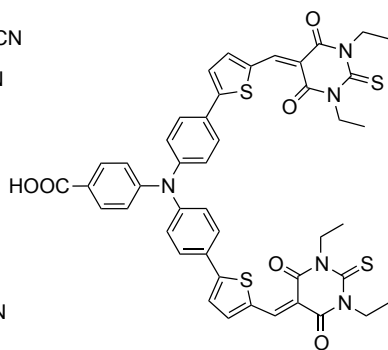
Table 3: High performance donor-acceptor-type dyes studied in p-DSCs with their corresponding J-V performance parameters.

Sensitizer	V _{OC} (mV)	J _{SC} (mA/Cm ²)	η (%)	Reference
P1	84	5.48	0.15	50, 60
	132	2.31	0.101	68
	110	2.51	0.08	49
	131	1.24	0.055	63
	150 ^[a]	0.95	0.054	74
	110	1.52	0.05	58
	110	0.83	0.031	74
	180 ^[b]	0.384	0.026	77
	357 ^[c]	0.165	0.018	77
P2	63	3.37	0.07	60
P3	55	1.36	0.03	60
P4	100	2.48	0.09	49
P7	80	3.37	0.09	60
T1	104	2.64	0.075	79
T2	122	3.27	0.113	79
Arylamine 1	105	1.59	0.06	68
Arylamine 2	115	1.39	0.058	68
Arylamine 3	113	1.38	0.053	68
Arylamine 4	125	2.25	0.093	68
Arylamine 5	122	2.18	0.092	68
Arylamine 5	123	2.18	0.35	72
Arylamine 6	131	2.05	0.087	68
Arylamine 6	131	2.05	0.32	72
O2	94	1.43	0.05	64
O6	97	1.04	0.037	64
O7	90	1.74	0.06	64
PMI-2T-TPA	153	2.06	0.09	47
PMI-4T-TPA	176	3.4	0.19	47
PMI-6T-TPA	218	5.35	0.41	47
	301	2.6	0.33	78
	292	3.3	0.4	78
	294	5.11	0.61	51
	305	1.32	0.14	69
	333 ^[d]	0.3	0.041	66
66-28	146	1.77	0.08	179
66-28i	122	1.06	0.04	179
66-37	147	2.24	0.1	179
66-37i	136	1.23	0.05	179

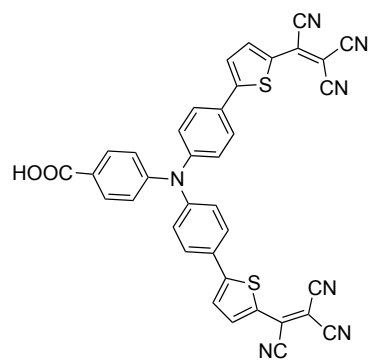
The sensitizers that have been used in conjunction with [a] NiO/alumina, [b] CuGaO₂, [c] CuGaO₂ and the cobalt-based electrolyte [d] CuAlO₂



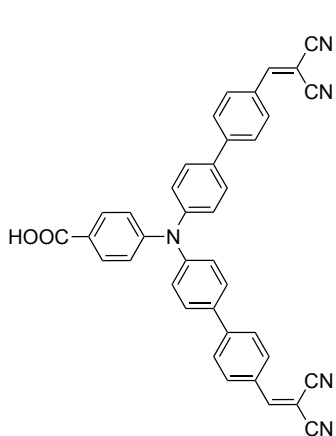
P1



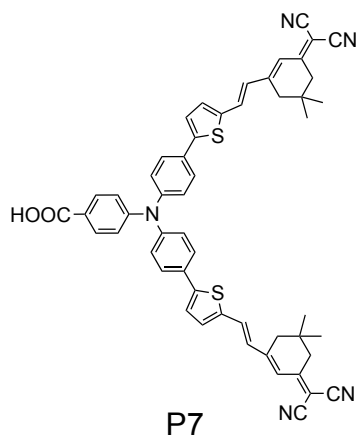
P2



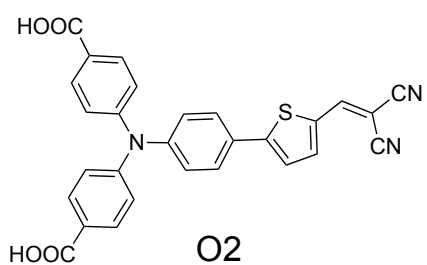
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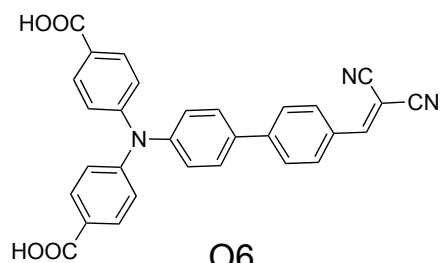
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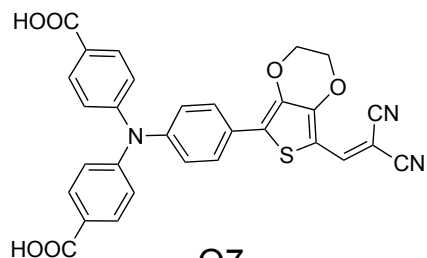
P7



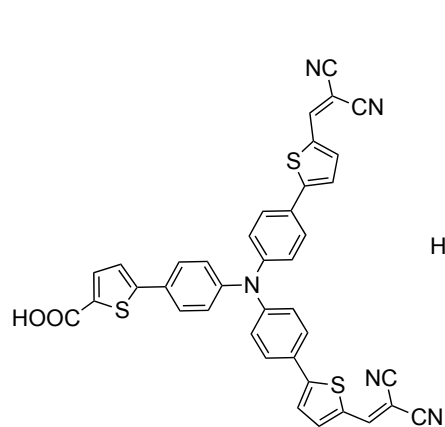
O2



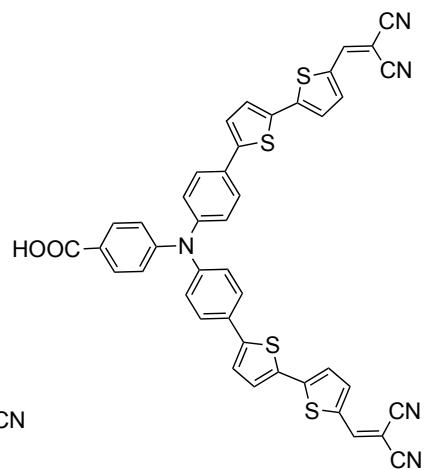
O6



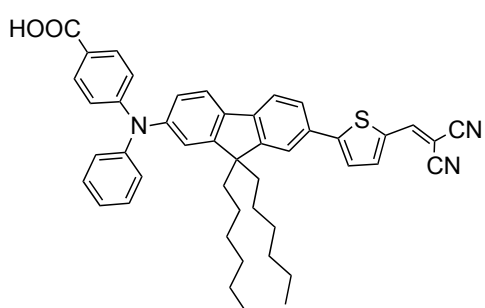
O7



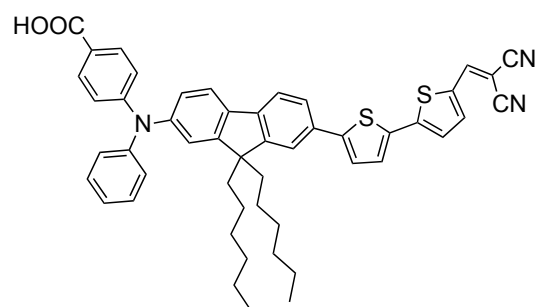
T1



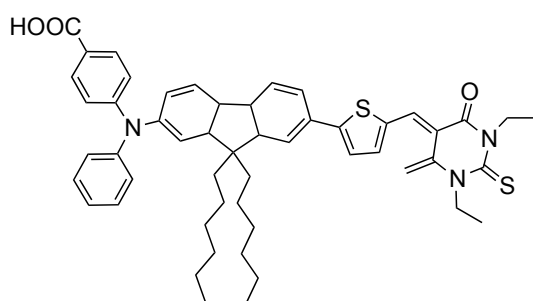
T2



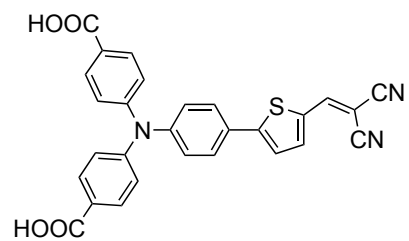
Arylamine 1



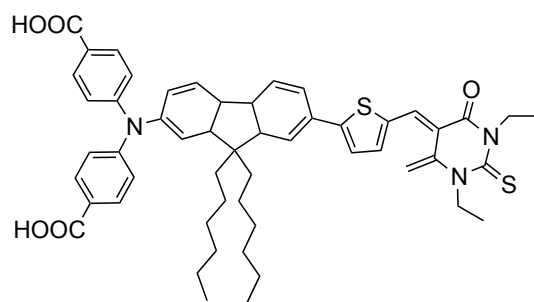
Arylamine 2



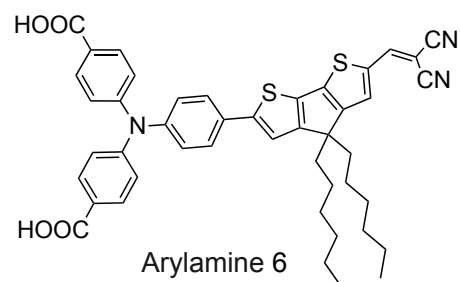
Arylamine 3



Arylamine 4



Arylamine 5



Arylamine 6

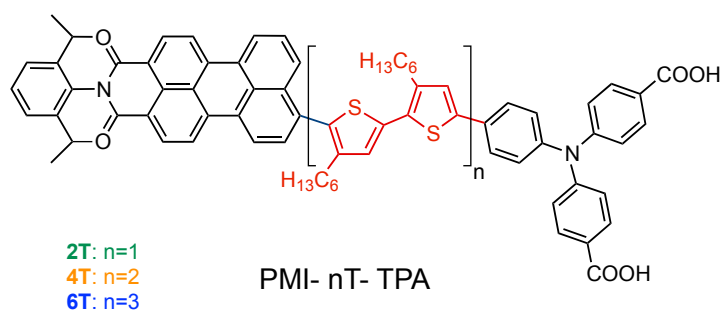
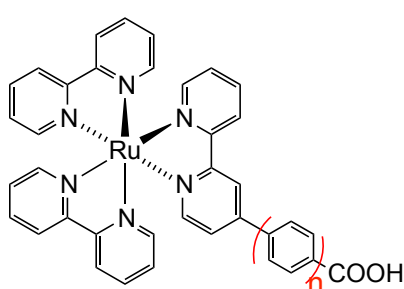


Figure 19: Chemical structures of high-performance donor-acceptor-type p-DSC dyes. The J-V performance parameters are shown in Table 3.

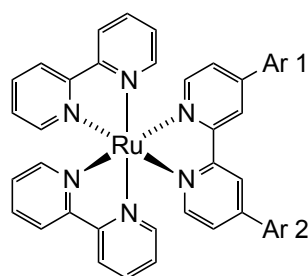
Recently, Pellegrin *et al.* and Ji *et al.* reported ruthenium-based sensitizers for p-DSCs. The highest reported p-DSC efficiencies using ruthenium-based dyes have reached 0.05%. Ji *et al.* studied and reported the same effect of increasing the conjugation length to improve the photocurrent and efficiency. Figure 20 shows the chemical structures of the studied ruthenium-based sensitizers, and Table 4 summarizes the corresponding J-V performance data.

Table 4: Ruthenium-based dyes studied in p-DSCs with their corresponding J-V performance parameters.

Sensitizer	V_{OC} (mV)	J_{SC} (mA/Cm ²)	η (%)	Reference
Ru-Py 1	85	0.63	0.019	67
Ru-Py 2	95	0.78	0.025	67
Ru-Py 3	75	0.25	0.0065	67
Ru-Py 4	85	0.65	0.018	67
O8	63	0.44	0.009	73
O11	79	1.16	0.033	73
O12	82	1.84	0.051	73



n = 0, O8
n = 1, O11
n = 2, O12



Ru polypyridine dye

Ru-Py 1
Ar 1 = Ar 2 = $-\text{COOH}$

Ru-Py 3
Ar 1 = Ar 2 = $-\text{CS}_2\text{H}$

Ru-Py 2
Ar 1 = Ar 2 =

Ru-Py 4
Ar 2 =

Figure 20: Chemical structures of the ruthenium-based dyes studied in p-DSCs. The J-V performance parameters are shown in Table 4.

2.5.4 Electrolytes

An electrolyte typically contains a redox couple and some additives that are designed to optimize the solar cell performance. The electrolyte enables charge transport between the working electrode and the counter electrode. The electrolyte is primarily responsible for dye regeneration in DSCs. The rest potential of the redox couple determines the maximum (theoretical) V_{OC} of a DSC.

Iodide-triiodide is the most popular redox couple in DSCs. The n-DSCs that use an iodide redox couple have reached efficiencies of close to 12%.¹¹ p-DSCs have attained conversion efficiencies of up to 0.6% with the devices that use iodide electrolytes.⁵¹ Despite this high performance, iodide redox couples are not the best-suited redox couple. Iodide redox couples have a corrosive nature, and these redox couples exhibit a complex redox chemistry.¹³ The corrosive nature of an iodide redox couple makes it challenging to integrate this couple into commercial modules and limits the choice for alternative counter electrode materials. Iodide redox couples have extremely high absorptivity below 450 nm. In pn-DSCs, the incident light travels through the electrolyte before reaching the second electrode.

To address these problems, researchers are analyzing alternative redox couples to replace iodide electrolytes.

n-DSCs

The potential difference between the rest potential of the electrolyte and the quasi-Fermi level of the n-type semiconductor defines the V_{OC} of n-DSCs. In recent years, the applications of cobalt, iron and copper complexes, as well as ferrocene- and thiolate-based redox couples, as replacements for iodide electrolytes are under investigation.^{171, 180-187}

p-DSCs

As mentioned earlier, iodide is the most commonly used redox couple for p-DSC studies. However, apart from the aforementioned challenges, the rest potential of iodide electrolytes is not favorable for their application in p-DSCs. The valence band of NiO, which was estimated using photoelectron spectroscopy in air (PESA), was 0.6 V (vs. NHE).⁶⁶ The rest potential of iodide was measured to be 0.35 V (vs. NHE); therefore, the maximum V_{OC} for NiO-based p-DSCs

would be limited to only ~250 mV.¹³ However, the p-DSC V_{OC} using iodide electrolyte has been reported to be 350 mV. The spectroelectrochemistry measurements were based on a Li^+ -containing supporting electrolyte. Li^+ is a flat band potential determining ion, and the influence of Li^+ on the valence band edge of NiO is unknown.^{180, 188-190} Despite the effect of lithium, the V_{OC} of p-DSCs are very limited in combination with electrolytes that are based on an iodide redox couple. The iodide electrolyte needs to be replaced by a redox couple with a lower (more negative vs. NHE) rest potential than iodide-based electrolytes to achieve higher V_{OC} s for p-DSCs. The other possible solution is to replace NiO by another p-type semiconductor with a higher ionization potential than NiO.

Zhang et al. reported that the fine-tuning of NiO crystallinity can influence the valence band edge and the device V_{OC} . The maximum reported V_{OC} of photocathodes that are based on finely tuned NiO and iodide electrolytes is 305 mV.⁶⁹ Aside from these fine-tuned nanocrystals, Nattestad et al. reported a V_{OC} of 218 mV for photocathodes that were based on commercial NiO and iodide electrolytes.⁴⁷ In another report, Nattestad et al. reported a V_{OC} of 333 mV after replacing NiO with $CuAlO_2$.⁶⁶

To overcome these limitations, recent reports have focused on cobalt-based electrolytes. Le Pleux *et al.* reportedly used tris(4,4'-di-tert-butyl-2,2'-dipyridyl)cobalt(II/III) perchlorate $[Co(dtbpy)_3]^{2+/3+}$ in p-DSCs along with NiO that was sensitized with PMI-NDI, which yielded a V_{OC} of 370 mV.¹³² Renaud et al. reported the highest V_{OC} (375 mV) for p-DSCs that use a similar sensitizer and electrolyte but replaced NiO with $CuGaO_2$. However, the efficiency was limited to 0.015%.⁷⁵

Other studied cobalt complexes in p-DSCs include $[Co(ttb-tpy)_2]^{2+/3+}$, $[Co(dMeO-bpy)_3]^{2+/3+}$ and $[Co(dm-bpy)_3]^{2+/3+}$ (where $ttb-tpy$ = 4,4'4''-tri-tert-butyl-tripyridine, $dMeO-bpy$ = 4,4'-dimethoxyl-bipyridine, and $dm-bpy$ = 4,4'4''-dimethyl-bipyridine).^{52, 62} However, none of these approaches have resulted in an overall increase in the energy conversion efficiency of p-DSCs beyond the 0.5% mark. Figure 21 shows the chemical structures and relative rest potentials of these complexes in comparison with those of the iodide electrolyte.

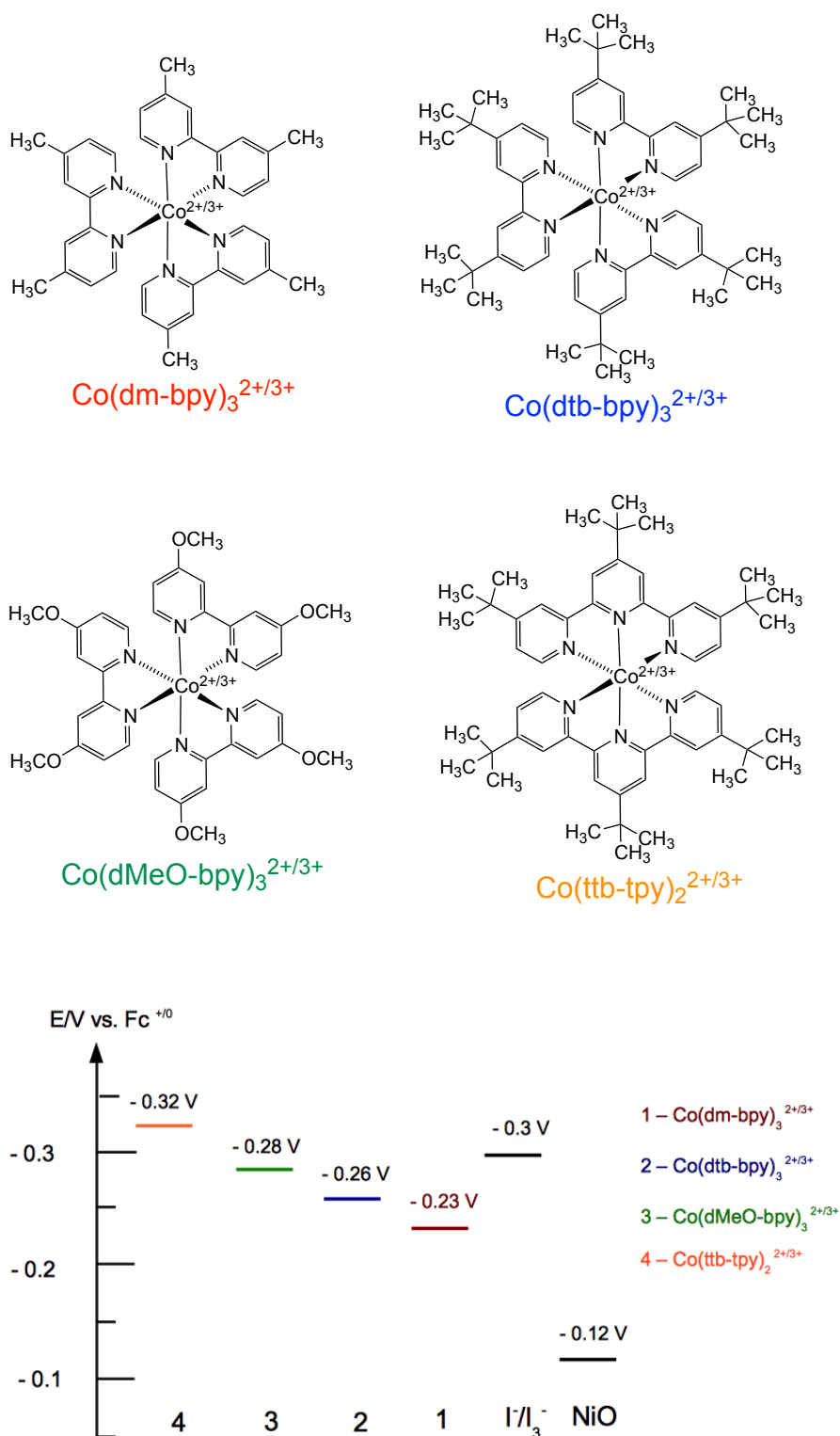


Figure 21: a) Chemical structures of the cobalt complexes studied in p-DSCs. b) Schematic rest potential energy levels of the cobalt complex (shown in Figure 21 a) based electrolytes and the iodide electrolyte.

2.5.5 Counter electrode

The counter electrode in DSCs is a conducting substrate that is coated with a catalyst layer. In n-DSCs, the catalyst reduces the oxidized species of the redox couple, and, in p-DSCs, it oxidizes the reduced species under operation. The choice of the catalytic material depends on the used redox couple. For the most popular iodide electrolyte system, platinum is typically the preferred catalyst. Platinum is deposited on the counter electrode surface either by thermal decomposition at high temperatures (400 °C) or by electrochemical deposition at room temperature.¹⁹¹

Other reported catalytic materials that have been coated onto substrates and used in conjunction with a suitable redox couple are carbon-based materials,^{192, 193} Poly(3,4-ethylenedioxythiophene) (PEDOT),¹⁹⁴ PEDOT doped with p-toluenesulfonate (PEDOT:TsO),¹⁹⁵ PEDOT doped with polystyrene sulfonate (PEDOT:PSS),¹⁹⁶ gold¹⁹⁷ and cobalt sulfide (CoS).^{198, 199}

Carbon-based materials are attractive due to their reasonable costs but are less electrochemically active. Conducting polymers are another alternative to expensive platinum counter electrodes. PEDOT is used in the display and electronics industries. PEDOT and its doped forms can be deposited on substrates by electrodeposition and, in some cases, by screen-printing. Gold is not an appropriate catalyst for an iodide redox system due to the corrosive nature of iodide, but it has been used with alternative redox mediators. Mixed composites include polymer-platinum composites, polymer-carbon composites, a Ni/Pt mixed deposition²⁰⁰ and carbon fiber (CF) and poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS).²⁰¹ In pn-DSCs, the counter electrodes are replaced with a photoactive electrode.

2.6 Scope of this thesis

A dye-sensitized solar cell (DSC) is a second-generation thin-film technology and an attractive alternative to conventional silicon solar cells. A DSC works in a different manner than other second-generation solar cell technologies in that the light absorbing sensitizer is anchored to the surface of a wide bandgap semiconductor. The wide bandgap semiconductor acts as a charge collector.

Photoanodic DSCs (n-DSCs – based on an n-type semiconductor) yield efficiencies of up to 12.3%. However, these efficiencies still lag behind those of first-generation silicon solar cells and of some other second-generation thin-film solar cell technologies. One way to improve these efficiencies is to create a tandem solar cell. Photocurrent generation in n-DSCs results from dye-sensitized electron injection into n-type semiconductors, such as TiO_2 . Photocurrent generation in photocathodic dye-sensitized solar cells (p-DSCs) results from electron transfer from the valence band of the p-type semiconductor to the photoexcited dye. The complementary nature of the charge flow in a p-DSC and an n-DSC provides an opportunity for assembling these cells in a sandwich structure to produce a tandem dye-sensitized solar cell (pn-DSC). This pn-DSC tandem architecture, which was proposed by He et al., can theoretically achieve higher efficiencies than single junction n-DSCs.⁴⁸

According to Kirchhoff's circuit law, the photovoltages are additive in this type of tandem architecture.^{46, 47} However, the photocurrent is limited by the lower performing electrode. Although the theoretical efficiencies of pn-DSCs could be higher than the maximum attained efficiency of single junction n-DSCs (12.3%), the maximum achieved pn-DSC efficiency is limited to 2.42% due to underperforming p-DSCs.⁴⁷ The maximum reported efficiency, V_{OC} and J_{SC} values for n-DSC are 12.3%, 935 mV and 17.66 mA/cm^2 , respectively.⁹ Theoretically, a p-DSC should perform as efficiently as an n-DSC. However, the highest reported p-DSC efficiency, V_{OC} and J_{SC} are limited to 0.61%, 350 mV and 5.48 mA/cm^2 .^{51, 52, 62}

Reported pn-DSCs have several other limitations. The overlapping absorption spectrum of the most efficient p-DSC sensitizer with that of the used n-DSC sensitizer (N719) means that both photoelectrodes are competing for photons in a similar wavelength range, thus limiting the attainable pn-DSC photocurrent. Furthermore, the tandem devices were utilizing electrolytes based on the I^-/I_3^- redox couple, which strongly absorbs at wavelengths below 500 nm.⁴⁷ In pn-DSCs, the incident light must travel through the electrolyte before reaching the second electrode.

Visible light absorption by the electrolyte reduces the achievable photocurrent of the second electrode and therefore lowers the attainable efficiency of these devices.

The drive toward high-efficiency tandem solar cells would require i) the development of p-DSC and n-DSC sensitizers with complementary absorption spectra, ii) new p-type semiconductors with higher ionization potentials and/or alternative n-type semiconductors with lower conduction band edges to improve the V_{OC} and iii) optically transparent electrolytes. Changing the electrolyte would not increase the V_{OC} of pn-DSCs because the gain on one side would be equivalent to the loss on the other side. However, higher potential mediators may allow us to use the effective IR sensitization on n-DSC side that will help in complementary absorption.

This thesis work has pursued different avenues to improve p-DSC performance for application in a pn-DSC.

Chapter 3 of this thesis describes the application of a hierarchical NiO nanomaterial (NiO microballs (NiO- μ B)) that consists of highly crystalline nanosheets in p-DSCs. The commercial NiO nanoparticles (NiO-NPs) produce low photocurrents due to their low surface area and high self-absorption. The new synthesized material has a high specific surface area and a low self-absorption. By employing NiO- μ B in p-DSCs, high photocurrents (7.0 mA/cm^2) and IPCE (74%) values were achieved under one-sun solar illumination conditions (1000 W/m^2 , AM 1.5 G).

The p-DSC photovoltage is limited to the difference between the rest potential of the electrolyte and the quasi-Fermi level of the p-type semiconductor. Chapter 4 introduces the use of $[\text{Co}(\text{en})_3]^{2+/3+}$ -based electrolytes in p-DSCs. The rest potential of a $[\text{Co}(\text{en})_3]^{2+/3+}$ -based electrolyte is more negative (-0.025 V vs. NHE) than those of previously studied p-DSC electrolytes. The favorable rest potential of the $[\text{Co}(\text{en})_3]^{2+/3+}$ electrolyte produced exceptionally high V_{OC} values (709 mV) for p-DSCs with record conversion efficiencies of 1.30%.

Chapter 5 explains the application of a transparent thiolate/disulfide-based electrolyte in p-DSCs and pn-DSCs. Photocathode and photoanode dyes with complementary absorption spectra were used in combination with the thiolate/disulfide-based electrolyte. p-DSC conversion efficiencies of 0.51% were achieved. The pn-DSCs achieved conversion efficiencies of up to 1.33%.

Chapter 6 describes the analysis of CuCrO_2 as an alternative p-type semiconductor for application in p-DSCs. The favorable rest potential of CuCrO_2 produced the highest V_{OC} (734 mV) for p-DSCs in conjunction with the $[\text{Co}(\text{en})_3]^{2+/3+}$ -based electrolyte.

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Chapter 3

**Improved photocurrents for p-type
dye-sensitized solar cells using
nano- structured nickel(II) oxide
microballs**

Monash University

Declaration for Thesis Chapter 3

Title: Improved photocurrents for p-type dye-sensitized solar cells using nano-structured nickel(II) oxide microballs

Declaration by candidate

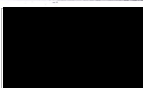
In the case of Chapter 3, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
All experimental work except synthesis; preparation of the manuscript and editing	60%

The following co-authors contributed to the work. Co-authors who are students at Monash University must also indicate the extent of their contribution in percentage terms:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
Qiang Wu	NiO synthesis, drafting and editing	N.A.
Martin Weidener	Dye synthesis, drafting and editing	N.A.
Andrew Nattestad	Data analysis, drafting and editing	N.A.
Zheng Hu	Drafting and editing	N.A.
Amaresh Mishra	Drafting and editing	N.A.
Peter Bäuerle	Drafting and editing	N.A.
Leone Spiccia	Drafting and editing	N.A.
Yi-Bing Cheng	Drafting and editing	N.A.
Udo Bach	Experimental design and planning, drafting and editing	N.A.

**Candidate's
Signature**

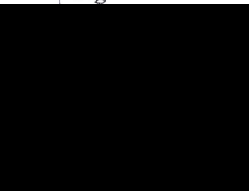
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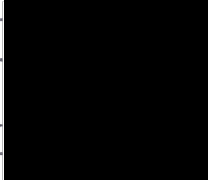
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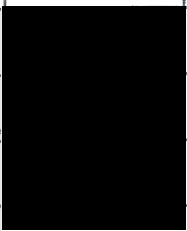
Declaration by co-authors

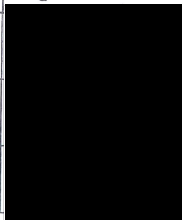
The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (6) the original data are stored at the following location(s) and will be held for at least five years from the date indicated below:

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Cite this: *Energy Environ. Sci.*, 2012, **5**, 8896

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COMMUNICATION

Improved photocurrents for p-type dye-sensitized solar cells using nano-structured nickel(II) oxide microballs†

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Received 3rd May 2012, Accepted 20th July 2012

DOI: 10.1039/c2ee22127f

Highly crystalline nanostructured nickel(II) oxide microballs (NiO-μBs) were developed for use in p-type dye-sensitized solar cells (p-DSC). Their high specific surface area and favorable optical properties yielded unprecedented photocurrent densities of 7.0 mA cm⁻² under simulated sunlight (AM1.5; 1000 W m⁻²) and incident photon to charge carrier conversion efficiencies of 74% when applied in p-DSCs. This is an important step towards matching the performance of p-DSCs with their n-type counterparts for future tandem applications.

Dye-sensitized solar cells (DSC) have attracted much attention as an alternative to conventional solar cells due to their projected low cost.^{9,10} In conventional photoanodic DSCs (n-DSCs) the photocurrent results from dye-sensitized electron injection into n-type semiconductors such as TiO₂. These photoanodes yield efficiencies of up to 12.3% and photocurrent densities (J_{SC}) of up to 17.66 mA cm⁻² under simulated sunlight (1000 W m⁻², AM1.5).¹¹ In dye-sensitized photocathodes (p-DSC) electron transfer takes place from the valence band of the p-type semiconductor (NiO being the most commonly used to date) to the lowest energy SOMO (singularly occupied molecular orbit) of the dye, following photo excitation.^{12,13} Photoanodes and photocathodes can be assembled together to produce tandem dye-sensitized solar cells (pn-DSCs) with a simple sandwich structure. According to Kirchhoff's circuit law, photovoltages are additives in this type of tandem architecture while the photocurrent is limited by the weakest performing photoelectrode, which is generally the photocathode.^{12,14}

The highest photocurrent density reported to date for p-DSCs (5.48 mA cm⁻²) under simulated sunlight (1000 W m⁻², AM1.5) is significantly lower than those typically reported for high efficiency n-DSCs.⁵

This photocurrent mismatch represents one of the major obstacles towards the realization of high efficiency tandem pn-DSCs, calling for the development of photocathodes with improved current densities.

Using a novel sensitizer (PMI-6T-TPA) (Fig. 1(a)) in conjunction with a mesoporous film comprised of commercially available NiO

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Broader context

This work describes the synthesis of hierarchical and highly crystalline NiO and their application in p-DSC. Employing these microballs in p-DSC, record photocurrent (7.0 mA cm⁻²) and IPCE (74%) values under solar illumination conditions were achieved. At low illumination levels photocurrents equivalent to 10.7 mA cm⁻² under full sun illumination were recorded, providing further evidence that full current matching of p-DSCs and n-DSCs could soon be at hands. The new hierarchical nanomaterial (NiO microballs consisting of highly crystalline nanosheets) presented here provides these performance improvements through two intrinsic advantages over conventional nanomaterials: (1) its high specific surface area and (2) its low self-absorption. Light absorption by the NiO semiconductor (self-absorption) does not generate any photocurrents and is in competition to the desired photon absorption by the dye. This is the first paper that clearly identifies and quantifies this self-absorption process as a major efficiency limitation. At the same time, we show that its limitations can partly be overcome through the use of tailor-made materials with defined nano- and micro-structure.

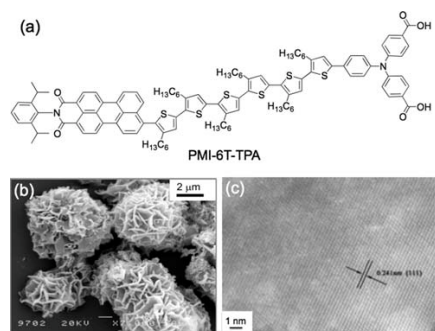


Fig. 1 (a) Chemical structure of PMI-6T-TPA sensitizer (b) SEM and (c) HRTEM images of as-synthesized NiO-μB.

nanoparticles (NiO-NPs) we were recently able to achieve a J_{SC} of 5.35 mA cm^{-2} under simulated sunlight (1000 W m^{-2} , AM1.5).¹ While those devices showed *absorbed* photon to charge carrier conversion efficiencies (APCE) of up to 96%, the highest *incident* photon to electron conversion efficiency (IPCE) recorded for these photocathodes was only 62%. A detailed optical analysis showed that about 30–40% of overall incident light was absorbed by the mesoporous semiconductor (NiO), which did not contribute to the cathodic photocurrent.¹ Consequently, the light harvesting efficiency (LHE) of the dye was limited. This clearly defines a need for novel p-type nanomaterials with improved optical properties.

Here, we report the synthesis of nanostructured NiO microballs (NiO-μBs) and their application in p-DSCs. These NiO-μBs were synthesized by a thermolysis method. An aqueous solution (50 mL) of 4 mM oxalic acid dihydrate and 20 mM hexamethylenetetramine were slowly added to 100 mL of 20 mM solution (aq.) of nickel(II) nitrate at room temperature. The mixed solution was heated to 100°C and refluxed for 5 hours, after which time a green precipitate was collected by filtration and washed with water and ethanol several times. After drying at 60°C , the product was heated in a muffle furnace in air at 400°C for 2 hours, resulting in a fine grey powder.

Fig. 1(b) shows a SEM micrograph of as synthesized NiO-μBs revealing a hierarchical structure of porous spheres with a diameter of $\sim 3 \mu\text{m}$ composed of nanosheets (see also Fig. S1, ESI†). HR-TEM micrographs (Fig. 1(c)) of these nanosheets reveal a high crystallinity with an interplanar spacing of about 0.241 nm , in agreement with the d_{111} value of cubic NiO. As synthesized NiO-μBs and commercially available NiO-NPs were compared using X-ray diffraction (XRD) analysis. The obtained XRD patterns (Fig. 2) feature similar peak heights and widths suggesting similar crystal domain sizes. The two

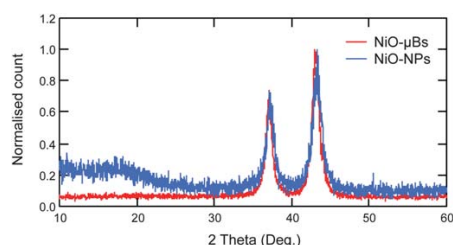


Fig. 2 XRD spectra of synthesized NiO-μBs (red) and as-received NiO-NPs (blue).

Table 1 BET results for unsintered and sintered NiO-μBs and NiO-NPs

	Surface area ($\text{m}^2 \text{g}^{-1}$)		Porosity (%)	
	Powder	Sintered film	Powder	Sintered film
NiO-NPs	122	56	59	51
NiO-μBs	85	65	73	68

materials show a distinct difference at 2θ values of $10\text{--}30^\circ$ where the commercial NiO nanopowder shows a broad feature, indicative of the presence of amorphous NiO. This hump is absent in the XRD spectrum of NiO-μBs, providing further evidence for the high crystallinity of this material.

Screen printing pastes were prepared by mixing 13.3 wt% NiO, 40% ethyl cellulose solution (5 wt% in ethanol) and 46.7% terpineol using synthesized NiO-μBs and as-received NiO-NPs. After removing ethanol by rotary evaporation, these two pastes were printed on FTO glass ($\text{NSG} - 8 \Omega \square^{-1}$) using a commercial semi-automatic screen printer. Single, double and triple layers were printed using each paste, with a 125°C drying period between subsequent printing steps. The screen-printed electrodes were sintered at 400°C for 30 min and 550°C for 10 min. The thicknesses of the sintered electrodes were measured using a Veeco Dektak 6M stylus profilometer. The thicknesses of electrodes consisting of NiO-NPs were $2.2 \mu\text{m}$, $5.0 \mu\text{m}$ and $6.3 \mu\text{m}$, while NiO-μBs films featured average thicknesses of $2.8 \mu\text{m}$, $4.2 \mu\text{m}$ and $6.0 \mu\text{m}$ for one, two and three layers respectively. Owing to the large size of the NiO-μBs ($\sim 3 \mu\text{m}$), the single layer NiO-μBs film corresponded to roughly monolayer coverage of microballs with high roughness and numerous pinholes. The subsequent prints yielded more uniform films.

The specific surface area and porosity of NiO-μBs and NiO-NPs before and after sintering were analyzed using Brunauer–Emmett–Teller (BET) analysis of N_2 adsorption–desorption studies (Fig. S2, ESI†). The results (Table 1) show that the specific surface area of the unsintered NiO-μB material is lower than that of the commercial NiO-NPs. Following the sintering process; the NiO-μB-based films show a surface area that is about 16% higher than that of films based on NiO-NPs. A dye adsorption/desorption study was performed (Fig. S3, and experimental details in ESI†) to verify if the increase in specific surface area translates into higher dye loading for sintered NiO-μBs films. The amount of dye desorbed from the NiO-μBs film (228 mol m^{-3}) was about twice as high as that desorbed from the NiO-NPs film (106 moles m^{-3}) indicating better pore space accessibility for the sintered NiO-μBs film. The analysis of the differential pore volume distribution as a function of pore size (Fig. S2, ESI†) confirmed that a significant fraction of the pores in sintered NiO-NPs film had a diameter of $<10 \text{ nm}$.

Dye-sensitized photocathodes were constructed following a procedure previously described.¹ In brief, sintered electrodes were sensitized in a 0.2 mM PMI-6T-TPA dye solution (in DMF) for 2 hours, before they were used to construct p-DSCs with platinized conductive glass counter electrodes and an I^-/I_3^- based electrolyte (0.03 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-terbutylpyridine and 0.1 M guanidinium thiocyanate in $85:15$ acetonitrile : valeronitrile).

Table 2 summarizes the photovoltaic performance of p-DSCs with varying thicknesses of NiO-μBs and NiO-NPs films under simulated

Table 2 Photovoltaic performances of NiO-NPs and NiO- μ Bs photocathodes (0.16 cm² NiO films) with different film thicknesses sensitized with PMI-6T-TPA dye under simulated sunlight (AM1.5, 1000 W m⁻²)

Film thickness (μ m)	NiO-NPs		
	2.2 (1 Print)	5.0 (2 Prints)	6.3 (3 Prints)
V_{OC} (mV)	199 $\pm$ 3	203 $\pm$ 10	198 $\pm$ 5
J_{SC} (mA cm ⁻²)	4.51 $\pm$ 0.16	5.01 $\pm$ 0.19	5.34 $\pm$ 0.13
Fill factor	0.34 $\pm$ 0.01	0.34 $\pm$ 0.01	0.33 $\pm$ 0.01
Efficiency (%)	0.30 $\pm$ 0.01	0.34 $\pm$ 0.03	0.36 $\pm$ 0.04
Film thickness (μ m)	NiO- μ Bs		
	2.8 (1 Print)	4.2 (2 Prints)	6.0 (3 Prints)
V_{OC} (mV)	214 $\pm$ 8	208 $\pm$ 3	185 $\pm$ 3
J_{SC} (mA cm ⁻²)	5.15 $\pm$ 0.15	6.36 $\pm$ 0.15	7.0 $\pm$ 0.30
Fill factor	0.34 $\pm$ 0.01	0.34 $\pm$ 0.01	0.33 $\pm$ 0.01
Efficiency (%)	0.38 $\pm$ 0.01	0.46 $\pm$ 0.02	0.43 $\pm$ 0.01

sunlight (1000 W m⁻², AM1.5; see also Fig. S4†). The best performing p-DSCs were constructed using 4.2 μ m and 6.0 μ m thick NiO- μ Bs electrodes. A 6.0 μ m thick NiO- μ Bs electrode yielded a J_{SC} of 7.0 mA cm⁻² and an overall device efficiency of 0.43%. The devices based on 4.2 μ m thick NiO- μ Bs generated slightly lower J_{SC} value of 6.36 mA cm⁻² and higher V_{OC} of 208 mV resulting in a higher efficiency of 0.46%. These are the highest values reported to date for p-DSCs.¹⁻⁸ Fig. 3(a) illustrates the relationship of photocurrent and NiO film thickness for both types of NiO electrodes. For a given film thickness p-DSCs based on NiO- μ Bs clearly outperform those made from NiO-NPs.

Photocathodes based on NiO- μ Bs show a stronger increase in J_{SC} than NiO-NPs based p-DSCs. In this side-by-side comparison we could show that the replacement of conventional NiO-NPs with NiO- μ Bs results in an increase in J_{SC} of p-DSCs by 31%. The trends observed for the short-circuit current are also reflected in the incident photon-to-charge carrier conversion efficiency (IPCE) spectra shown in Fig. 4. IPCE values for NiO- μ Bs based DSCs are generally higher

than that of NiO-NPs based DSCs. The highest IPCE value of 74% was recorded for a 6.0 μ m thick NiO- μ Bs electrode. Generally thicker NiO films result in a slightly improved red-response.

A detailed optical analysis of the light harvesting properties of the sensitized films was performed in order to clarify the origin of the improved performance of NiO- μ Bs based p-DSCs. If the improvement was solely due to the higher surface area of NiO- μ B electrodes it could be postulated that the lack in specific surface area for the NiO-NPs can be compensated simply by using thicker films.

As discussed above the overall light harvesting in p-DSCs based on conventional NiO-NPs is mostly limited by the parasitic light-absorption of the NiO material in the sensitized film. The absorption properties of dyed and undyed films were recorded before and after dye absorption, using a Perkin Elmer Lambda 950 spectrophotometer, equipped with an integrating sphere (see Fig. 5(a)). Dye absorptions on NiO films were calculated using eqn (1). Dye absorption on NiO- μ Bs film at the peak absorption wavelength of 436 nm was calculated to be 1.02, twice as high compared to NiO-NPs (0.48), in agreement with the dye-desorption studies (shown in Fig. S3, ESI†). In order to quantify and compare parasitic light absorption in both types of films the ratio of dye to NiO absorption was determined according to eqn (2).

$$A_{(Dye)}(\lambda) = A_{(Dyed\ NiO)}(\lambda) - A_{(NiO)}(\lambda) \quad (1)$$

where $A_{(NiO)}(\lambda)$ and $A_{(Dyed\ NiO)}(\lambda)$ are the absorptions of the NiO film prior to and following dye absorption respectively.

$$\text{Absorption ratio (Dye:NiO)}(\lambda) = \frac{A_{(Dye)}(\lambda)}{A_{(NiO)}(\lambda)} \quad (2)$$

$$\text{LHE}_{(dye)}(\lambda, d) = \frac{A_{(Dye)}(\lambda)}{A_{(Dyed\ NiO)}(\lambda)} \cdot \left(1 - 10^{-\tilde{A}_{(Dyed\ NiO)}(\lambda) \cdot d}\right) \quad (3)$$

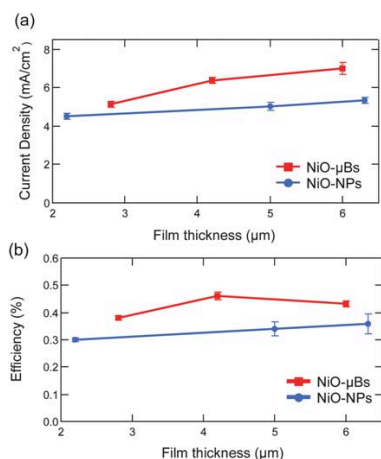
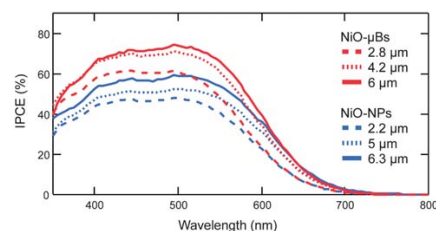
where $\tilde{A}_{(NiO+Dye)}(\lambda)$ is absorption of dyed NiO film per μ m and d is the film thickness in μ m.

$$J_{SC}^{\max} = \frac{e}{hc} \int \phi_p \text{AM1.5G}(\lambda) \text{LHE}(\lambda) \phi_{inj} \phi_{cc} d\lambda \quad (4a)$$

since

$$\text{LHE}(\lambda) \phi_{inj} \phi_{cc} = \text{IPCE}$$

$$J_{SC}^{\text{int}} = \frac{e}{hc} \int \phi_p \text{AM1.5G}(\lambda) \text{IPCE} d\lambda \quad (4b)$$

**Fig. 3** (a) Short circuit current density and (b) efficiency of p-DSCs sensitized with PMI-6T-TPA dye as a function of film thickness for photocathodes composed of NiO- μ Bs (red squares) and NiO-NPs (blue disks).**Fig. 4** IPCE spectra of p-DSC with different electrode thicknesses using NiO- μ Bs (red) and NiO-NPs (blue).

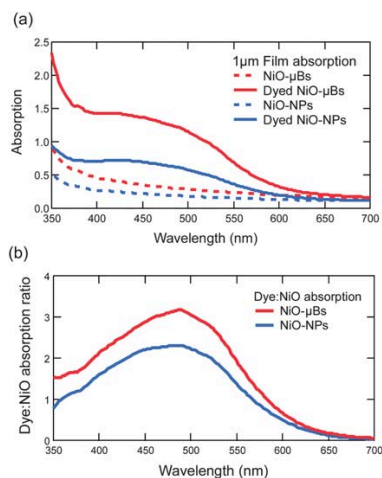


Fig. 5 (a) Absorption spectra of 1 μm thick undyed (dotted lines) and PMI-6T-TPA sensitized (solid lines) of NiO-NP and NiO- μB films, (b) the calculated ratio of dye to NiO absorption for both films. Plain FTO glass was used for baseline corrections for all spectra. NiO- μB films were printed from crushed microballs (low energy ball milling for 24 h) to realize pin-hole free films with homogeneous thickness appropriate for optical analysis according to Lambert-Beer's law.

where ϕ_p is photon flux, ϕ_{inj} is charge injection efficiency and ϕ_{cc} is charge collection efficiency.

Fig. 5(b) shows the ratio of dye to NiO absorption for both types of NiO films, further revealing more favorable light harvesting properties for the sensitized NiO- μBs film. At the peak absorption wavelength of 490 nm, the NiO in NiO-NPs-based DSCs, absorbs about 31% of the incident photons. For NiO- μBs based DSCs it is about 24%. The reduced self absorption of NiO- μBs can simply be explained based on the higher specific surface area of NiO- μBs compared to NiO-NPs after the sintering step. A lower degree of defects in the more crystalline NiO- μB material could also be a possible reason for the observed reduced self-absorption.

The higher photocurrents observed for NiO- μBs DSCs can therefore be rationalized in terms of (1) their superior light harvesting properties, as well as (2) a significant reduction in parasitic light absorption by NiO, compared to NiO-NPs DSCs. From the latter observation it can also be expected that the shortfall in light harvesting for the sensitized NiO-NPs based NiO electrodes cannot simply be compensated by increasing the NiO film thickness.

Based on the optical analysis of the 1 μm thick films shown in Fig. 5(a), eqn (3) can be used to calculate the expected light-harvesting efficiency as a function of film thickness for both types of NiO electrodes. Knowing the percentage of photons absorbed by the dye for a given film thickness at any given wavelength it is possible to calculate the maximum theoretical short-circuit current (J_{SC}^{max}) of NiO- μBs and NiO-NPs DSCs as a function of film thickness (eqn (4a)), assuming that light harvesting is the only limiting step in charge generation (APCE = 100%). Fig. 6 shows a plot of the calculated J_{SC}^{max} as a function of film thickness for NiO- μBs and NiO-NPs DSCs (solid lines). For comparison, the short-circuit currents calculated from the measured IPCE spectra (J_{SC}^{int}) according to eqn (4b) are also shown. For both NiO film types, the J_{SC}^{max} values plateau at a thickness of about 4 μm . Any further increase in film thickness does not

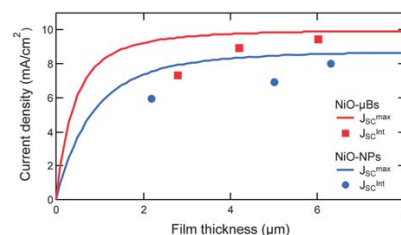


Fig. 6 Calculated maximum short-circuit current densities (J_{SC}^{max}) derived from the light-harvesting properties according to eqn (3a) for NiO- μBs (red) and NiO-NPs (blue) as a function of NiO thickness. For comparison the expected short-circuit currents based on the integration of IPCE and AM1.5 photon flux (eqn (4b)) for NiO- μBs (red squares) and NiO-NPs (blue disks) are also shown.

result in any significant increase in J_{SC}^{max} . As expected from the more favorable dye-to-NiO absorption ratio J_{SC}^{max} plateaus are at higher current values for NiO- μB than NiO-NP films. For a 6 μm film, J_{SC}^{max} for a NiO- μB DSC was calculated to be 9.9 mA cm^{-2} . This value is about 15% higher than the J_{SC}^{max} calculated for a 6 μm thick NiO-NPs DSC and corresponds to about 96% of the J_{SC}^{int} value calculated from the measured IPCE spectrum of a 6 μm thick NiO- μBs DSC (9.5 mA cm^{-2}). The close match between J_{SC}^{max} and J_{SC}^{int} for three layered NiO- μBs and NiO-NPs DSCs is consistent with the high APCE values reported earlier for these systems.¹ The differences between the calculated J_{SC}^{int} and the measured J_{SC} under simulated full sun (Table 2) can be rationalized in terms to the observed non-linear dependence between J_{SC} and the incident light intensity (Table S1, ESI†) and the circumstance that IPCE measurements were performed at low illumination levels, in the order of 0.01 suns. Short-circuit current at 0.10 sun of around 1 mA cm^{-2} were observed, indicating the superior performance at lower light intensities. Additional optimizations targeted at suppressing the current losses at higher light intensities therefore should have the potential to further increase the J_{SC} to close to 10 mA cm^{-2} for PMI-6T-TPA-sensitized NiO p-DSCs at one sun illumination. Generally all J_{SC}^{int} values are within a range of 85–100% of the expected photocurrent, except for the result of the single layer NiO- μBs film. This can be rationalized in terms of the irregularity of these films and the presence of pinholes due to the fact that the film thickness and the average microball size are in a comparable range. In this case, the light harvesting within the microball film cannot be modeled according to Beer-Lambert law, as it's based on the assumption of a flat homogeneous film.

Conclusion

We have demonstrated that the application of nanostructured NiO microballs to p-DSC provides a substantial improvement in J_{SC} compared to previous p-DSC reports. The high surface area and favorable pore size distribution of NiO- μBs after sintering facilitates higher dye loading. Sensitized NiO- μBs have substantially less parasitic absorption by the NiO itself, resulting in better light harvesting efficiencies. Consequently, p-DSC based on NiO- μBs were able to provide record J_{SC} (7.0 mA cm^{-2}) and IPCE values of up to 74% with an overall conversion efficiency of 0.43%. Devices using slightly thinner NiO- μBs films have achieved slightly higher efficiencies of 0.46%. J_{SC} of up to 10 mA cm^{-2} appear feasible with

PMI-6T-TPA-sensitized NiO p-DSCs. The J_{SC} values measured and projected in this work are getting closer to the current-densities required to match those of conventional high-efficiency photoanodic solar cells (n-DSCs) based on dye-sensitized TiO_2 . This clearly shows the feasibility of producing p-DSCs that are current matched with record-performing n-DSCs with the potential to boost the performance of tandem DSCs beyond current efficiency limitations of n-DSCs. What remains is the challenge to develop p-DSC sensitizers that harvest photons from a spectral range that is complementary to the absorption range of current high-efficiency n-DSC sensitizers. Considering the renewed interest in p-DSCs and given the recent progress in this field the gap between n-DSC and p-DSC performances is likely to be bridged even further, such that highly efficient tandem DSCs could soon be within reach.

Acknowledgements

The authors acknowledge financial support from the Australian Research Council through an Australian Research Fellowship (UB) and LIEF programs. Further financial support has been received from the Victorian State Government Department of Primary Industry (SERD Program, Victorian Organic Solar Cells Consortium), the Victorian Science Agenda (VSA), the Australia-Germany Solar Photovoltaics Research Program 2010–2011 as well as the Commonwealth Scientific and Industrial Research Organization through an OCE Science Leader position (UB). The Authors would also like to thank the NSFC (20873057) and the German Federal Ministry of Education and Research (BMBF) for financial support.

This work was also supported by the German Science Foundation (DFG) in the frame of a Collaborative Research Center (SFB) 569.

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Improved photocurrents for p-type dye-sensitized solar cells using nano-structured nickel(II) oxide microballs

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Supplementary information

NiO-NPs (NiO nanoparticle powder) were used as received from Inframat (73.22 wt% Ni) with a nominal particle size of 20 nm. All other chemicals and solvents were purchased from Sigma-Aldrich and used as received. Transmission electron microscopy (TEM) was performed on a JEOL-2100 microscope. X-ray diffraction (XRD) analyses were carried out on a Phillips powder diffractometer. The thicknesses of sintered electrodes were measured using a Veeco Dektak 6M stylus profilometer. The surface area was analyzed using Brunauer-Emmett-Teller (BET) analysis of N₂ adsorption-desorption studies (Fig. S2, ESI †) on a Micrometrics Tristar 3000 equipment. The counter electrode preparation and photocathode assembly was carried out as explained elsewhere.² The back filling hole was sealed using an aluminum-Surlyn sheet, which was prepared by heating aluminum foil with a 25 µm Surlyn sheet on a hot plate at 120 °C. Photocathodes were tested using an Oriel sun simulator (1,000 Wm⁻² Xe lamp) fitted with an AM 1.5 filter. The light intensity was calibrated using a calibrated silicon reference diode equipped with a KG3 filter provided and calibrated by the Fraunhofer Institute Freiburg (Germany). Current-voltage characteristics were measured using a Keithley 2400 source meter. The spectral response (IPCE) was measured using a 300 W Xe lamp fitted with an Oriel Cornstone

monochromator and recorded on a Keithley 2400 source meter. NiO- μ Bs and NiO-NPs films of about one micron thickness were printed for UV-vis spectroscopic studies. NiO- μ Bs were crushed by low energy ball milling for 24h to get a homogeneous film for optical analysis according to Lambert-Beer's law. The absorption properties of these films were measured before and after dye absorption, using a Perkin Elmer Lambda 950 spectrophotometer with integrating sphere attachment. A 2-step process was used to achieve quantitative dye desorption of PMI-6T-TPA off the NiO surface. The dyed films were first immersed in an aqueous dipotassium monohydrogen phosphate solution (0.7 M) for 10 min, this process did not result in any observable dye desorption. The electrodes were then rinsed with H₂O and ethanol before being immersed into a phosphoric acid solution in DMF (0.6 M) for 5 min to perform the actual dye desorption. The absorption spectra of desorbed dye solutions in DMF were measured using a Perkin Elmer Lambda 950 spectrophotometer. Baseline corrections were performed with a 0.6 M phosphoric acid solution.

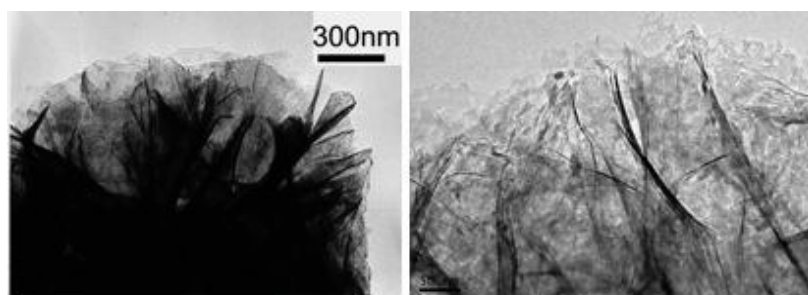


Fig.S1 TEM and HR-TEM images of synthesized NiO- μ Bs

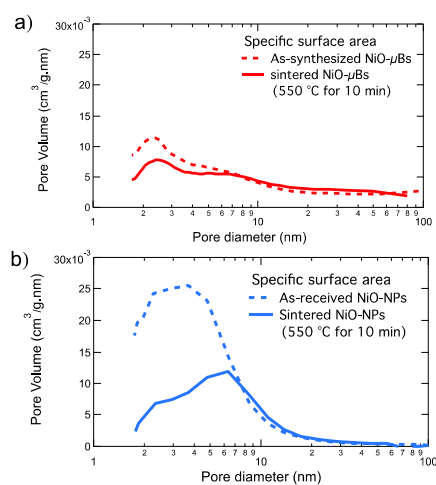


Fig.S2 Pore volume distribution for NiO powder and powder collected from NiO films sintered for 10 min at 550°C (a) NiO-μBs; and (b) NiO-NPs.

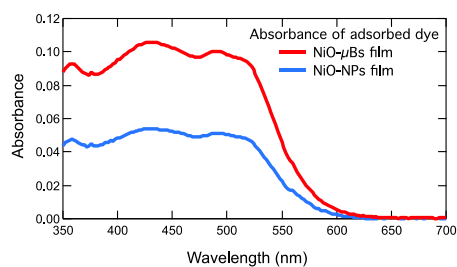


Fig.S3 Absorption spectra of desorbed dye from 1 μm thick (7 mm x 7 mm) NiO-NPs and NiO-μBs films. The amount of dye desorbed per film volume (0.049 mm³) from the NiO-μBs film was 11 nmoles and that of a NiO-NP film was 5.2 nmoles.

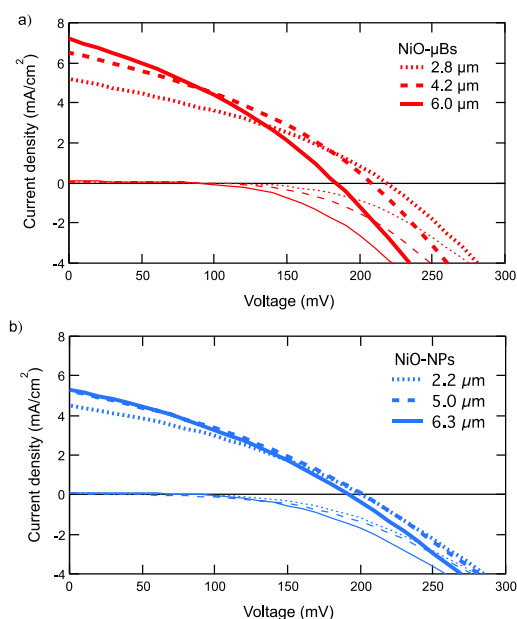


Fig.S4 Current density vs. voltage characteristics in the dark and under simulated 1 sun irradiation ($1,000 \text{ W/cm}^2$, AM1.5) of PMI-6T-TPA sensitized (a) NiO- μ Bs and (b) NiO-NPs films of various thicknesses.

Table S1: Photovoltaic performance of a $6.3 \mu\text{m}$ thick NiO-NPs and $6.0 \mu\text{m}$ thick NiO- μ Bs photocathodes (0.16 cm^2 NiO films) sensitized with PMI-6T-TPA dye under different incident light intensities of simulated sunlight (AM 1.5, 100% sun = $1,000 \text{ W/m}^2$).

	<i>NiO – NPs</i>			<i>NiO – μBs</i>		
Light intensity	10 % sun	38.5% sun	100% Sun	10 % sun	38.5% sun	100% Sun
V_{oc} (mV)	136	166	192	136	162	184
J_{sc} (mA/cm^2)	0.90	2.54	5.32	1.07	3.28	7.21
Fill Factor	0.38	0.35	0.32	0.40	0.36	0.33
Efficiency (%)	0.45	0.38	0.33	0.56	0.5	0.44

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Chapter 4

Highly Efficient p-Type Dye-Sensitized Solar Cells based on Tris(1,2- diaminoethane) Cobalt(II)/(III) Electrolytes

Monash University

Declaration for Thesis Chapter 4

Title: Highly Efficient p-Type Dye-Sensitized Solar Cells based on Tris(1,2-diaminoethane)Cobalt(II)/(III) Electrolytes

Declaration by candidate

In the case of Chapter 4, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
All experimental work except synthesis; preparation of the manuscript and editing	60%

The following co-authors contributed to the work. Co-authors who are students at Monash University must also indicate the extent of their contribution in percentage terms:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
Torben Daeneke	Cobalt synthesis, drafting and editing	N.A.
Michelle T. Ma	Cobalt synthesis, drafting and editing	N.A.
Dongchuan Fu	Data analysis, drafting and editing	N.A.
Noel W. Duffy	Data analysis, drafting and editing	N.A.
Günther Götz	Dye synthesis, drafting and editing	N.A.
Martin Weidelener	Dye synthesis, drafting and editing	N.A.
Amaresh Mishra	Drafting and editing	N.A.
Peter Bäuerle	Drafting and editing	N.A.
Leone Spiccia	Experimental design and planning, drafting and editing	N.A.
Udo Bach	Experimental design and planning, drafting and editing	N.A.

Candidate's Signature

	Date 01.05.2013
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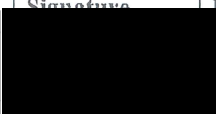
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Declaration by co-authors

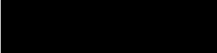
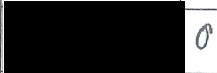
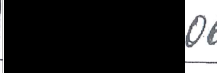
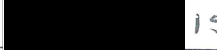
The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (6) the original data are stored at the following location(s) and will be held for at least five years from the date indicated below:

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Highly Efficient p-Type Dye-Sensitized Solar Cells based on Tris(1,2-diaminoethane)Cobalt(II)/(III) Electrolytes**

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The projected low manufacturing costs of dye-sensitized solar cells (DSCs) has made them attractive alternatives to traditional solar cells.^[1] In the conventional photoanodic DSCs (n-DSCs), photocurrent generation results from dye-sensitized electron injection into n-type semiconductors, such as TiO₂. In contrast, for dye-sensitized photocathodes (p-DSC), electron transfer takes place from the valence band of the p-type semiconductor (NiO being the most commonly used to date) to the photoexcited dye.^[2] The prospect of using p-DSCs as components in dye-sensitized tandem devices (pn-DSCs) has recently generated renewed interest in p-DSCs.^[3] Photocathodes employing the most efficient p-DSC sensitizer (PMI-6T-TPA; see Figure 1) reported to date in conjunction with a mesoporous NiO nanoparticles film and an I[−]/I₃[−] based electrolyte achieved efficiencies of up to 0.41 % under simulated sunlight (1000 W m^{−2}, AM 1.5 G). The PMI-6T-TPA-sensitized photocathode exhibits open-circuit voltages (V_{OC}) of up to 218 mV and short-circuit current densities (J_{SC}) of up to 5.35 mA cm^{−2}. Absorbed photon to charge carrier conversion efficiencies (APCE) up to 96 % have been observed for these p-DSCs.^[3] Despite this major advance-

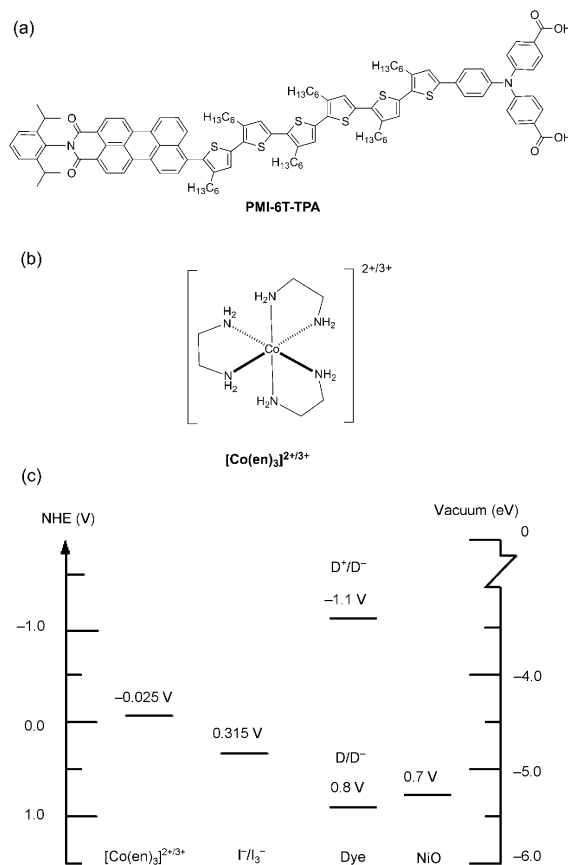


Figure 1. a) Structure of the PMI-6T-TPA sensitizer b) [Co(en)₃]^{2+/3+} and c) schematic energy diagram of the p-DSC device components used in this study (D = dye; NHE = normal hydrogen electrode). Electrolyte redox potentials were measured according to reference.^[7] The valence band edge of NiO was measured using photoelectron spectroscopy (PESA).

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[**] We acknowledge the Australian Research Council for providing equipment and fellowship support and the Australian Solar Institute, the Victorian State Government (DBI-VSA and DPI-ETIS) for financial support. The Commonwealth Scientific and Industrial Research Organization is acknowledged for providing support through an OCE Science Leader position (U.B.).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201206219>.

ment, p-DSCs are still lagging behind their n-type counterparts. Low open-circuit potentials represent a major performance limitation of these p-DSCs. Their V_{OC} is defined by the difference of the quasi-Fermi-level in the p-type semiconductor and the redox potential of the electrolyte. Strategies to increase the overall V_{OC} of p-DSCs, therefore, involve either a fine-tuning of the electronic properties of NiO, the replacement of NiO with a p-type material with a higher ionization potential or the replacement of I[−]/I₃[−] with a redox mediator

that is more easily oxidized. Some progress in this direction was recently achieved through the use of more crystalline NiO ($V_{OC}=350$ mV), p-type semiconductors with larger ionization energy, such as CuAlO₂ ($V_{OC}=333$ mV), CuGaO₂ ($V_{OC}=357$ mV) and the use of alternative electrolytes.^[4] In particular cobalt(II/III) complexes, such as [Co(ttb-tpy)]^{2+/3+}, [Co(dMeO-bpy)]^{2+/3+}, [Co(dtb-bpy)]^{2+/3+}, and [Co(dm-bpy)]^{2+/3+} (ttb-tpy = 4,4'-tri-*tert*-butyl tripyridine, dMeO-bpy = 4,4'-dimethoxyl bipyridine, dtb-bpy = 4,4'-di-*tert*-butyl bipyridine, and dm-bpy = 4,4'-dimethyl bipyridine) have found application in p-DSCs, affording open-circuit potentials of up to 350 mV.^[5] However, none of these approaches has resulted in an overall increase in energy conversion efficiency of p-DSCs beyond the 0.5% mark. Herein we report the use of tris(1,2-diaminoethane)cobalt(II/III) complexes ([Co(en)]^{2+/3+}) as redox mediators in p-DSCs. Application of this redox couple resulted in more than a twofold increase in photocathode efficiency (1.3%) and a twofold increase in V_{OC} (709 mV) compared to previously reported values.^[2b,3,4,5b,6] Importantly, a J_{SC} of 4.44 mA cm⁻² was also produced when I⁻/I₃⁻ electrolytes were replaced by [Co(en)]^{2+/3+} based electrolytes.

The redox potential of [Co(en)]^{2+/3+} based electrolytes is about 340 mV more negative than that of typical I⁻/I₃⁻ based p-DSC electrolytes, offering the scope to dramatically increase the V_{OC} of p-DSCs. At the same time, the driving force for dye-regeneration is still high (more than 1.0 eV) when [Co(en)]^{2+/3+} electrolytes are used in conjunction with PMI-6T-TPA as sensitizer.

Three electrolytes (EL1, EL2, and EL3, see Table 1) were prepared as described in the Experimental Section. The photovoltaic performances of p-DSCs with these three different electrolytes were measured under simulated sunlight (AM 1.5 G) with different light intensities. Table 1 summa-

rizes the photovoltaic performance at two different light intensities (100% sun and 10% sun). Photocathodes employing a classical I⁻/I₃⁻ electrolyte (EL1) generated a V_{OC} of 284 mV with a J_{SC} of 5.35 mA cm⁻² yielding 0.56% conversion efficiency at 100% sun condition. Replacing EL1 with the [Co(en)]^{2+/3+} based electrolytes (EL2, EL3) resulted in a 2.3 and 2.8-fold increase in device performance at 100% and 10% sun illumination, respectively. Photocathodes using EL2 produced the highest V_{OC} of 709 mV with an efficiency of 1.3%. This corresponds to a 2.5-fold increase in V_{OC} compared to EL1 based devices. A higher concentration of LiTFSI (0.5 M) in the EL3 electrolyte lowered both the V_{OC} (660 mV) and J_{SC} (4.35 mA cm⁻²) values but improved the fill factor (FF = 0.46) with similar power conversion efficiency (1.30%) compared to the EL2 electrolyte containing a lower LiTFSI concentration (0.1 M).

The J_{SC} values at lower sun intensities (10% sun) were as high as 0.57 mA cm⁻² and 0.56 mA cm⁻² for photocathodes based on EL2 and EL3 electrolytes. Photocathodes based on EL3 electrolytes achieved the highest FF of 0.52 and overall efficiency of 1.67% at 10% sunlight intensity. The solar cell data presented was measured with settling time of 1 s for EL1 and 3 s for EL2 and EL3, where the front bias and reverse bias efficiencies co-incite with each other. For shorter settling times, hysteresis was found to affect the results (See Supporting Information, Figure S4–S9).

The stability of the electrolytes is another important aspect to explore. Aging tests were performed on p-DSC employing EL3 electrolyte at room temperature in the dark. The efficiency improved due to improvements in FF over time. Figure S2 shows the photocathodes stability data for 624 h.

To further characterize the p-DSCs, majority charge carrier lifetimes (hole lifetimes τ_p) were measured using intensity modulated photovoltage spectroscopy (IMVS). The hole lifetime describes the average time a photogenerated hole will remain in the NiO film before it crosses the NiO–electrolyte interface and recombines with the reduced redox mediator. IMVS analysis is usually combined with intensity modulated photocurrent spectroscopy (IMPS) and charge extraction measurements. IMPS measurements allow the quantification of charge transport times in the semiconductor while charge extraction analysis can be used to identify shifts in the conduction and valence bands of the semiconductor. Similar to the TiO₂ conduction band, the NiO valence band edge is known to shift with pH value.^[8] Differences in the electrolyte composition, especially the addition of excess 1,2-diaminoethane, may alter the proton activity of the electrolyte. This change can lead to a shift in the NiO valence band and a change in open-circuit voltage. We found that the capacitive nature of NiO films interfered with IMPS measurements conducted at short circuit and prohibited the determination of possible valence-band shifts and changes of the charge transport times (See Figure S3 for charge extraction data).^[9]

For all further analysis, p-DSCs based on EL1 electrolytes were compared with high efficiency devices based on the EL3 electrolytes. Figure 2 shows the dependence of the hole lifetime on J_{SC} . The hole lifetimes for the EL1 and EL3 based

Table 1: Photovoltaic performance of p-DSCs based on mesoporous NiO electrodes.^[a]

100% Sun	EL1 ^[b]	EL2 ^[c]	EL3 ^[d]
V_{OC} [mV]	284 ± 15	709 ± 10	660 ± 14
J_{SC} [mA cm ⁻²]	5.35 ± 0.17	4.44 ± 0.22	4.35 ± 0.40
Fill Factor	0.37 ± 0.01	0.42 ± 0.02	0.46 ± 0.05
Efficiency [%]	0.56 ± 0.04	1.30 ± 0.09	1.30 ± 0.08
10% Sun	EL1 ^[b]	EL2 ^[c]	EL3 ^[d]
V_{OC} [mV]	219 ± 15	640 ± 11	587 ± 17
J_{SC} [mA cm ⁻²]	0.66 ± 0.01	0.57 ± 0.03	0.56 ± 0.04
Fill Factor	0.40 ± 0.03	0.45 ± 0.06	0.52 ± 0.02
Efficiency [%]	0.58 ± 0.06	1.61 ± 0.13	1.67 ± 0.12

[a] Film thickness = 2.5 μm and surface area = 0.16 cm²; sensitized with PMI-6T-TPA under simulated sunlight. All p-DSCs were tested in front-illumination mode (light incident on the dye-sensitized NiO electrode) with settling time of 1 s/10 mV for EL1 and 3 s/10 mV for EL2 and EL3 measured from positive bias to negative bias. The corresponding IV curves are shown in Figure S1. [b] EL1: (0.03 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-*tert*-butylpyridine, and 0.1 M guanidinium thiocyanate in 85:15 acetonitrile:valeronitrile), [c] EL2: (0.07 M [Co(en)](BF₄)₃, 0.3 M Co(BF₄)₂·6 H₂O, 0.1 M lithium bis(trifluoromethanesulfonyl)imide) (LiTFSI), 1.67 M 1,2-diaminoethane in acetonitrile) and [d] EL3: (0.07 M [Co(en)](BF₄)₃, 0.3 M Co(BF₄)₂·6 H₂O, 0.5 M LiTFSI, 1.67 M 1,2-diaminoethane in acetonitrile).

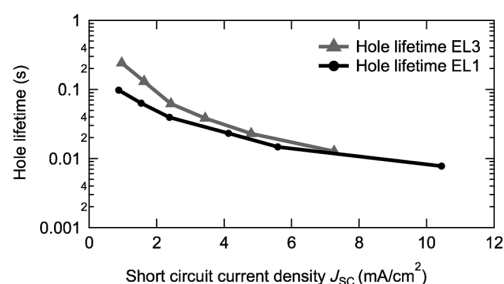


Figure 2. Hole lifetime as a function of short-circuit density (J_{sc}) for the photocathodes employing I^-/I_3^- based (black circles) and $[Co(en)_3]^{2+/3+}$ based (gray triangles) electrolytes.

devices were found to be approximately similar at a given J_{sc} , indicating similar recombination losses for I^-/I_3^- and $[Co(en)_3]^{2+/3+}$ based electrolytes. These results are encouraging since single-electron redox couples for n-DSCs usually suffer from increased recombination losses compared to two-electron redox couples.^[10] Furthermore, the observed hole lifetime of 66 ms at 100% sun is similar to electron lifetimes observed for typical high performance n-DSCs.^[11]

Incident photon to electron conversion efficiency (IPCE) spectra of p-DSCs using EL3 and EL1 electrolytes are shown in Figure 3. Under front-illumination (light incident from the sensitized NiO electrode) $[Co(en)_3]^{2+/3+}$ and I^-/I_3^- based p-DSCs display almost identical IPCE spectra that feature a broad plateau between 400 and 520 nm with similar peak IPCE values of 66% (EL1) and 57% (EL3). To determine the redox mediator's applicability in tandem solar cells (pn-DSCs); back-illumination IPCE spectra were measured by illuminating light from the counter-electrode side. The measured IPCEs under back illumination were corrected for the transmission losses that occurred at the counter electrodes to calculate the 'corrected back-IPCEs'. The shape of the curves can easily be explained based on the absorption properties of the 22.5 μm thick electrolyte layer located between the counter electrode and the sensitized NiO film (see Figure 3c). Above 500 nm, the corrected back-IPCEs closely follow the front IPCE for both electrolyte systems whereas below 500 nm the corrected back-IPCE of iodide based DSCs (EL1) drops down steadily to reach a value close to 0% at about 380 nm. This drop is caused by the strong absorptivity of I^-/I_3^- based electrolytes in this wavelength range. For $[Co(en)_3]^{2+/3+}$ based DSCs (EL3), the front and corrected back IPCE follow each other closely throughout the wavelength range. At around 480 nm, the corrected back-IPCE for EL3-based DSCs shows a shallow minimum, which was not observed in front-illumination mode. This is caused by a weak absorption maximum (7.9% absorptivity) for the $[Co(en)_3]^{2+/3+}$ electrolyte in this spectral region. Generally, the absorptivity of the $[Co(en)_3]^{2+/3+}$ based electrolyte remains well below 10% over most of the wavelength range, making it an excellent choice for tandem solar cells where one of the two photoelectrodes inevitably needs to operate in back-illumination mode.

In conclusion, we have shown that the $[Co(en)_3]^{2+/3+}$ redox couple is an excellent mediator for p-DSCs, affording energy

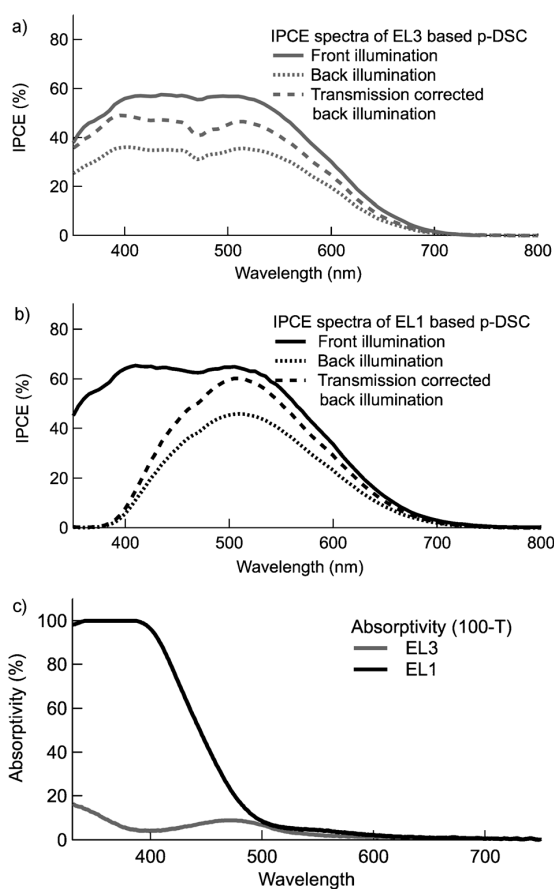


Figure 3. IPCE spectra of p-DSCs with illumination through the working electrode (front illumination), counter electrode (back illumination) and the back-illumination IPCE corrected for the transmission losses that occur at the counter electrode is also shown: a) EL3 electrolyte ($[Co(en)_3]^{2+/3+}$); and b) EL1 electrolyte (iodide/triiodide) c) Absorptivity spectra of EL3 (gray line) and EL1 (black line) electrolytes in a cell with 25 μm optical pathlength. (See Experimental Section for electrolyte compositions.)

conversion efficiencies of 1.3% at 100% sun (1.67% at 10% sun) and open-circuit voltages as high as 709 mV. This corresponds to a 2.3-fold increase in η and twofold in V_{OC} , compared to the best performing p-DSCs known to date. Surprisingly, the lifetimes of photoinjected holes in the valence band of NiO were almost identical for the one-electron redox couple $[Co(en)_3]^{2+/3+}$ and the two-electron I^-/I_3^- redox system. These hole lifetimes were also comparable to the electron lifetimes in conventional TiO_2 -based DSCs.

Electrolytes based on $[Co(en)_3]^{2+/3+}$ are optically transparent, making them very suitable for application in tandem solar cells, where one of the two dye-sensitized electrodes needs to operate in back-illumination mode. The use of $[Co(en)_3]^{2+/3+}$ in conjunction with dye-sensitized TiO_2 electrode, affords low built-in voltages of around 475 mV. This could provide an opportunity to develop NIR-sensitive n-DSCs, which are difficult to achieve for conventional TiO_2 /dye/ I^-/I_3^- DSCs owing to insufficient driving forces for either

dye regeneration or charge injection. Moreover, the use of $[\text{Co}(\text{en})_3]^{2+/3+}$ based p-DSCs in conjunction with alternative n-type materials with higher-lying conduction band edges could provide an opportunity to realize tandem DSCs with unprecedentedly high V_{oc} .

Experimental Section

Dye-sensitized photocathodes were constructed following literature procedures.^[3,12] In brief, NiO nanoparticle (Inframat) based screen-printing paste was printed on plain FTO glass (NSG—8 $\Omega/\square$, 4 mm thick) using a semi-automatic screen printer. 2.5 μm thick NiO electrodes were sensitized in a 0.2 mM PMI-6T-TPA dye solution (in DMF) for 2 h, before they were used to construct photocathodes with platinized conductive glass counter electrodes. Three electrolytes were prepared; an optimized I^-/I_3^- electrolyte (EL1); and two $[\text{Co}(\text{en})_3]^{2+/3+}$ based electrolytes (EL2, EL3) with different LiTFSI concentrations (0.1M and 0.5M). The I^-/I_3^- based electrolyte (EL1) was composed of 0.03M iodine, 0.6M 1-butyl-3-methylimidazolium iodide, 0.5M 4-*tert*-butylpyridine, and 0.1M guanidinium thiocyanate in 85:15 acetonitrile:valeronitrile. The $[\text{Co}(\text{en})_3]^{2+/3+}$ based electrolyte (EL2) contained 0.07M $[\text{Co}(\text{en})_3](\text{BF}_4)_3$, 0.3M $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, 0.1M lithium bis(trifluoromethanesulfonylimide) (LiTFSI), 1.67M 1,2-diaminoethane in acetonitrile. EL3 contained a higher LiTFSI concentration of 0.5M. $[\text{Co}(\text{en})_3]^{2+/3+}$ electrolytes were prepared in the glovebox. Exclusion of oxygen during electrolyte preparation and cell construction was important as $[\text{Co}(\text{en})_3]^{2+}$ can oxidize to $[\text{Co}(\text{en})_3]^{3+}$ in the presence of air.^[13] Devices were characterized at slow scan rates (1 s for EL1 and 3 s for EL2 and EL3). Electrochemically deposited platinum counter electrodes were used for the front and back illumination IPCE studies.^[14]

Received: August 3, 2012

Published online: November 21, 2012

Keywords: cobalt · dye-sensitized solar cells · electrolytes · photocathodes

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Supporting Information

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**Highly Efficient p-Type Dye-Sensitized Solar Cells based on
Tris(1,2-diaminoethane)Cobalt(II)/(III) Electrolytes****

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Udo Bach**

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Supporting information

NiO working electrode preparation:

NiO nanoparticle powder was used as received from Inframat (73.22 wt % Ni) with a nominal particle size of 20 nm. All other chemicals and solvents were purchased from Sigma-Aldrich and used as received. Screen-printing pastes were prepared by mixing 8 wt % NiO, 46 % ethyl cellulose solution (5 wt % in ethanol) and 46 % terpineol using as-received NiO nanoparticle powder. The paste was printed on FTO glass (NSG - 8 $\Omega/\square$, 4 mm thick) using a commercial semiautomatic screen printer. The thicknesses of the sintered electrodes were measured using a Veeco Dektak 6M stylus profilometer.

Synthesis of $[\text{Co}(\text{en})_3](\text{BF}_4)_3$:

Synthesis of $[\text{Co}(\text{en})_3]\text{Cl}_3$ was carried out according to reported procedures.^[13] Typically, $[\text{Co}(\text{en})]\text{Cl}_3$ (3 – 4 g) was dissolved in tetrafluoroboric acid (100 – 150 mL) with gentle heating. Nitrogen gas was bubbled through the solution, followed by heating under reduced pressure (to remove HCl). Addition of one – two parts diethyl ether resulted in precipitation of a fine orange powder. This was collected on a sintered glass frit, washed with diethyl ether and allowed to dry, providing $[\text{Co}(\text{en})_3](\text{BF}_4)_3$ in quantitative yield. Addition of aqueous AgNO_3 to an aqueous solution of this salt did not result in precipitation of any silver salts.

Microanalysis found C 14.43 %, H 4.81 %, N 16.78 %; requires C 14.42 %, H 4.84 %, N 16.82 %. ^1H NMR (400.17 MHz in CD_3CN , solvent reference δ 1.94): δ 2.75, broad s, 6H, diastereotopic CH_2 ; 2.80 broad s, 6H, diastereotopic CH_2 ; δ 3.95 broad s, 6H, diastereotopic NH_2 ; 4.35, broad s, 6H, diastereotopic NH_2 . ^{13}C NMR (100.6 MHz, CD_3CN , solvent reference δ 1.32): δ 45.6 CH_2 . ^{19}F NMR (376.5 MHz, CD_3CN , 10% trifluoroacetic acid external reference δ 0): δ -73.7 BF_4^- .

1,2-Diaminoethane used in electrolyte solution was dried (KOH, Na metal for 4 hours, 4 Å sieves for 48 hours) and then distilled under a dry, inert atmosphere.

Cell assembly:

The counter electrode was prepared using 3 mm thick (NSG – 15 $\Omega/\square$). The dyed NiO working electrode and the counter electrode were assembled together using a 25 μm thick surlyn gasket. Pneumatic finger press was used to press the working electrode while heating counter electrode. The electrolyte was vacuum backfilled in the cell cavity. The back filled hole was sealed using an aluminum-Surlyn sheet, which was prepared by heating aluminum foil with a 25 μm Surlyn sheet on a hot plate at 120 °C.

Electrochemical measurement:

Electrochemical experiments were performed at room temperature in the glove box using a potentiostat. The redox potential of the electrolytes was determined from the potential difference between a platinum wire, immersed in the redox electrolyte, and a Ag/Ag⁺ reference electrode.^[7] The reference electrode was calibrated against the freshly prepared ferrocene/ferrocenium redox couple.

Device characterization:

An Oriel sun simulator (1,000 Wm⁻² Xe lamp) fitted with an AM 1.5 filter resembling solar spectrum was used to test the photocathodes. The light intensity was calibrated with a calibrated silicon reference diode (Fraunhofer) equipped with a KG3 filter to reduce spectral mismatch between calibrated diode and measured photocathode. Current-voltage characteristics were measured using a Keithley 2400 source meter and a custom made labview software.

The spectral response (IPCE) of the photocathode was measured using an Oriel 300 W Xe lamp fitted with a Cornstone monochromator and recorded on a Keithley 2400 source meter. The light intensity was quantified using a calibrated Fraunhofer reference diode.

IMVS/IMPS measurements:

For the IMPS and IMVS measurements, a circular LED array (Luxeonstar) consisting of seven green (530 nm) LEDs (LXML-PM01-010) equipped with a concentrating cluster lens (Polymer 263 - Fibre Optic Concentrator) was modulated to a depth of ca. 2 % using a purpose built LED driver with an adjustable DC offset and Stanford lock-in-amplifier (SR810). A set of neutral density filters was used to vary illumination intensity. Performing the experiment in an earthed Faraday dark-box eliminated electrical noise at low light intensities. Photocurrents were measured using a battery powered current preamplifier (Stanford SR570) and photovoltages measured using a purpose built battery powered high impedance voltage follower (input impedance 10¹² Ω). The phase and amplitude of the resultant AC photocurrent (or photovoltage) were captured using the lock-in amplifier (SR810) under computer control (Labview).

Charge Extraction Measurements:

A charge extraction setup identical as explained by Duffy *et al.*^[15] The same light source used in IMVS/IMPS was used for charge extraction measurement. Ni USB 6251 BNC data acquisition board was used to record the data.

Absorption spectroscopy measurements:

Two microscopic slides were assembled together with 25 μm thick surlyn gasket. The electrolyte was backfilled in the cavity through a pre-drilled hole. The absorption of electrolytes was measured using a Perkin Elmer Lambda 950 spectrophotometer with integrating sphere attachment.

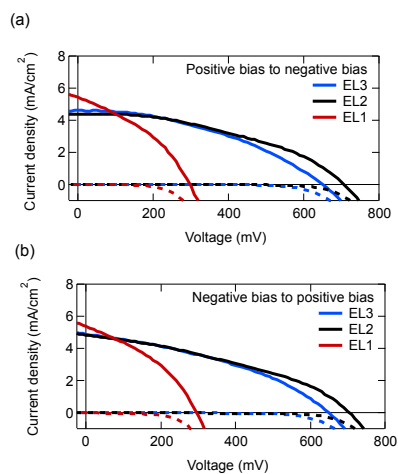


Figure S1: Current density vs. voltage characteristics in the dark (dotted lines) and under simulated 1 sun irradiation (1,000 W/cm², AM 1.5) (solid lines) of PMI-6T-TPA sensitized NiO photocathodes employing I⁻/I₃⁻ based EL1 electrolyte (red lines); [Co(en)₃]^{2+/3+} based EL2 electrolyte containing 0.1 M LiTFSI (black lines) and 0.5 M LiTFSI EL3 electrolyte (blue lines).

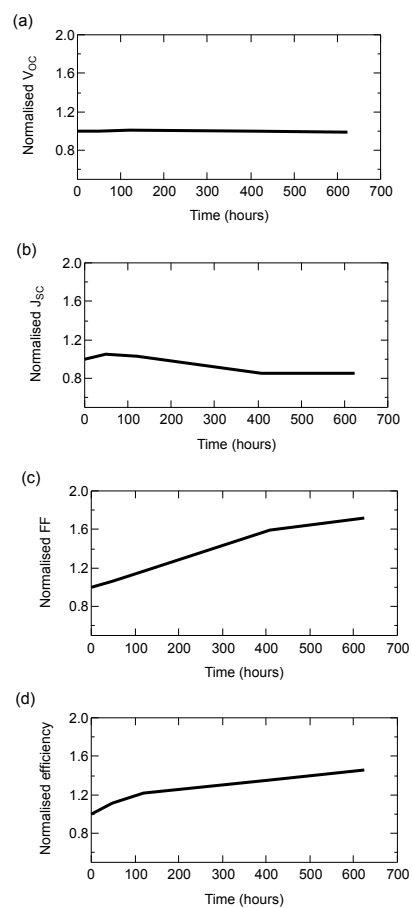


Figure S2 Normalized photocathode stability data with $[\text{Co}(\text{en})_3]^{2+/3+}$ based EL3 electrolyte; stored at room temperature in dark and characterized at 100 % sun (AM1.5G).

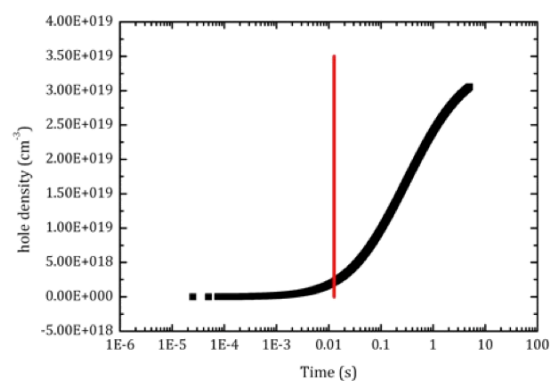


Figure S3 Extracted charge vs. time plot of photocathode with EL3 based electrolyte at 140 % sun. Vertical line represents the hole lifetime determined by IMVS.

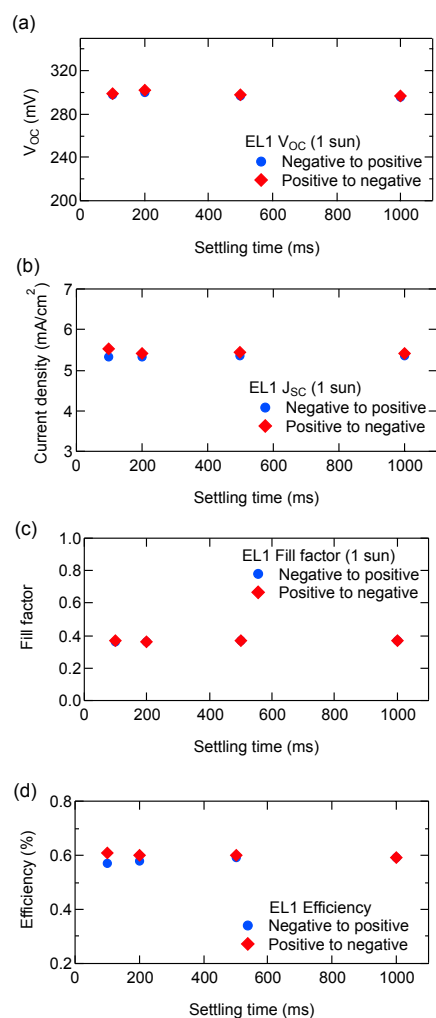


Figure S4 Summary of current density vs. voltage characteristics under simulated 100% sun irradiation (1,000 W/cm², AM 1.5G) of PMI-6T-TPA sensitized NiO photocathodes employing I⁺/I₃⁻ based EL1 electrolyte with different settling times and scan directions

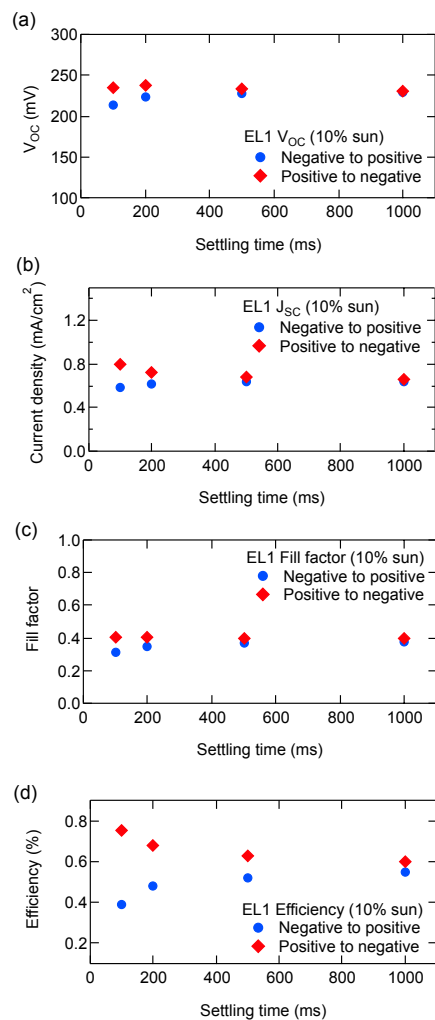


Figure S5 Summary of current density vs. voltage characteristics under simulated 10% sun irradiation (100 W/cm², AM 1.5G) of PMI-6T-TPA sensitized NiO photocathodes employing I/I₃⁺ based EL1 electrolyte with different settling times and scan directions

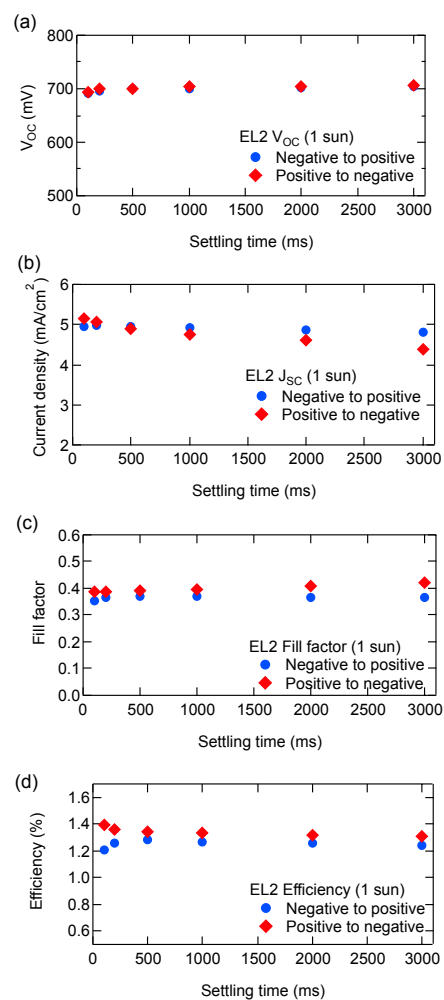


Figure S6 Summary of current density vs. voltage characteristics under simulated 100% sun irradiation (1,000 W/cm², AM 1.5G) of PMI-6T-TPA sensitized NiO photocathodes employing [Co(en)₃]^{2+/3+} based EL2 with different settling times and scan directions

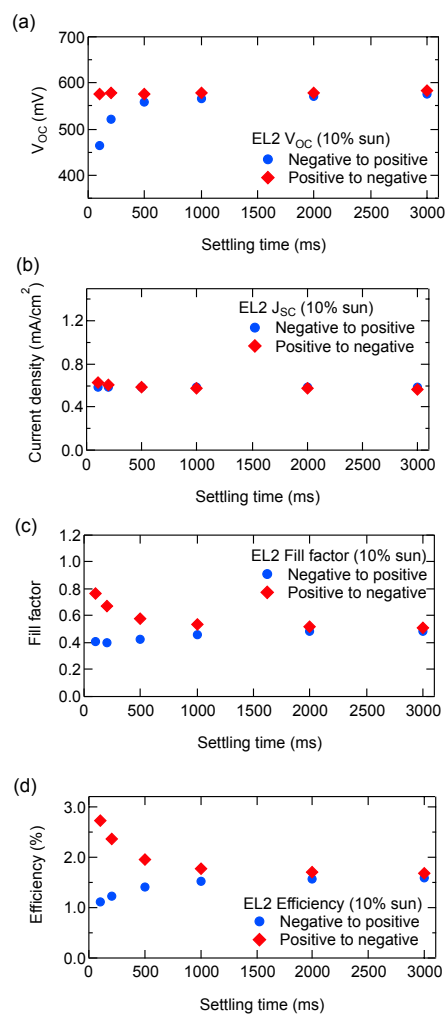


Figure S7 Summary of current density vs. voltage characteristics under simulated 10% sun irradiation (100 W/cm², AM 1.5G) of PMI-6T-TPA sensitized NiO photocathodes employing [Co(en)₃]^{2+/3+} based EL2 electrolyte with different settling times and scan directions

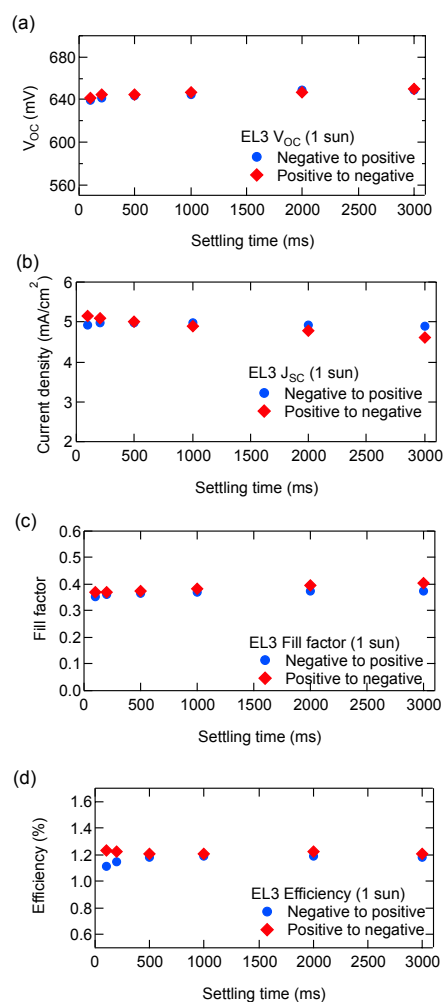


Figure S8 Summary of current density vs. voltage characteristics under simulated 100% sun irradiation (1,000 W/cm², AM 1.5G) of PMI-6T-TPA sensitized NiO photocathodes employing [Co(en)₃]^{2+/3+} based EL3 electrolyte with different settling times and scan directions

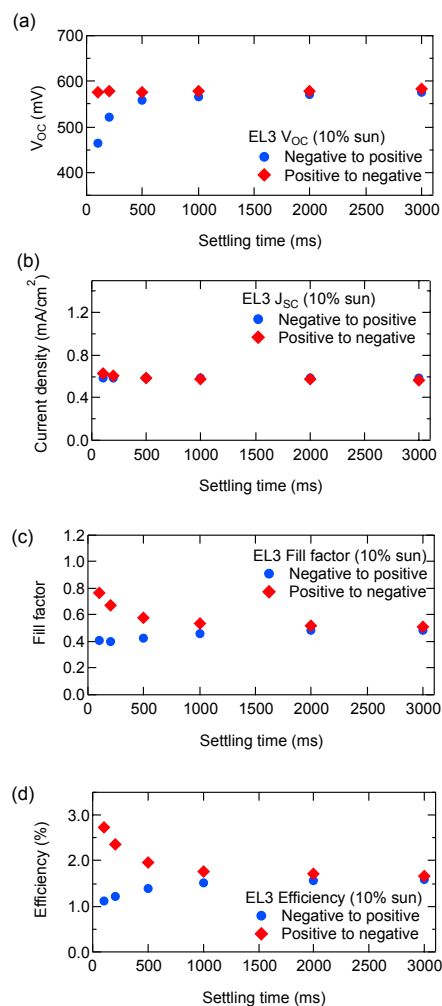


Figure S9 Summary of current density vs. voltage characteristics under simulated 10% sun irradiation (100 W/cm², AM 1.5G) of PMI-6T-TPA sensitized NiO photocathodes employing [Co(en)₃]^{2+/3+} based EL3 electrolyte with different settling times and scan directions

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Chapter 5

Improved Photovoltages for p-Type Dye-sensitized Solar Cells Using CuCrO₂ Nanoparticles

Monash University

Declaration for Thesis Chapter 5

Title: Improved Photovoltages for p-Type Dye-sensitized Solar Cells Using CuCrO₂ Nanoparticles

Declaration by candidate

In the case of Chapter 5, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Experimental work except synthesis and transient absorption spectroscopy (TAS); preparation of the manuscript and editing	60%

The following co-authors contributed to the work. Co-authors who are students at Monash University must also indicate the extent of their contribution in percentage terms:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
Dehua Xiong	CuCrO ₂ synthesis, drafting and editing	N.A.
Torben Daeneke	TAS analysis, drafting and editing	N.A.
Michelle T. Ma	Cobalt synthesis, drafting and editing	N.A.
Akhil Gupta	AC2 measurement, drafting and editing	5 %
George Lee	TEM imaging, drafting and editing	N.A.
Satoshi Makuta	TAS measurement, drafting and editing	N.A.
Yasuhiro Tachibana	TAS analysis, drafting and editing	N.A.
Wei Chen	Drafting and editing	N.A.
Leone Spiccia	Drafting and editing	N.A.
Yi-Bing Cheng	Drafting and editing	N.A.
Günther Götz	Dye synthesis, drafting and editing	N.A.
Peter Bäuerle	Drafting and editing	N.A.
Udo Bach	Experimental design and planning, drafting and editing	N.A.

Candidate's
Signature

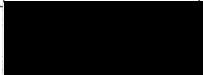
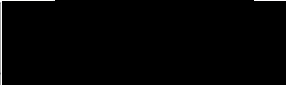
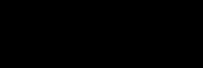
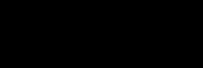
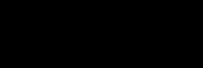
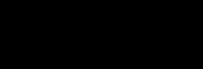
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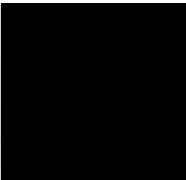
Declaration by co-authors

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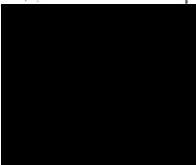
- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
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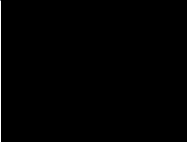
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DOI: 10.1002/cssc.201((will be completed by the editorial staff))

Improved Photovoltages for p-Type Dye-sensitized Solar Cells Using CuCrO₂ Nanoparticles

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Dedication ((optional))

The photocurrent generation in photoanodic DSCs (n-DSCs), results from dye-sensitized electron injection into n-type semiconductors such as TiO₂.^[1] In photocathodic dye-sensitized solar cells (p-DSCs) the photocurrent results from photoinduced electron transfer from the valence band of a p-type semiconductor to the photoexcited dye.^[2] Photoanodes and photocathodes can be combined in simple sandwich structures to form a tandem dye-sensitized solar cell (pn-DSC). According to Kirchhoff's circuit law, the photovoltages of p-DSC and n-DSC are additive in this type of tandem architecture.^[2]

Tandem solar cells can overcome the Shockley-Queisser efficiency limitation that applies to single junction photovoltaic devices,^[3] offering the scope to improve the efficiency of DSCs beyond current limits. This, however, is conditional on the availability of p-DSCs that match the requirements DSCs in terms of photocurrent generation and energy level positions.

The donor-acceptor dye, PMI-6T-TPA (see Figure 1a) is an efficient sensitizer for photocathodes which can achieve absorbed photon to charge carrier conversion efficiencies (APCEs) of up to 96%.^[2b, 4] In our recent study we showed that employing the [Co(en)₃]^{2+/3+} redox mediator (Figure S1, ESI †) in p-DSCs based on PMI-6T-TPA sensitized NiO allowed to double the best previously reported p-DSCs open circuit voltage (V_{OC}) to 709 mV.^[5] Despite these improvements, the best conversion efficiency reported to date for p-DSCs is 1.3 %, a value that is still lagging behind the best n-DSCs conversion efficiency (12.3 %).^[6]

One of the obstacles in the design of high efficiency p-DSCs is thought to be the p-type semiconductor. NiO limits the p-DSCs performance, due to its intrinsic properties, such as the capacitive nature, which interferes with charge extraction.^[5, 7] The hole diffusion coefficient of NiO (10⁻⁸ to 10⁻⁷ cm² s⁻¹ depending on preparation method) is at least two orders of magnitude smaller than the electron diffusion coefficient in TiO₂.^[8] Furthermore, the photo-inactive NiO was shown to absorb about 30-40% of the overall incident light in p-DSCs, thus limiting the achievable photocurrent. Due to the position of its valence band, the theoretical limit of the achievable open circuit voltage (V_{OC}) of NiO is 385 mV when used in conjunction with I⁻/I₃⁻ based electrolytes.^[2b, 5]

One strategy to improve the p-DSC performance would be to replace NiO with an alternative p-type material with a higher ionization potential. This strategy would also assist to improve the V_{OC} of tandem pn-DSCs, which is defined by the difference

between the quasi-Fermi level near the valence band in the p-type semiconductor and that near the conduction band of the n-type semiconductor. Hence, the introduction of a new p-type semiconductor could potentially result in higher V_{OC}s, for the pn-tandem DSC. Some advances to replace NiO in p-DSCs were recently reported, introducing p-type semiconductors such as CuO (V_{OC} = 150 mV), CuAlO₂ (V_{OC} = 333 mV) and CuGaO₂ (V_{OC} = 375 mV) in conjunction with either I⁻/I₃⁻ or cobalt polypyridyl redox mediators.^[9]

Herein, we report the synthesis of CuCrO₂ nanoparticles (CuCrO₂-NPs) and their successful conversion to mesoporous CuCrO₂ films for p-DSCs with unprecedentedly high V_{OC}s (734 mV).^[5, 10] Mesoporous NiO and CuCrO₂ films were compared in p-DSCs. Photoelectron spectroscopy in air revealed an ionization potential (valence band edge) of - 5.3 eV vs. vacuum for the as-synthesized CuCrO₂, 0.1 eV lower than that of NiO-NPs, offering an opportunity to improve the overall V_{OC} of p-DSCs. Figure 1(b) shows the energy schematics of the major p-DSC components.

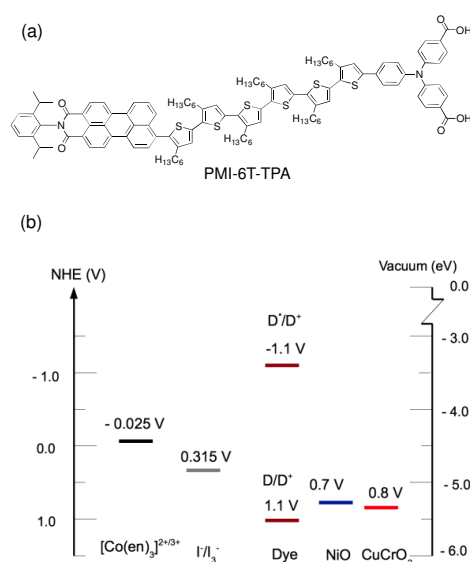


Figure 1. (a) Chemical structure of PMI-6T-TPA sensitizer, (b) energy diagram representation of the p-DSC components used in this study. The valence band edges of NiO and CuCrO₂ were measured by photoelectron

spectroscopy in the air (PESA, see Figure S2, ESI †). The electrolyte redox potentials were measured as described by Boschloo *et al.*^[11]

PMI-6T-TPA-sensitized p-DSCs employing iodine and [Co(en)₃]^{2+/3+} based electrolytes were constructed from CuCrO₂ and NiO films as previously described.^[12] Their photovoltaic performances were measured under simulated sunlight (1000 W m⁻², AM 1.5G) and are summarized in Table 1 (photocurrent-voltage characteristics curves, Figure S4 ESI †). DSCs constructed from CuCrO₂ films showed improved V_{OC}s, compared to their NiO counterparts, with increases of 42 and 94 mV for iodine and [Co(en)₃]^{2+/3+} based electrolytes respectively. The latter matches well with the V_{OC} increase expected from the ionization potential difference measured for the two semiconductor materials (100 mV), resulting in the highest V_{OC} (734 mV) that has ever been reported for a p-DSC to date.^[4-5, 13]

Table 1. Photovoltaic performance parameters of NiO and CuCrO ₂ photocathodes (film thickness = 1.8 μm and film area = 0.16 cm ²) sensitized with PMI-6T-TPA dye under simulated sunlight (AM 1.5G, 1,000 W m ⁻²).				
	NiO		CuCrO₂	
Redox Couple	I ⁻ /I ₃ ⁻	[Co(en) ₃] ^{2+/3+}	I ⁻ /I ₃ ⁻	[Co(en) ₃] ^{2+/3+}
V _{OC} (mV)	226 ± 4	640 ± 10	268 ± 10	734 ± 9
J _{SC} (mA cm ⁻²)	5.40 ± 0.24	3.72 ± 0.14	1.98 ± 0.05	1.23 ± 0.17
Fill Factor	0.36 ± 0.01	0.42 ± 0.04	0.44 ± 0.03	0.53 ± 0.04
Efficiency (%)	0.45 ± 0.02	1.00 ± 0.01	0.23 ± 0.02	0.48 ± 0.08
For the electrolyte composition, see Experimental Section.				

Photocurrent densities (J_{SC}s) recorded for CuCrO₂ p-DSCs were generally lower than for those employing NiO. This is consistent with the low incident photon to charge carrier conversion efficiency (IPCE) observed for these devices (Figure 2). The peak IPCE value for NiO-NPs photocathodes employing the I⁻/I₃⁻ electrolyte was 59 % compared to 16 % for CuCrO₂ photocathode. The corresponding IPCE values for [Co(en)₃]^{2+/3+} based p-DSCs were 40 % (NiO) and 8 % (CuCrO₂). Despite the high V_{OC}, the overall conversion efficiencies of CuCrO₂-NPs based devices were limited by the low photocurrents and reached 0.23% for I⁻/I₃⁻ and 0.48% for the [Co(en)₃]^{2+/3+} electrolytes. The photocurrent density (J_{SC}) generated by a photocathode is a function of the light harvesting efficiency (LHE) and the absorbed photon to charge carrier conversion efficiency (equation 1). The APCE itself is the product of charge injection efficiency (φ_{inj}) and charge collection efficiency (φ_{cc}).

$$J_{SC} = \frac{e}{hc} \int \phi_p \text{AM1.5G}(\lambda) \cdot \text{LHE}(\lambda) \cdot \text{APCE} \cdot d\lambda \quad (1)$$

$$A_{(\text{Dye})}(\lambda) = A_{(\text{Dyed SC})}(\lambda) - A_{(\text{SC})}(\lambda) \quad (2)$$

$$\text{LHE}_{(\text{dye})}(\lambda, d) = \frac{A_{(\text{Dye})}(\lambda)}{A_{(\text{Dyed SC})}(\lambda)} \cdot (1 - 10^{-\tilde{A}_{(\text{Dyed SC})}(\lambda) \cdot d}) \quad (3)$$

$$\text{APCE}(\lambda) = \frac{\text{IPCE}(\lambda)}{\text{LHE}(\lambda)} \quad (4)$$

Where where (φ_p) is the photon flux, A_(SC)(λ) and A_(Dyed SC)(λ) are the absorptions of the semiconductor film prior to and following dye absorption respectively. $\tilde{A}_{(\text{Dyed SC})}(\lambda)$ is the absorption of the dyed semiconductor film per μm and d is the film thickness in μm.

A detailed optical analysis was carried out to compare the light harvesting properties of CuCrO₂ and NiO based films. The dye absorption on 1.8 μm thick semiconductor film was measured by comparing the film absorption before and after dye-uptake (Equation 2). Based on these results the light harvesting efficiency (Figure 3b) was calculated according to Equation 3. The light harvesting of sensitized NiO films is superior to that of sensitized CuCrO₂ films of the same thickness. At the dye's absorption maximum (436 nm) the light harvesting of the 1.8 μm thick NiO film is 61 %, compared to 48 % for the CuCrO₂ film. However, the lower LHE cannot account for the three-fold difference in short-circuit photocurrent between CuCrO₂ and NiO based p-DSCs.

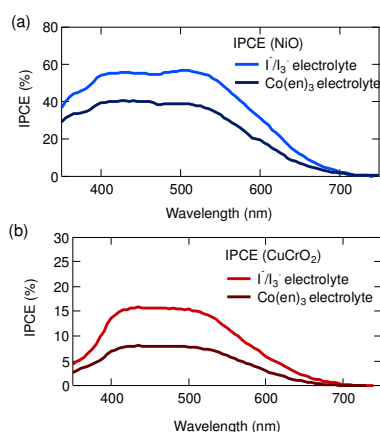


Figure 2. IPCE spectra of (a) NiO-NPs based p-DSC employing I⁻/I₃⁻ (blue) and [Co(en)₃]^{2+/3+} (navy blue) electrolytes (b) CuCrO₂-NPs based p-DSC employing I⁻/I₃⁻ (red) and [Co(en)₃]^{2+/3+} (brown) electrolytes.

APCE calculations according to Equation 4 (see Figure S5 and Table S2, ESI †) revealed drastically reduced APCE values for CuCrO₂ (40% for I⁻/I₃⁻; 26% for [Co(en)₃]^{2+/3+}) compared to NiO DSCs (96% for I⁻/I₃⁻; 70% [Co(en)₃]^{2+/3+}) as the main reason for the reduced photocurrents in CuCrO₂ DSCs (see Figure S5, ESI †). The expected photocurrents as a function of device thickness were calculated (see Figure S6, ESI †) according to Equation 1.

As expected for devices limited by their low APCE a thickness increase is not expected to solve the low photocurrent issue. This has been confirmed experimentally for a series of DSCs employing an iodide electrolyte with CuCrO₂ film thicknesses ranging from 0.6 μm to 3.6 μm (see Figure S6, ESI †). An increase in CuCrO₂ film thicknesses from 0.6 μm to 3.6 μm only resulted in a marginal increase in J_{SC} from 1.49 to 2.26 mA cm⁻².

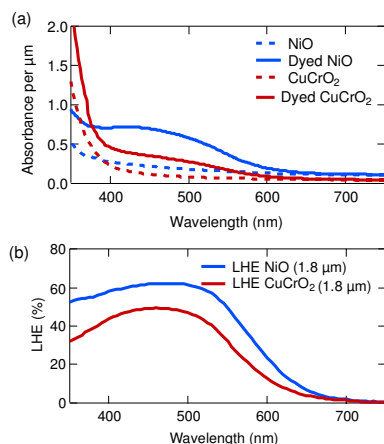


Figure 3. (a) Absorption spectra of 1.0 μm thick undyed (dotted lines) and PMI-6T-TPA sensitized (solid lines) films of NiO (blue) and CuCrO_2 (red), (b) Calculated light harvesting efficiency of p-DSCs incorporating 1.8 μm thick NiO (blue) and CuCrO_2 (red) films.

One reason for the lower APCE of the CuCrO_2 based p-DSCs could be increased recombination losses. Transient absorption spectroscopy (TAS) was performed to gain insight into the charge recombination process between the photo-generated dye anion and the electron vacancy (hole) in the p-type semiconductor. Devices were constructed in absence of any redox mediator in the electrolyte to measure the dye anion lifetime. The film thickness was adjusted to yield similar light absorption by the sensitizer (2.2 μm for CuCrO_2 and 1 μm for NiO). Figure 4 shows the transient absorption decay signal of PMI-6T-TPA-sensitized semiconductor films at 900 nm, which can be assigned to the transient appearance of the dye anion.^[2b] The comparable transient lifetime observed in CuCrO_2 and NiO DSCs indicate that similar recombination time constants prevail in both p-DSC types. However, significant differences were observed in the overall signal amplitude, which is ~60% smaller for sensitized CuCrO_2 , compared to NiO films. This is despite the fact that a similar number of dye molecules per device area were excited, as laser excitation energies and dye-loading were similar in both cases. This provides a strong indication that the low photocurrent yields observed for CuCrO_2 DSCs stem from low photoinduced hole injection yields of PMI-6T-TPA into CuCrO_2 .

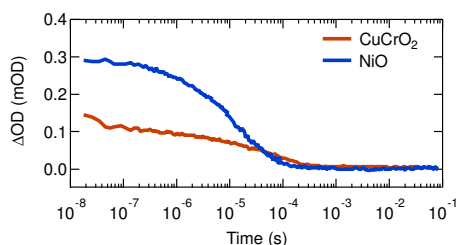


Figure 4. Transient absorption decay observed at 900 nm for dye-sensitized semiconductor films, CuCrO_2 (red) and NiO (blue). Laser excitation wavelength: 532 nm, pulse energy: 14 $\mu\text{J}/\text{cm}^2$, repetition rate: 10 and 2 Hz for nanosecond and microsecond-millisecond transient spectroscopies, respectively. Film thicknesses: 2.2 μm for CuCrO_2 and 1.0 μm for NiO.

The driving forces for hole injection from PMI-6T-TPA* into the valence bands of CuCrO_2 and NiO are ~ 0.3 and ~ 0.4 eV respectively. Mori *et al.* recently reported that hole-injection rates scaled with driving forces up to ΔE values of 0.6 eV,^[14] thus providing a strong indication that insufficient hole injection driving forces are hampering the performance of PMI-6T-TPA-sensitized CuCrO_2 p-DSCs. Overcoming this limitation will require the development of customized p-DSC sensitizers with higher HOMO (highest occupied molecular orbital) levels or superior electronic coupling to warrant quantitative photoinduced hole injection.

In conclusion, we have demonstrated the application of mesoporous CuCrO_2 films in p-DSCs. The 0.1 eV difference in valence band edge energy levels of CuCrO_2 and conventionally used NiO, resulted in an improvement in the V_{OC} of CuCrO_2 based p-DSCs. Application of PMI-6T-TPA sensitized CuCrO_2 electrodes in conjunction with $[\text{Co}(\text{en})_3]^{2+/3+}$ in p-DSCs resulted in a V_{OC} value of 734 mV, the highest reported to date. The overall efficiency of p-DSCs based on CuCrO_2 -NPs was 0.48% as a consequence of the lower J_{SC} values that arise from the IPCE being limited to ~16%. Transient absorption spectroscopy indicates inefficient charge injection as the main reason for the low photocurrents. This reveals that upcoming new generations of mesoporous p-type semiconductor materials for p-DSCs will require a new line of specifically engineered sensitizers to exploit their full potential.

Experimental Section

CuCrO_2 nanoparticles (CuCrO_2 -NPs) were synthesized following a reported literature procedure.^[15] The as-synthesized CuCrO_2 NPs and its mesoporous films were characterized by transmission electron microscopy, X-ray diffraction and Brunauer-Emmett-Teller (BET) analysis of N_2 adsorption-desorption isotherms (Figure S3 ESI †). Mesoporous CuCrO_2 films were screen-printed from CuCrO_2 -NP based pastes followed by sintering at 400°C as described in more detail in the ESI †. The sintered CuCrO_2 films showed a specific surface area of 72 m^2g^{-1} , compared to 56 m^2g^{-1} for the sintered NiO films (Table S1, ESI †). PMI-6T-TPA-sensitized p-DSCs employing iodine and $[\text{Co}(\text{en})_3]^{2+/3+}$ based electrolytes were constructed from CuCrO_2 and NiO films as previously described.^[12] The I^-/I_3^- based electrolyte was composed of 0.03 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-terbutylpyridine and 0.1 M guanidinium thiocyanate in 85:15 acetonitrile: valeronitrile. The $[\text{Co}(\text{en})_3]^{2+/3+}$ based electrolyte contained 0.07 M $[\text{Co}(\text{en})_3](\text{BF}_4)_3$, 0.3 M $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, 0.1 M lithium bis(trifluoromethanesulfonyl)imide, 1.67 M 1,2-diaminoethane in acetonitrile. The $[\text{Co}(\text{en})_3]^{2+/3+}$ electrolyte preparation and cell construction was carried out in glovebox in order to exclude oxygen.^[5]

Acknowledgements

The authors acknowledge financial support from the Australian Research Council through an Australian Research Fellowship (UB) and LIEF programs. Further financial support has been received from the Victorian State Government Department of Primary Industry (SERD Program, Victorian Organic Solar Cells Consortium), the Victorian Science Agenda (VSA), the Australia-

Germany Solar Photovoltaic Research Program 2010-2011 as well as the Commonwealth Scientific and Industrial Research Organization through an OCE Science Leader position (UB). WC and YBC wish to acknowledge the financial support by the 973 Program of China (2011CBA00703). YT acknowledges funding support from the JST PRESTO program (Photoenergy Conversion Systems and Materials for the Next Generation Solar Cells). The Authors would also like to thank the German Federal Ministry of Education and Research (BMBF) for financial support. The German Science Foundation (DFG) in the frame of a Collaborative Research Center (SFB) also supported this work.

Keywords: p-type dye-sensitized solar cells • photocathodes • Copper chromium oxide • cobalt electrolyte • keyword 5

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Received: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cssc.20xxxxxxx>. ((Please delete if not appropriate))

Supplementary information

All other chemicals and solvents were purchased from Sigma-Aldrich and used as received.

CuCrO₂ synthesis:

CuCrO₂ nanoplates were synthesized in high yield following reported literature procedure.^[15] Typically, 6 g of chromium nitrate [Cr(NO₃)₃·9H₂O] and 3.62 g cupric nitric trihydrate [Cr(NO₃)₂·3H₂O] were dissolved in deionized water with magnetic stirring, followed by the addition of sodium hydroxide (NaOH) (0.7 mol/L) as a mineralized. After stirring for 10 min, the obtained homogeneous solution was transferred into a 100 ml Teflon-lined autoclave, which was sealed and heated to 240 °C for 60 h. The autoclave was allowed to cool down to the room temperature (approximately 25 °C). The precipitate was several times washed with diluted hydrochloric acid and absolute alcohol in sequence. The nanoplates were then stored in absolute alcohol until further use. 2.0 g. CuCrO₂-NPs with hexagonal nanoplate like structures (Fig. S2) could be isolated. The synthesized CuCrO₂-NPs were characterized by X-ray diffraction (Fig. S3) using a Phillips (include model) powder diffractometer..

NiO and CuCrO₂ electrodes preparation:

Screen printing pastes were prepared by mixing 7 wt % semiconductor nanopowder (synthesized CuCrO₂-NPs or commercial NiO-NPs (Inframat 73 wt % Ni)), 46.5 % ethyl cellulose solution (5 wt % in ethanol) and 46.5 % terpineol. The ethanol was then removed by rotary evaporation. Semiconductor films were prepared by printing both pastes onto FTO glass (NSG - 8 Ω/□) using a commercial semi-automatic screen printer. The screen-printed NiO-NPs electrodes were sintered at 400 °C for 30 min and 550 °C for 10 min. The screen-printed CuCrO₂-NPs electrodes were sintered at 400 °C for 60 min. Higher temperatures were avoided in the case of CuCrO₂-NPs electrodes to avoid chemical decomposition.^[15] The thicknesses of the sintered electrodes were measured using a Veeco Dektak 6M stylus profilometer and found to be 1.8 μm.

BET Characterization:

The specific surface area and porosity of sintered CuCrO_2 -NPs and NiO -NPs were analyzed using Brunauer-Emmett-Teller (BET) analysis of N_2 adsorption-desorption isotherms (Fig. S5). The results (Table S1) show that the specific surface area of CuCrO_2 -NPs material is slightly higher than that of NiO -NPs.

Table S1. BET results for sintered NiO and CuCrO_2

	Surface area (m^2/g)	Porosity (%)
NiO -NPs	56	51
CuCrO_2 -NPs	72	79

Photocathode assembly:

Dye-sensitized photocathodes were fabricated following previously described methods.^[16] In brief, sintered electrodes were sensitized in a 0.2 mM PMI-6T-TPA dye solution (in DMF) for two hours. The counter electrodes were prepared using 3 mm thick TCO glass (NSG – $15 \Omega/\square$). The dyed working electrodes were used to construct p-DSCs with platinized conductive glass counter electrodes using a 25 μm surlyn gasket. Pneumatic finger press was used to press the working electrode while heating the counter electrode. The photocathodes were filled with the redox mediator by vacuum back-filling. Two different redox mediators (electrolytes) were investigated: a) I/I_3^- based electrolyte [0.03 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-terbutylpyridine and 0.1 M guanidinium thiocyanate in 85:15 acetonitrile: valeronitrile] and b) $[\text{Co}(\text{en})_3]^{2+/3+}$ based electrolyte [0.07 M $[\text{Co}(\text{en})_3](\text{BF}_4)_3$, 0.3 M $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, 0.1 M lithium bis(trifluoromethanesulfonylimide), 1.67 M 1,2-diaminoethane in acetonitrile]. The back filled hole was sealed using an aluminum-Surlyn sheet, which was prepared by heating aluminum foil with a 25 μm Surlyn sheet on a hot plate at 120 °C. Cobalt electrolyte solar cells

were fabricated in a glovebox.

Electrochemical measurement:

Electrochemical experiments were performed at room temperature in the glove box using a potentiostat. The redox potentials of the electrolytes were determined from the potential difference between a platinum wire, immersed in the redox electrolyte, and a freshly prepared Ag/Ag⁺ reference electrode.^[11] The reference electrode was calibrated against in a reference experiment against the ferrocene/ferrocenium redox couple.^[17]

Device characterization:

An Oriel sun simulator (1,000 Wm⁻² Xe lamp) fitted with an AM 1.5 filter resembling solar spectrum was used to test the photocathodes. The light intensity was calibrated with a calibrated silicon reference diode (Fraunhofer) equipped with a KG3 filter to reduce spectral mismatch between calibrated diode and measured photocathode. Current-voltage characteristics were measured using a Keithley 2400 source meter and a custom made Labview software.

The spectral response (IPCE) of the photocathode was measured using an Oriel 300 W Xe lamp fitted with a Cornstone monochromator and recorded on a Keithley 2400 source meter. The light intensity was quantified using a calibrated Fraunhofer reference diode.

Transient absorption spectroscopy was performed on 2 custom built transient absorption spectrometers, one optimized for measurements in the nanosecond domain and the other one optimized for longer time scales. The same laser was used for both spectrometers. A N₂-dye laser (LTB Lasertechnik Berlin GmbH) was used to deliver the pump pulse (532 nm, ~700 ps pulse width, pulse intensity of 14 μJ cm⁻²). For measurements with a timescale of ~1 ns – 10 μs, monochromatic probe light at 900 nm was selected from a Xe lamp (Photon Technology International) through two monochromators (Acton,

Princeton Instruments). Transient data were collected by a sub-nanosecond detection system (Unisoku Co., Ltd.) with an oscilloscope (Tektronix) at 10 Hz laser excitation. On slower time scales (1 μ s – 1 s), transient data were collected by a sub-microsecond transient absorption spectrometer at 2 Hz laser excitation, the details of the spectrometer were described previously.^[18] Laser shots of 1280 and 300 were averaged in each time domain for the nanosecond and the microsecond-millisecond transient spectrometers, respectively. The measured data were combined to show transient decays over a time range of 10 ns – 100 ms.

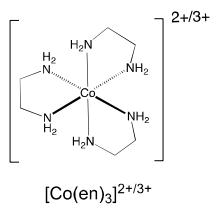


Figure S1: Chemical structure of $[\text{Co}(\text{en})_3]^{2+/3+}$ redox mediator

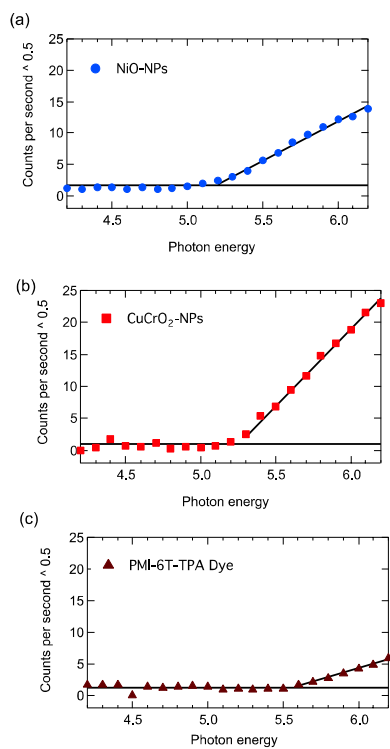


Figure S2: PES measurement of ionization potentials of (a) NiO-NPs (blue disks), (b) CuCrO₂-NPs (red squares) and (c) Dye (brown triangles)

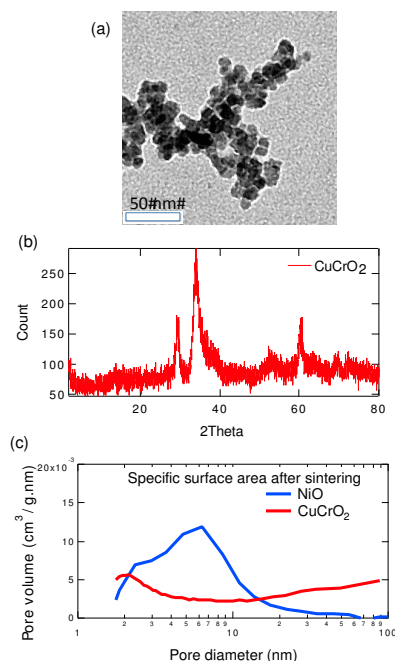


Figure S3: TEM image of the hexagonal nanoplate-like CuCrO_2 (b) XRD spectra of the synthesized CuCrO_2 (c) Pore volume distribution for semiconductor powder collected from sintered films CuCrO_2 -NPs; (red) NiO -NPs (blue).

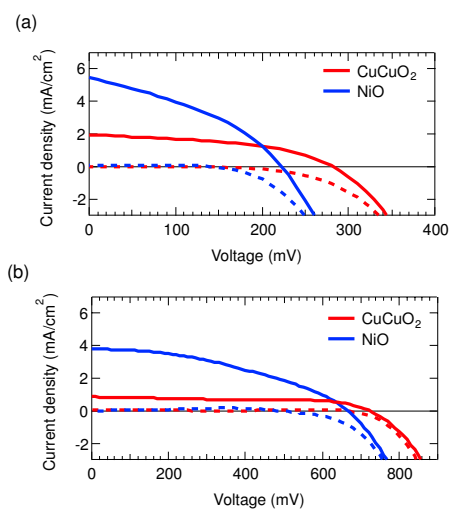


Figure S4: Current density vs. voltage characteristics in the dark and under simulated 1 sun irradiation ($1,000 \text{ W/cm}^2$, AM1.5G) of PMI-6T-TPA sensitized CuCrO_2 -NPs (red) and NiO -NPs (blue) based photocathodes in conjunction with (a) I^-/I_3^- based electrolytes (b) $[\text{Co}(\text{en})_3]^{2+/3+}$ based electrolytes

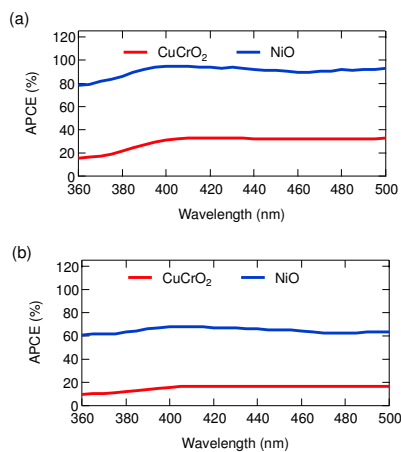


Figure S5: Calculated APCE spectra of p-DSC based on CuCrO₂ (red) and NiO (blue) employing (a) iodide electrolyte and (b) [Co(en)₃]^{2+/3+} based electrolyte. Corresponding values are shown in Table S1.

Table S2. The experimentally determined APCE values for p-DSCs based on NiO-NPs and CuCrO₂-NPs, sensitized with PMI-6T-TPA employing [Co(en)₃]^{2+/3+} and iodide electrolytes.

	Iodide electrolyte	Co(en) ₃ electrolyte
NiO-NPs	0.96	0.70
CuCrO ₂ -NPS	0.40	0.25

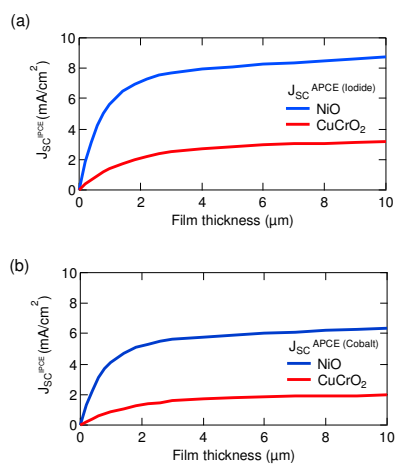


Figure S6: Calculated short-circuit current densities (J_{SC}) for p-DSCs based on $CuCrO_2$ -NPs films (red lines) and NiO-NPs (blue lines) as a function of film thickness (a) using calculated APCE values (Table S2) for p-DSCs employing iodide electrolyte (b) using calculated APCE values (table S2) for p-DSCs employing $[Co(en)_3]^{2+/3+}$ electrolyte.

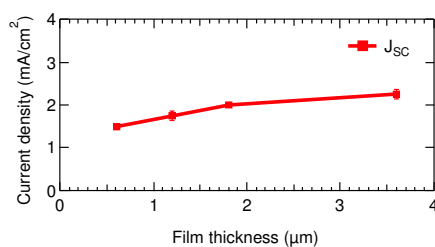


Figure S7: Short circuit current density of p-DSCs sensitized with PMI-6T-TPA dye as a function of film thickness for photocathodes composed of $CuCrO_2$ -NPs

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Chapter 6

Thiolate/Disulfide Based Electrolytes for p-type and Tandem Dye- Sensitized Solar Cells

Monash University

Declaration for Thesis Chapter 6

Title: Thiolate/Disulfide Based Electrolytes for p-type and Tandem Dye-Sensitized Solar Cells

Declaration by candidate

In the case of Chapter 6, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
All experimental work except synthesis; preparation of the manuscript and editing	60%

The following co-authors contributed to the work. Co-authors who are students at Monash University must also indicate the extent of their contribution in percentage terms:

Name	Nature of contribution	Extent of contribution (%) for student co-authors only
Rishabh Bhargava	Electrolyte and counter electrode preparations, drafting and editing	10%
Torben Daeneke	Help in data analysis, drafting and editing	N.A.
Günther Götz	Dye synthesis, drafting and editing	N.A.
Peter Bäuerle	Drafting and editing	N.A.
Thomas Geiger	Dye synthesis, drafting and editing	N.A.
Simon Kuster	Dye synthesis, drafting and editing	N.A.
Frank A. Nüesch	Drafting and editing	N.A.
Leone Spiccia	Drafting and editing	N.A.
Udo Bach	Experimental design and planning, drafting and editing	N.A.

Candidate's Signature

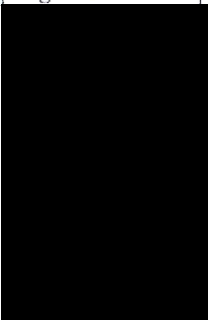
	Date 01.05.2013
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Location: Monash University, Australia

Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (6) the original data are stored at the following location(s) and will be held for at least five years from the date indicated below:

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE

Thiolate/Disulfide Based Electrolytes for p-type and Tandem Dye-Sensitized Solar Cells

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⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

This article presents the first report of a tandem dye-sensitized solar cell employing optically transparent, non-corrosive metal-free thiolate/disulfide based electrolytes and a set of sensitizers with complementary absorption spectra. Sodium 1-phenyl-1H-tetrazole-5-thiolate and its reduced form 5,5'-dithiobis(1-phenyl-1H-tetrazole) (thiolate/disulfide) were used as redox mediators for photocathodic dye-sensitized solar cells (p-DSCs), yielding higher open circuit voltages (285 mV) compared to the more commonly used iodide-based redox couple (226 mV). The herein achieved efficiencies of p-DSCs (0.51 %) and pn-DSCs (1.33 %) employing the thiolate/disulfide-based electrolytes were comparable to p-DSCs and pn-DSCs employing conventional iodide-based electrolytes (0.44 % and 1.19 %).

Dye-sensitized solar cells (DSCs) with their low projected costs have increasingly attracted attention as an alternative to silicon solar cells.^{1, 2} The highest reported conversion efficiencies for dye-sensitized photoanodes (n-DSCs) and dye-sensitized photocathodes (p-DSCs) are 12.3% and 1.3% respectively, under simulated sunlight (1000 W/m², AM1.5 G).^{3, 4} These record efficiencies still lag behind the conventional silicon solar cells and some other thin film solar cell technologies. Researchers have been endeavouring to improve the efficiencies of n-DSC and p-DSC by altering the semiconductors, sensitizers and redox couples.³⁻²² One attractive approach to improve efficiencies is to construct third generation tandem dye-sensitized solar cells (pn-DSCs). In the n-DSCs, the photocurrent results from dye-sensitized electron injection into n-type semiconductors, e.g. TiO₂, whereas in p-DSC electron transfer occurs from the valence band of the p-type semiconductor (NiO being the most commonly used to date) to the photoexcited dye.^{22, 23} These charge separation mechanisms are complementary and provide the opportunity to assemble n-DSCs and p-DSCs in a simple sandwich structure to produce tandem dye-sensitized solar cells (pn-DSCs).²⁴ According to Kirchhoff's circuit law photovoltages are additive for this type of pn-DSCs, as the photoelectrodes are connected in series. However, the photocurrent is limited by the weaker performing photoelectrode.^{22, 24}

Previously reported pn-DSC efficiencies have been higher than their individual components (n-DSCs and p-DSCs). However,

those devices still shared several limitations. The overlapping absorption spectra of the most efficient p-DSC sensitizer (PMI-6T-TPA – see Figure. 1a) with that of the applied n-DSC sensitizers (N719) meant that both photoelectrodes were competing for photons in a similar wavelength range, limiting the attainable pn-DSC photocurrent. Furthermore, the tandem devices were utilizing electrolytes based on the I/I₃⁻ redox couple which absorbs strongly at wavelengths below 500 nm.⁴

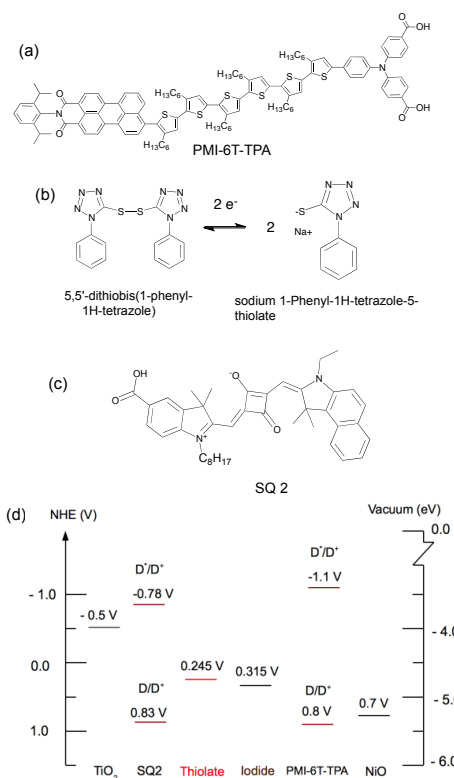


Fig.1 (a) Structure of the PMI-6T-TPA sensitizer; (b) structures of the oxidized (5,5'-dithiobis(1-phenyl-1H-tetrazole)) and reduced (sodium 1-phenyl-1H-tetrazole-5-thiolate) forms of the redox couple; (c) structure of the SQ2 sensitizer; (d) approximate energy diagram for the components used in the tandem solar cells with the rest potentials of the iodide and

thiolate electrolytes (measured according to a literature procedure).²⁵ The work function of NiO (~5.2 eV) was measured using photoelectron spectroscopy (PESA) (Figure S1, ESI †) and the conduction band edge of TiO₂ (~4.0 eV) was taken from the literature.^{9, 26, 27}

Iodide/triiodide had been the most commonly applied redox couple for both n-DSCs and p-DSCs. Concerns over the corrosive nature and complex redox chemistry of this redox couple has led researchers to explore alternative redox mediators.²⁸ In recent years major advances have been made resulting in the application of metal complexes (Co, Fe and Ni) and organic thiolate based redox mediators.^{8, 29-34} Interest in thiolate/disulfide as alternative redox couple in n-DSCs has been growing very rapidly, due to its non-corrosive properties and optical transparency.^{8, 29-33}

Overall, the realization of high efficiency pn-DSCs requires: (i) the development of p-DSC and n-DSC sensitizers with complementary absorption spectra; (ii) new p-type semiconductors with higher ionization potential and/or alternative n-type semiconductors with lower conduction band edge to improve the open circuit voltage (V_{OC}); and (iii) optically transparent electrolytes. This report is attempting to address requirements (i) and (iii).

Here, we report the application of an optically transparent thiolate/disulfide electrolyte based on (5,5'-dithiobis(1-phenyl-1H-tetrazole)) and sodium 1-phenyl-1H-tetrazole-5-thiolate as redox couple (see Figure 1(b)) in p-DSCs and tandem pn-DSCs. The redox potential of the thiolate electrolyte (245 mV vs. NHE) is about 70 mV more negative than that of the iodide electrolyte (315 mV vs. NHE), offering an opportunity to improve the V_{OC} of p-DSCs.

The photovoltaic performances of p-DSCs employing these two electrolytes were measured under simulated sunlight (1000 W/m², AM 1.5G) and are summarized in Table 1 (photocurrent-voltage characteristics are shown in Figure S2, ESI †). The V_{OC} of iodide-based p-DSCs (226 mV) together with the short-circuit current (J_{SC}) of 5.3 mA/cm² yielded an overall efficiency of 0.44 %, comparable to literature reports.^{15, 22} Replacing the iodide electrolyte with a thiolate electrolyte improved the V_{OC} by ~60 mV (285 mV). This V_{OC} improvement is very close to the expected V_{OC} shift due to difference in the electrolyte redox potentials (~70 mV). The improved V_{OC} and identical J_{SC} values (5.3 mA/cm²) lead to an increase in the overall efficiency of thiolate/disulfide based p-DSCs to 0.51 %, compared to iodide based p-DSCs (0.44 %).

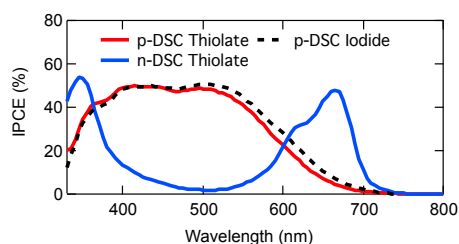


Fig. 2 IPCE spectra of a p-DSCs (red line) and n-DSC (blue line) comprising a thiolate electrolyte. For comparison the IPCE of a p-DSCs in conjunction with an iodide-based electrolyte (black dotted line) is also shown. p-DSCs were constructed from PMI-6T-TPA sensitized mesoporous NiO electrodes (thickness: 1.8 μ m). n-DSCs were

constructed from SQ2 sensitized mesoporous TiO₂ electrodes (thickness: 2 μ m). For the electrolyte composition see Experimental Section.

Table 1 Photovoltaic performance parameters for p-DSCs, n-DSCs and pn-DSCs under one sun simulated sunlight (1000 W/m², AM1.5 G). The tandem pn-DSCs and n-DSCs were illuminated through the n-side (TiO₂) and the p-DSCs were illuminated through the p-side (NiO).

	Thiolate electrolyte ^[a]		
	p-DSC	n-DSC	pn-DSC
V_{OC} (mV)	285 $\pm$ 10	595 $\pm$ 6	814 $\pm$ 18
J_{SC} (mA/cm ²)	5.3 $\pm$ 0.5	2.6 $\pm$ 0.3	2.5 $\pm$ 0.2
Fill Factor	0.34 $\pm$ 0.01	0.64 $\pm$ 0.04	0.65 $\pm$ 0.05
Efficiency (%)	0.51 $\pm$ 0.03	1.00 $\pm$ 0.05	1.33 $\pm$ 0.02
	Iodide electrolyte ^[b]		
	p-DSC	n-DSC	pn-DSC
V_{OC} (mV)	226 $\pm$ 4	718 $\pm$ 8	924 $\pm$ 13
J_{SC} (mA/cm ²)	5.3 $\pm$ 0.3	3.6 $\pm$ 0.1	1.9 $\pm$ 0.1
Fill Factor	0.36 $\pm$ 0.01	0.77 $\pm$ 0.01	0.67 $\pm$ 0.02
Efficiency (%)	0.44 $\pm$ 0.02	1.97 $\pm$ 0.05	1.19 $\pm$ 0.04

^a [a],[b] See Experimental Section for electrolyte compositions. The p-DSCs were based on mesoporous NiO electrodes (film thickness = 1.8 μ m and surface area = 0.16 cm²) sensitized with PMI-6T-TPA, n-DSC were based on mesoporous TiO₂ electrodes (film thickness = 2 μ m and surface area = 0.16 cm²) sensitized with SQ2 dye.

The incident photon-to-current conversion efficiency (IPCE) spectra measured for p-DSCs employing thiolate and iodide based electrolytes show an identical spectral response with peak IPCE values reaching up to 50% (Figure 2), indicating that the absorbed photon-to-current conversion efficiency observed for iodide-based p-DSCs sensitized with PMI-6T-TPA also prevails for the thiolate electrolytes. The sensitizer SQ2 also yielded peak IPCE values of 50% when used in conjunction with thiolate electrolytes in n-DSCs.

In order to realize high pn-DSC efficiency, either of the two electrodes is required to absorb and efficiently convert photons from the red and near infrared section of the solar spectrum. Near infrared (near IR) dyes can be applied to either the p-DSC or n-DSC. However, infrared sensitizers reported in the literature are limited to n-DSCs.^{27, 35-37} The squaraine-based sensitizer SQ2 (Figure 1 c) developed by the groups of Nüesch and Grätzel features a strong absorption peak at 675 nm and a window of low absorption in the range from 400 nm to 580 nm.²⁷ It is spectrally complementary to the best performing p-type sensitizer PMI-6T-TPA. Figure 2 shows IPCE spectra of p-DSC and n-DSC employing the thiolate based electrolyte. The p-DSC and n-DSC sensitizers show complementary absorption spectrum.

Since the overall J_{SC} value of a series connected tandem solar cell is limited by the electrode producing the lower J_{SC} , both photoelectrodes have to be carefully optimized and matched, to maximize the efficiency of pn-DSCs. The light harvesting properties of each electrode can be adjusted by controlling the film thickness of the NiO and TiO₂ films.

The maximum theoretical photocurrent of a single junction dye-sensitized solar cell can be calculated based on its light harvesting efficiency and absorbed photon to charge carrier conversion efficiencies (APCE) (equation 1).¹⁵ Based on the single junction solar cell calculation model, we have extended the J_{SC} calculation model to assist in tandem solar cell electrode thickness optimization. In the pn-DSC calculations, the light reaching the second photoelectrode was estimated by taking into account the transmission losses that occur in the top electrode and electrolyte

layer. The expected J_{SC} values of pn-DSCs for a range of photoelectrode film thicknesses were calculated based on the absorption properties of the individual cell components and the APCEs for both photoelectrodes. A detailed derivation can be found in the ESI †.

$$J_{SC} = \frac{e}{hc} \int \phi_p \text{AM1.5G}(\lambda) \cdot LHE(\lambda) \cdot \phi_{inj} \cdot \phi_{cc} \cdot d\lambda \quad (1)$$

The absorptivity of both electrolytes was measured using a 22.5 μm path length cuvette; corresponding to the electrolyte layer thickness in DSCs (Figure S3). In accordance with previous reports,^{8, 29-33} the thiolate electrolyte showed negligible absorption in the visible spectral range, while the iodide electrolyte significantly absorbs light at wavelengths below 490 nm. The results highlight the advantage of the new thiolate based electrolyte for pn-DSCs in which the incident light has to pass through the electrolyte compartment to reach the bottom electrode. APCE values for p-DSCs and n-DSCs employing thiolate and iodide electrolytes were determined experimentally (see Table S1) and assumed to be independent of the layer thickness. The APCEs for p-DSCs sensitized with PMI-6T-TPA, employing thiolate and iodide electrolytes were determined to be 0.92 and 0.95, respectively. The measured APCE values for SQ2 sensitized n-DSCs employing thiolate and iodide electrolyte were 0.38 and 0.40 respectively, much lower compared to p-DSCs.

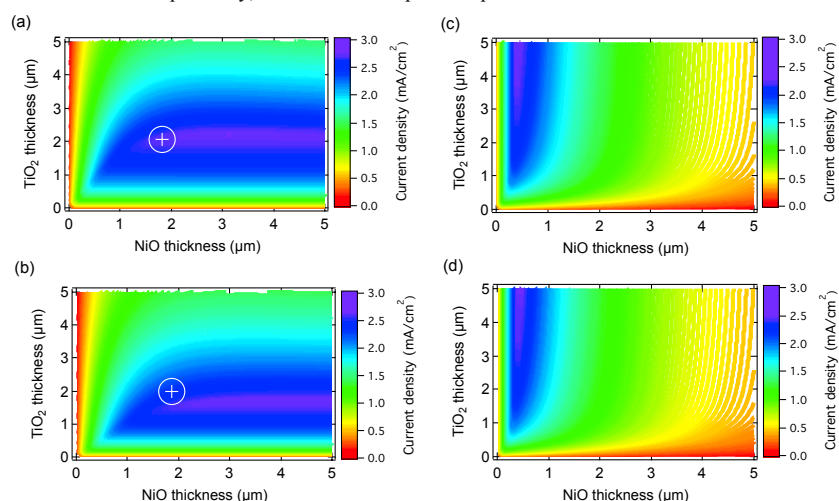


Fig. 3 Calculated photocurrent density (J_{SC}) estimate at one sun irradiation (1000 W/m², AM 1.5 G) of tandem pn-DSCs [illuminated through the TiO₂ electrode side (a),(b) and the NiO electrode side (c),(d)] using a thiolate electrolyte (a),(c); and an iodide electrolyte (b),(d). The crosshair shows the respective film thicknesses used to prepare the DSCs reported in Table 1.

Figure 3 shows a contour graph of the calculated tandem solar cell J_{SC} values, illuminated through TiO₂, as a function of TiO₂ and NiO film thicknesses for both electrolytes. The calculation predicts maximum photocurrents of about 2.82 mA/cm² and 2.24 mA/cm² in tandem pn-DSCs for optimized TiO₂ thicknesses of 2 μm and 1.6 μm in conjunction with thiolate and iodide electrolytes respectively. This indicates that the absorption of the iodide electrolyte imposes additional restrictions to the top

electrode thickness. The stronger inner filter effect in iodide-based tandem cells needs to be compensated by employing a thinner TiO₂ top electrode, to ensure sufficient light penetration to the underlying NiO electrode.

The tandem solar cell J_{SC} contour graphs for pn-DSCs using thiolate electrolyte and iodide electrolyte with an illumination through the NiO electrode are shown in Figure 3 c and d respectively. A similar maximum J_{SC} of ~2.54 mA/cm² can be expected in this illumination mode with comparably thin NiO top electrodes (0.5 μm). Here the self-absorption of the NiO semiconductor film introduces an additional inner filter effect.

Table 1 summarizes the J-V performance data of p-DSCs, n-DSCs and the tandem pn-DSCs, measured under simulated sunlight (1000 W/m², AM 1.5 G). The corresponding J-V curves are shown in Figure S2 (ESI †). The pn-DSCs using the thiolate electrolytes were found to be slightly more efficient (1.33 %) than those comprising an iodide electrolyte (1.19 %), even though the efficiency of n-DSC using the thiolate electrolyte (1.00 %) was lower than for the iodide-based n-DSC (1.97 %).

The NiO and TiO₂ film thicknesses used for these devices were optimized for pn-DSCs employing a thiolate-based electrolyte.

According to the results of our simple photocurrent calculation in Figure 3 the semiconductor film thickness used for the devices reported in Table 1 are not ideal for iodide based pn-DSCs. Assembling pn-DSCs with film thicknesses optimized for iodide-based cells according to Figure 3b indeed yielded an improved photocurrent (2.6 mA/cm²) and device efficiency (1.28 %; see Table S2, ESI †), comparable to the optimized thiolate-electrolyte based pn-DSC.

Generally, the photocurrent trends observed in pn-DSCs follow the calculations depicted in Figure 3, while the magnitude of the measured photocurrents at full sun illumination generally turned out lower than predicted. This effect can be attributed to the sub-linear dependence of photocurrent and illumination intensity, generally observed for the DSCs presented here. Table S3 shows the performance data of the devices described in Table 1 at 1/10 sun simulated sunlight (100 W/m², AM 1.5 G). Here the photocurrents of 0.27 and 0.30 mA/cm² for iodide and thiolate electrolyte based pn-DSCs respectively are generally in good agreement with the calculated values illustrated in Figure 3.

The V_{OC} for iodide based pn-DSCs characterized in Table 1 is about 110 mV higher than for thiolate-based tandem DSCs. The nature of the redox mediator should, however, not directly affect the V_{OC} , which should correspond to the difference of the quasi-Fermi levels in the NiO and TiO₂ electrode under illumination. An interpretation of the difference in V_{OC} between these tandem solar cells is difficult, as the optimized thiolate and iodide electrolytes employed here varied strongly in their composition

(see Experimental Section). Above all, the absence of flatband determining lithium ions in the iodine electrolyte and the presence of 50 mM Li⁺ in the thiolate electrolyte is expected to strongly affect the V_{OC} of n-DSCs. Indeed we observe that the addition of 50 mM Li⁺ to iodide electrolyte drastically drops the V_{OC} of the iodide-based pn-DSC (750 mV) below that of the thiolate pn-DSC (see Table S3 ESI †).

Experimental

Two electrolytes were prepared; (a) an optimized thiolate electrolyte [0.05 M 5,5'-dithiobis(1-phenyl-1H-tetrazole), 0.40 M sodium 1-phenyl-1H-tetrazole-5-thiolate, 0.05 M lithium bis(trifluoromethanesulfonylimide), 0.50 M 4-tert-butylpyridine in acetonitrile]; and (b) an optimized iodide electrolyte [0.03 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-tert-butylpyridine and 0.1 M guanidinium thiocyanate in 85:15 acetonitrile: valeronitrile]. p-DSC were constructed following the literature procedures (see ESI † for details).³⁸ Briefly, for p-DSCs sintered 1.8 μm thick mesoporous nickel(II) oxide (NiO) electrodes were sensitized in a 0.2 mM PMI-6T-TPA dye solution (in DMF) for 2 hours and rinsed before they were used to construct p-DSCs with counter electrodes. The electrolytes were vacuum back filled through a predrilled hole on the counter electrode. Platinized conducting glass counter electrodes were used for the iodide electrolyte based devices. However, since the thiolate based electrolytes have a very high charge transfer resistance on platinum, poly(3,4-ethylenedioxythiophene) (PEDOT) counter electrodes were used in thiolate based p-DSCs (Figure S5, ESI †).³³ For n-DSCs 2 μm thick TiO₂ electrodes were sensitized in 0.2 mM SQ2 dye solution (in ethanol), with the addition of 10 mM chenodeoxycholic acid. For tandem solar cells TiO₂ electrodes were drilled for electrolyte back filling, prior to dyeing. The tandem solar cells were assembled using dyed TiO₂ electrodes and NiO electrodes. More details on experimental procedures are in ESI †.

Conclusions

We have demonstrated a tandem dye-sensitized solar cell with complementary absorption of the photocathodic and photoanodic sensitizers that utilize an optically transparent, non-corrosive organic thiolate based electrolyte. We have developed a simple model for optimizing the film thicknesses of photoelectrodes for tandem DSC applications. The developed thiolate based electrolyte resulted in an improvement in V_{OC} in p-DSCs compared to the devices based on iodide electrolytes, while maintaining similar J_{SC} (5.3 mA/cm²) values. When employed in tandem DSCs with film thicknesses optimized for the two respective electrolytes the tandem cells based on the non-corrosive thiolate electrolyte exhibited similar conversion efficiencies (1.33 %) to those based on iodide electrolytes (1.28 %). Our results reveal the great potential of thiolate based electrolytes for future applications in p-DSCs and pn-DSCs. The optical transparency in the visible region, favorable rest potential and the noncorrosive nature of the thiolate redox couple makes it more suitable than the iodide based redox couple for these applications. Future studies should focus on developing novel

near IR dyes with the potential to generate higher photocurrents, which can boost the efficiencies even further.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

ACKNOWLEDGMENT

- The authors acknowledge the Australian Research Council for providing equipment and fellowship support and the Australian Solar Institute, the Victorian State Government (DBI-VSA and DPI-ETIS) for financial support. The Commonwealth Scientific and Industrial Research Organization is acknowledged for providing support through an OCE Science Leader position (UB). This work was performed partly at the Melbourne Centre for Nanofabrication, an initiative partly funded by the Commonwealth of Australia and the Victorian Government.

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Thiolate/Disulfide Based Electrolytes for p-type and Tandem Dye-Sensitized Solar Cells

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ASSOCIATED CONTENT

Materials and methods

The materials (NiO, fluorine doped tin oxide coated conducting glass, SQ2 dye and the redox couple components) were purchased from commercial suppliers and used as received unless stated otherwise. PMI-6T-TPA dye was synthesized in-house.

Working electrode materials

NiO electrode preparation:

NiO nanoparticle powder was used as received from Inframat (73 wt% Ni, nominal particle size: 20 nm). All other chemicals and solvents were purchased from Sigma-Aldrich and used as received. Screen-printing pastes were prepared by mixing 8 wt % NiO, 46% ethyl cellulose solution (5 wt % in ethanol) and 46% terpineol using as-received NiO nanoparticle powder. The substrates were cleaned in an ultrasonic bath for 10 min in 5 % Hellmanex dissolved in water followed by rinsing with clean water and further sonication (10 min) in ethanol. The paste was printed on FTO glass (NSG - 8 $\Omega/\square$, 4 mm thick) using a commercial semi-automatic screen printer. The thicknesses of the sintered electrodes were measured using a Veeco Dektak 6M stylus profilometer.

Just before dye-sensitization, the working electrodes were reheated to 550 °C for 10 minutes using a heat gun to remove absorbed water and organics from the NiO surface. After cooling to 60 °C the films were immersed into the dye bath. Dye deposition was achieved from a 0.2 mM

PMI-6T-TPA dye solution (see Figure 1) in DMF. After two hours of dye deposition the films were rinsed in DMF and assembled to p-DSCs.

TiO₂ electrode preparation

The TiO₂ pastes (PST-18NR) were purchased from JGC Catalysts and Chemicals. The substrates were cleaned in an ultrasonic bath for 10 min in 5 % Helmanex dissolved in water followed by rinsing with clean water and further sonication (10 min) in ethanol. The substrates were coated with a dense TiO₂ blocking layer by spray pyrolysis at 450 °C using a 7.5 wt % titanium diisopropoxide bis(acetylacetonate) in isopropanol. TiO₂ paste (PST-18R, JGC Catalysts and Chemicals) was screen printed on FTO glass (NSG - 8 Ω/□, 4 mm thick) using a commercial semi-automatic screen printer, with a 90 T mesh. One print was found to deposit 2 μm thick TiO₂ layers. The films were sintered under a stream of compressed air at 450 °C for 30 minutes followed by 15 minutes at 500 °C. After initial sintering, all films were treated with an aqueous TiCl₄ solution (20 mM, 70 °C, 30 min). The films were sintered again and stored until use. The printed transparent TiO₂ film thickness was measured to be 2 μm. The dimensions of the printed films were 4 x 4 mm (area 0.16 cm²).

Just before dye-sensitization, the working electrodes were reheated to 500 °C for 30 minutes using a heat gun to remove absorbed water and organics from the TiO₂ surface. After cooling to 60 °C the films were immersed into the dye bath. Dye deposition was achieved from a 0.2 mM SQ2 dye solution (see Figure 1b) in ethanol containing 10 mM chenodeoxycholic acid, used as a co-adsorbent. After two hours of dye deposition the films were rinsed in acetonitrile and assembled to n-DSCs.

Counter electrode preparation

For n-DSCs and p-DSCs, the counter electrode glass was cut to size and a hole was drilled (~1mm diameter) to fill in the electrolyte. The hole was drilled using a Dremmel bench drill with a dental burr. The separated counter electrodes were cleaned in ultrasonic bath following the same procedure described for the working electrodes. The prepared counter electrodes were stored in ethanol until use. The counter electrodes were coated with a drop of a 10 mM solution of hexachloroplatinic acid in isopropanol. The counter electrodes were then sintered at 400 °C for 15 minutes. For pn-DSCs, holes were drilled on TiO₂ electrodes prior to dyeing process.

PEDOT counter electrode preparation

The PEDOT counter electrodes were prepared following literature procedure.¹ The pulse potentiostatic electropolymerization of PEDOT thin films onto FTO glass substrates were carried out using a simple aqueous solution (50 mL) containing 2.0 mM 3,4-ethylenedioxythiophene monomer (ARCOS, 99%), 10 mM sodium dodecyl sulfate, and 10 mM lithium perchlorate (LiClO₄) in a three-compartment cell at ambient atmosphere, which was controlled by EC-lab software. The parameters for the electropolymerization of PEDOT were set under the pulse-on potential of 1.2 V vs. Ag/AgCl, the pulse reversal potential of 0.2 V vs. Ag/AgCl, the pulse-on period of 1 s, the pulse-reversal period of 0.5 s and total duration interval of 500 s. A Pt wire and an Ag/AgCl reference electrode were used as a counter electrode and a reference electrode, respectively. The obtained PEDOT CEs were rinsed in distilled water and dried under a cool air flow.

Device assembly

p-DSCs and n-DSCs were assembled by inserting a laser cut 25 mm thick surlyn gasket (inner dimensions 6 x 7 mm) in between the working and counter electrodes. Pneumatic finger press was used to press the working electrode while heating counter electrode. The electrolyte was vacuum backfilled in the cell cavity. The back filled hole was sealed using an aluminum-Surlyn sheet, which was prepared by heating aluminum foil with a 25 μ m Surlyn sheet on a hot plate at 120 °C.

The tandem solar cells were assembled in similar way, replacing the counter electrode with pre-drilled TiO₂ working electrode. The TiO₂ electrodes and NiO electrodes were assembled with a laser cut 25 μ m thick surlyn gasket (inner dimensions 6 x 7 mm) in between. Following the same procedure as p-DSCs/n-DSCs.

Rest potential measurement:

Electrochemical experiments were performed at room temperature in the glove box using a potentiostat. The redox potential of the electrolytes was determined from the potential difference between a platinum wire, immersed in the redox electrolyte, and a Ag/Ag⁺ reference electrode.² The reference electrode was calibrated against the freshly prepared solution of ferrocene/ferrocenium redox couple.

Device characterization:

An Oriel sun simulator (1,000 W/m² Xe lamp) fitted with an AM 1.5 filter resembling the solar spectrum was used to test the photocathodes. The light intensity was calibrated with a calibrated

silicon reference diode (Fraunhofer) equipped with a KG3 filter to reduce spectral mismatch between calibrated diode and measured photocathode. Current-voltage characteristics were measured using a Keithley 2400 source meter and a custom made Lab view software.

The spectral response (IPCE) of the photocathode was measured using an Oriel 300 W Xe lamp fitted with a Cornstone monochromator and recorded on a Keithley 2400 source meter. The light intensity was quantified using a calibrated Fraunhofer reference diode.

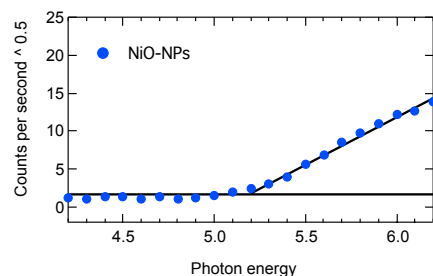


Fig S1: Photoelectron spectroscopy (PESA) measurements of ionization potential of NiO in eV (Vs Vacuum)

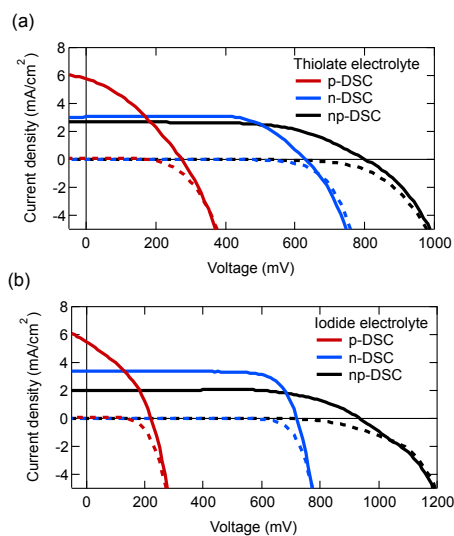


Figure S2. Photocurrent density – voltage (J-V) curves under simulated one sun (1000 W/m^2) irradiation (AM 1.5 G) of p-DSC, n-DSC and tandem np-DSC using (a) a thiolate electrolyte; and (b) an iodide electrolyte. The tandem pn-DSCs and n-DSCs were illuminated through the n-side and the p-DSCs were illuminated through p-side. Table 1 shows the corresponding the J-V characteristics.

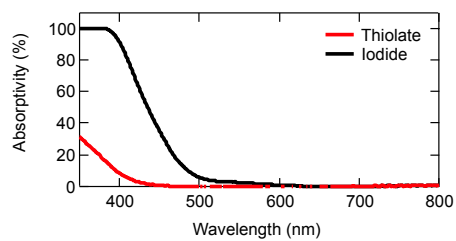


Figure S3. Absorptivity spectra of thiolate (red line) and iodide (black line) electrolytes with path length of 22.5 μm , corresponding to a typical electrolyte layer thickness in DSCs.

The photocurrent (J_{SC}) calculations:

The theoretical photocurrent densities (J_{SC}) generated by dye-sensitized solar cells can be calculated using equation (1), where LHE is light harvesting efficiency. For LHE calculations equation (2), detailed optical analysis was carried on TiO_2 and NiO films before and after dyeing process ($A_{(SC)}(\lambda)$) and $A_{(Dyed SC)}(\lambda)$ respectively. The dye absorption on the film ($A_{(dye)}(\lambda)$) was calculated by subtracting absorption of the semiconductor [$A_{(SC)}(\lambda)$] from $A_{(dyed SC)}(\lambda)$. The electrolyte absorptions were measured with a $22.5 \mu m$ path length.

Based on the optical analysis, film absorptions were normalized to $1 \mu m$ thick films. The expected light-harvesting efficiencies as a function of film thickness for both types of sensitized semiconductor electrodes were calculated. Assuming $APCE = 1$, theoretical maximum photocurrents ($J_{SC \text{ max}}$) were calculated using equation (3) as a function of film thickness. The p-DSC and n-DSC IPCEs of known film thickness were measured and compared with equation 3 to calculate APCE values for both n-DSC and p-DSC. The calculated $APCE_{MAX}$ values for n-DSC and p-DSC are shown in table S3.

$$J_{SC} = \frac{e}{hc} \int \phi_p AM1.5G(\lambda) \cdot LHE(\lambda) \cdot \phi_{inj} \cdot \phi_{cc} \cdot d\lambda \quad (1)$$

where e is electric charge, h is Planck's constant, c is speed of light, ϕ_p is photon flux, LHE is light harvesting efficiency, ϕ_{inj} is charge injection efficiency and ϕ_{cc} is charge collection efficiency.

$$LHE_{(dye)}(\lambda, d) = \frac{A_{(Dye)}(\lambda)}{A_{(Dyed SC)}(\lambda)} \cdot (1 - 10^{-\bar{A}_{(Dyed SC)}(\lambda) \cdot d}) \quad (2)$$

$$\text{When } APCE = \phi_{inj} \cdot \phi_{cc} = 1$$

$$J_{SC}^{max}(d) = \frac{e}{hc} \int \phi_p \text{AM1.5G}(\lambda) \cdot LHE(\lambda, d) \cdot d\lambda \quad (3)$$

$$\text{Since } LHE(\lambda) \cdot \phi_{inj} \cdot \phi_{cc} = IPCE(\lambda) \quad (4)$$

$$J_{SC}^{IPCE} = \frac{e}{hc} \int \phi_p \text{AM1.5G}(\lambda) \cdot IPCE(\lambda) \cdot d\lambda \quad (5)$$

$$APCE(\lambda) = \phi_{inj} \cdot \phi_{cc} = \frac{IPCE(\lambda)}{LHE(\lambda)} \quad (6)$$

$$J_{SC}^{APCE}(d) = \frac{e}{hc} \int \phi_p \text{AM1.5G}(\lambda) \cdot LHE(\lambda, d) \cdot APCE(\lambda) \cdot d\lambda \quad (7)$$

Where $A_{(\text{dyed SC})}(\lambda)$ are absorption of the dyed semiconductor. $\tilde{A}_{(\text{Dyed SC})}(\lambda)$ is absorption of dyed NiO film per μm and d is the film thickness in μm .

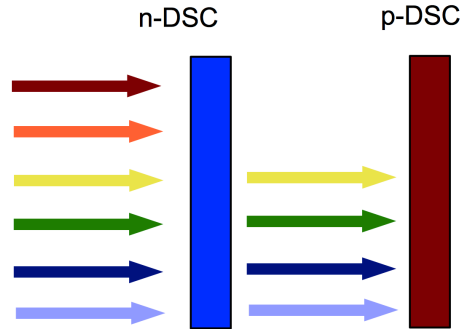


Fig S4. Schematic representation of pn-DSC absorption with n-DSC and p-DSC electrodes

Figure S4 shows a tandem structure for pn-DSC with illumination through photoanode (TiO_2) side. In tandem structures, the light reaching the second electrode was estimated by subtracting absorptivity of first electrode and absorptivity of electrolyte from incident light as a function of wavelength. The light harvesting efficiencies of second electrodes were recalculated according to the corrected incident light. Theoretical J_{SC} s were estimated from the calculated LHE and APCE values as a function of film thickness. According to the Kirchoff's circuit law, the photocurrent

of a tandem solar cell is governed by, low photocurrent producing electrode. The minimum estimated photocurrents was recorded for a given TiO_2 and NiO film thicknesses. Based on the different film thickness matrix, the photocurrents were estimated and a countour was plotted.

Table S1. The experimentally determined APCE values for p-DSCs sensitized with PMI-6T-TPA and n-DSCs sensitized with SQ2 employing thiolate and iodide electrolytes.

	Iodide electrolyte	Thiolate electrolyte
p-DSC	0.95	0.92
n-DSC	0.40	0.38

Table S2. Photovoltaic performance parameters for pn-DSCs under 100% sun simulated sunlight (1000 W/m², AM1.5 G) using 1.6 μ m TiO₂ and 2 μ m NiO. The tandem pn-DSCs and n-DSCs were illuminated through the n-side (TiO₂). The effect of Li⁺ ions on the device performance of pn- DSCs was studied by comparing the iodide-based electrolyte with its analogue containing Li⁺ ions.

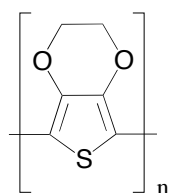
	Iodide electrolyte	Lithium added iodide electrolyte
	pn-DSC	pn-DSC
V _{oc} (mV)	936 $\pm$ 16	750 $\pm$ 29
J _{sc} (mA/cm ²)	2.6 $\pm$ 0.1	2.6 $\pm$ 0.2
Fill Factor	0.52 $\pm$ 0.04	0.60 $\pm$ 0.01
Efficiency (%)	1.28 $\pm$ 0.01	1.18 $\pm$ 0.01

Composition of iodide electrolyte: 0.03 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-tert-butylpyridine and 0.1 M guanidinium thiocyanate in 85:15 acetonitrile: valeronitrile.

Composition of Li added iodide electrolyte: 0.03 M iodine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.5 M 4-tert-butylpyridine, 0.1 M guanidinium thiocyanate and 0.05 M lithium in 85:15 acetonitrile: valeronitrile

Table S3. Photovoltaic performance parameters for p-DSCs, n-DSCs and pn-DSCs under 10% sun simulated sunlight (100 W/m², AM1.5 G) using 2 μ m TiO₂ and 1.8 μ m NiO. The tandem pn-DSCs and n-DSCs were illuminated through the n-side (TiO₂) and the p-DSCs were illuminated through the p-side (NiO).

	Thiolate electrolyte			Iodide electrolyte		
	p-DSC	n-DSC	pn-DSC	p-DSC	n-DSC	pn-DSC
V _{oc} (mV)	224 ± 9	507 ± 7	663 ± 20	175 ± 3	657 ± 10	819 ± 19
J _{sc} (mA/cm ²)	0.79 ± 0.08	0.31 ± 0.05	0.30 ± 0.04	0.75 ± 0.04	0.35 ± 0.01	0.27 ± 0.07
Fill Factor	0.40 ± 0.04	0.62 ± 0.04	0.69 ± 0.03	0.41 ± 0.01	0.78 ± 0.01	0.70 ± 0.01
Efficiency (%)	0.71 ± 0.07	0.98 ± 0.26	1.35 ± 0.08	0.52 ± 0.03	1.78 ± 0.05	1.55 ± 0.06



Poly(3,4-ethylenedioxythiophene)

Figure S5. Chemical structure of PEDOT [poly(3,4-ethylenedioxythiophene)]

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Chapter 7

Conclusion

Conclusion

Dye-sensitized solar cells (DSCs) are an attractive alternative to traditional solar cells with an advantage of projected low manufacturing costs. DSCs based on n-type semiconductors (n-DSCs) generate photocurrent from dye-sensitized electron injection into n-type semiconductors such as TiO_2 . In contrast, for dye-sensitized photocathodes (p-DSC), electron transfer takes place from the valence band of the p-type semiconductor to the photoexcited dye. The use of p-DSCs as components in dye-sensitized tandem devices (pn-DSCs) can theoretically improve the efficiencies of single junction dye-sensitized solar cells. However, p-DSCs are still lagging behind their n-type counterparts. The most efficient photocathodes reported outside this work had maximum efficiencies, photovoltages and photocurrents of up to 0.41%, 350 mV and 5.4 mA/cm^2 respectively, under simulated sunlight ($1,000 \text{ W/m}^2$, AM 1.5G). Throughout this thesis many of the important issues relating to the development of more efficient photocathodes have been addressed and improved efficiencies have been achieved.

The low surface area and strong light absorption of commercial NiO nanoparticles have previously limited the photocurrents of photocathodes. A NiO film based on commercial nanoparticles with a thickness of $\sim 2 \text{ }\mu\text{m}$ absorbs about 30% to 40% of the incident visible light compromising efficient light harvesting and limiting the overall achievable efficiency. In chapter 3 of this thesis a novel hierarchical NiO nanomaterial was studied. Utilizing NiO microballs consisting of highly crystalline nanosheets with high specific surface area and low light absorption, improved cathodic photocurrents could be realized. Optimized p-DSCs based on these microballs showed high photocurrents (7.0 mA/cm^2) and record peak IPCE values (74%). The high specific area and low NiO light absorption could lead to more efficient utilization of the incident light and improve the photocurrents by about 30% compared to the previously reported highest photocurrent values. Figure 1a compares reported photocurrent from the literature with the results achieved in this thesis highlighting the progress that has been achieved in the field over the recent years.

A second major limitation of p-DSC efficiency was addressed in Chapter 4. The typically low open circuit voltage of photocathodes is the main limiting factor of the photoconversion efficiency. The application of $[\text{Co}(\text{en})_3]^{2+/3+}$ based electrolytes with a more negative rest potential (-0.025 V vs. NHE) compared to iodide based electrolytes (0.35 V vs. NHE) in p-DSCs could

improved the photovoltage of the resulting device. The more favorable rest potential of the $[\text{Co}(\text{en})_3]^{2+/3+}$ electrolyte produced record V_{OC} values of up to 709 mV for p-DSCs with the highest reported conversion efficiency of 1.30%. The $[\text{Co}(\text{en})_3]^{2+/3+}$ based-electrolytes also have the advantage of low light absorption in the visible spectral region, where the most efficient photocathode/photoanode sensitizers absorb.

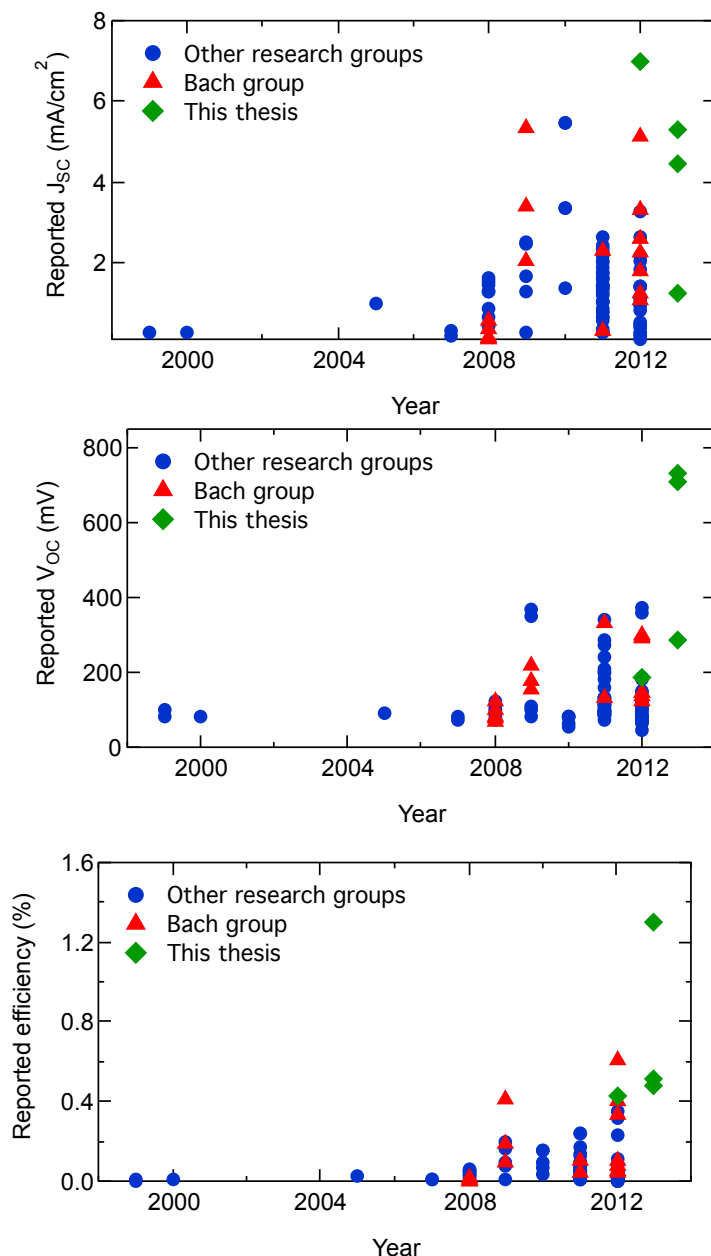


Figure 1. The reported photocathode a) short circuit current (J_{sc}); (b) open circuit voltage (V_{oc}) values; and c) efficiency values against time, taken from the literature; red triangles indicate the values reported by Bach group and blue dots represent the values reported by other research groups. The green squares represent the values reported as a part of this thesis.

To improve the photocathode open circuit voltages further, CuCrO_2 , a p-type semiconductor with higher ionization potential compared to NiO , was investigated in Chapter 5. The favorable valence band position improved the photocathode V_{OC} (734 mV) in conjunction with a $[\text{Co}(\text{en})_3]^{2+/3+}$ based electrolyte. The resulting devices showed low photoconversion efficiencies due to reduced photocurrents. Transient absorption laser spectroscopy indicated that inefficient charge injection is the likely reason for the low photocurrents. Novel dyes with more appropriate energy levels may result in increased performance of this type of p-DSC.

In Chapter 6, a novel transparent electrolyte was developed, in order to achieve improved pn-DSCs efficiencies. Two sensitizers with complementary absorption were utilized for the p-DSC and n-DSC part of the device. The developed device featured the general advantage that neither the front electrode, nor the electrolyte, competed with the back electrode for the incident light. The overall device efficiency however was still limited. Improved transparent electrolytes and infrared light absorbing sensitizers may ultimately lead to higher efficiencies.

In conclusion, a range of approaches was studied to improve the efficiency of photocathodes by improving their photocurrent and photovoltage. NiO in p-DSC has performance limitation due to self-absorption (parasitic light absorption). This limitation was addressed with an application of $\text{NiO-}\mu\text{Bs}$ that minimized the self-absorption leading to higher photocurrents. However, at the peak wavelength where dye absorbs $\text{NiO-}\mu\text{Bs}$ still absorb about 5-7% of incident visible light. The alternative p-type semiconductor (CuCrO_2) was studied as an alternative to conventional NiO . The application of CuCrO_2 in p-DSCs offered higher V_{OC} compared to NiO based p-DSCs due to its higher ionization potential compared to NiO . However, CuCrO_2 has low charge injection efficiency. The future work could be focused on finding an alternative p-type semiconductor with higher ionization potential to replace NiO . The change in semiconductor with higher ionization potential will reduce the driving force for dye regeneration. The parallel efforts are required to develop p-DSC dyes with lower (more positive vs. NHE) HOMO levels. To improve tandem DSC efficiencies more red shifted sensitizers could be a promising direction of research. The fill factors of p-DSCs are much lower compared to n-DSCs, for unknown reasons. There is an immediate need to tackle this issue.