Studies of Semiconductors Modified with Nanoscale Light Absorbers for Solar Cell Application

BY
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Abstract

Recently, materials such as hole conductors (CuI, CuSCN) and light absorbers (Ru-complexes, CulnS$_2$) have been actively investigated for application in nanocrystalline solar cells. In this thesis combinations of these materials have been studied.

In the first part of the thesis, various methods were applied to characterize the electronic structure and photoconversion mechanism of the dye molecule Ru(debpyH$_2$)$_2$(NCS)$_2$, when combined with materials for the use in photovoltaic devices. Specifically, the adsorption and electronic structure of the dye molecules adsorbed to semiconductors were investigated by means of photoelectron spectroscopy. The results indicate a chemical bond between the dye molecules and the hole conductors (CuI, CuSCN) via the NCS- groups. In addition, preparation of a TiO$_2$/Ru-dye/Cul solid state model system was studied in situ. These experiments showed a partial breaking of the TiO$_2$-dye bond caused by CuI evaporation. Photovoltage measurements were also performed. These investigations showed a shift in the light absorption threshold of the dye molecules adsorbed onto the hole conductors (CuI and CuSCN), indicating new defect states at the dye/CuSCN interface. Also, charge accumulation and transport in solar cells with CuSCN were compared to liquid electrolyte cells. Measurements showed that the lifetime and transport time of electrons in solar cells with CuSCN are much shorter than in electrolyte cells.

In the second part of the thesis, the deposition of CulnS$_2$ onto various metal oxides by spray pyrolysis has been studied with x-ray diffraction and photoelectron spectroscopy. The measurements showed that the morphologies of the substrates play a significant role in the formation of CulnS$_2$ layers. Also, the presence of CdS at TiO$_2$ has a positive influence on the formation of CulnS$_2$.

Keywords: photoelectron spectroscopy, dye-sensitized, solar cells, inorganic light absorber, nanostructure, mesoporous, photovoltaic devices

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To my family and friends
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Introduction

The demand for clean and renewable sources of energy is growing with every year. One of the obvious choices is the use of solar energy. The solar energy derives from a nuclear fusion reaction in the sun interior and the amount of energy emitted in the ultraviolet to infrared spectral regions is sufficient for any human activity today and for future demands. Solar energy is converted to chemical energy by photosynthesis in the plants and can be converted to heat by solar collectors or to electricity by solar cells.

Chapin, Fuller, and Pearson made the first development of a solar cell in 1954 using silicon [1]. Subsequently, the first thin layer cadmium-sulfide solar cells were developed by Raynolds et al. [2].

The functional and reasonably effective crystalline silicon based solar cells are already available on the market. However, at present time this technology is not a low cost alternative for the large scale energy production. The cell design requires high purity and relative large amounts of the material. The device is based on a p-n junction, commonly formed by diffusion of dopants into n-type and p-type silicon wafers.

To date, solar cells have been made of various choices of materials employing single-crystal, polycrystalline, and thin film structures. Regardless what future will bring, it will require different types of solar cells: for indoor or outdoor activities, with different cost performance, light and flexible, different colors and shapes. Specific environment conditions will also dictate the use of special types of solar cells. In order to protect environment and human health, the use of some components will be restricted and will force scientists to look for alternatives.

A recently developed solar cell type is based on a photoelectrochemical approach. The dye-sensitized nanocrystalline solar cells (DNSC) have been under active investigation in the last decade, [3-5]. In such solar cells dye molecules are used as light absorbers, a nanocrystalline metal oxide and electrolyte are used as electron and hole conductors, respectively. The main advantages are the potentially low manufacturing cost, the possibilities to have them lighter and thinner, and the use of flexible substrate and the possibility to choose colors. Encapsulation of the conventionally used liquid electrolyte in these cell leads, however, to several technological problems such as solvent evaporation, degradation of the components by for example water and oxygen entering the cell through an imperfect sealing. These problems have encouraged studies in which the liquid redox electrolyte in dye-
sensitized solar cells is replaced with solid-state equivalents, such as polymer-gel electrolytes [6], conducting organic polymers [7], ionic conductive polymer electrolytes [8], organic hole conductors [9], and inorganic semiconductors [10-18]. In this thesis, two alternatives were investigated. Firstly, p-type semiconductors CuI and CuSCN were applied as hole conductors in dye-sensitized solar cells. The other approach to the problem was to replace the dye molecule by an extremely thin inorganic solid state light absorbers (ETA cells), such as CuInS₂, [19-21]. Later research has shown that CuInS₂ also can be used also as a hole conductor [22]. In particular, the chemical bonding of organic dye molecules to the p–semiconductors and the charge separation and transport process at the solid-state DNSC interface have been investigated. The formation and purity of the CuInS₂ layer on metal oxides and CdS (for ETA cells) has been studied.

This thesis is divided into five chapters: following the introduction, a brief review of the basic concepts of photovoltaics is presented in Chapter 1. Structure and function of the nanocrystalline solar cells are given in Chapter 2. In Chapter 3, the experimental methods used in the thesis are described. Finally, Chapter 4 and 5 summarize some of the results obtained in the papers included in this thesis.
1. Basic concepts of Photovoltaic Systems

1.1. p-n junction

This section gives the basic concepts of photovoltaic systems using the example of the silicon p-n junction solar cell that often serves as a reference device for solar cells.

The electronic structure of semiconductors is characterized by an energy gap between the valence band, which is filled with electrons, and the essentially empty conduction band. The electronic properties of semiconductors can be controlled by incorporation of a small concentration of foreign atoms (doping). Depending on the valency and the lattice position of these atoms, they can be electron donors, acceptors, or electronically inactive. In n-type semiconductors donors are present with energy levels close to the conduction band edge. Thermal excitation of electrons from donors to the conduction band leads to electronic conductivity. In p-type semiconductors, acceptors with energy levels close to the valence band edge can capture electrons from this band, which results in valence band holes.

The typical conventional solar cells (Si based) consist of a p-n junction, a front ohmic contact and a back ohmic contact that covers the entire back surface. The junction is formed when two surfaces with different doping of n- and p- type are contacted. Such a system has a single bandgap $E_g$. Close to the interface there exists a depletion region (or space charge region) where free charge carriers are absent and an electric field is present. This built-in electric field is responsible for the photovoltaic effect. A photon with energy $h\nu$ greater than $E_g$ can be absorbed and can contribute at most an energy $E_g$ to the cell output, Figure 1.1. The excess over $E_g$ is wasted as heat due to thermalization of the charges to the band edges. Electron – hole pairs that are generated inside the space-charge region and those able to diffuse into this region are effectively separated and contribute to the photocurrent and photovoltage of the p-n junction solar cell. A detailed description can be found in [23].
One of the factors that lowers the efficiency of solar cells is recombination of electron–hole pairs. This can occur in the bulk as well as at the interfaces of the materials. Recombination can largely be avoided by using defect-free single crystalline materials. However, this type of material appears to be too expensive for large-scale photovoltaic applications.

**Figure 1.1** Energy–band diagram of p-n junction solar cell under solar irradiation. 

- **a,b** – excitation of an electron from valence into the conductive band of p-type semiconductor.
- **c** – injection of electron into the conductive band of n-type semiconductor.
- **d** – recombination of electron-hole pairs.
1.2. Photoelectrochemical solar cell

From the early 1970s, there have been made efforts in many laboratories around the world to develop photoelectrochemical systems based on semiconductor materials for the utilization of solar energy. An electrochemical photovoltaic cell consists of a semiconductor electrode, an electrolyte containing a redox system and an inert counter electrode. The energy diagram for a cell with an n-type semiconductor and a redox system with a potential close to the valence band is shown in Figure 1.2.

![Energy level diagram for an electrochemical photovoltaic cell using an n-type semiconductor electrode](image)

**Figure 1.2 Energy level diagram for an electrochemical photovoltaic cell using an n-type semiconductor electrode**

In this figure, the short-circuit condition is presented, i.e. the Fermi level is constant through the system and the voltage between the two electrodes is zero. The Fermi level represents the electrochemical potential of the electrons in the material, i.e. normally referred to as the redox potential in the electrolyte. Upon illumination of such a cell, holes are created and transferred to the reduced species of the redox system. The electrons reach the rear ohmic metal contact of the semiconductor electrode, traverse the external circuit, do useful work, and then reduce the oxidized component of the redox couple at the metal counter electrode. Since no net consumption of components in the electrolyte occurs, this cell is regenerative [24].
It should be mentioned that a p-type electrode could also be used in a photovoltaic cell. In such a cell electrons are the minority carriers created by light, and a redox system with a standard potential close to the conduction band should be selected. In this case, the electrons are driven toward the semiconductor surface where they are transferred to the oxidized species of the redox system. Here, holes are collected at the back contact.

The conversion efficiencies depend on the semiconductor bandgap in semiconductor solid and solid-liquid devices, as given by thermodynamic calculations. The maximum theoretical efficiency, for a single bandgap device, is about 30% for a bandgap around 1.3 eV.
2. Nanostructured solar cells

2.1. Dye-Sensitized Nanocrystalline Solar Cell

Dye-sensitized solar cells are photoelectrochemical cells that usually consist of a wide-bandgap semiconductor, such as TiO₂, ZnO, or SnO₂, in combination with dye molecules and an electrolyte. The bandgap of the semiconductor exceeds 3 eV, causing them to absorb only a few percent of the solar spectrum, i.e. the ultra-violet region. In general, wide-bandgap semiconductors are stable and cheap photoelectrodes. Attachment of dye molecules to the semiconductor surface makes the system sensitive to the visible part of the solar spectrum. Many types of dyes have been used, but the best result has been achieved with ruthenium bipyridyl complexes, for example (Ru(dcbpyH₂)₂(NCS)₂) Figure 2.1 [25-26].

A monolayer of dye on a flat semiconductor electrode does not absorb more than a few percent of the incident light and, therefore, such a system can not form an efficient solar cell. A breakthrough in dye-sensitized solar cells was made by Grätzel and co-workers [3]. They developed porous nanocrystalline TiO₂ electrodes, which have a very high internal surface area. The electrode consists of numerous TiO₂ particles of colloidal size (5-50 nm), that are interconnected by a low-temperature sintering step. A monolayer of dye adsorbed on such an electrode is sufficient to absorb a major part of the solar spectrum. Porous nanocrystalline metal oxide electrodes have been made from, for example TiO₂, ZnO, SnO₂, Fe₂O₃ and WO₃.

The working principle of a dye-sensitized solar cell is shown in Figure 2.2a. After absorption of a photon by a dye molecule, the excited electron is injected into the conduction band of the semiconductor. At the back contact of the semiconductor the electron is collected and can perform work in an external circuit, before returning into the system at the counter electrode, where it reduces oxidized species. Meanwhile, the oxidized dye is regenerated by acceptance of an electron from reduced species in the electrolyte. Apart from these desired reactions, several reactions can occur that will lower the overall efficiency of the dye-sensitized process. First, the excita-
tion of dye molecules may be lost by radiative or non-radiative decay. Second, injected electrons can be transferred back to the oxidized dye, and third, injected electrons may react with oxidizing agents in the electrolyte.

In contrast to conventional solar cells, nanocrystalline dye-sensitized solar cells do not operate through a built-in electric field but rather the kinetics of interfacial electron transfer processes are responsible for the photovoltaic effect [5]. The rate constants for electron injection from an excited dye into the conduction band are very fast, in the sub-pico second region [27], provided that the energy of the excited state is higher than that of the conduction band edge. The reduction of the oxidized dye by electrolyte occurs on a time scale in the order of tens nanoseconds. The back-reaction of the electron to the oxidized dye occur at much lower rates, in the micro second regime [28].

The use of the liquid electrolyte leads to several technological problems such as solvent evaporation, degradation and seal imperfection. Using a solid state hole conductor can solve those problems. CuI and CuSCN are p-type semiconductors that are suitable as hole conductors in dye-sensitized solar cells and a number of attempts in the preparation of devices have been made [10-18]. These materials are transparent, have good conductivity, and possess favorable valence band positions, which allows hole injection from oxidized or excited dye molecules. Furthermore they can be applied onto dye-sensitized TiO₂ electrodes using low-temperature methods. For solar cells based on TiO₂ sensitized with Ru(dcbpyH₂)₂(NCS)₂ efficiencies in the order of 2% are achieved with CuSCN [29] and up to 3.8% with CuI as the hole conductor [30], Figure 2.2b.

The photoconversion yields of these heterojunctions depend largely on the electron transfer processes between the dye molecule and the hole conductor surface. This in turn is related to the geometrical and electronic structure of the dye in the heterojunction environment. Part of the current study focuses on the specific dye adsorption from solution of Ru(dcbpyH₂)₂(NCS)₂ at CuI and CuSCN substrates and on possible changes in the upper valence electronic structure (e.g. in the highest occupied orbital, HOMO), when the dye interacts with the substrate. In Chapter 4 we show a detailed investigation of this subject.
Figure 2.1 Ru(dcbpyH$_2$)$_2$(NCS)$_2$

Figure 2.2 Electrochemical photovoltaic cell based on dye sensitization of a wide bandgap semiconductor with electrolyte (a) and p-type semiconductor (b) as hole conductor.
2.2. Solar Cells with Extremely Thin Light Absorbers

The concept discussed below is based on the application of an extremely thin absorber (eta-solar cell), such as CuInS$_2$ [19-21]. This concept is similar to those using a dye for light absorption, which is embedded between semiconductor and electrolyte. To attain high light absorption, the absorber is embedded in a porous and transparent structure, Figure 2.3.

One of the suitable materials is CuInS$_2$ (CIS). CIS is formed from type I-III-VI$_2$ group of semiconductors with chalcopyrite structure. During the last years it is used for photovoltaic applications, because it is stable, non-toxic, inexpensive, has a high absorption coefficient (more than $10^4$ cm$^{-1}$) and a direct band gap of 1.5 eV. Later research has shown that CuInS$_2$ can be used also as a hole conductor [22]. There are a number of methods for the deposition of CuInS$_2$ such as: atomic layer deposition (ALD) [31], ion layer gas reaction (ILGAR) [32], vacuum deposition [33] and spray pyrolysis [34-37]. The latter method is of interest because of its potential for a low cost production process. However, the main difficulty in spraying CuInS$_2$ onto TiO$_2$ is to obtain a pure chalcopyrite structure at the interface [38], especially when the film is exposed to air [39]. The photoconversion power output of these heterojunctions depends largely on the electron transfer processes between the absorber layer and the semiconductor. This in turn is related to the electronic structure of the absorber layer in the heterojunction environment. In Chapter 5 we discuss some of the problems related with spray pyrolysis deposition of eta-layers onto different metal oxides.

![Figure 2.3 Energy – band diagram of ETA – solar cell](image)
3. Experimental Methods

This chapter describes the experimental techniques that have been used for the preparation and characterization of the samples. The chapter is divided into four sections: photovoltage measurements, solar cell characterization, photoelectron spectroscopy and sample preparation.

3.1. Photovoltage Measurements

The optical and transport properties of materials are frequently determined by the surface conditions. Contactless characterization methods is therefore an important experimental requirement for their investigation.

Photovoltage measurements is a method to investigate transport (time resolved features of photovoltage) and optical (spectral features of photovoltage) properties of semiconductor materials. O. E. Johnson [40], investigated the transient photovoltage first and its spectral modification was applied by Goodman [41].

The photovoltage measurements were carried out in the fixed parallel-plate capacitor arrangement that consists of the investigated material on a conductive glass substrate, a 10 μm thick mica spacer and a semitransparent Cr-electrode evaporated on a quartz homogenizer, Figure 3.1. A Xe lamp with a quartz-prism monochromator is used to excite the sample in the spectral dependent photovoltage. The light is chopped with the required frequency. Laser pulse excitation is used for the photovoltage transients. The photovoltage signal is registered by an oscilloscope or lock-in amplifier from the Cr electrode as a voltage drop on a load resistor (about 1 GΩ). Investigation of transient photovoltage is performed on the time scale between 1 ns and 0.1 s. A detailed description of the setup can be found in [42].

The basic processes (light absorption, charge separation and charge transport) that are involved in the generation of a photovoltage signal are depicted in Figure 3.2 for the case of charge injection from a dye molecule into a hole conductor. The photovoltage signal arises due to the spatial charge separation between the two electrodes. The signal increases with increasing number of separated charge carriers and with increasing charge separation length.
Figure 3.3 shows, as an example, photovoltage transients of bare SnO$_2$:F (open circles) and SnO$_2$:F covered by a monolayer of dye molecules (solid circles). The photovoltage signal appears within the laser pulse and rises within 3 ns (bare SnO$_2$:F) and 30 ns (SnO$_2$:F covered by a monolayer of dye molecules). The photovoltage signal is negative and small (2 mV) for the bare SnO$_2$:F while it is positive and much larger (15 mV) for SnO$_2$:F covered by a monolayer of dye molecules. A positive photovoltage signal means that negative charge is injected into the SnO$_2$:F while positive charge remains at the dye molecules. The insert shows the dependence of the maximum of the photovoltage transient on the excitation intensity. The photovoltage signal increases linearly with increasing excitation intensity at lower intensities and bends to saturation at higher intensities.

Figure 3.1 Basic cell for photovoltage measurements.
Figure 3.2 Schematic band diagram of the structure used for photovoltage measurements in the fixed parallel-plate capacitor arrangement. The numbers (1-3) denote the processes of photon absorption, charge injection and charge transport.

Figure 3.3 Photovoltage transients of bare SnO$_2$:F (open circles) and SnO$_2$:F covered by a monolayer of dye molecules (solid circles). The insert shows the dependence of the maximum of the photovoltage transient on the excitation intensity.
3.2. Solar Cell Characterization

3.2.1. IPCE

The spectral response is a characteristic property of a photovoltaic system. Experimentally, the photocurrent is recorded during illumination with monochromatic light. Measuring the photoresponse and illumination intensity, the incident photon to current conversion efficiency (IPCE) can be calculated according to:

\[
IPCE = \frac{\text{No. of el. generating the photocurrent}}{\text{Incident photons}} = \frac{1240 \cdot j_{ph}}{\lambda \text{[nm]} \cdot P_{in}} \quad (3.2.1.1)
\]

where \( j_{ph} \) is the photocurrent density, \( P_{in} \) is the light power density and \( \lambda \) is the wavelength in nanometers. More detailed information can be obtained by correcting for the absorption and reflection in the glass support and in the film, respectively. However, it is difficult to accurately measure absorption and reflection in nanostructured systems.

Although photocurrent measurements are relatively simple they can give valuable information. The photocurrent results from a number of sequential events; absorption, electron injection, recombination and transport.

3.2.2. IMPS

In Intensity Modulated Photocurrent Spectroscopy (IMPS) a small sinusoidal perturbation is superimposed onto a large dc illumination level. The time-dependent incident illumination is therefore of the form in equation 3.2.2.1, where \( \delta \) is the depth of modulation and \( I_o \) is the mean intensity. The phase and amplitude of the resulting ac photocurrent is measured as function of modulation frequency. The experimental arrangement is shown in Figure 3.4. In IMPS, the photocurrent signals (in-phase and 90° phase shifted) are measured in a large frequency range, Figure 3.5. The method was used in this work to study the charge transport of the solar cell under short-circuit conditions. It has been mainly applied in characterization of electrolyte solar cells [43-48].
In a nanostructured semiconductor electrode the IMPS response reflects the electron transport through the nanocrystalline film to the back contact, under the assumption that the electron lifetime is much larger than the required transport time. The time constant associated with the charge transport can be calculated from the angular frequency at which the absolute maximum of the 90º phase-shifted photocurrent occurs $\omega_{\text{max}}$, equation 3.2.2.2. For nanocrystalline systems it has been shown that $\omega_{\text{max}}$ depends on the light intensity [49].

\[
I(t) = I_0 \left( 1 + \delta \cdot \sin(\omega t) \right) \quad (3.2.2.1)
\]

\[
\tau = \omega_{\text{max}}^{-1} \quad (3.2.2.2)
\]

Figure 3.4 Experimental arrangement for intensity modulated photocurrent spectroscopy (IMPS).
3.2.3. Photovoltage and Photocurrent decay

Laser induced photocurrent and photovoltage transients were recorded in paper IV. The intensity dependent current transients were integrated numerically to obtain the extracted charge, i.e. the electronic charge that was present in the nanostructured electron conductor under illumination. The charge recorded in the absence of laser excitation was subtracted in order to correct for the offset of the instrument.

The voltage decay is directly related to the recombination of the charge carriers in the interpenetrated dye-sensitized junctions. Zaban and co-workers derived the following expression for the electron lifetime ($\tau_e$) in nanostructured dye-sensitized solar cells with electrolyte [50]:

$$\tau_e = \frac{kT}{e} \left(\frac{dV_{OC}}{dt}\right)^{-1} \quad (3.2.3.1),$$

where $kT$ is the thermal energy and $e$ the elementary charge.
3.3. Photoelectron Spectroscopy

In photoelectron spectroscopy, PES, the sample is irradiated with monochromatic radiation with energy larger than the work function of the sample, and the kinetic energy of the emitted electrons is analyzed, Figure 3.6.

\[I_{BE} = KE \text{hv}\]  
\[E_{B}^f = E_{B}^{l} - \Phi_s\]

The ionization energy, \(E_{B}^{l}\), is calculated from the relation

\[E_{B}^{l} = h\nu - E_K\]  
\[E_b^e = E_{B}^{l} - \Phi_s\]

Here \(E_K\) denotes the kinetic energy of the emitted electron and \(h\nu\) the energy of the incident radiation. The ionization energy \(E_{B}^{l}\) is referred to the vacuum level and \(E_K\) is the kinetic energy of the electron just outside the surface. For condensed phase samples the Fermi level, \(E_{B}^{f}\), is often used as reference level for the binding energy scale. The difference between the scales is the work function \(\Phi_s\) of the sample:

If the electrons are inelastically scattered during their path through the material they do not contribute to the main elastic photoelectron peak. The prob-
ing depth is therefore usually 5-50 Å and the method is therefore generally considered to be surface sensitive at the molecular level. Varying the excitation energy can alter the surface sensitivity, since the kinetic energy of the electrons is changed. The intensity of electrons from a sample can be described as [51]:

\[ I \propto \lambda(E_k) \left[ 1 - \exp \left( -\frac{d}{\lambda(E_k)} \right) \right] \]  

(3.3.3)

where \( \lambda \) is the electron inelastic mean free path and \( d \) is the sample thickness. \( \lambda \) is dependent of the kinetic energy, \( E_k \), following the so-called universal curve, see [51]. Thus, in order to vary the surface sensitivity a light source with variable wavelength, such as a synchrotron radiation source is needed. A similar effect can also be obtained by varying the take-off angle on a flat substrate.

The surface coverage can be estimated from photoelectron peak intensities. For example, by measuring the substrate peaks before \( (I_0) \) and after \( (I) \) dye-sensitization the thickness of the dye layers can be calculated. This is done by using the expression \( I = I_0 \exp \left[ -d/(\lambda \sin \theta) \right] \), where \( d \) is the layer thickness and \( \theta \) is a take-off angle.

### Line width and shape

The resolution in a PES spectrum depends on several factors. The lifetime of the core hole broadens the line; the shorter the lifetime the broader the peak. The line shape due to the lifetime broadening is Lorentzian. Experimental factors, such as energy width of the incident radiation and the resolution of the analyzer, contribute to the total line width generally with a Gaussian distribution. The resulting line shape can be approximated by a convolution of Lorentzian and Gaussian distributions - a shape known as a Voigt shape.

### Chemical shift

An important advantage of PES is the ability to obtain information on chemical states from the variations in core level binding energies, or chemical shifts, of the photoelectron lines. Neighboring atoms affect the core level peak position in several ways. For example the charge redistribution causes changes in the oxidation state of the atom, which leads to a change in the electronic potential of the core electrons. Also, the potential exerted by the
atom neighbors influences the core level energies. Final state effects, i.e. charge redistribution due to the ionization process, may also be important.

**Synchrotron radiation**

PES measurements can be performed using a number of different light sources. The common denominator is that the energy of the excitation light must exceed the work function of the sample. UV light has been widely used to study valence bands. Characteristic x-rays, e.g. Al $K_{\alpha}$ and Mg $K_{\alpha}$, are used to study core levels. The most versatile light source is, however synchrotron radiation (SR). SR is emitted when charged particles are accelerated while they are traveling at a very high, relativistic, speed.

Synchrotron radiation has several advantages over characteristic x-ray radiation. In particular, the photon energy may be varied continuously over wide ranges, using monochromators. This makes it possible to choose the most suitable energy for the experiment, for example with respect to surface sensitivity.

The light beam is directed towards the experimental set-up through a beamline (BL) and the experiments are performed at end-stations. End-stations are generally designed for specific experiments such as photoelectron spectroscopy, crystallography etc.

At Max – Lab in Lund, two beamlines have been used in this work, I411 and D1011, both operating in the energy range 50 – 1500 eV. The latter beamline is equipped for UHV work (below $10^{-10}$ mbar) and the former for more moderate vacuum conditions ($>10^{-8}$ mbar). D1011 allows *in situ* sample preparation.
3.4. Sample Preparations

Various methods have been applied for sample preparations to match the requirements for different characterization methods.

3.4.1. Preparation of TiO$_2$ electrodes

In papers I and III - VI, two ways of preparation of the mesoporous TiO$_2$ films were applied. Firstly, a colloidal paste of TiO$_2$ [3] was spread onto TEC-8 (a glass covered by 0.5 µm fluorine doped tin oxide) and annealed at 450 °C, yielding a 1 – 2 µm transparent film. Secondly a TiO$_2$ powder (Degussa, P25) was compressed at 500 kg/cm$^2$, yielding a 4 µm film [52].

Thin dense films of TiO$_2$ (30-100 nm) have been deposited onto TEC-8 by spray pyrolysis. A solution of titanium (IV) isopropoxide (2.4 ml), acetyl acetone (3.6 ml) in ethanol (54 ml) was spread on heated surfaces at 450°C [53].

3.4.2. Spray Vaporization of CuI and CuSCN

In paper I and III, CuI and CuSCN were prepared by spray vaporization. The characterization methods required the dye to be adsorbed onto the p-type semiconductor without any contact to the underlying substrate. That demands a homogeneous layer of CuI or CuSCN onto the FTO glass substrate (TEC-8), which is rather difficult to achieve. For this purpose the CuI and CuSCN films were deposited by spraying a solution at 50°C (CuI was dissolved in acetonitrile, CuSCN in n-propylsulfide, 1% by mass) onto a conductive glass, TEC-8, covered with a mesoporous TiO$_2$, [10,11,54]. The substrates were subsequently completely covered with the p-type semiconductor materials.

3.4.3. Pore filling with CuSCN

In paper IV, the deposition of CuSCN into the pores of dye-sensitized nanocrystalline TiO$_2$ electrodes was performed on a custom-built apparatus at the Energy Research Center of the Netherlands, as described by B. O'Regan in [55].
3.4.4. Dye-sensitization

In paper I and III, the CuSCN and CuI films were soaked in solutions of the dye Ru(dcbpyH₂)₂(NCS)₂ and ethanol (Kemetyl, 99.6%). For the dye-sensitization of the CuSCN substrate a 0.5 mM dye solution was used while a 0.05 mM dye solution was used for the CuI substrate. All dye-sensitized p-type semiconductor films were rinsed by dipping them into ethanol. The procedures reported here yield close to monolayer coverage.

For the preparation of films containing dye molecules that are not specifically bonded to a substrate, a substrate layers of dense TiO₂ (thickness about 200 nm) on TEC-8 conducting glass were used. These substrates were soaked for 30 min in a 0.5 mM dye solutions of Ru(dcbpyH₂)₂(NCS)₂ in ethanol but they were not rinsed. This preparation gave multilayer coverage of the dye with only minor effects from the substrate itself and is hereafter referred to as non-bonded dye molecules.

3.4.5. Sample preparation for UHV measurements

In paper II, the titanium dioxide film was grown under UHV conditions on Si(111) (Virginia Semiconductors, resistivity 0.1-1.0 Ω cm) by means of chemical vapor deposition (CVD) using titanium (IV) isopropoxide (TTIP) as precursor molecule. The dose was 5×10⁻⁷ Torr for two minutes and the sample temperature was kept at 500 °C during dosing. This produces a TiO₂ film consisting of anatase grains, approximately 10 nm wide. The thickness of the anatase layer was estimated to be between 50 and 100 Å. Consequently, this film forms a most suitable basis for modeling the properties of a nanostructured anatase film.

After the deposition of the TiO₂ film the sample was transferred in an Ar-filled module to a glove box with an Ar-atmosphere. In the glove box the film was dye-coated Ru(dcbpyH₂)₂(NCS)₂, purchased from (Solaronix, Aubonne, Switzerland) by immersing it into a saturated solution (ethanol, Kemetyl 99.6 %, spectroscopic quality) of the dye for 40 minutes. Using the Ar-filled module the sample was transferred back to the UHV system.

The evaporation source consisted of a directly heated Ta-pocket filled with CuI powder (Aldrich, purity 99.999 %). Before evaporation the pocket was first heated up to 400 °C for one minute. During evaporation the temperature was kept at 400 °C and the pressure during deposition was below 1×10⁻⁸ Torr.
3.4.6. Spray Pyrolysis of CuInS$_2$

In paper V and VI, thin films of CuInS$_2$ were deposited by spray pyrolysis of a solution of copper chloride (CuCl$_2$), indium chloride (InCl$_3$) and thiourea (CS(NH$_2$)$_2$ dissolved in deionized water. Films were deposited on dense and mesoporous surfaces of a number of metal oxides (such as ZnO, SnO$_2$ and TiO$_2$). The concentration of Cu$^{2+}$ in the spray solutions was 2 mmol/l. The molar ratio of Cu:In:S was kept to 1:1:3. The bath temperatures for different sets of samples were 400°C and 340°C. The distance between nozzle and substrate was kept at 29 cm during the depositions. Purified and compressed nitrogen was used as a carrier gas with a flow rate of 7 l/min. The parameters during the spray procedure were kept constant. Films were prepared at the Tallinn Technical University (Estonia).

3.4.7. Chemical Bath Deposition of CdS

In paper VI, thin films of CdS (applied as buffer layer) were prepared by the chemical bath deposition technique. The titanium oxide electrodes were immersed in a solution of CdCl$_2$·2.5·H$_2$O, NH$_3$, NH$_4$Cl, CS(NH$_3$)$_2$ at 80°C [56].
4. Studies of the dye / hole conductor interface

Previous work has shown that the p-type semiconductors CuI and CuSCN can be used as hole conductors in dye-sensitized nanocrystalline solar cells. Although these materials are relatively similar, they give different stability and overall efficiency [29,30]. Optimization of these photovoltaic devices requires therefore more fundamental knowledge of the dye-semiconductor interfacial and electronic structures, as well as better understanding of charge accumulation, injection and transport. Below, a summary of the results of an investigation in these materials is given.

As a first step, the adsorption of dye molecules onto p-type semiconductors was studied by means of photoelectron spectroscopy (paper I). The schematic structure of the dye Ru(dcbpyH2)2(NCS)2 (the red dye) was shown in Figure 2.1. Previous investigations have shown that the red dye molecule is bonded to TiO2 surface via the carboxylic groups [57-62]. In contrast, the red dye molecule anchors to CuI and CuSCN via the NCS- ligands. This configuration is favorable for the solar cell function, in which photoexcitation is followed by electron injection in the TiO2 and hole injection into the p-type semiconductor. In the red dye the highest occupied molecular orbital (HOMO) consists of electronic levels from Ru and the NCS- ligand and the lowest unoccupied molecular orbital (LUMO) is localized on the bipyridine rings [63,64]. The adsorption and electronic structure were studied via the shift of the core-levels of oxygen, nitrogen and sulfur. Examples are presented in Figure 4.1 and Figure 4.2. Figure 4.1 shows O 1s spectra originating from the non-bonded red dye molecules and the dye sensitized TiO2 substrate. Figure 4.2 shows the shift of S 2p level due to adsorption onto a CuI surface. Because of the complexity of the investigated system, the deconvolution of the spectra requires a complex curve fit analysis. The information from different samples and core levels was combined. From the curve fit analysis we conclude that only half of dye molecules are connected to the CuSCN surface via both NCS- groups, and the rest are connected through one NCS- ligand. Similarly the interaction between the red dye and the CuI surface via both of the NCS ligands as well as one carboxylic group was deduced. In addition, aggregation of dye molecules onto the CuI surface during sensitization time longer than 10 seconds was observed.
The shifts of the core levels indicate substantial charge redistribution in the red dye molecule upon adsorption. Also a shift to higher binding energy of the Ru 3d_{5/2} core-level was detected. The shifts of the core-levels are accompanied with changes also in the upper valence structure and are therefore important for the function of solar cell. Such effects are discussed further below.

In the conventional preparation method of solid-state DNSC the hole conductor is deposited onto a dye-sensitized TiO₂. Therefore in the complete system additional constrains may be of importance when forming the functional heterojunction. In paper II, layer by layer formation of the heterostructure was followed by PES. The TiO₂ and CuI layers were prepared in ultra high vacuum and the dye-sensitization was performed in argon atmosphere. The PES measurements indicate the adsorption of dye molecules onto TiO₂ via carboxylic groups and connection to CuI through the NCS⁻ ligand. A majority of NCS⁻ groups is connected to the CuI surface (around 60-70%). After a certain amount of CuI deposition, CuI grows in the form of particles and displace the dye molecules at the TiO₂ surface. Moreover, bond breaking between TiO₂ and the dye was observed, which probably affects the charge transport channels.

Figure 4.1 The O1s core-level spectra of the red dye molecules adsorbed onto TiO₂ (solid line) and non-bonded. After adsorption, the shape of initial double oxygen peak is changed indicating the bond between dye molecules and TiO₂ surface.
Figure 4.2 The S2p core-level spectra of the red dye molecules. The peak position of adsorbed dye molecules (solid line) is shifted to higher bonding energy indicating the bonding between the red dye molecules and CuI surface.

Although there are similarities in red dye-hole conductor (CuI and CuSCN) connection, the effect on the electronic structure within the red dye may vary for the two different materials. The core levels of nitrogen and sulfur in the NCS’ ligand have different shifts on the two materials. Another aspect that must be taken into consideration is that CuI and CuSCN could have different energy position of the valence band. All these factors combined together will influence the dye-semiconductor interface function.

A further step was to investigate the charge injection from dye molecules into the hole and electron conductors (paper III). The dye was connected to only one semiconductor surface at a time, in order to observe the influence of the particular surface. This required special sample preparation and measurements methods. The contactless photovoltage method, described in chapter 3, is well suited for such measurements.

In paper III, the injection of charge carriers from dye molecules adsorbed on transparent electron and hole conductors was investigated by transient and spectral photovoltage measurements in a parallel plate capacitor arrangement [65]. The dye-sensitized n- and p-type semiconductors were illuminated by monochromatic light and the photovoltage was measured as function of wavelength. The spectral photovoltage measurements show that if the red dye molecule was adsorbed onto CuI or CuSCN the dye’s light absorption threshold moved from 1.7 eV (for the dye on TiO2) to 1.9 eV, Figure 4.3. Additional defect states were observed around 1.2 eV for the dye-sensitized CuSCN surface. The introduction of such states could increase recombination in a solid state DNSC based on CuSCN.
An overall goal is that hole conductors will replace the electrolyte in DNSC. The heterostructure should give a similar energy output as the electrolyte cells. The last step in the present studies was more focused on a complete device. A comparison of charge accumulation and transport in nanostructured dye-sensitized solar cell with electrolyte or CuSCN was thus investigated.

In paper IV, the lifetime of the electrons, charge extraction and transport were investigated. The influence of the buffer layer (Al$_2$O$_3$) was also studied. Previous studies have demonstrated improvements in DNSC performance after employing a buffer layer such as a very thin layer of Al$_2$O$_3$ [66-68]. The buffer layer was employed between the red dye and the metal oxide (TiO$_2$).

The IPCE spectra and the light absorption spectra correlate well with the light absorption spectrum of the dye. No spectral shifts are observed in contrast to photovoltage and PES measurements.

For dye-sensitized heterojunctions the short-circuit photocurrent density ($J_{sc}$) increases linearly with light intensity, in accordance with electrolyte-based dye-sensitized nanocrystalline solar cells [44]. The open-circuit poten-
tial ($V_{oc}$) is clearly affected by the $\text{Al}_2\text{O}_3$ layer: higher $V_{oc}$ values are observed for both the electrolyte and the CuSCN cells. The $V_{oc}$ decays after switching off the light to half of its initial value in less than 0.5 s in the CuSCN cells, compared to $>5$ s for the electrolyte cells. The electron lifetime under open circuit conditions was 100 ms for electrolyte cells and 10 ms for CuSCN cells, and estimated to be 1 s for the electrolyte and 80 ms for CuSCN cells under short circuit conditions. The implementation of a buffer layer increases the electron lifetime in all samples. Integration of the photocurrent decay transients gives information on the stored charge. There is significantly more charge present in the electrolyte cells. Samples with buffer layer resulted in more extracted charge at a given light intensity. This is directly related to the decreased recombination in these samples. Intensity-modulated photocurrent spectroscopy was used to study the charge transport of the solar cells under short-circuit conditions. The IMPS time constant was determined as function of the extracted charge, see Figure 4.4. For a certain electron transport speed or $\tau_{\text{IMPS}}$, much less charge needs to be accumulated in the nanostructured TiO$_2$ in the CuSCN cells.

In summary, paper IV shows that there is definitely a positive effect of the buffer layer for both types of photovoltaic devices. The lifetime and transport time of the electrons is shorter in CuSCN cells in comparison to electrolyte cells. Based on values of extracted charge, we find that the recombination is higher in CuSCN cells (as expected from paper III).

![Figure 4.4 Transport time ($\tau_{\text{IMPS}}$) as function of extracted charge ($Q_{\text{ext}}$) from the solar cell. The following abbreviations were used to describe the samples: TDE, TADE, TDC and TADC, where T stands for TiO$_2$, A for $\text{Al}_2\text{O}_3$, D for dye, C for CuSCN and E for electrolyte.](image-url)
5. Investigations of CuInS$_2$ deposition onto TiO$_2$

As mentioned above (chapter 2), spray pyrolysis is a low cost alternative method of light absorber deposition, for ETA solar cells. The deposition is performed in oxygen atmosphere at high temperature (340-450 °C). A difficulty under such experimental conditions is to prepare clean CuInS$_2$ (CIS) layers especially onto metal oxide surfaces. Any impurity in the films or the interface region could cause a drop of photovoltaic efficiency.

Papers V and VI are concerned with the preparation and investigation of CIS layers on metal oxides. X-ray diffraction (XRD) and photoelectron spectroscopy (PES) were used for characterization. The work was performed in collaboration with Tallinn University of Technology (Estonia), Hahn-Meitner Institute (Berlin, Germany) and the Energy Research Center of the Netherlands.

In paper V we have investigated the growth of CIS films (thickness 300 – 400 nm) by spray pyrolysis on dense and highly structured nanocrystalline titanium oxide electrodes. According to these measurements, an In$_2$O$_3$ phase was observed in the CIS films deposited onto nanocrystalline TiO$_2$ at 430 °C, indicating an oxidation process. It may be proposed that the nanocrystalline structure is responsible for this oxidation. The indium oxide was not detected on dense electrodes under the same experimental conditions. A decreased growth temperature (380 °C) results in a CIS film on the nanocrystalline electrode without an oxide phase. In this work, we have shown that CIS layers can be deposited onto TiO$_2$ electrodes and that they show photovoltaic properties. The thickness of the layers investigated in paper V is however too large to determine the purity of the CIS/TiO$_2$ interface.

Therefore, the interface between CIS and TiO$_2$ was investigated in more detail. At the same time a CdS layer was introduced, which increases the photovoltage and photocurrent of the photovoltaic device [69]. The CdS layer is referred to as a buffer layer and may function as a tunnel barrier to reduce the recombination of the injected electrons.

In paper VI, we investigated the deposition of CIS onto clean and CdS coated nanocrystalline and dense TiO$_2$ electrodes. This work was focused on the TiO$_2$-CIS (TiO$_2$-CdS-CIS) interface. The amount of sprayed solution was here kept minimal. The PES characterization revealed that during CIS deposition onto nanocrystalline TiO$_2$ surface an indium oxide layer was formed.
We did not detect any signal from sulfur or copper, see Figure 5.1. An explanation for this could be that CuS is converted into CuSO₄ upon oxidation on nanocrystalline TiO₂. The latter compound is easily dissolved in an aqueous medium. As a result, Cu and S are removed while indium is left at the surface.

On the contrary, if the electrode is only partly covered by CdS, the CIS was formed without any sign of indium oxide. The CdS layer of nanocrystalline TiO₂ (mixture of rutile and anatase) exhibited pinholes, whereas the dense layer of TiO₂ (anatase) was completely covered by CdS. This comparison between deposition of small amounts onto dense TiO₂ and nanocrystalline TiO₂ show that the surface morphology has a big influence on the growth mechanism of the CIS layer.

Figure 5.1 Cu2p, In3d and S2p core-levels of CuInS₂ from different substrates (where d – dense and n – nanocrystalline). No copper and sulfur signals were detected from nanocrystalline TiO₂ substrate.
Sammanfattning

Syftet med alla solceller är att omvandla solenergi, i form av ljus, till elektrisk energi. Idag finns många typer av solceller tillverkade av olika material. Applikationsområdena bestäms utför solcellens specifika egenskaper. Krav på nya egenskaper utgör en utmaning för vidare forskning.


Figur 5.2 En schematisk bild på en nanokristallin solcell. Det inkommande ljuset (1) tas upp av det absorberande lagret, varefter en elektron hoppar över till metalloxiden (2). Det absorberande lagret får en elektron från elektrolyten eller ett annat material som kan ge elektroner (3). Därför byggs en laddningsskillnad upp på de olika sidorna om det absorberande skiktet. Laddningarna kan ledas ut från solcellen och utföra ett arbete i en elektrisk krets t.ex. en lampa (4).
Två olika typer av absorberande skikt har undersökts, ett monolager av Ru(dcbpy)$_2$(NCS)$_2$-molekyler och ett tunt lager av ett oorganiskt material. Det oorganiska materialet är en sammansättning av koppar, indium och sva-
vel, CuInS$_2$. Ru(dcbpy)$_2$(NCS)$_2$-molekylerna har en diameter på ungefär 1 nanometer och det oorganiska materialet har en tjocklek på några nanometer.

Den nanokristallina solcellen har undersöks aktivt under det senaste årti-
ondet. En stor fördel med en sådan solcell, jämfört med en konventionell
solcell, är den enkla tillverkningsproceduren. Andra fördelar är liten mate-
rialåtgång, de stora variationsmöjligheterna vad gäller färgämne och möjlig-
heten att tillverka solcellen på ett flexibelt material. Det extremt tunna oor-
ganiska materialet (CuInS$_2$) är känt för stor absorptionsförmåga, stabilitet i
en syrerik miljö, olika framställningsmetoder och låg kostnad.

Ett av problemen med nanokristallina solceller är relaterat till det faktum
att elektrolyten är en vätska. Detta har uppmuntrat forskare att försöka ersät-
ta vätskan med material i fast form, till exempel CuI och CuSCN. Största
delen av avhandlingsarbetet har fokuserat på bindningen av Ru(dcbpy)$_2$(NCS)$_2$-molekyler till fasta material, exempelvis CuI and CuSCN.

Uppbyggnaget av tunna oorganiska ljusabsorberande material, såsom Cu-
InS$_2$, har också undersöks. Föroreningar i lagren kan vara ett problem, spe-
ciellt då tillverkningen sker i atmosfäriska förhållanden vid höga temperatu-
er. Undersökningarna visar att kvalitén hos filmerna kan förbättras genom
att addera ett tunt lager CdS mellan metalloxiden och CuInS$_2$. 

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Comments on my participation

I had the main responsibility for the experiments, sample preparation, data analysis in papers I, III and IV. In paper II, I participated in the experimental work and interpretation of the results. In paper V, I took part in sample preparation, discussions and interpretation of the results. In paper VI, I had main responsibility for characterization, data analysis and interpretation of the results.

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Boriss Mahrov
Uppsala, 2004
References


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series *Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology*. (Prior to October, 1993, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science”.)