

5 Cell preparation

The cell assembly of liquid dye sensitized solar cells (DSSC) and nano surface conductivity solar cells (NSCSC) is described in this chapter. The procedure given refers to the standard (reference) cell of each type. That means whenever measurement data is given without experimental details a standard (reference) cell was used. Briefly, the cell assembly comprises the following steps:

A fluorine doped tin oxide (FTO)-glass is cleaned and characterized (chapter 5.1). Then, a layer of nanoporous TiO_2 is screen printed onto it (chapter 5.2) and the TiO_2 -particles are sensitized with an organometallic Ru-complex (chapter 5.3). Chapter 5.4 describes the cell assembly of a liquid DSSC, which includes the sealing and the injection of the electrolyte.

Chapter 5.5 describes the preparation of a NSCSC. A supersaturated electrolyte film based on iodine/iodide is precipitated on the TiO_2 -particles. On top a porous layer of carbon particles is deposited. In the reference NSCSC, the deposition was done with the doctor blade method. Other deposition techniques are discussed in chapter 6.5.6.

5.1 FTO-glass

Transparent conducting glass (F:SnO₂-doped, FTO) was purchased from Pilkington and used for all experiments. Four-point probe measurements revealed a sheet resistance of $R_{\text{sheet}} = 8.5 \Omega/\square$. To convert the sheet resistance into the specific resistance ρ_{FTO} of the FTO, the layer thickness d_{FTO} had to be determined. Two techniques were used:

- 1) A profile of the FTO-layer was made with a DEKTAK-profilometer. Therefore, a band of ca. 3.5 mm width was covered with a polyimide tape to protect the underlying FTO. The rest of the FTO-substrate was covered with a thin layer of zinc-powder. By adding some drops of 2 M hydrochloric acid (HCl)-solution, the FTO-layer was reduced by the evolving hydrogen and could be almost completely removed. The sheet resistance after the HCl-treatment increased to ca. $1 \text{ M}\Omega/\square$.

Then the polyimide tape was removed and the remaining FTO could be measured with a profilometer (Fig. 5.1a). The thickness of the layer was determined to be ca. 660 nm.

- 2) An SEM-picture of a cross section of the FTO-coated glass was taken (Fig. 5.1b). The longish crystals in the lower part of the picture are identified as the FTO and the thickness was determined to be around 610 nm

The measured layer thickness with both methods is in good agreement. For the calculation, the average value of 635 nm was used.

$$\rho_{\text{FTO}} = R_{\text{sheet}} * d_{\text{FTO}} \quad (5.1)$$

Thus the specific resistance of the substrate was $5.4 * 10^{-4} \Omega\text{cm}$.

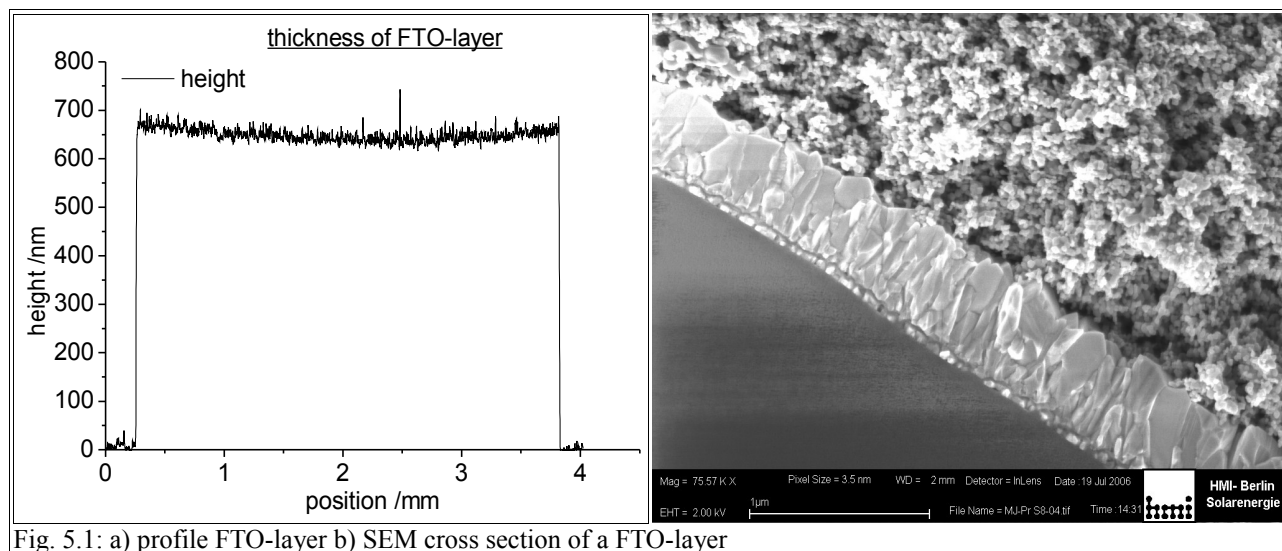


Fig. 5.1: a) profile FTO-layer b) SEM cross section of a FTO-layer

The initial size of the FTO-plates was $3.5 * 10$ cm. The plates were scratched but not broken with a glass cutter into pieces of $1.75 * 2$ cm. Prior to use the FTO-glass was cleaned in an ultrasonic bath for 15 min in acetone and for 15 min in deionized water. If the cleaned FTO-glass was not directly used for cell assembly, it was stored in ethanol for up to 1 month.

For NSCSCs, the FTO was etched except the area where the TiO_2 is screen printed and the cell is contacted. Detached carbon particles (chapter 5.5) might otherwise short circuit the cell. The FTO-etching is done according to the procedure described above.

5.2 Preparation of the titanium dioxide layer

The deposition of the TiO₂-layer was done by screen printing. Though other techniques have been applied in the past [154][126], the deposition with screen printing was found to be superior both in reproducibility of the layer thickness and the mechanic stability of the layer.

The pastes for the screen printing were kindly provided by the ECN, Netherlands. The synthesis of the TiO₂ nanoparticles in these pastes followed the standard procedure described in the literature [155][6]. The modification of the titanium dioxide was anatase.

The TiO₂-particle diameter was around 22 nm. The films had a porosity of 55 % and an average pore size diameter of 16 nm. The BET-surface area was 52 m²g⁻¹. This data was measured at the ECN and not confirmed within this PhD-thesis.

The screen printing apparatus “MEC Präzisions-Handsiebdrucktisch” was purchased from Seritechnica GmbH, München with 61 T polyester fibers. A picture of the apparatus can be seen in Fig. 5.3. On a FTO-glass substrate of 3.5 * 10 cm, ten TiO₂-electrodes were printed, each of them having an area of 1 cm². The arrangement of the electrodes is depicted in Fig. 5.2.

A printing cycle comprised the following steps:

- 1) With the screen in the upright position, the mesh openings were filled with the TiO₂-paste. Then the screen was placed above the FTO-glass substrate and a squeegee was used to press the paste through the mesh openings.
- 2) The TiO₂ was kept at room temperature for 5 min to decrease the mechanic tension within the layer.
- 3) The layer was dried at 120 °C on a hot plate for 10 min to evaporate volatile components of the paste.

Each printing cycle increased the layer thickness of the TiO₂ by ca. 5 μm. Depending on the desired thickness of the layer, the printing cycle was repeated up to 4 times.

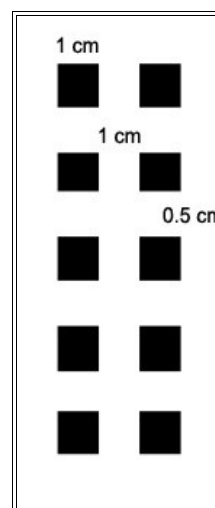


Fig 5.2:
arrangement of
TiO₂-electrodes

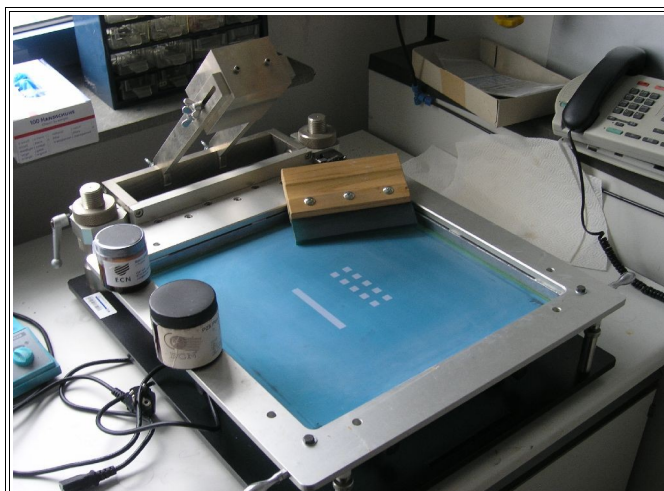


Fig. 5.3: screen printing of nanoporous TiO₂-layer

Then the dried TiO₂-layers were fired at high temperature to burn the organic components of the TiO₂-paste and to improve the mechanic contact of the nanoporous TiO₂-particles. The scratched glass plates were broken into pieces of 1.75 * 2 cm prior to the heating because the glass softens at a temperature >400 °C and breaks uncontrollably after the heating. The temperature profile used in the sintering process has a great impact on the quality of the film. The profile given in table 5.1 is based on the following observations:

- 1) the maximum temperature should not exceed 550 °C, because the phase transition from anatase to the thermodynamically more stable rutile starts in this temperature region.
- 2) the heating rate should be very slow. Initially the layer contains a lot of organic material, which decomposes in the temperature interval 200 °C < T < 350 °C. The decomposition process induces mechanic tension into the TiO₂-layer. If the heating is done too fast, the adhesion to the FTO-substrate is less firm. As a consequence cracks form within the layer.
- 3) the cooling rate of the sintered TiO₂-electrode also needs to be slow in order to minimize the tension within the glass substrate and the TiO₂-layer.

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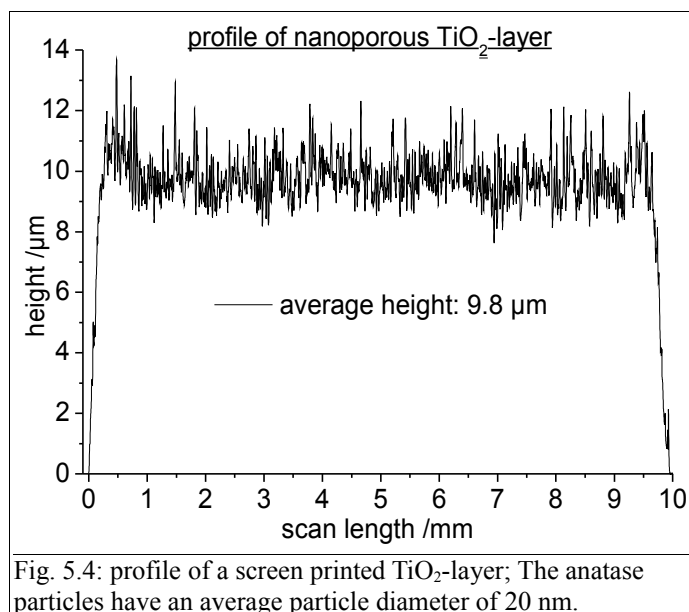
	time	final temperature	total time
heating	10	280	10
isotherm	10		20
heating	5	380	25
isotherm	15		40
heating	10	520	50
isotherm	30		80
cooling	ca. 60		140

Table 5.1: temperature profile used for the sintering of the TiO₂-films.

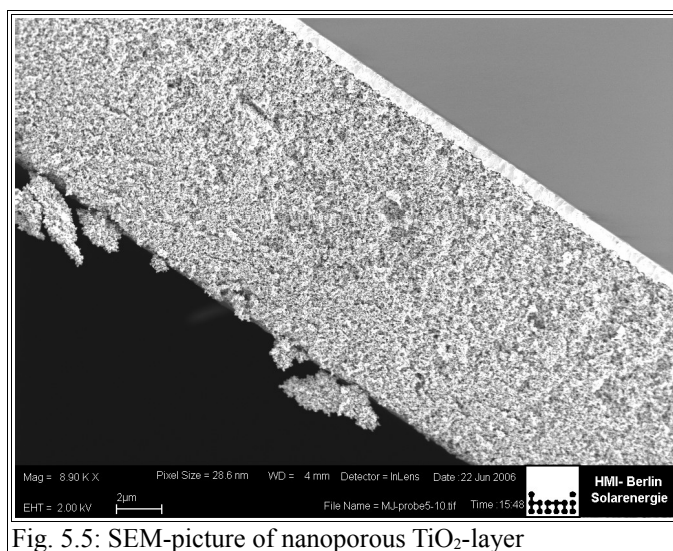
Out of ten TiO₂-electrodes on each glass-plate, two were measured with a DEKTAK-profilometer to determine the layer thickness (Fig. 5.4). About 50 profiles from TiO₂-films were measured within this PhD-thesis, that were made on four different days. The following standard deviation for the layer thickness was found:

	standard deviation of layer thickness
Layers on the same glass sheet	< 0.1 μm
Layers made on the same day but on different glass sheets	< 0.5 μm
Layers made on different days	< 1.5 μm

The average layer thickness used in a standard cell was about 10 μm .



The DEKTAK-profile (Fig. 5.4) also reveal that the surface of the TiO₂-film is very rough. It is believed that loosely attached TiO₂-clusters mainly account for the rough surface, which can be seen on the SEM-picture 5.5.



Prior to the staining of the electrodes, the TiO₂-films were immersed into a 50 mM solution of TiCl₄*2THF in water for 30 min at 70 °C and rinsed with water and ethanol afterwards. This treatment causes the growth of a thin TiO₂-layer on top of the nanoparticles, which has a positive effect on the short circuit current of a DSSC/NSCSC. After the dip-coating, the TiO₂-electrodes

were fired for 30 min at 450 °C again.

After the second heat treatment, the TiO₂ electrodes were either immediately sensitized or stored in a box. If the electrodes were stored, they were again heated to 450 °C for 30 min prior to sensitization because it was found that the quality of the TiO₂-film worsen with time due to the adsorption of pollutants (CO₂, dust, ...) from the gas phase.

5.3 Sensitization of the titanium dioxide electrode

The TiO₂-films were immersed into a dye solution after they have cooled down to ca. 60 °C. The composition of the dye solution is listed in table 5.2. Typically the sensitization was done over night for 14-20 hours. The standard DSSC and NSCSC were sensitized with the N719-dye.

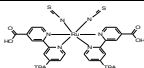
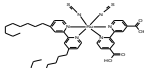
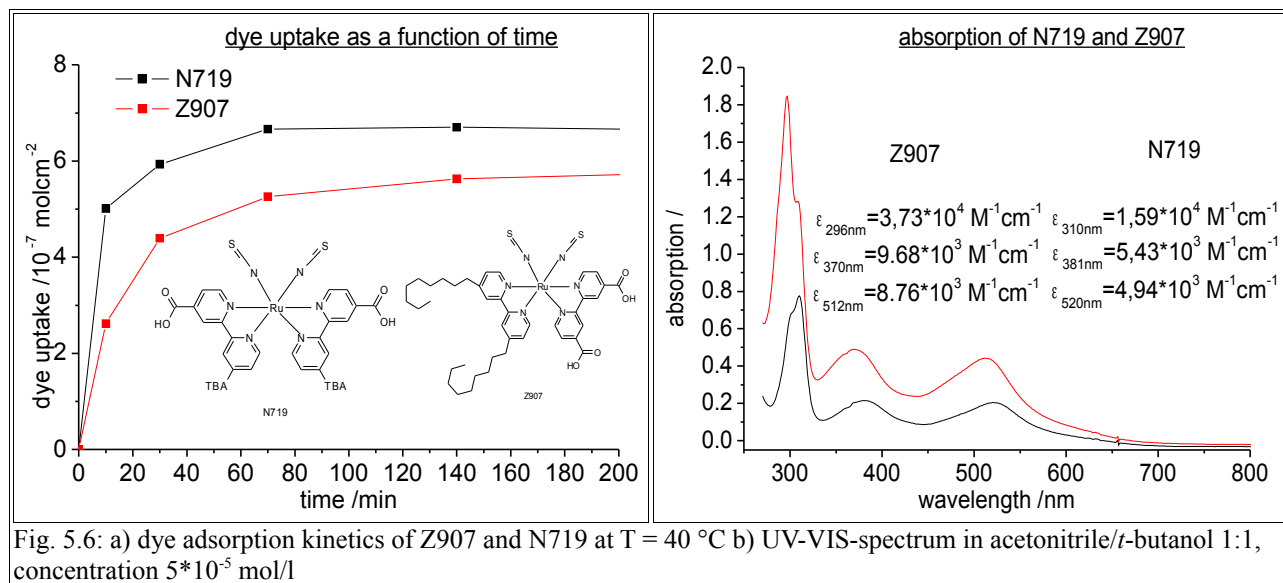
name	formula	molar mass [g/mol]	mass [mg]	density [g/ml]	volume [ml]	amount [mmol]	manufacturer
N719		1187.7	71			0.06	Solaronix
Z907		936.3	56			0.06	Solaronix
acetonitrile	CH ₃ CN	41.05		0,79	30		Merck
<i>t</i> -butanol	C ₄ H ₁₀ O	74.12		0.78	30		Merck

Table 5.2: composition of dye-solution

To monitor the adsorption kinetics of the dye, samples of the dye solution were analyzed by UV-VIS-spectroscopy. The absorption peak in the UV-region at $\lambda = 296$ nm (Z907) and $\lambda = 310$ nm (N719) was taken as the reference point. First the absorption was measured for different concentrations to determine the absorption coefficient (Fig. 5.6 b). It was noted that agglomerates form in the Z907-solution for a concentration $> 5 \cdot 10^{-5}$ mol/l. Therefore the dye solution was diluted tenfold prior to the measurement.

A fixed volume of 20 ml was used for the staining of the electrode. By measuring the concentration of the dye solution at different times, the adsorption rate could be monitored, which is shown in Fig. 5.6 a. It is interesting to note that the dye adsorption already levels off after three hours indicating that standard value of 15 hours, which is usually given in the literature, might not be needed to stain the TiO₂-film.



5.4 Assembly of a liquid Dye Sensitized Solar Cell

5.4.1 Preparation of the counter electrode

FTO-glass plates of 3.5 * 10 cm were scratched but not broken into ten pieces of 1.75 * 2 cm. A conical hole was drilled into each piece using a sandblaster Microjet 2 from Gläser Sandstrahltechnik GmbH. The small opening of the conus was on the outer (not FTO-covered) side of the substrate to make the hole closure after the electrolyte filling easier. Both front- and back side were covered with a polyimide foil to protect the surface of the FTO-glass.

After the hole was drilled, a square of 1 * 1 cm around the hole was roughened with the sandblaster to improve the adhesion of the Surlyn[®] foil in the sealing process.

Then the polyimide foil was removed and the FTO-glass was cleaned in an ultrasonic bath for 30 min (15 min deionized water, 15 min ethanol). If the FTO-substrates were not immediately processed, they could be stored in ethanol for up to one month without cleaning them again.

After cleaning 2-3 drops of H₂PtCl₆-solution were spread on the FTO-substrate with a glass rod (composition in table 5.3). The solvent evaporated at room temperature within a few minutes. Then the substrates were fired at 380 °C for 15 min in air. Small clusters of catalytically highly active platinum form.

name	formula	molar mass [g/mol]	mass [mg]	density [g/ml]	volume [μl]	amount [mmol]	manufacturer
platinhexachloro- acid hexahydrate	H ₂ PtCl ₆ ·6H ₂ O	517.92	2.58	1.08	2.4	0.005	Merck
propan-2-ol	C ₃ H ₈ O	60.1		0.79	1000		Fluka

Table 5.3: composition of the H₂PtCl₆·6H₂O-solution

remark:

The firing of the TiO₂-film and the counter electrode should not be done in the same oven. At high temperature, traces of platinum tend to detach from a given substrate, which then deposits in the oven. If the TiO₂ is sintered in the same oven, platinum might contaminate the TiO₂-surface, which significantly decreases the cell performance [126].

The platinized counter electrodes should be processed within a few hours because the catalytic activity of the platinum decreases when being exposed to air at room temperature. It is possible to recover the catalytic activity by heating the electrode again at 380 °C for 15 min.

5.4.2 Sealing of the cell

The front- and counter electrode were sealed using Surlyn[®] 1702 hot melt foil from Dupont. Surlyn[®] is an ionomer with a melting point of about 90 °C. The thickness of the foil used in a standard DSSC was 30 µm. The gasket had a layout as depicted in Fig. 5.7. It was stored at least one day in an exsiccator before the cell was sealed. Otherwise water adsorbs on the surface, which decreases the adhesion to the FTO-substrate.

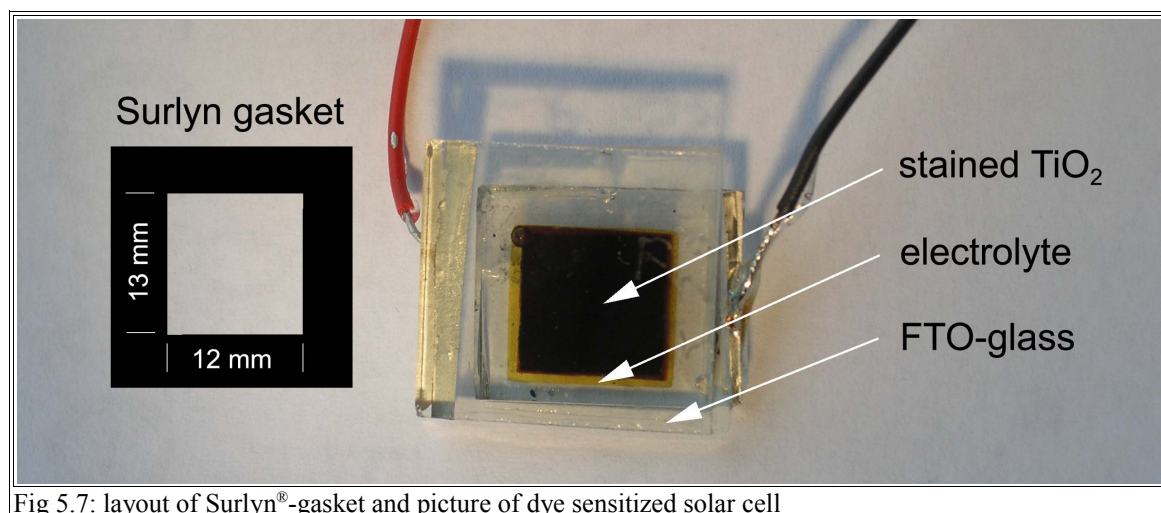


Fig 5.7: layout of Surlyn[®]-gasket and picture of dye sensitized solar cell

The Surlyn[®] gasket was sandwiched between the front and counter electrode and pressed for 90 s at 1.5 kN and 100 °C using a hot press. The front and counter electrode have to overlap partly in order to have room for the cell contacts.

After the sealing a piece of Surlyn[®] 1702 (ca. 3 mm * 3mm) was pressed on the roughened area around the hole in the counter electrode for 10 s at 1 kN and 100 °C. To avoid sticking of the Surlyn[®] foil to the hot press, it is covered with a PET-foil, which can be easily removed after the heating.

remark:

It was found that the sealed cell can be stored for several hours without a noticeable degradation of the sensitizer. Thus, if the cell assembly needs to be interrupted at some point, this is the best time to do so.

5.4.3 Filling of the electrolyte

Finally the electrolyte is filled through the hole in the counter electrode employing the vacuum method. The composition of the standard electrolyte for liquid DSSCs is given in table 5.4.

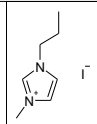
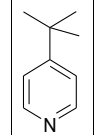
Name	formula	molar mass [g/mol]	mass [mg]	concentration [mol/l]	volume [ml]	amount [mmol]	manufacturer
PMII		252.1	152	0.6		0.6	Iolitec
iodine	I ₂	253.8	25.4	0.1		0.1	Merck
TBP		135.2	67.6	0.5	0.074	0.5	Fluka
acetonitrile	CH ₃ CN	41.05			1		Merck

Table 5.4: composition of the standard electrolyte for liquid DSSCs

The Surlyn[®] foil, that was placed on the hole in the counter electrode, was punctured with a needle. Two drops of the electrolyte were spread on the hole. Then the cell was covered with a funnel and placed on a soft pad (e.g. mouse pad). The funnel was attached to a vacuum pump and evacuated between 10-30 s. The air between front- and counter electrode started to escape, which could be seen when the electrolyte started to bubble.

When the electrolyte stopped to bubble, the funnel was carefully lifted using a flat metal stick. The inflowing air pressed the electrolyte between front and counter electrode.

remark:

The pressure within the funnel needs to be carefully adjusted. If the pressure is too low, the solvent of the electrolyte evaporates, if it is too high, the air between the electrodes does not escape.

The vacuum method works very well with low viscous solvents like acetonitrile. If a solvent with a higher viscosity is used, the vacuum method might be repeated several times before the cell is completely filled.

Finally the hole in the counter electrode was closed. First the rest of the electrolyte solution was carefully removed from the Surlyn[®]-foil with a tissue. Then another piece of Surlyn[®] and a roughened piece of cover glass were put on the hole in the counter electrode. Both Surlyn[®] foil and glass were pressed for 10 s at 0.8 kN and 100 °C.

remark:

It is important to keep the pressure < 0.8 kN for the hole closure. Otherwise the thin cover glass plate tends to break and the cell might leak.

5.4.4 Contacting of the cell

The cell was contacted with Scotch 3M electrical tape, which could be directly adhered on the FTO-substrate. It was possible to solder copper cables on electrical tape so in principal the contacting was a very fast and easy process. However, it was found that the conductivity of the electrical tape decreased with time and it tended to peel off the FTO-substrate. Therefore a low-viscous silver paste (Leitsilber from Hans Wolbring GmbH) was deposited on the tape and the copper wire to ensure a good electric contact for several years.

5.5 Assembly of a Nano Surface Conductivity Solar Cell

In a standard NSCSC, a suspension of carbon nanoparticles and polyacryl-coated carbon glue in propan-2-ol was spread on a sensitized TiO_2 -film by the doctor blade method. Other deposition techniques have been tested and are discussed in chapter 6.5.7.

The composition of the carbon suspension was developed empirically. Some characteristics of the suspension correlated with the quality of the resulting NSCSC, however, a general mechanism for the charge transport in the carbon layer is still missing.

1) carbon glue

The carbon glue employed in this study was “C-Leit” from Provac GmbH. It is a highly viscous paste of polyacryl-coated carbon particles, which have an average diameter of ca. $10\ \mu\text{m}$. The paste mainly contains xylene and toluene as a solvent. After the paste was applied to the substrate, the solvents evaporated at room temperature and a mechanically very stable

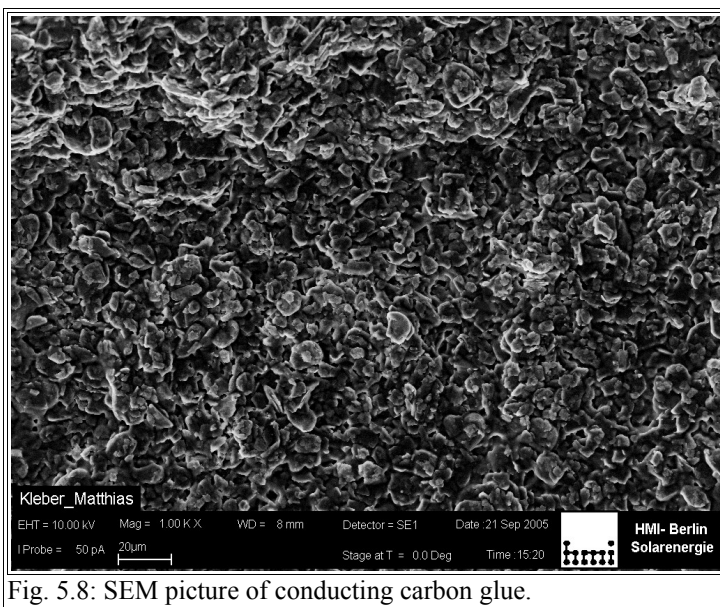


Fig. 5.8: SEM picture of conducting carbon glue.

network of interconnected carbon-flakes formed. A SEM-picture is shown in Fig. 5.8. The carbon glue adhered very well to the FTO-substrate and had a good electric conductivity. It greatly improved the mechanical stability of the layer, however the catalytic activity for the iodine reduction was found to be only modest.

2) carbon nanoparticles

In contrast to the carbon glue, the carbon nanoparticles showed an excellent catalytic activity for the reduction of iodine, why they are frequently applied as a counter electrode

material in DSSCs [156]. Furthermore they were found to enhance the electric conductivity of the carbon layer significantly, which lowered ohmic losses. In a standard NSCSC Printex XE 2 950812 (Degussa) carbon particles were employed, which had an average particle diameter of around 50 nm and a surface area of about 1100 m²/g.

3) solvent

The solvent for the suspension was propan-2-ol. It was chosen because it had a reasonable low boiling point (82 °C) and was able to suspend the carbon particles homogeneously. In more polar solvents like water or ethanol the carbon particles agglomerated.

18 mg of Printex 2 was mixed with 150 mg of carbon glue. 1 ml propan-2-ol was added and the suspension was homogenized for 1 min in an ultrasonic bath. The viscosity of the suspension was found to be determined by the amount of Printex 2, that was added. 30 µl of the suspension was dropped next to the TiO₂ film and evenly spread with a glass rod. The propan-2-ol evaporated at room temperature. Depending on the desired film thickness the deposition/evaporation steps were repeated up to four times.

Then excessive carbon paste on the glass-substrate was removed with a tissue.

Afterwards, the front electrode was kept at ca. 10⁻⁴ mbar at room temperature for 15 min to remove the rest of the volatile compounds in the carbon layer.

Then ca. 10 µl of the electrolyte solution with the composition given in table 5.5 was spread on the TiO₂ with a pipette. Ethanol proved to be the best solvent for this purpose because it had a sufficient solubility for LiI and could penetrate the carbon layer without effecting its mechanical stability. Other solvents could either not penetrate the carbon layer at all or they peeled off the carbon-layer from the TiO₂-film.

Again the film was kept at ca. 10⁻⁴ mbar for 30 min to remove volatile compounds from the layer.

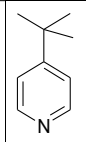
name	formula	molar mass [g/mol]	mass [mg]	concentration [mol/l]	volume [ml]	deposition amount [μmol]	manufacturer
lithium iodide	LiI	136.84	137	1		10	Alfa
iodine	I ₂	253.8	2.53	0.01		0.1	Merck
TBP		135.2	13.5	0.1	0.015	1	Fluka
ethanol	C ₂ H ₅ O H	40.07		0,79	1		Merck

Table 5.5: composition of the standard electrolyte solution for NSCSC

Finally a FTO-coated glass was pressed on top of the front electrode with the help of two clamps. For long term stability test epoxy resin was used to fix the electrodes and keep a constant distance between front- and counter electrode.

The contacting was done according to the procedure described in chapter 5.4.4.

A SEM-cross-section of the NSCSC is shown in Fig. 5.9 and a scheme of the cell in Fig. 5.10.

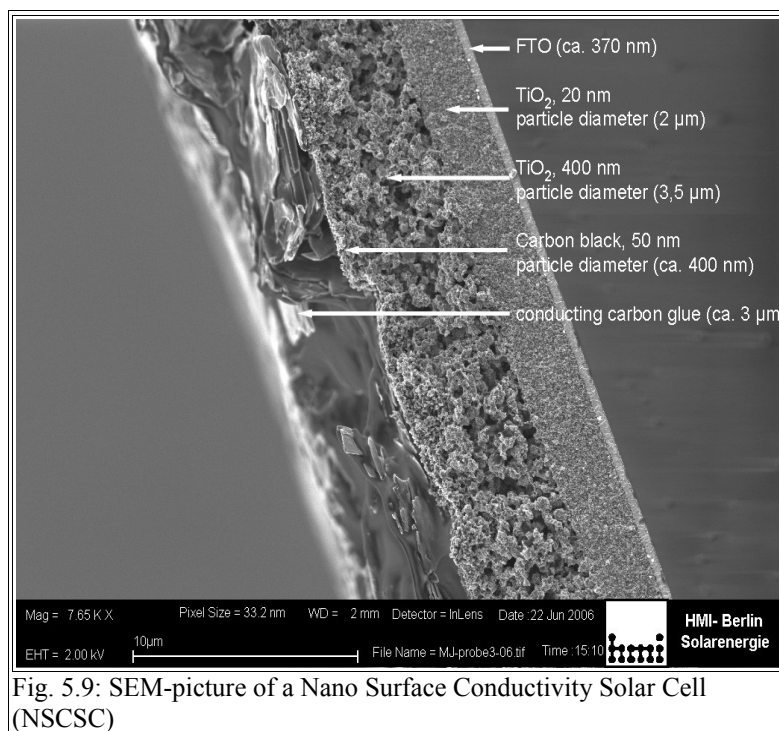


Fig. 5.9: SEM-picture of a Nano Surface Conductivity Solar Cell (NSCSC)

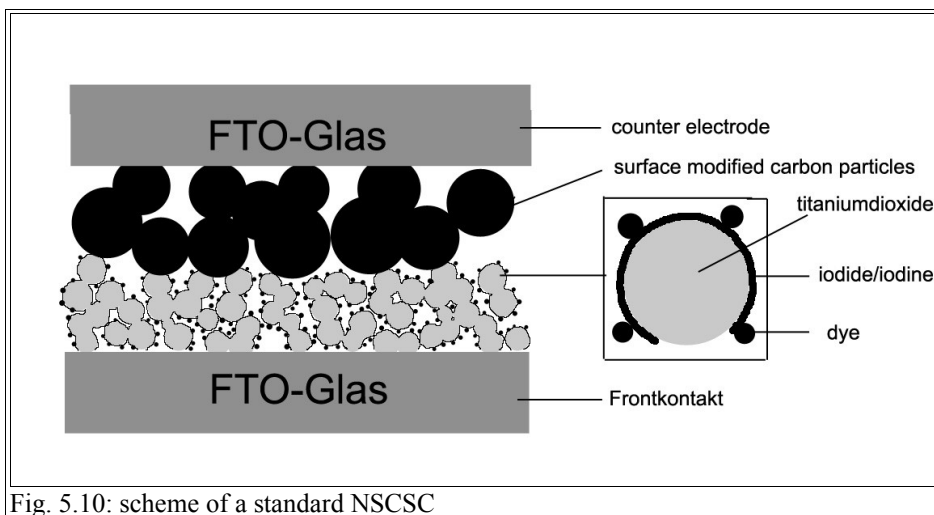


Fig. 5.10: scheme of a standard NSCSC