Carbon nanomaterials as counter electrodes for dye solar cells

Kerttu Aitola





DOCTORAL DISSERTATIONS

Carbon nanomaterials as counter electrodes for dye solar cells

Kerttu Aitola

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Abstract

The dye solar cell (DSC) is an interesting emerging technology for photovoltaic conversion of solar electromagnetic energy to electrical energy. The DSC is based mainly on cheap starting materials and it can be manufactured by roll-to-roll deposition techniques on flexible substrates, which is considered as one option for cost-effective large-scale solar cell production.

The most expensive component of the DSC is the transparent conductive oxide glass substrate, and considerable cost reductions can be achieved by changing it to e.g. a plastic substrate. Plastic substrates are very flexible, lightweight and transparent. The state of the art DSC catalyst is thermally deposited or sputtered platinum, but platinum is a rare and expensive metal. Carbon, on the other hand, is widely available and some of its nanomaterials conduct electricity and are catalytic toward the DSC counter electrode (CE) reduction reaction.

In this work, carbon nanomaterials and their composites were studied as the DSC CE active material. The materials were random network single-walled carbon nanotube (SWCNT) film on glass and plastic substrate, vertically aligned multiwalled carbon nanotube "forest" film on steel and quartz substrate and carbon nanoparticle composite film on indium tin oxide-polyethylene terephthalate (ITO-PET) substrate. After comparison of the materials, the SWCNT network film on PET was chosen as the main CE type of this study, since it offers superior conductivity, transparency and flexibility over the other carbon-based CEs, it is also the thinnest and contains only one active material component. When a 30 % transparent SWCNT network film on PET was tested as a DSC CE, it was found out that such a film is not catalytic and conductive enough for a full 1 sun illumination DSC device, but the film could be suitable for a indoor illumination level application. The catalytic properties of a 10 % transparent SWCNT film were improved by depositing conductive PEDOT polymer on the film, and the DSC with such film as the CE had similar efficiency than the reference DSC with a sputtered Pt on ITO-PET CE. The PEDOT-SWCNT film had superior catalytic perfomance over the studied Pt films.

Thus, it can be concluded that carbon nanotube network films and their composite films are a feasible alternative flexible, roll-to-roll depositable DSC CE material.

Keywords Dye solar cell, counter electrode, carbon, nanomaterial, nanotube, nanoparticle, flexible, plastic

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Tiivistelmä

Väriaineaurinkokenno on lupaava uusi teknologia auringonvalon energian muuntamiseen sähköenergiaksi. Väriainekenno voidaan valmistaa pääosin melko edullisista materiaaleista ja se sopii teolliseen rullalta rullalle -tuotantoon joustaville alustoille, mitä pidetään yhtenä mahdollisuutena edulliseen ja laajamittaiseen teolliseen aurinkokennotuotantoon.

Väriainekennon kallein komponentti on läpinäkyvällä johtavalla pinnoituksella päällystetty lasialusta, ja merkittäviä kustannussäästöjä voidaan saavuttaa vaihtamalla lasi muovialustaan. Muovialustat ovat erittäin taipuisia, kevyitä ja läpinäkyviä. Kennon standardikatalyytti on termisesti pinnoittamalla tai sputteroimalla valmistettu platinakalvo, mutta platina on harvinainen ja arvokas metalli. Hiiltä taas on runsaasti saatavilla ja jotkut sen nanomateriaalit johtavat sähköä ja ovat katalyyttisiä kennon vastalektrodin pelkistysreaktiolle.

Tässä työssä tutkittiin hiilinanomateriaaleja ja niiden komposiitteja väriaineaurinkokennon vastaelektrodin aktiivisena materiaalina: satunnaisesti järjestäytyneistä yksiseinäisistä hiilinanoputkista koostuvaa kalvoa lasilla ja muovilla, vertikaalisesti järjestäytyneistä moniseinäisistä hiilinanoputkista koostuvaa kalvoa kvartsilla ja teräksellä ja hiilinanopartikkelikomposiittikalvoa indium-tinaoksidi-muovilla (ITO-muovi). Vertailun jälkeen satunnaisesti järjestäytyneistä yksiseinäisistä hiilinanoputkista koostuva kalvoa muovilla valittiin päätutkimuskohteeksi, koska se oli kalvotyypeistä parhaiten sähköä johtava, läpinäkyvin ja taipuisin. Lisäksi se oli ohuin ja sisälsi vain yhden aktiivisen materiaalin komponentin. 30 % läpinäkyvä satunnaisesti järjestäytynyt hiilinanoputkikalvo muovilla ei ollut tarpeeksi katalyyttinen eikä johtava täyden auringonvalon ulkosovelluksiin, mutta sisävalaistussovelluksiin sen ominaisuudet olivat riittävät. Kun 10 % läpinäkyvä hiilinanoputkikalvo muovilla pinnoitettiin johtavalla PEDOT-polymeerillä ja kalvoa testattiin kennossa, kennon hyötysuhteeksi saatiin suunnilleen sama kuin vertailukennon, jossa oli vastaelektrodina sputteroitu platinakatalyytti ITO-muovilla. PEDOT-hiilinanoputki-kalvolla oli myös parempi katalyyttinen suorituskyky kuin tutkituilla platinakalvoilla.

Tutkimuksen johtopäätöksenä voidaan todeta, että hiilinanoputkikalvot ja -komposiittikalvot muovilla ovat toteuttamiskelpoisia vaihtoehtoisia materiaaleja taipuisille väriainekennovastaelektrodeille.

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Avainsanat Väriaineaurinkokenno, vastaelektrodi, hiili, nanomateriaali, nanoputki, nanopartikkeli, taipuisa, muovi

Preface

This work was carried out in the New Energy Technologies Group of the Department of Applied Physics, Aalto University School of Science, under the supervision of Professor Peter Lund. The financial support came from the Graduate School of Nordic Center of Excellence in Photovoltaics, the TKK/Aalto University project MIDE/CNB-E and the Graduate School of Energy Technology in the form of travel grants.

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Preface

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Espoo, April 26, 2012,

Kerttu Aitola

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List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.

- I K. Aitola, J. Halme, N. Halonen, A. Kaskela, M. Toivola, A. G. Nasibulin, K. Kordás, G. Tóth, E. I. Kauppinen, and P. D. Lund. Comparison of dye solar cell counter electrodes based on different carbon nanostructures. *Thin Solid Films*, 519, p. 8125–8134, June 2011.
- II K. Aitola, A. Kaskela, J. Halme, V. Ruiz, A. G. Nasibulin, E. I. Kauppinen, and P. D. Lund. Single-walled carbon nanotube thin-film counter electrodes for indium tin oxide-free plastic dye solar cells. *Journal of the Electrochemical Society*, 157, p. B1831-B1837, October 2010.
- III K. Aitola, M. Borghei, A. Kaskela, E. Kemppainen, A. G. Nasibulin, E. I. Kauppinen, P. D. Lund, V. Ruiz, and J. Halme. Flexible metal-free counter electrode for dye solar cells based on conductive polymer and carbon nanotubes. *Submitted to Journal of Electroanalytical Chemistry*, January 2012.
- IV M. Toivola, J. Halme, K. Miettunen, K. Aitola, and P. Lund. Nanostructured dye solar cells on flexible substrates - Review. *International Journal of Energy Research*, 33, p. 1145-1160, September 2009.
- V G. Hashmi, K. Miettunen, T. Peltola, J. Halme, I. Asghar, K. Aitola, M. Toivola, and P. Lund. Review of materials and manufacturing options for large area flexible dye solar cells. *Renewable and Sustainable Energy*

Reviews, 15, p. 3713-3732, October 2011.

Author's Contribution

Publication I: "Comparison of dye solar cell counter electrodes based on different carbon nanostructures"

The author planned and conducted the carbon nanomaterial film testing in the CE-CE cell configuration and coordinated the multidisciplinary work between the three different research groups. The author participated in the random network carbon nanotube film preparation, built all the CE-CE cells, did all the measurements related to them, analyzed the data, wrote most of the paper and integrated others' parts to the text.

Publication II: "Single-walled carbon nanotube thin-film counter electrodes for indium tin oxide-free plastic dye solar cells"

The author planned the work, coordinated the multi-disciplinary research cooperation, participated in the carbon nanotube film manufacturing, electrochemical treatment and characterization, modified the solar cell configuration to meet the carbon nanotube film requirements, built the solar cells, carried out the solar cell characterization, analyzed the data, wrote most of the paper and integrated others' parts to the text.

Publication III: "Flexible metal-free counter electrode for dye solar cells based on conductive polymer and carbon nanotubes"

The author planned the study, coordinated the research cooperation, participated in the composite film manufacturing and electrochemical characterization and carried out the different film testing in the solar cells. Author analyzed the solar cell data, wrote most of the paper and integrated others' parts to the text, and coordinated the practical work with the other authors from two research groups.

Publication IV: "Nanostructured dye solar cells on flexible substrates - Review"

The author made a critical analysis and a review of carbon nanomaterials for flexible DSCs and wrote the section on these materials. In addition, the author gave minor contributions for the rest of the paper.

Publication V: "Review of materials and manufacturing options for large area flexible dye solar cells"

The author made a critical review on carbon materials for large-area DSCs and contributed to the writing.

Other publications by the author

M.I. Asghar, K. Miettunen, J. Halme, M. Toivola, K. Aitola, P. Vahermaa, and P. Lund. Stability issues of improved dye sensitized solar cells. 24th European Photovoltaic Solar Energy Conference, Proceedings of 24th European Photovoltaic Solar Energy Conference, p. 93-96, 2009.

M. Toivola, T. Peltola, K. Miettunen, J. Halme, K. Aitola, and P. Lund. Large Area Optimized Thin Film Nano Solar Cells on Metal Sheets. *12th NSTI Nanotech Conference, Proceedings of 12th NSTI Nanotech Confer ence*, p. 126-129, 2009.

M.I. Asghar, K. Miettunen, J. Halme, P. Vahermaa, M. Toivola, K. Aitola, and P. Lund. Review of stability for advanced dye solar cells. *Energy & Environmental Science*, 3, p. 418-426, 2010.

T. Nikitin, K. Aitola, S. Novikov, M. Räsänen, R. Velagapudi, J. Sainio, J. Lahtinen, K. Mizohata, T. Ahlgren, and L. Khriachtchev. Optical and structural properties of silicon-rich silicon oxide films: Comparison of ion implantation and molecular beam deposition methods. *physica status solidi* (*a*), 208, p. 2176-2181, 2011.

Other publications by the author

Abbreviations and Symbols

Abbreviations

CE	counter electrode
CIGS	copper indium gallium diselenide
CNT	carbon nanotube
CV	cyclic voltammetry
CVD	chemical vapor deposition
DSC	dye solar cell
DWCNT	double-walled carbon nanotube
EDOT	3,4-ethylenedioxylthiophene
EIS	electrochemical impedance spectroscopy
FTO	fluorine-doped tin oxide
HOMO	highest occupied molecular orbital
IL	ionic liquid
IPCE	incident photon to collected electron efficiency $% \left({{{\bf{n}}_{{\rm{s}}}}} \right)$
ITO	indium tin oxide
LUMO	lowest unoccupied molecular orbital
MWCNT	multi-walled carbon nanotube
PANI	polyaniline
PE	photoelectrode
PEDOT	poly(3,4-ethylenedioxythiophene
PEN	polyethylene naphthalate
PET	polyethylene terephthalate
PMII	1-methyl-3-propylimidazolium iodide
PV	photovoltaics
SEM	scanning electron microscope
SWCNT	single-walled carbon nanotube

- TCO transparent conductive oxide
- QE quantum efficiency

List of symbols

B_0	electrochemical double-layer "charge"
β	exponent of a constant phase element
$C_{\rm CE}$	electrochemical double-layer capacitance
$C_{\rm CO}$	contact capacitance
c_{μ}	chemical capacitance
D	electron diffusion coefficient
d	(film) thickness
$E_{\mathbf{F}}$	Fermi level
$E_{\rm redox}$	electrolyte redox potential
ϵ_{λ}	extinction (absorptivity) coefficient
η	efficiency
F.F.	fill factor
g	electron generation rate
i_{CELL}	(dye solar) cell current
$I_{\rm MPP}$	current at maximum power point
Iox	oxidation current
$i_{\rm PH}$	photocurrent
$I_{\rm red}$	reduction current
$i_{\rm SC}$	short-circuit current
j	imaginary symbol
L	electron diffusion length
λ	light wavelength
M	electrical mobility
m	empirical (non)ideality factor
n	charge carrier concentration
$n_{\rm e}$	free electron density
n_0	equilibrium electron concentration (in the dark)
ω	characteristic frequency
p	porosity
$P_{\rm IN}$	incident power
P_{MAX}	maximum power
$R_{\rm CE}$	counter electrode charge-transfer resistance
$r_{\rm CE}$	counter electrode charge-transfer resistance (per volume)
$R_{\rm CO}$	contact resistance
$R_{\rm REC}$	(PE) recombination resistance
$r_{\rm REC}$	(PE) recombination resistance (per volume)

$R_{\mathbf{S}}$	series resistance
$R_{\rm sh}$	sheet resistance
r_{T}	transport resistance
$\rho_{\rm e}$	electrical resistivity
S^0	ground state of the dye
S^*	excited state of the dye
S^+	oxidized state of the dye
σ	conductivity
T	optical transmittance
au	RC time constant
$ au_e$	electron lifetime
$V_{\rm MPP}$	voltage at maximum power point
$V_{\rm OC}$	open-circuit voltage
W_p	peak-watt
Ζ	impedance
Z'	real component of impedance
Z''	imaginary component of impedance
$Z_{\rm D}$	Warburg diffusion impedance

1. Introduction

In recent years, the rising global temperature has raised concern over the link between global warming and increased levels of atmospheric green house gases, such as carbon dioxide and methane. The CO_2 level increase is most likely due to the ever-growing fossil fuel (oil, coal, natural gas) usage in the developed and developing world. The energy consumption of the world was about 8000 million tonnes of oil equivalent (roughly 340 EJ) in 2009, of which much more than half was covered with fossil fuels, and the consumption is only growing [1].

Fossil fuels are a finite source of energy: it is estimated that the peak of "conventional" oil production has already been reached or will be reached in the very near future [2]. Unknown resources may lie either in unconventional oil, such as oil sand, of which extracting the energy source is difficult, or in high drilling-risk deepwater areas. In addition, it is estimated that hundreds of thousands of people die every year because of illnesses related to the small particle emissions from fossil fuel combustion [3].

One means of tackling the increased green house gas emissions, as well as small particle emissions and growing energy demand, is using more renewable energy: photovoltaic (PV), solar thermal, hydropower, biomass or wind energy. About 120 000 TW of solar energy (sunlight) reaches the Earth surface [4], which is thousands of times the amount humankind consumes. All the aforementioned forms of renewable energy are based on solar energy, but photovoltaics is the only form were sunlight is tranformed directly into electrical energy. In the end of 2010, the total installed PV capacity in the world was about 40 GW [5] and the PV market and production grows rapidly, but as the numbers indicate, there is still a lot of room for solar electricity.

Developing cheap and efficient solar cells and panels, where several cells are connected together for a larger energy harvesting unit, has not been an easy task. The photovoltaic effect was observed already in the 19th century, and the first modern solar cell was developed at Bell Laboratories in the 1950s. For decades, solar cells were considered suitable only for space applications and as an electricity production method in remote areas where other energy production or transfer means would not be worthwhile. This thought has however been challenged during the past years, because of the increased interest towards renewable energy and lowered solar cell and panel prices.

The so called price per watt of photovoltaics, which means the capital costs of a PV system cabable of producing 1 watt of power, has fallen rapidly during the past few years. In photovoltaics, the nominal power is expressed with the concept of peak-watt, W_p , which is the power production capability of a PV device in standard laboratory conditions (1000 W/m² illumination at air mass 1.5 global, AM1.5G). The current price per watt for silicon based PV is about 2.4 EUR/W_p, but prices as low as 1 EUR/W_p have also been reported [6].

As a consequence of the falling prices - and government support in the form of a feed-in tariff (the PV electricity producers can sell their overproduction to the grid with a set price) - the share of PV in total electricity production has reached 2 % in Germany in 2010 [7]. However, to reach grid parity, where the PV electricity costs as much as other electricity forms bought from the grid, and even better price competition with the other electricity production methods, the PV price has to drop even further. There are two ways of reaching this: increasing the solar cell efficiencies or reducing the cost of the materials or manufacturing through scientific or technological innovations.

1.1 Background

The solar cell type of this study is the dye solar cell (DSC) [8]. It has been estimated that the DSC production costs would be 3 - 4 EUR/W_p with the current manufacturing techniques and materials (Publication IV). This cannot at the moment compete even with the module prices of silicon (1 - 2 EUR/W_p). The DSC cannot either answer the question of high efficiencies (record 12.3 % [9]) compared to the commercial Si panel efficiencies of ~ 20 %). However, the DSC technology holds promise for very low-cost production because of the inherently cheap and non-poisonous materials, and cheap and easy manufacturing methods, of which roll-to-roll produc-

tion on flexible plastic and metal substrates seems the most industrially relevant one. With roll-to-roll methods large areas of solar cell materials can be deposited fast - faster than with the complex batch-processing techniques used in the silicon solar cell production - and the speed affects the final cost of the product. In addition to the complicated processing, other disadvantages of silicon solar cells are the energy-intensive silica reduction to produce the silicon starting material, the high purity requirement for the raw material and the poisonous chemicals used in the solar cell production. It must be also kept in mind, that the price of a a technological product typically drops rapidly in the industrial phase, following a "learning curve" - and the DSC technology is currently only in its preindustrial stage.

The most expensive component of the state of the art rigid, glass-based DSC is the transparent conductive oxide (TCO) glass substrate (fluorinedoped tin oxide, FTO, or indium tin oxide, ITO, covered glass, Publication IV) used both at the photoelectrode (PE) and counter electrode (CE). The standard CE contains also a few nanometer thick layer of platinum catalyst, which, like the indium in ITO, is a precious metal. The increased usage of indium in electro-optical applications raised its price from 10 cents (USD) per gram of the early 2000s to 60 cents of the late 2000s [10].

With flexible plastic substrates, the substrate cost could already be cut down by about 35 % (Publication IV). The standard flexible CE is manufactured by sputtering Pt on ITO-polyethylene terephthalate (PET) or polyethylene naphthalate (PEN), and also the ITO is deposited on the plastic by sputtering. From roll-to-roll manufacturing point of view, printing deposition methods of the conductive and catalytic layers might be more advantageous [11]. For these reasons, the DSC CE active materials should be replaced with cheaper and more printing-friendly materials.

1.2 Objectives of this study

The objective of this study was to develop potentially cheap CE materials for flexible plastic dye solar cells. Flexibility is an important feature of DSC substrates and active materials, since only such materials are compatible with the fast and low-cost roll-to-roll manufacturing techniques.

Some of the current state of the art DSC materials are not very flexible and contain rare and expensive metals. Carbon, on the other hand, is an interesting alternative material for flexible (and also rigid) DSCs,

Introduction

since it is abundantly available, and some of its allotropes are conductive, catalytic and suitable for the printing deposition methods. Carbon nanotubes (CNT) are very conductive, strong, flexible and catalytic, and they are thus an attractive optional material for flexible, transparent electronics and DSCs. CNTs were chosen as the alternative DSC material of this study because of the aforementioned intriguing properties. CNTs are not especially cheap yet, but they may improve a host material's properties already at a low weight-percentage and they hold a promise for becoming more affordable once the synthesis methods develop further. This applies to other carbon nanomaterials, such as nanoparticles and graphene, too.

Today, CNTs are utilized commercially for instance in composite materials as strength enhancers, and the CNT market has reached the billion USD scale [12]. An Israeli company, 3GSolar, aiming at commercializing glass-based DSCs, has announced utilizing multi-walled carbon nanotubes (MWCNTs) as additives in their carbon nanomaterial counter electrodes [13].

The initial aim of this study was to test CNTs at all the cell components, but the most fruitful line of research turned out to be the flexible random network single-walled carbon nanotube (SWCNT) CE on plastic substrate, and most of the work concentrated on it, on its fundamental properties and in improving its properties (electrochemically). The SWCNT network film can be deposited on a substrate by a simple press-transfer method, which is perhaps integratable to a roll-to-roll process, and the electrochemical methods are fast an upscalable. Also vertically aligned MWCNT "forest" film and carbon nanoparticle composite film were tested as the CE catalyst, of which especially the carbon nanoparticle composite is interesting from the printing point of view.

In addition to the material development objective, another aim of this study was to develop the methods of characterizing and comparing the different carbon nanomaterials further.

1.3 Thesis outline

The structure of the thesis is as follows. Chapter 1 presents the general introduction, background and objectives of the study. In chapter 2, more thorough introduction to the topic is given covering photovoltaics in general, dye solar cells and carbon nanotubes, explaining why this study was carried out and what is worthwhile about it. The experimental methods

are described in Chapter 3: the manufacturing methods of the carbon nanomaterials and the solar cells and the material and cell characterization techniques. The results of the study are presented and discussed in Chapter 4, divided in subsections by the publications. Chapter 5 summarizes and concludes the study. Introduction

2. Photovoltaics and materials

Photovoltaics or solar cells are a technique for transforming the electromagnetic energy of light (direct sunlight or indoor light) into electrical energy. A photovoltaic decive must have a means to create an electronic excitation, an electron-hole pair, and separate the electron-hole pair to create electric current.

The silicon solar cell - as well as the other solid-state semiconductor solar cells - is based on p-n junction technology, where areas of different dopants form an "internal electrical field", which separates the charges when an exciton is created in the semiconductor by the incident light with energy matching the energy gap of the semiconductor. The concept of the dye solar cell, the cell type of this thesis, is very different from the materials and operation point of view, and it will be addressed in the following chapters.

There are many solar cell types of which those based on solid state silicon are the dominant type in research and industry. The different solar cell types are divided in "generations". The first generation comprises of the first generation of commercial solar cells, such as crystalline and multicrystalline silicon. The second generation consists of solar cell types based on material reduction attempts: thin film solar cells of cadmium telluride, copper indium gallium diselenide (CIGS), amorphous silicon (a-Si) or nanocrystalline silicon. The third generation comprises both of solar cells with efficiencies higher than the maximum theoretical Shockley-Queisser limit of a p-n junction solar cell, that is either multijunction solar cells or cells with light concentrators, and "new" technologies such as dye solar cells and polymer solar cells.

2.1 Dye solar cells

Dye solar cells or dye-sensitized solar cells were first invented by Michael Grätzel and his colleagues in the early 1990s [8]. The DSC is a photoelectrochemical system, based somewhat on the work done on photoelectrochemical semiconductor-electrolyte cells in the preceding decades and inspired by the concept of photosynthesis [4].

The dye solar cell comprises of a photoelectrode, a counter electrode and an electrolyte sandwiched between the electrodes. The photoelectrode is a nanoporous TiO_2 film covered with a monolayer of dye molecules, for instance ruthenium polypyridines, usually in the thickness of 15 μ m, on a conductive substrate. In a DSC, the electronic excitation happens in the dye molecule, but the charge separation is carried out by the semiconductor/electrolyte interface. The DSC PE nanoporous structure is required for achieving a large microscopic area for the dye to harvest light efficiently. The counter electrode utilizes a catalyst, usually platinum, on a conductive substrate, and the most common electrolyte type is the iodide/triiodide redox couple in an organic solvent. Alternatives to the materials have been developed, for instance ZnO to replace the TiO₂, carbon nanoparticle composites instead of platinum, and cobalt complex redox couples instead of iodide/triiodide or solid state electrolytes, but many of the alternative materials suffer from for instance low performance or bad stability.

TiO₂ is a large band gap semiconductor ($E_g = 3.2 \text{ eV}$ in the bulk anathase phase), thus it absorbs directly only a small quantity of the solar spectrum, namely the high-energy UV light. However, TiO₂ can be made photoconductive with the help of the dye adhered on its surface. In the light harvesting process of the dye, an electron is excited from the highest occupied molecular orbital (HOMO) level to the lowest unoccupied molecular orbital (LUMO) level, and the excited electron is injected directly from the dye LUMO level to the TiO₂ conduction band (as well as to the lower energy defects states in the TiO₂ band gap). The electrons diffuse through the TiO₂ film to the contact, to the external circuit, and finally to the counter electrode. The oxidized dye is regenerated by the iodide ions in the electrolyte, which in turn oxidize to triiodide. The triiodide ions diffuse toward the counter electrode, where they are reduced back to iodide. The largest obtainable DSC voltage corresponds to the difference between the Fermi level of the electrons in the TiO₂ film and the redox potential of



Figure 2.1. A schematic image of a DSC and its operating principle. Reproduced with permission from Adv. Mater., 22, E210 (2010). Copyright 2010 Wiley-VHC Verlag.

 I^-/I_3^- in the electrolyte.

The overall photochemical reactions at the DSC PE are as follows (S^0 refers to the ground state of the dye, S^* to the excited state, S^+ to the oxidized state):

$$S^0 + h\nu \to S^* \tag{2.1}$$

$$S^* \to S^+ + e^-(\text{TiO}_2) \tag{2.2}$$

$$2S^+ + 3I^- \to 2S^0 + I_3^-$$
 (2.3)

$$3I^- + 2h\nu \to I_3^- + 2e^-(TiO_2)$$
 (2.4)

and at the CE

$$I_3^- + 2e^- \to 3I^-.$$
 (2.5)

It has been suggested that the dye regeneration reaction (2.3) actually consists of complex formation steps between the oxidized dye and I^- ion and I^-_2 radical [14] (it has been proven experimentally that I^-_2 is also present in the electrolyte), but the intermediate reactions are not presented here.

A schematic image of a DSC and its operating principle and energy level diagram are presented in Figures 2.1 and 2.2.

The reason for utilizing the I^-/I_3^- redox couple in the DSC lies in the fact



Figure 2.2. A schematic image of a DSC and its energy level diagram. Reproduced with permission Adv. Mater., 22, E210 (2010). Copyright 2010 Wiley-VHC Verlag.

that the I_3^- reduction reaction is a two electron transfer process, which involves a dissociation reaction. This is a prerequisite for slow enough direct recombination from the TiO₂ conduction band to the I_3^- ions present in the PE pores. The iodine-based electrolytes have however their disadvantages: iodine is very volatile (even though in solution very little of it is present [15]), and the triiodide ion causes optical losses and is a very strong oxidant that, through corrosion, prevents usage of for instance cheap steel substrates [16] and silver current collecting grids without protective layers.

The only one-electron-transfer redox mediator producing comparable or even better - DSC efficiencies is the cobalt bipyridine complex [9, 17], which requires the usage of dyes with long organic sidechains to prevent direct contact of the redox mediator and the TiO_2 film and thus direct recombination. The cobalt complex redox couple has poorer diffusion properties than iodide/triiodide, but this is compensated with its more favorable redox potential and thus larger photovoltage of the cells, and the DSC record efficiency of 12.3 % has been achieved utilizing this redox couple [9]. The poorer diffusion can be further compensated by using thin PE films and dyes with large extinction coefficients. An additional advantage of this redox couple type is that is does not absorb light as efficiently as the iodide/triiodide couple, causing less optical losses.

An operating DSC is always subject to current and voltage losses. A certain type of dye has a certain type of absorption spectrum. This can be matched for instance with the sunlight spectrum peak, which is at the green wavelength, but one dye can not absorb all the available light wavelengths. This can be at least partially overcome with e.g. cosensitization

[18] where several dyes with different spectral responses are used simultaneously, however so far with modest results. Losses happen also by e.g. recombination from the PE and from the FTO on the PE side to the triiodide in the electrolyte. Further losses happen via the transport resistance at PE, the charge-transfer resistance at CE, the diffusion resistance in the electrolyte and the electrical contact resistances.

The dye solar cell is by nature based on relatively cheap materials and the typical manufacturing processes do not require especially high temperatures or a very controlled atmosphere. It can also be produced on flexible plastic or metal substrates by roll-to-roll printing techniques, which is one means to achieve cheap production costs. For instance, a 7.6 % efficiency has been achieved with a pressed TiO₂ film on an ITO-PET substrate when MPa-scale pressure is used [19]. Other advantages of the DSC are for instance its good light-harvesting properties at low light intensities [20], thus the DSC could be used in low-intensity applications, such as mobile phone chargers or light detectors. In indoor lighting conditions, the DSCs would not be subjected to extreme temperatures or drastic temperature changes, which would also relax the temperature durability requirements.

The challenges of this solar cell type are the relatively low efficiency and the long-term stability issues. The state of the art record efficiency, 12.3 %, cannot compete with those of commercial silicon (~ 20 %). The long-term stability issues are ascribed to for instance the liquid electrolyte leakage or unwanted chemical reactions in the cells [21], even though promising durability results have been obtained with careful material selection and cell sealing.

In the solar cell world, the DSC has to compete with the other solar cell types. For instance thin film silicon solar cells have properties similar to those of DSCs: flexibility, transparency, low material consumption and good light-harvesting properties at low light intensities. The DSC is however still a relatively young technology and it is currently only in the early stages of commercialization. Some companies, such as G24 Innovations, already sell products, such as a bag equipped with a flexible DSC panel on a metal substrate.

2.1.1 The IV curve of the dye solar cell

Perhaps the simplest way to obtain the IV curve of the DSC is to start from the recombination current density, i_{REC} , of the photoelectrode film [22].

Assuming uniform electron density, that is electron diffusion lenght L is larger than the PE film thickness d, the i_{REC} is

$$i_{\text{REC}} = q_{\text{e}}dk(n^{\beta} - n_{0}^{\beta}) = q_{\text{e}}d\frac{n^{\beta} - n_{0}^{\beta}}{\tau}$$
 (2.6)

where k is the first-order rate constant of the recombination reaction, τ the electron lifetime, assumed here independent on the position in the film, and β is an exponential factor describing nonlinear recombination. By inserting to it the equation that relates the electron density and voltage,

$$n(x=0) = n_0 e^{\frac{-q_e V_{\text{TiO}_2}}{k_{\text{B}}T}}$$
(2.7)

we get

$$i_{\text{REC}}(V_{\text{TiO}_2}) = i_{\text{REC},0} \left(e^{-\frac{\beta q_e V_{\text{TiO}_2}}{k_B T}} - 1 \right),$$
 (2.8)

where

$$i_{\text{REC},0} = \frac{q_{\text{e}} dn_0}{\tau} \tag{2.9}$$

is the exchange current of the recombination reaction. The IV curve of the cell can be obtained by subtracting Equation 2.8 from the i_{SC} (the short-circuit current or the photocurrent):

$$i_{\text{CELL}}(V_{\text{TiO}_2}) = i_{\text{SC,TiO}_2} - i_{\text{REC,0}} \left(e^{-\frac{\beta q_e V_{\text{TiO}_2}}{k_B T}} - 1 \right).$$
 (2.10)

This produces the IV curve of a DSC (for a good quality PE, L > d), and the shape of the curve resembles the diode-like IV curve of a solid state solar cell based on a p-n junction. If there are electron diffusion problems in the PE, the IV curve takes the form

$$i_{\text{CELL}}(V_{\text{TiO}_2}) = i_{\text{SC,TiO}_2} - i_{\text{REC,0}} \left(e^{-\frac{\beta q_e V_{\text{TiO}_2}}{k_B T}} - 1 \right) \left(\tanh \frac{\tanh(d/L)}{(d/L)} \right), \quad (2.11)$$

as deduced elsewhere [22].

2.2 Carbon nanotubes

Carbon nanotubes are cylindrical nanostructures of carbon, which can be thought of as a rolled up graphene [23] sheet (Figure 2.3). They were



Figure 2.3. A schematic image of a single-walled carbon nanotube. Adapted from Wikimedia Commons.

first observed by Sumio Iijima in 1991 [24] and are a "one-dimensional" allotrope of carbon, other allotropes being for instance diamond, graphite, and fullerenes. What makes them interesting from the applications point of view is their unique electrical and mechanical properties that stem from their structure: carbon nanotubes can conduct electrons ballistically, they are one of the strongest known materials and they conduct heat very well, to mention a few.

The diameter of a CNT is in the nanometer range but its length can be micrometers or even centimeters [25], they can be single-walled or multiwalled, stacked cup-type, or functionalized with e.g. carboxyl groups or fullerenes [26]. The atoms in the CNT "honeycomb" graphene lattice have three nearest neighbours and are sp² hybridized, thus there is also a delocalized π bond. In carbon nanotube synthesis, a broad range of structurally different CNTs are formed, even though they are usually more or less all either of the SWCNT or MWCNT type. The structural property that varies is the *chirality*, which has an effect on the electronic properties as well.

The chirality of a SWCNT (or a MWCNT wall) can be described by the chiral indices (Figure 2.4). The chiral indices are the coefficients of the chiral vector, which is composed of multiples of the unit vectors of the hexagonal CNT lattice. If m = 0, the CNT is called "zigzag". If n = m, it is "armchair" and otherwise "chiral". Depending on the chirality, CNTs are either metallic or semiconducting. Armchair CNTs are metallic. If n - m is divisible by 3, the CNT is a small band gap semiconductor, and for other m and n values they are semiconductors. About two thirds of the SWCNTs formed in bulk quantities are semiconducting, one third metallic.

In a CNT wall, electrons are quantum confined around the CNT circumference (in the graphene sheet monolayer) and periodic boundary conditions apply [27]. Electrons can propagate only along the nanotube axis, so that their wavevectors point at this direction, and the resulting number of one-dimensional conduction and valence bands depends on the standing waves set up around the CNT circumference. The dispersion relations of the one-dimensional bands for CNTs can be calculated based on these principles.



Figure 2.4. The chiral indices and the chiral vector of a carbon nanotube. Adapted from Wikimedia Commons.

Graphene is a semi-metal or a zero band gap semiconductor. The electronic structure of CNTs is closely related to that of graphene [25]. The graphene Fermi surface consists of the corner points of the hexagonal Brillouin zone (K point), and the electronic states of a CNT are parallel lines in the reciprocal k space. For armchair tubes, there are states crossing the corner points of the (first) Brillouin zone, making those tubes metallic, and other tubes semiconducting.

A downside of the strong carbon sp² bond is that CNTs are chemically very inert and it is relatively difficult to form bonds between them and some compound of for instance a composite matrix host material. One method of modifying CNTs is chemical functionalization, where for instance a carboxyl group is introduced to the CNT wall by treating the tubes with acid. By ultrasonication in a mixture of concentrated nitric and sulfuric acid, the CNTs can be oxidized, which results in carboxyl group addition, end cap opening and tube shortening [28]. With less vigorous treatment, only carboxyl groups are introduced. However, the chemical functionalization breaks the perfect graphene structure of the (outermost) wall and affects the electronic properties too, at least to some extent.

Another issue related to CNTs is their tendency to form bundles of tubes, where the nanotubes are held together by weak van der Waals force, making the bundle internally mechanically weak but the bundling phenomenon strong enough to complicate dispersion. CNTs can be dispersed in a solution by ultrasonication, possibly with the help of a surfactant, but the treatment is not long-term stable and leaves the surfactant in the solution.


Figure 2.5. A SEM image of a randomly oriented SWCNT network film. The bright spots are iron catalyst particles present in the film from the SWCNT synthesis.

2.2.1 Carbon nanotube films

It is possible to manufacture many kind of films out of carbon nanotubes: randomly oriented network films, vertically aligned "forest" films and horizontally aligned films [29] or composite films. A conductive but still semitransparent film can be made out of SWCNTs [30], and double-walled carbon nanotube (DWCNT) films seem to have even better optical transmittance versus sheet resistance properties [31]. A scanning electron microscope (SEM) image of a random network SWCNT film is shown in Figure 2.5.

Carbon nanotubes are very flexible, and this applies to CNT films too. A randomly oriented SWCNT film clearly outperforms for instance ITO in flexure resistance: ITO's conductivity properties worsen considerably when bending, whereas a SWCNT film does not exhibit changes [32]. A downside of CNT films is that the CNT bundles or agglomerates do not adhere to each other or to some substrate very well.

The superior electrical conductivity - and mechanical strength - of CNTs is difficult to utilize in macroscopic structures. In randomly oriented CNT films, the conductivity is known to be restricted by the high contact resistance between the individual tubes and bundles [33]. This should be resolved by some means, e.g. by forming interlinking bonds between the individual CNTs [34, 35, 36] or between the CNTs and some other material in a composite, before the advantageous CNT properties can be fully utilized in thin, transparent films. The electrical conduction in a CNT film is for the most part via the metallic CNTs, so that the semiconducting tubes are "unnecessary" in the structure. However, efficient methods for sorting them out according to their electronic properties (or chirality) do not presently exist.

The CNT film conductivity can be improved by acid doping [37]: the film is immersed in a concentrated acid solution and NO_x groups are deposited on the film. The result of the procedure is p-doping of the films. Acid doping is however known unstable in the long run, but in one study the stability problem was overcome by depositing a conductive polymer layer on top of the dopant layer [38]. Individual CNTs have also been nitrogen doped, meaning that some of the carbon atoms in the CNTs have been substituted with nitrogen atoms, that have five valence electrons. The individual N-doped semiconducting CNTs become more n-type, but this does not apply in the bulk scale, since in the present manufacturing processes for the N-doped CNTs, the tubes are formed shorter and more defective compared to pristine CNTs, which impairs the conductivity [39].

Carbon nanotubes are also catalytic toward e.g. the triiodide reduction reaction of the DSC CE - carbon is somewhat catalytic and its performance as a catalyst can be improved by utilizing it as a porous film with large microscopic surface area, and CNT films are intrinsically porous. A CNT film catalytic performance is most likely dependent on its microscopic surface area, which in turn depends on the film thickness [40] (Publication I), so that the catalytic performance and transparency functions have different requirements for the film thickness, unless the film catalytic performance is enhanced by other some means than just increasing its thickness. The catalytic activity of a CNT film is most often ascribed to defects in the (outermost) CNT wall and to the CNT endcaps, where the wall curvature is high, but some studies claim that also the sidewalls play a role [41].

The sheet resistance of a conductive film, $R_{\rm sh}$ (Ω , or " Ω /sq"), is given by

$$R_{\rm sh} = \rho_{\epsilon} d^{-1} = (\sigma d)^{-1}, \qquad (2.12)$$

where ρ_{ϵ} (Ω m) and σ (S/m) are the electrical resistivity and conductivity of the film parallel to the substrate. respectively. The $R_{\rm sh}$ depends on the nature and quality of the carbon nanomaterial (e.g. nanotubes vs. nanoparticles) and the structure of the film, and can therefore vary greatly from one type of film to another. The electrical conductivity of CNT films thicker than a few monolayers obeys a bulk material conductivity law,

$$\sigma = enM, \tag{2.13}$$

where e is the elementary charge, n is the charge carrier concentration (per unit volume of the film), and M is the electrical mobility.

Measuring a nanometer-range thickness - where a CNT films' thickness often falls - is difficult. For instance profilometry fails because of the thinness and the unevenness of the CNT films. However, the thickness of a CNT film can alternatively be described by optical transmittance, T, measured at 550 nm light wavelength. Because the transmittance is related to the amount of carbon (layers) in the film, and light scattering and reflection may be omitted, the transmittance can be related to the film thickness by the Beer-Lambert law

$$T = e^{-\epsilon(\lambda)(p-1)d} \tag{2.14}$$

where $\epsilon(\lambda)$ is an extinction (or absorptivity) coefficient, which depends on the wavelength, λ , of light, and p is the porosity of the film. The electrical and optical properties of CNT films are often presented as a dependence of the sheet resistance on the transmittance. Using equations 2.12, 2.13 and 2.14 the dependence can be expressed as follows:

$$R_{\rm sh} = \frac{\epsilon(1-p)}{enM\ln(T)}.$$
(2.15)

This dependence is in good agreement with experimental results obtained from SWCNT networks. Obviously, for a certain type of CNTs (ϵ = const) with a certain porosity (p = const), the electrical quality of the film will be determined by the concentration and mobility of the charge carriers. The first parameter can be affected by the CNT doping level, and the length of the tubes determines the mobility of charge-carriers in the CNT film.

Figure 2.6 displays optical transmittance vs. sheet resistance correlation for the random network SWCNT films used in this study, as well as a typical optical transmittance spectrum and a Raman spectrum. With best ITO-PEN films, 15 Ω /sq sheet resistance at 80 % transmittance can be achieved, so that in this respect the SWCNT films cannot yet compete with ITO (for similar sheet resistance values the SWCNT network film has a transmittance of the order of 10 %).

In this work, the SWCNT film transmittance is used mainly as a measure of the film thickness (since it cannot be determined by other means, e.g. with profilometry, as mentioned above). Transparency is considered as one of the advantages of the DSC technology in for instance building integrated PV, and in this regard it is a desired property for the CE too.



Figure 2.6. a) The optical transmittance versus sheet resistance of (an ethanol-densified) SWCNT network film, b) optical transmittance and c) Raman spectrum. Reproduced with permission from J. Electrochem. Soc., 157, B1831 (2010).

From the DSC operating point of view it is not an indispensable quality (the DSC can be lit from the PE side).

2.3 Carbon nanotubes in dye solar cells

It is possible to manufacture transparent but conductive films out of SWC-NTs and DWCNTs, as mentioned before, and CNTs are known catalytic. In addition to replacing the conductive and/or catalytic layer of a DSC electrode, carbon nanotubes can be mixed with the PE TiO_2 film to improve conductivity, perhaps especially in the pressed TiO_2 films, in which the conductivity is sometimes insufficient. Carbon nanotube-ionic liquid composite electrolytes have also been succesfully used in the DSC. CNT films could also act as the conductive layer on the PE side, but in that case the catalytic property should be blocked by some means, so that the electrons in the film would not recombine with the triiodide in the electrolyte, and so far this has not been studied.

2.3.1 Carbon nanotube films as dye solar cell counter electrode

Carbon nanotube films, being both conductive and catalytic, can carry out both of these functions of the DSC CE. What makes them even more interesting is the fact that CNTs and at least random network CNT films are very flexible [32] and it is possible to manufacture conductive, yet somewhat transparent films out of SWCNTs [30, 32] and DWCNTs [31]. CNT films have also shown promising stability in the DSC (electrolyte) [42].

Different kind of CNT films have been utilized at the DSC CE, though usually only as the catalyst on some conductive substrate. There are only two studies, where a random network SWCNT film carried both the catalytic and conductive functions: ni the other study the film was however not transparent [43]; in the other it was semitransparent but the catalytic performance was only moderate (Publication II).

When a random network SWCNT film on FTO glass has been utilized as the DSC catalyst, low CE charge-transfer resistances, R_{CE} , (see Chapter 3.2.2.) and good DSC efficiencies have been obtained [40, 43, 44, 45, 46, 47]. Trancik et al. conducted a comparative study of different SWCNT film thicknesses (as determined by their transmittance) on FTO glass substrate and found out that the R_{CE} lowers as the SWCNT film thickness increases [40]. They also caused defects in the SWCNTs by ozone treatment and observed a R_{CE} decrease up to a certain duration of the ozone treatment (until the treatment started to worsen the film R_{sh}), thus concluding defects as catalytically active sites. A stainless steel substrate worked well in concert with a SWCNT film [48]. Composite films, MWCNT-Nafion [49] and TiN-nanoparticle-decorated MWCNTs [50], have also been good catalysts.

A vertically aligned MWCNT "forest" film has yielded good [51] and fair [46, 52, 53] efficiencies, always on a conductive substrate.

An issue with CNT films is the poor chirality control in the synthesis, which results in a mixture of semiconducting and conducting CNTs, which should be solved - unless CNT sorting methods according to e.g. chirality develop further. Other issue is the poor adherence of CNTs' and for instance the random network CNT films', which calls for improved chemical functionalization or interlinking with bonds [34, 35, 36]. The latter alternative might tackle the CNT or CNT bundle contact resistance problem too.

A natural point of comparison to the CNT films is the carbon black CE: carbon nanoparticles mixed with conductivity improving graphite flakes and adherence improving TiO₂ particles and pressed or sintered on FTO glass or ITO-PET substrate [54, 55, 56, 57, 58, 59, 60]. To obtain sufficient catalytic performance, the films have to be very thick, in the 10 μ m range, thus they are completely opaque and not very flexible. Chen et al. fabricated a pure carbon CE by depositing activated carbon on a flexible graphite sheet and obtained even better DSC performance than with thermally deposited Pt on FTO glass [61]. Also a flexible carbon nanoparticlegelator film on ITO-PEN has been reported [62]. There are some preliminary results with graphene films [63] or graphene composites [64, 65] as DSC catalyst.

One option for DSC CE material could be a composite of CNTs and carbon nanoparticles, which has already been tested as an electrode in the lithium ion battery [66], but not in the DSC so far.

2.3.2 Carbon nanotubes at the dye solar cell photoelectrode and in the electrolyte

Carbon nanotubes have also been utilized as conductivity improving additives in the DSC PE in many different forms: SWCNT [67, 68, 69], MWCNT [70, 71, 72] and functionalized SWCNT [73, 74], in high and low temperature [72] PE manufacturing. The TiO₂-CNT composite materials have been tested in order to find out whether the CNTs could improve the titania conductivity, which is a problem especially in the low-temperature processed, pressed PE films. The result has usually been a moderate i_{SC} increase, the open-circuit voltage, V_{OC} , staying more or less the same, yielding a small efficiency, η , improvement (see Chapter 3.2.1 for the parameter definitions). Brown et al. showed that electrons in a SWCNT-TiO₂ composite PE film had a 50 % higher lifetime than electrons in a plain TiO₂ film, thus the DSC with such a PE had a higher photocurrent, but the V_{OC} was lower due to a "charge equilibration" phenomenon between the TiO₂ and the SWCNTs (more positive Fermi level in the composite film) [69].

CNT films could also act as the conductive layer on the PE side, but in that case the catalytic property should be blocked by some means, so that the electrons in the film would not recombine with the triiodide in the electrolyte, and so far this has not been studied.

CNTs have been exploited in DSC ionic liquid electrolytes too. Ionic liquids (IL) are a promising non-volatile DSC electrolyte type [75]. They are organic salts, comprising usually of a large organic cation and an inorganic anion. Their structure prevents them from forming solid crystals in room temperature (apart from some exceptions), but the electrostatic force between the anion and cation on the other hand prevents evaporating, making them an interesting electrolyte type. Their disadvantage is that they are much more viscous than the common organic solvents

(e.g. acetonitrile or 3-methoxypropionitrile) used in the standard DSC electrolytes. The most commonly utilized ionic liquid in the DSC is 1-methyl-3-propylimidazolium iodide (PMII), but a mixture of three different imidazolium iodides has yielded a DSC efficiency of 8.2 % [76].

Both SWCNTs [77] and MWCNTs [78] have been utilized as IL electrolyte additives. The SWCNTs improved the DSC performance considerably and the MWCNTs somewhat, however carbon black nanoparticles and TiO₂ nanoparticles even more. The i_{SC} and V_{OC} were the highest for the MWCNT case but the fill factor lowest, but the authors did not present an explanation for the observations.

The mechanism via which the CNTs improve the IL performance is not known; it could be via improved ionic conductivity due to improved Grotthus mechanism (the CNT would function as a catalyst for the Grotthusstype conduction, where an I_2 molecule is exchanged between an iodide and a triiodide ion). This adds to the ionic conduction without actual ionic mass transfer. Other means could be improved charge-transfer at the CE or electron conduction along the CNT, which would shorten the distance the ions have to travel between the PE and the CE.

It is theoretized that in SWCNT-IL composites, when ground, the SWCNT delocalized benzene ring and the imidazolium five ring interact somehow and form a gel via that mechanism [79]. In the gel, the SWCNTs are also less bundled than in the pristine form.

2.4 Conducting polymers

Conducting polymers are organic polymers that can conduct electricity. Their electricity conducting mechanism resembles that of CNTs: also in them there is sp^2 hybridized carbon that forms a conjucated p bond, in which electrons have high mobility. Some of them, such as polyaniline [80] (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT, Figure 2.7) [81] and its poly(styrenesulfonate)-[82, 83] and *p*-toluenesulfonate-doped versions [84], work as DSC catalysts. PEDOT has also been mixed with carbon nanotubes [85, 86, 87], carbon black [88] and graphene [64] with good results. The lateral conductivity of a PEDOT film on a plain polyester [89] or glass substrate (as a large-area DSC) [90] is however not sufficient for the DSC purposes, thus an additional conductive layer is required. With PEDOT nanotubes lower R_{CE} values than with Pt have been obtained [91].



Figure 2.7. Poly(3,4-ethylenedioxythiophene). Reproduced from Wikimedia Commons.

The most common deposition method of the above mentioned conducting polymers is spin-coating or doctor-blading the polymer solution on the TCO substrate and letting the paste dry in air in around 110 °C. Another option is oxidative electropolymerization of EDOT by chronocoulometry, which offers a precise control of the amount of the deposited PEDOT.

PEDOT functions also as a DSC solid state electrolyte [92, 93]. Liu et al. obtained a 6.1 % DSC efficiency, when the PEDOT polymerization was started from the bis-3,4-ethylenedioxylthiophene dimer, so that the dimer solution effectively penetrated all the PE pores, ensuring a uniform structure and hole transport in the resulting polymer film [92].

2.5 Graphene

Graphene, the two-dimensional carbon monolayer structure [23] is an emerging DSC additive. Being a zero-band gap semiconductor or a semimetal with extremely high electron mobilities, its conductive properties are even better than those of carbon nanotubes, but so far the large-scale synthesis is an open question - graphene is produced mainly in small flakes. There are already some reports where graphene has been used as a catalyst on the DSC CE [63, 64, 65] and as a conductivity improving agent in the TiO₂ film [94]. Roy-Mayhew et al. showed that "oxygencontaining cites" in the graphene flakes are responsible for the catalytic activity [65].

3. Methods

3.1 Manufacturing methods

The main research topic of this thesis was carbon nanomaterials and films made out of them as DSC CE, and the most important manufacturing methods are presented in this chapter.

The SWCNTs used as the DSC CE active material (Publication I, Publication II, Publication III) were synthesized by a floating catalyst (aerosol) chemical vapor deposition (CVD) method [95]. In the process, carbon monoxide (CO), mixed with 1 % of carbon dioxide (CO₂), is passed through a ferrocene cartridge in room temperature. The ferrocene sublimes to the passing gas and the gas mixture is directed via a water cooled injector to the tube furnace. The walls of the furnace are inert to prevent CNT growth on them and the reactor is kept at maximum in temperature of 880 °C. A temperature gradient between the injector and the tube walls causes ferrocene decomposition and formation of supersaturated iron vapor. This in turn leads to the formation of Fe nanoparticles. The metal nanoparticle acts both as the catalyst for the carbon source decomposition and as the CNT formation site. The SWCNTs form bundles in the gas phase and the bundles can be collected on a porous membrane filter at the reactor outlet. The film thickness depends on the collection time.

The use of CO as carbon precursor is advantageous in the sense that the CO disproportionation reaction (2CO (g) \rightarrow C (s) + CO2 (g)) requires a catalyst surface and cannot decompose thermally by itself, unlike many other carbon sources, such as hydrocarbons and alcohols, that decompose and form byproducts (amorphous carbon, soot). The gas-phase CVD methods shows also potential for upscaling [95], since it is a continuous process that involves both the catalyst particle formation and the SWCNT forma-

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tion and growth. Also the direct product collection from the gas phase and the lack of a substrate (in the SWCNT synthesis) reduces the amount of process steps.

The formed SWCNT film can be transferred on many substrates, for instance plastic, glass or quartz, by a simple and fast room temperature press-transfer method [30]. The film on the low-adhesion membrane filter is pressed on the substrate so that the CNT film faces the substrate. Then a pressure in the order of 1 kPa is applied on the membrane filter and the SWCNT film transfers on the substrate. After the transfer, the film can be densified by applying ethanol on it and letting the ethanol evaporate, which makes the SWCNT film more dense and thereby improves its conductivity.

The iron catalyst particles present in the SWCNT film can be removed from the films electrochemically by anodic stripping in 1 M HNO₃, which removes the particles efficiently but does not worsen the film quality, as proven by Raman spectroscopy and unaltered conductivity and electrochemical performance [96]. The iron nanoparticles need to be removed prior to the DSC assembly, since iron is oxidized by the triiodide in the electrolyte and iron precipitates on the TiO₂ particles are known harmful for the DSC performance [97]. It has been observed that non-purified SWCNT films have an adverse affect on the DSC PE behaviour (Publication II).

The MWCNT forest films (Publication I) were grown directly on quartz and stainless steel (Inconel) sheets by catalytic CVD [98]. First a 250 nm titanium layer was deposited on the quartz and Inconel steel (Ni 72 wt.-%, 16 % Cr, and 7 % Fe) substrates by physical vapor deposition and the Ti was patterned with a lift-off process resulting in Ti covered surface with square openings to the substrate to enable MWCNT growth. On the steel substrate the opening had the size 6 x 14 mm. On the quartz substrate, the openings formed an array of squares, with a square size of 100 x 100 μ m and a 50 μ m spacing. The purpose of the Ti layer was to ensure areas of no MWCNT growth and for the quartz substrate, sufficient lateral current collection. The MWCNT film deposition was carried out in a horizontal tube reactor pumped to a low pressure and purged with argon. The argon flow was maintained and the furnace heated to 785 °C. Ferrocene in xylene solution was evaporated and preheated, and this precursor gas was injected to the reactor. The films were grown to about 10-50 μ m thickness, aiming at 10 μ m, but due to process uncertainty some areas had thicknesses of even 50 μm . Platinum nanoparticles were deposited on some of the films by drop-casting platinum bis(acetylacetonate) in toluene on them and reducing the platinum bis(acetylacetonate) by H₂/Ar (5/95%) gas.

The carbon nanoparticle composite film (Publication I) was prepared by mixing carbon nanoparticles (diameter 30 nm), graphite and TiO_2 nanoparticles in a mortar in a small amount of ethanol. Then more ethanol was added to the mixture and it was stirred overnight. The films were deposited by spray-coating the suspension on ITO-PET substrates and the dried film was pressed in a hydraulic press to ensure mechanical integrity [60].

The PEDOT deposition on the SWCNT on PET and ITO-PET films (Publication III) was carried out by chronocoulometry in EDOT aqueous solution. The dye solar cells were manufactured according to our normal procedures, reported several times before [99, 100]. In these studies the PEs were always deposited by doctor-blading. The electrolyte used was our common electrolyte.

3.2 Measurement methods

The SWCNT films were characterized with sheet resistance measurements and optical absorption spectroscopy. All the studied carbon nanomaterial films were imaged with scanning electron microscopy and the SWCNT films (the efficiency of the iron removal and the PEDOT deposition) with energy-dispersive X ray spectroscopy. The optimal PE-DOT amount in the PEDOT-SWCNT films, as indicated by the deposition charge in the chronocoulometry method (mC/cm²), was chosen by cyclic voltammetry in 1 mM I₂, 10 mM LiI and 0.1 M LiClO₄ in acetonitrile.

The solar cells were characterized by IV measurements in the solar solar simulator, by electrochemical impedance spectroscopy (EIS) measurements with a potentiostat (as well as the "symmetrical" CE-CE cells with two CEs, see Chapter 3.2.2.) and by incident photon to collected electron efficiency (IPCE) method with a spectral response measurement system. The impedance of the solar cells was taken in the dark and by polarizing the cells up to voltages similar to their open-circuit voltage and of the CE-CE cells at 0 V. The equivalent circuits were fitted to the EIS spectra with Zview2 program.



Figure 3.1. An IV curve of a solar cell and its characteristic parameters.

3.2.1 IV measurement

In an IV measurement, the solar cell is placed under a defined light intensity and its current-voltage properties are measured over some range. The standard light intensity is 1000 mW/cm^2 , AM1.5G, which is the intensity of the average solar spectrum with air mass 1.5, which means that the light has traveled 1.5 times the distance in the Earth's atmosphere if 1 is the distance when the Sun is in zenith.

The efficiency, η , of a solar cell is calculated by dividing the power of the maximum power point (see Figure 3.1) by the incident light power:

$$\eta = \frac{P_{\text{MAX}}}{P_{\text{IN}}} = \frac{I_{\text{MPP}}V_{\text{MPP}}}{P_{\text{IN}}},$$
(3.1)

where P_{MAX} is the maximum power obtainable from the solar cell, P_{IN} is the incident power (usually 1000 W/m²), I_{MPP} is the current at the maximum power point and V_{MPP} the voltage at the maximum power point.

The other solar cell figures of merit, alongside with the efficiency, are the short circuit current, I_{SC} , the open circuit voltage, V_{OC} , and the fill factor, *F.F.*. The two former define the absolute maximum current and voltage obtainable from a solar cell. The fill factor of the solar cell describes how "lossy" the solar energy conversion in the solar cells is (how "square" the IV curve is, i.e. how large the voltage and current losses are at the maximum power point):

$$F.F. = \frac{I_{\rm MPP}V_{\rm MPP}}{I_{\rm SC}V_{\rm OC}}.$$
(3.2)

3.2.2 Electrochemical impedance spectroscopy

The photovoltaic parameters of a solar cell can be obtained from the IV curve, but the IV curve does not reveal exactly which losses happen at which component at a certain current and voltage value. Such information can be obtained with electrochemical impedance spectroscopy, in which the electrochemical system in equilibrium is exposed to a small amplitude perturbation (alternating current) and its response (impedance, Z) is measured as a function of the perturbation frequency. The definition of impedance is

$$Z(\omega) = \frac{V_{\rm AC}(\omega)}{I_{\rm AC}(\omega)},\tag{3.3}$$

where V_{AC} is alternating voltage and I_{AC} alternating current. The most common interface type in an electrochemical cell is an electrode surface that has both resistive (the charge-transfer through the interface can be described as a resistance, even though it is not a real ohmic resistance) and capacitive properties (ability to store charge for instance in the elecrochemical double layer).

The inverse impedance of a parallel connected resistor and capacitor is the sum of the individual components' inverse impedances:

$$\frac{1}{Z} = \frac{1}{R} + j\omega C = \frac{1 + j\omega RC}{R} = \frac{1 + j\omega\tau}{R}$$
(3.4)

where *j* is the imaginary symbol and τ the time constant ($\tau = RC$). The impedance then becomes

$$Z = \frac{R(1 - j\omega\tau)}{1 + \omega^2\tau^2}.$$
(3.5)

If the real (Z') and imaginary component (Z") are taken, and by noticing that $-Z''/Z' = \omega \tau$, the equation can be written in the form

$$(Z' - \frac{R}{2})^2 + (-Z'')^2 = \frac{R^2}{4},$$
(3.6)

which is an equation of a (semi)circle with a radius of R/2. Thus, when the EIS response (spectrum) is plotted in the (Z', Z'') plane, a parallel connected RC-element produces a (semi)circle. The (Z', Z'')-plane representation is called the Nyquist plot (Figure 3.2), whereas in a Bode plot, for instance the Z' and Z'' components are plotted as a function of frequency (Figure 3.3).



Figure 3.2. A Nyquist plot representation of a DSC EIS spectrum. The first semicircle is ascribed to the CE, the second to the PE.



Figure 3.3. A Bode plot representation (Z''(frequency)) of a DSC EIS spectrum.

Since the different cell components usually have different characteristic frequencies or time constants ($\omega = \tau^{-1} = (RC)^{-1}$), the different components appear at different parts of the spectrum and an equivalent circuit containing the different cell components can be fitted to the spectrum. Thus the electrochemical properties, such as the charge-transfer resistance or electrochemical double layer capacitance of the DSC CE, can be obtained from the impedance spectrum.

The above described RC model is suitable only for a real resistor and capacitor and does not apply e.g. in the case of a real DSC CE. For a DSC CE, the capacitor should be replaced with a constant phase element (CPE), whose impedance is

$$Z_{\text{CPE}} = \frac{1}{B_0} (i \cdot \omega)^{-\beta}, \qquad (3.7)$$

where B_0 describes the double-layer charge and β the "flatness" of the EIS semicircle, that is $\beta = 1$ for a real capacitor. The CPE is used in order to obtain a better fit for the resistor.

A porous DSC PE is better described by a transmission line model [101]. Figure 3.4 displays an equivalent circuit of an operating (illuminated) DSC with a PE transmission line model component, where R_S is the series resistance of the cell, emerging from for instance the ohmic resistance



Figure 3.4. A complete DSC equivalent circuit with a transmission line component representing the PE. Reproduced with permission from Adv. Mater., 22, E210 (2010). Copyright 2010 Wiley-VHC Verlag.

of the electrical contacts, $R_{\rm CO}$ is the contact resistance between the TiO₂ film and the substrate, $C_{\rm CO}$ is the capacitance of that contact, r_T is the transport resistance in the TiO₂ film, $r_{\rm CT}$ is the charge-transfer resistance at the TiO₂-electrolyte interface (also called the PE recombination resistance, $r_{\rm REC}$), c_{μ} is the chemical capacitance of the TiO₂ film, Z_D is the (Warburg) diffusion impedance, $r_{\rm CE}$ is the charge-transfer resistance of the CE and $C_{\rm CE}$ the capacitance of the electrochemical double-layer. The $i_{\rm PH}$ refers to the photocurrent produced in the cell. The r values are per unit volume of the film (Ω m³), and the R values (per macroscopic surface area) can be obtained by dividing the r values by the film thickness, d.

A counter electrode material can also be studied in the so called symmetrical CE-CE cell configuration at 0 V [102], where the other electrode is the studied CE and the other a similar CE or for instance a thermally deposited Pt on FTO glass. This produces either one semicircle in the Nyquist plot, which is a superposition of the two exactly identical semicircles, or two semicircles, each ascribed to the different CEs (with different time constants).

EIS in the dark

Since measuring EIS from individual solar cells in light in a solar simulator is rather laborous when an experiment consists of over 20 cells and it may take several hours to measure one cell, the cells can be measured more easily sequentially by placing them in a "black box" and connecting them to a multiplexer, which connects them to the potentiostat one by one. Since the measurement is carried out in the dark, the cells are polarized to voltages similar to the open-circuit voltage (or the measurement can be done as a function of voltage). In the method, the electrons are fed to the PE from the electrical contact, unlike in light, where the electrons are fed to the PE by the dye. In this way, the electronic states in the TiO_2 are filled

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in the same manner as in light, but because the electrons are fed from the PE contact and not by the dye, the current in the cells flows to the opposite direction than in a lit DSC. Therefore also the redox reactions occur to the opposite direction (iodide oxidation instead of triiodide reduction at the CE). It has been, however, proven experimentally that the "symmetry factor" in the Butler-Volmer model of several DSC CE materials is the same to both current directions, thus producing the same absolute CE IV curve slope values (or its inverse, resistance) to both voltage (or current) directions [103]. Dark EIS measurements have been used in conjunction with lit EIS measurements, yielding similar results [56, 104]. One advantage of the dark EIS over the lit EIS is the lack of temperature rise in the cells caused by the light source [104].

An issue related to the EIS in the dark is that if for instance the R_{CE} differs greatly among the studied cell types, it is not known exactly how the voltage is distributed among the different cell components and comparing the resistances as a function of V is unreliable. This can be compensated by deriving an estimate of the component voltage by integrating the component's resistance, but this method has certain limitations (see Chapter 4.4 and Publication III). However, dark EIS can be taken as a good, indicative method for comparing different CE materials in practice, if the results are interpreted with care. Moreover, dark EIS normally yields results that are consistent with other measurements, for instance the IV measurements.

In theory, EIS could also be measured in reverse bias so that the current would flow to the same direction and the same redox reactions would happen at the electrodes as in light, but in this reverse bias case the semiconducting PE is insulating and the current flows via the PE substrate (e.g. FTO glass) and not through the PE TiO_2 film. For using the method, it should be carefully verified that the substrate impedance does not overlap with the CE impedance in the impedance spectrum.

3.2.3 Incident photon to collected electron efficiency

Incident photon to collected electron efficiency or quantum efficiency (QE) means the ratio of charge carries to the number of photons at a certain wavelength. In the measurement, the studied device current production is measured as a function of varying light wavelength. This gives information about how the solar cell responses to a certain wavelength of light.

The QE of a DSC comprises of four different efficiencies multiplied by



Figure 3.5. An IPCE spectrum of a DSC.

each other:

$$\eta_{\text{IPCE}} = \eta_{\text{LH}}(\lambda)\eta_{\text{INJ}}(\lambda)\eta_{\text{COLL}}(\lambda)\eta_{\text{REG}}(\lambda), \qquad (3.8)$$

where η_{LH} is the dye light harvesting efficiency, η_{INJ} the dye electron injection efficiency, η_{COLL} the electron collection efficiency of the PE and η_{REG} the dye regeneration efficiency. These four different efficiencies cannot be directly determined from an IPCE spectrum, but for instance PE charge-collection issues can be observed with a QE measured from the CE side: in such case most of the charge-carries formed far from the TiO₂-TCO contact have to travel a long way in the PE film, and if there is a high risk of recombination, less electrons will reach the contact, resulting in a poor QE spectrum. A typical IPCE spectrum is displayed in Figure 3.5.

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4. Results

4.1 Publication IV and V: Review of dye solar cell manufacturing on flexible substrates and large areas

A review of dye solar cells on flexible substrates (Publication IV) and upscaling to large areas (Publication V) was carried out. Very different issues were covered: metal and plastic substrates, carbon nanomaterials as CE active material, PE and CE active material deposition techniques on flexible substrates, cost analysis, stability, electrolytes, sealing and module configurations. The work was mainly based on literature and somewhat on experiments.

It was estimated in Publication V that the production costs of rigid glass based DSC modules would be 3 - 4 USD/W_p with the current materials and manufacturing techniques, compared to those of silicon-based PV modules, 3 USD/W_p (during the time of the paper writing). But by manufacturing DSCs by roll-to-roll production techniques on flexible substrates, the costs could drop to less than 1 USD/W_p. It must be however kept in mind that when a new technology enters the industrial phase, its manufacturing costs drop rapidly following the learning curve, and it has been suggested that the costs of organic PV decrease quicker than those of silicon-based PV, and that this would apply to the DSC technology too. It was pointed out that in roll-to-roll manufacturing, already existing production concepts and non-vacuum techniques could be utilized, which is an advantage over some other thin film solar cell types, such as CIGS and a-Si.

The most expensive DSC component is the TCO glass substrate, and a 35 % price reduction can be obtained by replacing it with a flexible plastic ITO-PET or -PEN substrate. Other advantages of plastic substrates

are flexibility and light weight, but their permeability to water and oxygen and the restriction of cell manufacturing temperature below 150 °C are open questions. A stainless steel metal substrate could be even 80 % cheaper than TCO glass. Metal substrates (Publication IV, Publication V) are also very conductive (as compared to FTO/ITO) and flexible when thin enough, they are thus extremely interesting. The triiodide in the electrolyte is on the other hand a strong oxidant: a steel substrate ages rapidly either as the CE or the PE substrate in an operating DSC unless the steel is protected somehow. Other issues are for instance their opaqueness and the poor suitability of thermal platinization: the best efficiency, 9.15 %, has been obtained with a carbon catalyst. Thin titanium foils, which have a natural, protective TiO₂ layer, withstand the iodine-based electrolytes, but there the price of the precious metal is a problem.

Carbon black composites and gelatinized carbon black-based suspensions are an interesting catalyst option for flexible DSC CEs (Publication IV, Publication V). The carbon gel catalyst can be applied also in non-conventional cell configurations, such as the optical DSC fiber (Publication IV) - the gelatinized carbon composite can take more or less any shape. In Publication V it was remarked that when the carbon layer is as thick as 60 μ m, as opposed to the typical 10 - 20 μ m, no additional conductive layer is needed, which is important in particular for the monolithic DSC configuration. It was also found from the literature, that PEDOT is the most interesting organic DSC catalyst, since it forms uniform films, is transparent and stable and has a low $R_{\rm CE}$.

Carbon nanotubes could replace the TCO layers in several optoelectronic devices, but so far the best $R_{\rm sh}$ vs transmittance values cannot compete with those of ITO-PEN, but with improved CNT film engineering this can be achieved (Publication V). A cost estimate for a CNT film was given: 64 USD/m², which is still too high for practical purposes. Many kinds of carbon nanomaterials (SWCNTs, MWCNTs, carbon nanoparticles and their composites) function as DSC catalysts (Publication IV). They can also be used as conductivity enhancers in the TiO₂ film, yielding some $i_{\rm SC}$ improvements. The literature on CNTs in DSCs is however rather scarce and very varying (no systematic comparison on the matter), which makes drawing conclusions difficult.

There are several ways to manufacture a plastic PE, of which the press technique on ITO-PEN has proven most successful, producing efficiencies of even 7.6 % [19], which was achieved with a thorough optimization of the film manufacturing process. Often, an issue with the low-temperature PE preparation is unwanted adsorbed substances on the TiO_2 surface, which may block some of the dye from forming a good contact to the TiO_2 surface and thus cause low dye electron injection efficiency or unwanted recombination. In the high temperature sintering process, these substances burn out. Also the TiO_2 nanoparticle contacting may be insufficient in the low-temperature manufacturing, leading to a short electron diffusion length.

It was pointed out in Publication V that the ionic liquid viscosity may offer also advantages for e.g. screen printing of the electrolytes, not just diffusion problems.

It was concluded that roll-to-roll manufacturing methods of DSCs on flexible substrates are essential in achieving competetive prices for the technology, but the materials have to develop further and the stability questions have to be addressed more thoroughly than so far has been done before the DSC technology can be fully commercialized.

4.2 Publication I: Comparison of carbon nanomaterias as DSC CE

Since it was found from the literature that carbon nanomaterials are a promising alternative flexible DSC electrode material (Chapter 4.1), three different carbon nanomaterials were tested as DSC counter electrodes and compared in terms of their catalytic performance, conductivity, transparency, thickness, and flexibility. The CE materials were a randomly oriented SWCNT network film on a plain glass substrate, a vertically aligned MWCNT forest film on Inconel steel and quartz with and without Pt nanoparticles and a pressed carbon nanoparticle composite film (carbon nanoparticles, graphite and TiO_2 nanoparticles) on ITO-PET. These were also compared with thermally platinized Pt on FTO glass. Schematic images of the different carbon nanomaterial structures are shown in Figure 4.1 and SEM and TEM images in Figures 4.2, 4.3 and 4.4.

The carbon nanomaterials were tested in the symmetrical CE-CE cell configuration so that the other CE was a Pt on FTO glass CE and the other CE the studied nanomaterial, apart from the carbon nanoparticle composite CE were the cell consisted of two identical carbon CEs. In addition to EIS, the CEs were characterized with scanning electron microscopy, and transmittance, conductivity and thickness measurements, when possible.

Since the charge-transfer resistance obtainable from e.g. an EIS measurement is a quantity that is proportional to the geometric surface area



Figure 4.1. Schematic images of the different carbon nanostructures tested as DSC CEs. a) Random network SWCNT film, b) MWCNT forest film and c) carbon nanoparticle composite film. Reproduced with permission from Publication I. Copyright 2011 Elsevier.



Figure 4.2. a)-b) SEM and c) TEM images of the SWCNT network film at different magnifications. Reproduced with permission from Publication I. Copyright 2011 Elsevier.



Figure 4.3. a)-d) SEM images of the MWCNT forest film at different magnifications, in c) with the platinum nanoparticles. Reproduced with permission from Publication I. Copyright 2011 Elsevier.



Figure 4.4. a)-d) SEM images of the carbon nanoparticle composite film at different magnifications, b) is a close-up of a). G denotes graphite, C carbon nanoparticle and TiO_2 titania nanoparticle. Reproduced with permission from Publication I. Copyright 2011 Elsevier.

of an electrode, it does not reveal the microscopic catalytic activity of a material, $r_{\rm CE}$, whose relationship to $R_{\rm CE}$ is

$$R_{\rm CE} = r_{\rm CE} d^{-1},\tag{4.1}$$

where d is the CE film thickness. In the case of CEs based on different carbon nanomaterials with different thicknesses and altogether different microscopic properties, and when the microscopic surface areas are not known, it is not possible to compare the materials' $r_{\rm CE}$ s directly. A comparison can however be made with the product of $R_{\rm CE}$ and the electrode capacitance, $C_{\rm CE}$,

$$C_{\rm CE} = c_{\rm CE} d, \tag{4.2}$$

where c_{CE} is the capacitance per unit microscopic surface area of a material. The C_{CE} is one measure of the electrically active electrode surface area. This applies in the case of metallic materials, to which CNT films can be ranked, as most of the conduction in them is via the metallic CNTs.

In the product the surface area and the film thickness cancel out:

$$R_{\rm CE}C_{\rm CE} = r_{\rm CE}c_{\rm CE}.\tag{4.3}$$

Table 4.1 summarizes the properties of the different CEs: sheet resistance, transmittance, CE charge-transfer resistance, CE electrochemical double-layer capacitance, series resistance, and the product $R_{\text{CE}}C_{\text{CE}}$ and presents the numerical comparison that can be made.

It was found out that Pt had more than 100 times higher catalytic performance as compared with the other materials, it was also the thinnest (few nanometers) and the most transparent. Its disadvantages are, on the other hand, its price and the fact that it requires a brittle conductive layer below, ITO or FTO.

The SWCNT network was the second thinnest (few hundred nanometers), second most transparent, the most flexible (as deduced here from the literature as the substrate in this study was a plain microscope glass) but had only moderate catalyst performance for the iodine-based electrolyte, the substrate adherence was also an issue.

The MWCNT forest film was not as such catalytic enough for the normal DSC operating conditions. The platinum loading in the Pt-MWCNT forest films was quite high, about 200 times larger (by Pt mass per area) than in the standard thermally deposited Pt on FTO glass CEs. This

1																	
	$R_{CE}C_{CEave}$		0.088		6.4		12	16		19		1.3		3.3		2.9	
	$R_{CE}C_{CE}$	$(m\Omega F)$	0.083-	0.095	2.0-10		4.2 - 24	8.9-24		14-24		0.54 - 2.9		3.0 - 3.6		2.0-5.2	
i	$R_{S,ave}$	(Ωcm^2)	6.6		42		13	10		7.8		6.0		44			
	$R_{\rm S}$	(Ωcm^2)	9.1-10		27-54		9.6 - 17	8-12		6.5 - 9.0		5.4-7.0		42-46			
	$C_{CE,ave}$	(μFcm^{-2})	5.5		21		91	150		340		250		300		2400	
	$C_{\rm CE}$	$(\mu { m Fcm^{-2}})$	5.0-5.8		18-25		87-98	130-160		270-420		61-740		210-380		1200-	3700
	$R_{CE,ave}$	(Ωcm^2)	11		304		129	118		54		7.5		12		1.3	
	R_{CE}	(Ωcm^2)	10-13		107-	384	47-266	54 - 181		52-57		6.5 - 11		7.4 -17		0.6 - 1.8	
	T (%)		ca. 80		82		45	5	$q(\mu \mathbf{m})$	5-20		1-10		5-35		10-20	
	$R_{ m sh}$	(Ωcm^2)	15		214		80	20 - 30									
	No of cells		4		ŝ		4	2		ന		6		2		9	
1	CE type		Pt on FTO glass		SWCNT network	on glass				MWCNT (pris-	tine) on Inconel	MWCNT+Pt on	Inconel	MWCNT+Pt on	quartz	Carbon nanopar-	ticle composite

Table 4.1. Comparison of the R_{CB} and the C_{CB} of the different carbon nanomaterial CEs. The R_{s} for the carbon nanoparticle CE cells can not be compared with the other cells due to different cell geometries. Film thickness is given directly for the MWCNT (rough estimate) and the nanoparticle composite film, but can be indicated only b the optical transmittance at 550 nm for the SWCNT films. Also $R_{\text{CE}}C_{\text{CE}}$ values are shown. Reproduced with permission from Publication I. Copyright 2011 Elsevier

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helped us to determine whether the low $R_{\rm CE}$ was because of the intrinsically low catalytic activity of the MWCNT films, low conductivity along the perpendicular-to-the-plane direction or a contact problem between the MWCNTs and the substrate. The best $R_{\rm CE}$ for the Pt-MWCNT film was relatively high, ~ 7 Ω cm², even though the Pt loading was high and it was present as high surface area nanoparticles. This led us to the conclusion that there is a conductivity issue related to the MWCNT film, either the above mentioned contact problem or low conductivity along the tubes, resulting in charge-transfer to electrolyte already in the "root" of the forest and the charge not penetrating the whole forest "height".

The carbon nanoparticle film had good $R_{\rm CE}$, due to, not only the catalytic activity of the carbon nanoparticles, but its very large microscopic surface area, as confirmed by its highest capacitance value. It was however completely opaque and not very flexible: it flaked off easily when bent and its adherence to the substrate was altogether poor.

It was concluded that a proper quantitative comparison of the different carbon nanomaterials is difficult, since the materials are so different by nature. For instance carbon nanotubes synthesized in large quantities display a broad range of properties (e.g. chirality, length) and effective sorting methods according to a certain property do not presently exist, meaning that CNTs cannot be considered as a simple raw material. It was also suggested that a composite of carbon nanoparticles and carbon nanotubes would be a natural next step in the field of carbon nanomaterial CEs, to which also graphene is entering. Carbon nanotube interlinking or including them in some composite materials, e.g. with conducting polymers, would seem benefitable. However, the studied SWCNT network films were concluded promising because they were flexible without additional binders.

4.3 Publication II: Carbon nanotube films on plastic substrates as DSC CEs

Based on the preceding experimental work and literature review in comparing the carbon nanomaterials and flexible substrates, it was suggested that the SWCNT random network film on a plastic substrate is a very interesting carbon nanomaterial CE type for the DSC: there is only one active material component, SWCNTs, the film deposition is relatively easy and it is semitransparent and very flexible. The SWCNT film also adheres



Figure 4.5. Schematic images of the cell structure a) from above and b) from the side. Reproduced with permission from Publication II. Copyright 2010 The Electrochemical Society.

better to plastic than to glass, which is an advantage from the flexible DSC point of view.

In Publication II, a random network SWCNT film of 30 % transmittance on a PET plastic substrate was studied as a DSC CE. It was known from the previous CE-CE cell measurements that the CE type's catalytic performance would most likely not suffice for full one sun illumination (1000 W/m²), but it was studied whether the film would anyhow function as a CE in low intensity DSC applications, where a high CE chargetransfer resistance causes a less significant voltage drop because the current densities are low. Moreover, we wanted to find out whether these thin films would be mechanically durable enough to sustain processing to a solar cell and whether they would be chemically compatible with the other cell materials. Also the physical and chemical compatibility of the PET plastic substrate to the cell configuration and materials had to be investigated. A schematic image of the cell structure is shown in Figure 4.5.

In the IV measurement of the first solar cell experiment, it was noticed that the i_{SC} was lower than that of the reference DSCs with thermally deposited Pt on FTO glass as the CE (data not shown). When the IV was swept to both (IV) directions, the i_{SC} kept dropping even more. This was



Figure 4.6. The IV curves of the SWCNT on PET cells (CNT-DSC) and the reference Pt on FTO glass cells (ref. DSC) in full (1 sun), 43 % and 8 % light intensities. Reproduced with permission from Publication II. Copyright 2010 The Electrochemical Society.

hypothesized to be due to the fact that the SWCNT film contains iron nanoparticles from the CNT synthesis process. Some of the Fe nanoparticles are capped inside the tubes, but some of them are outside the tubes. The hypothesis was that the triiodide oxidizes the Fe, which makes the nanoparticles to dissolve in the electrolyte and the iron (or its compounds) to migrate to the PE - Fe is known detrimental to a DSC PE [97]. When the films were electrochemically purified from the Fe particles by cyclic voltammetry in 1 M HNO₃, the currents stabilized - but still to a lower lever as compared to the reference cells with platinum on FTO glass as CE, see Figure 4.6.

The effiency of the SWCNT-DSCs in full 1 sun illumination conditions was 0.7 %, compared to the 4.4 % of the reference DSC with a thermally deposited Pt on FTO glass CE. This result was expexted, knowing the modest catalytic performance of the SWCNT film. To find out the suitability for low-light intensity DSC applications, the low-intensity behaviour of the DSCs was probed by setting metal grid shades in front of the solar simulator lamps, so that the light intensity dropped to about 43 and 8 % of 1 sun intensity (estimated with a silicon calibration cell, from its $i_{\rm SC}$ values, which were assumed to depend linearly on the light intensity). The results of the IV measurements at different illumination levels are displayed in Figure 4.6. At lower intensities, the fill factors of the IV curves improved but the $i_{\rm SC}$ values never reached those of the reference DSCs. The linear shapes and the poor fill factors of the IV curves of the CNT-DSCs were linked with the high CE charge-transfer resistance and sheet resistance of the SWCNT film, which manifests itself in a high cell series resistance. The lack of a clear plateau in the IV curve near the shortcircuit condition is an indication of a high R_{CE} .

The EIS spectra (Nyquist plot) of the SWCNT-DSCs revealed atypical CE semicircles, which were "distorted" compared to the reference Pt CE semicircles, see Figure 4.7. The SWCNT-DSC CE semicircle had no clear high-frequency limit (at our typical 100 kHz maximum measured frequency) and seemed to be of the Gerischer case type of the transmission line impedance [101]. Also an "additional", high-frequency semicircle appeared in the spectra (see also Chapter 4.3.). These two features were in similar frequency range and produced a distorted Gerisher type semicircle with an additional "bump" at the straight line region. The Gerischer shape suggests that the resistance of current flow along the SWCNT film plane is higher than the resistance of charge-transfer to the electrolyte, so that the current leaks to the electrolyte far from the contact (since the EIS is taken in the dark by feeding electrons to the PE, the current flows to the other direction as it would in an illuminated DSC - in an illuminated cell the phenomenon would be more or less the opposite, the current leaking to the electrolyte near the contact). Such a Gerisher shape impedance can be seen for e.g. a pressed PE, where the PE transport resistance is a cell performance limiting factor [101]. This hypothesis was however not proven experimentally or theoretically.

The EIS taken in the dark did not reveal altered PE recombination properties (Figure 4.8, plotted here as a function of cell current density), which led us to suspect that the reason for the low i_{SC} lies in the residual Fe having somehow affected the light-harvesting or the electron injecting properties of the dye. It was suggested that the CNT film iron removal should be improved further and the CNT film catalytic performance increased for full sunlight DSC applications.

Based on this study, it could be seen that the SWCNT film on PET is a potential DSC CE from the DSC manufacturing point of view. The manufacturing steps were also studied in a separate experiment (data not shown neither in the paper nor in the thesis), where it was observed that the different steps, such as sealing and electrolyte addition, caused only neglibible increase to the cell series resistance.



Figure 4.7. Example EIS spectra (Nyquist plot) of a SWCNT-DSC and a reference DSC measured in the dark at similar current densities: -3.6 mA/cm² for the SWCNT-DSC and -3.3 mA/cm² for the reference cell. The SWCNT-DSC exhibits an atypical CE EIS response. Reproduced with permission from Publication II. Copyright 2010 The Electrochemical Society.



Figure 4.8. The inverse of the $R_{\rm CE}$ of the SWCNT-DSCs and the reference DSCs as a function of cell current density. Reproduced with permission from Publication II. Copyright 2010 The Electrochemical Society.



Figure 4.9. The cyclic voltammograms obtained for the different CE materials.

4.4 Publication III: Electrochemically deposited PEDOT polymer on SWCNT film on plastic as completely carbon-based flexible DSC CE

In order to find out whether the random network SWCNT film catalytic performance could be improved, conducting PEDOT polymer was electrochemically deposited on a 10 % transparent SWCNT film on a PET plastic substrate. Its performance as a DSC CE was compared with those of plain SWCNT film on PET, sputtered Pt on ITO-PET and thermally deposited Pt on FTO glass. The PEDOT-SWCNT film produced a 4 % efficiency compared to the 2.0 % of the plain SWCNT film, the 3.9 % of the sputtered Pt on ITO-PET and the 4.3 % of the thermally deposited Pt on FTO glass, thus realizing a thin, flexible completely carbon-based DSC CE.

The optimal PEDOT amount, as indicated by the deposition charge per unit area (mC/cm²), was studied with cyclic voltammetry and turned out to be about 30 mC/cm² (Figure 4.9). When the PEDOT amount was increased further, the peak spacing of I_{ox} and I_{red} (the peaks related to the oxidation and reduction of I_3^-/I^- ; the peak spacing is inversely proportional to the rate constant of the electrochemical reaction) started growing and the peak current density did not improve (optimization data not shown). The PEDOT and SWCNT also had a synergistic effect for the catalytic activity of the PEDOT-SWCNT film, when comparing it with those of plain PEDOT and SWCNT (Figure 4.9).

In the solar cells, the current production in the SWCNT and the PEDOT-SWCNT cells was still slightly lower than those of the both types of platinum cells - also that of the thermally platinized cells was significantly



Figure 4.10. The IV curves of the studied DSCs.

lower than that of the sputtered Pt cells (Figure 4.10). The possible effect of the residual iron from the SWCNT catalyst nanoparticles (see Chapter 4.3.) was tried to avoid by improved SWCNT and PEDOT-SWCNT film rinsing and soaking, on top of the electrochemical iron removal, see details in Publication III, but either the iron cleaning was still not sufficient or the reason for the lower current production lies elsewhere.

EIS taken in the dark revealed that the PEDOT-SWCNT CE had the lowest charge-transfer resistance of the studied CE materials (Figure 4.11) and that all the cells had similar series resistances. Taking this into account, it was surprising that the PEDOT-SWCNT and SWCNT cells had lower efficiencies than the Pt on FTO glass cells. The EIS measurements revealed unaltered PE recombination except for the SWCNT cells, see Figure 4.12 a). Because of this difference, we tried calculating the $V_{\rm PE}$ values from the PE recombination resistance, R_{REC} , values by integrating the differential resistances (first fitting a function to the data and then integrating the function, as done in an earlier publication [99]), but when plotting the R_{REC} as a function V_{PE} , the data of the most solar cell types became very scattered (Figure 4.12 b)), apparently because the integration is sensitive to the choice of the reference point. This led us to the conclusion that an EIS measurement in the dark is only indicative about the behaviour of the different cell components, and the results are commensurate only for cells with similar voltage losses at the other components than the studied one. Here this does not apply for instance for the SWCNT-DSCs, that have higher R_{CE} than the other cells.



Figure 4.11. The R_{CE} s of the different CE materials as a function of cell voltage.



Figure 4.12. The PE recombination resistance as a function of a) cell voltage and b) PE (voltage loss corrected) voltage.

Results

Also in this study an "additional" high-frequency impedance arc appeared in the spectra of the DSCs containing a porous CE (see Chapter 4.3). Roy-Mayhew et al. have attributed similar behavior to a porous graphene CE: to an additional Nernstian diffusion through the electrode pores at 100-2.5 kHz [65]. This should be included in the "total resistance" of the CE, but since it was of the order of one to few ohms only, it was neglegted. They also suggest that the simple resistor-constant phase element model is suitable only for a more or less flat Pt film on FTO or ITO, but does not work for the porous carbon CE. The EIS fitting of the PEDOT-SWCNT cells was further complicated because of the fact that the CE semicircle appeared at lower frequencies than that of the other CE types, resulting in an overlapping of the PE and CE semicircles. This seemed to be mainly because of the large CE capacitance (large microscopic surface area) value for the PEDOT-SWCNT CE (data not shown).

Optical modeling was also carried out to see whether the different reflectance properties of the sputtered Pt could explain the much larger i_{SC} in the cells with sputtered Pt CE, but the effect of the reflectance was found negligible. An explanation for the slightly smaller i_{SC} of the SWCNT and PEDOT-SWCNT DSCs could be the different substrate (plain PET) having an effect on the PE via for instance its different water and oxygen penetration properties as compared to ITO-PET. This has also been seen in our other studies (unpublished results), and calls for more attention to the substrate's effect on the DSC performance.

5. Summary and conclusions

Solar cells are a promising option for renewable electricity production. Once manufactured, they do not require any other source of energy than (sun)light for operation, and there are e.g. no moving parts that could break easily. At the moment, the price of the state of the art commercial solar cells, crystalline or multicrystalline silicon solar cells, drops rapidly and is on the verge of reaching grid parity, but there is anyhow a neverending quest for cheap electricity production.

The dye solar cell (DSC) may answer the question of even cheaper solar cell production costs: it is based mainly on abundant and nonpoisonous materials and its manufacturing techniques are relatively simple and non-energy intensive. One of the most interesting features of the DSC is that it can be built on flexible plastic and metal substrates, that allow economical roll-to-roll mass production. It is still however a somewhat open question how to transfer the DSC photoelectrode and the counter electrode (CE) active material manufacturing techniques on flexible substrates, and in this work the flexible CE materials were addressed.

As most metal substrates still have stability issues (e.g. stainless steel is corroded by the triiodide in the electrolyte without protective coatings), plastic substrates are more durable in this sense, even though they have their own stability issues, such as permeability for water and oxygen from ambient air. Plastic substrates are also transparent and light-weight properties that may be benefitable for instance in building and clothes integration of solar cells and in indoor applications. Plastic substrates were chosen as the main substrate type in this study, but the results may be applicable to metal and glass substrates too.

The state of the art plastic DSC CE comprises of a thin sputtered Pt layer on indium tin oxide-polyethylene terephthalate (ITO-PET) or ITOpolyethylene naphthalate plastic substrate. Pt and In are however rare and precious metals and ITO is not especially flexible, thus these materials should be replaced. Carbon is an interesting alternative CE material: it is abundantly available, it is catalytic and some of its allotropes (nanotubes, graphite, graphene) conduct electricity. With carbon nanotubes, transparency can be added to the list of carbon CE material properties.

In this work, different carbon nanomaterials were tested as flexible DSC CEs: a semitransparent random network single-walled carbon nanotube (SWCNT) film on PET plastic and glass substrate, a vertically aligned multi-walled carbon nanotube (MWCNT) forest film on Inconel steel and quartz substrate, and carbon nanoparticle composite on ITO-PET substrate. These were tested either in the CE-CE cell configuration or in the complete DSC, also the literature on the topic was covered.

It was found out that a 10-30 % transparent SWCNT film on PET or glass substrate is not catalytic enough for the iodide/triiodide redox couple of the DSC. The MWCNT forest film was only moderately catalytic without Pt nanoparticle decoration, and this was linked to its very high porosity (and low surface area), also the manufacturing method was complex and the films were thick. The carbon nanoparticle composite film had good catalytic performance but it was very thick, completely opaque, not very flexible and brittle. As a whole, it was somewhat difficult to compare the materials directly because of their very different microscopic properties, but it was concluded that the SWCNT network film on PET is the most interesting of the CE types for flexible DSCs, since it contains only one active material component and it is thin, very flexible and semitransparent. As such, it could be utilized only in low light intensity indoor applications due to the insufficient catalytic performance, and for full one sun illumination conditions its catalytic properties must be enhanced by some means.

In the next part of the work, conducting poly(3,4-ethylenedioxythiophene) (PEDOT) polymer was electrochemically deposited on a SWCNT film on PET substrate in order to improve the SWCNT film catalytic performance. It was observed that the catalytic property of the PEDOT-SWCNT film was better than those of thermally deposited Pt on FTO glass and sputtered Pt on ITO-PET, as well as that of PEDOT on ITO-PET. From the latter result, it was concluded that the SWCNT network film is a better substrate for PEDOT than ITO or FTO, since the SWCNT film has a porous structure and with it the PEDOT can be utilized as a porous film having a large-surface area, which is most likely beneficial for the
catalytic performance of a film.

Putting the SWCNT CE results in the DSC efficiency, η , context, the main results are as follows:

- For the SWCNT film on PET CE with a 30 % transparency $\eta=0.7$ %
- For the 10 % transparent SWCNT film on PET CE $\eta=2$ %
- + For the 10 % transparent SWCNT film with PEDOT layer deposited on it $\eta=4$ %

A reference DSC with a sputtered Pt on ITO-PET CE yielded a 3.9 % efficiency.

At best, the CE charge transfer resistance, $R_{\rm CE}$, of the PEDOT-SWCNT composite film was few $\Omega \rm cm^2$ (at -0.6 V in the dark solar cell EIS measurement), which is below the target value of $< 10 \ \Omega \rm cm^2$. For the other carbon nanomaterial CEs the $R_{\rm CE}$ s can be summarized as follows:

- $R_{\rm CE}$ for the SWCNT film decreased as the film thickness increased, for the pristine film it was at best around 50 Ω cm² at 5 % transmittance (EIS taken in the CE-CE cell at 0 V)
- For the pristine MWCNT forest film, the $R_{\rm CE}$ was around 50 Ω cm² (EIS taken in the CE-CE cell at 0 V)
- For the carbon nanoparticle composite film, the R_{CE} was around 10-20 Ωcm^2 (EIS taken in the CE-CE cell at 0 V)

To conclude, carbon nanotube films and CNT-composite films seem potential as conductive, catalytic, flexible and potentially cheap CE material for dye solar cells. The results presented in this thesis show that CNT films and composites can be deposited to flexible (plastic) substrates by methods that could be applied in industrial roll-to-roll solar cell production.

However, to really utilize carbon nanotubes and nanomaterials as films and composites in real devices, the synthesis, sorting and chemical functionalization methods of the materials should develop further. There is also of room for improvement in applying the materials in the DSC: the composites can be optimized further and for instance the adherence of the carbon nanomaterials to the substrates made better. Further work could include lifetime and degradation studies, too, to verify the long-term stabilities of these new materials in the DSC.

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