Nordic DSC
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Task 4: Develop nanostructures with well designed interfacial architectures

Task 5: Construct well integrated and interfaced multilayer assemblies of layered nanomaterials

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   Initial analysis of model TiO2 SP pastes with UV-treatment

   Preparation of plastic-based solar cells

2. Deposition of a photonic crystal (PC) (alternating layers of TiO2 and SiO2) by means of well-stablished printing techniques

   Ink characterization: Rheology

   Ink characterization: Spreading of SP TiO2 and SiO2 inks on glass, PET, and PEN substrates

   Production of a PC prototype by means of ink-jet printing

   Characterization of ink-jet printed single layers of SiO2 and TiO2

Task 3: Designing of barrier materials

   Plasma coatings

   ALD (Atomic Layer Deposition) coatings from Beneq

   ALD (Atomic Layer Deposition) coatings from Lotus Applied Technologoes (USA)

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Conclusions

Task 2: Designing of conductive substrate materials

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Collaboration with other national and international projects and programs

Dissemination of project results

Future outlook

Deviations from original milestone plan and rationale for deviation

Conclusions

AALTO UNIVERSITY SCHOOL OF SCIENCE AND TECHNOLOGY (AALTO)

Introduction

Experimental testing and refining of 1DPC DSC device structure

Electrical modeling ion diffusion through the porous 1DPC layer in DSCs

Optical – electrical modeling of light scattering designs for DSCs

Modeling of transparency, color and photovoltaic performance of DSCs from optical properties of the solar cell materials and components

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NORDIC DSC

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EXECUTIVE SUMMARY

On the whole, the 09053 NORDIC DSC was a success in terms reaching the tangible objectives of the project. The project had ambitious and visionary goals: Based on realistic customer needs, the project aimed at creating a new type of transparent solar cell with different colors and aesthetical appearance for future implementation in building facades. The work content consisted in developing new industrially viable nanomaterials to be used as solar cell components. The work content also included the development of new industrially viable processing methods for such materials. The end goal was the manufacturing of a flexible transparent solar cell containing a novel porous photonic crystal for increased efficiency and aesthetical colour control. As can be seen below, all the major goals and key problems in the program were addressed and resolved. Real life testing is currently being done and will be followed up during spring 2013.

Flexible cheap solar cells will be strategically important for integration both in consumer electronics products and building integration. The commercial value of this project is high as it proves the novel concept can be realized and it will spur future productification and commercialization of transparent DSC.

Below is a condensed list of highlights created during the course of the project, followed by the reports from each participant in the 09053_NORDIC DSC.

Highlights

- Commercial future was proven based on the final results

- A prototype consisting of a 9 cm x 8.5 cm large, flexible and transparent DSC with photonic crystal was manufactured using industrially viable methods. The device was based on a state of the art type of flexible, transparent and conductive glass substrate.

- Inks for industrial screen printing of photonic crystals were created. The inks were screen printed resulting in reproducible photonic crystals with well defined optical properties.

- Creation of a simulation model that accurately predicts the subjectively perceived transmitted or reflected visual colour of DSC’s with photonic crystals while it simultaneously predicts the conversion efficiency of such devices. In short, this means that designers and building architects in the future, in principle, can use a fully computerized software tool for designing aesthetically appealing DSC-photonic crystal covered building facades that also generate high electrical power.

- 4 new industrially screen printable high performance seals were introduced and tested.

- Nanoparticle dispersions for ink-jetting photonic crystals were created. Inkjetting tests were performed with promising results. Well defined single layers were obtained.
More than 20 different flexible plastic barrier materials were tested and evaluated for the permeability of water vapour.

2 novel low temperature methods of depositing TiO2 on conducting plastic were developed and tested. Efficiencies between 0.3% and 1.5% were obtained.

Interesting features of conductive coatings of graphite/graphene have been observed.

10 scientific publications including 1 master thesis were generated during this project.

Recommendations

**NLAB Solar**
Continue to develop the industrial methods for producing the materials even cheaper
Develop new current collectors optimized for the new seals developed by Danish Technological Institute (DTI)

**Danish Technological Institute (DTI)**
Increase printability of new seals
Optimize particle distribution and morphology of seals

**Aalto School of Science**
Further optimize the theoretical models into a complete software enabling Scheiwiller & Svensson (SSARK) and NLAB Solar to foresee the efficiency correlated to the visual appearance of the solar cell.

**Consejo Superior de Investigaciones Científicas (CSIC)**
Increase control over selected band gap reflection and electrolyte diffusion by improved monodispersity of nanoparticles and interparticle porosity.

**Fasadglas and Scheiwiller & Svensson (SSARK)**
Future work should be oriented towards deeper market analysis and insights. Coordinated with input from construction companies and real estate developers.
Introduction

NLAB Solar was the project owner of 09053 NORDIC DSC with partial responsibilities in WP1, main responsibilities in WP3, partial responsibilities in WP5 and partial responsibilities in WP6. However, NLAB also contributed significantly to WP2, as will be shown below.

WP1 - Roadmap

DTI was the leader of WP1 and NLAB Solar was partially responsible of performing tasks in WP1 together with DTI, SSARK and Fasadglas.

WP1 aimed at producing a “realistic description of the functional and aesthetic performance of the target product, and a roadmap describing possible development routes towards the target”. The leader of WP1 was DTI with its experience in multicolour facades and solar cells with various light transparency levels in different building architectures. However, the DTI project leader quitted the position at DTI in the beginning of the NORDIC DSC project and the core competence needed to fulfill WP1 was thereby lost. Accordingly, WP1 was simplified and DTI was reassigned to coasssist NLAB Solar in WP3/task 3 in designing and testing liquid and vapour barrier layers for DSC devices.

In spite of the competence loss in the NORDIC DSC program, WP1 was nevertheless partially fulfilled through prestudies of possible DSC patterns from both an a strict architectural view and also from a construction point of view in a collaboration between SSARK, Fasadglas and NLAB. This resulted in bench marking of existing solar panel systems and bench marking of world-wide architecture concerning the artistic expression of solar panels, and, finally in a full-scale mock-up of DSC solar panels for the ”100 house”-exhibition for a sustainable society. Additionally SSARK performed an internal project study on the commercial possibilities for using solar panels in buildings from a technical- and energy producing point of view.

WP2 – Designed nanomaterials

NLAB was not assigned to any of the tasks in WP2. However, NLAB made significant contributions to WP2 that, in a late stage, became crucial to a successful practical outcome in terms of a real working device in the NORDIC DSC project, as shown below.

Regarding task 2 and task 3 in WP2, NLAB inquired and sourced a new type of high temperature resistant, transparent, flexible conducting glass substrate with superior barrier properties. Based on this new glass substrate NLAB was able to build large area transparent flexible DSC solar cells with built in photonic crystals and test these solar cells. By using the
new type of glass substrate several of the crucial difficulties in the NORDIC DSC project could be resolved in an simple way. Key NORDIC DSC problems such as:

- Creating barrier materials capable of completely blocking the DSC outleakage of electrolyte and inleakage of water
- Creating a low temperature processable TiO2 ink compatible with heat sensitive plastic
- Creating a low temperature Pt ink compatible with heat sensitive plastic
- Creating new conducting layers to replace the expensive and scarce ITO covered plastic

could thereby be eliminated since the TiO2 and Pt inks could now be processed at high temperatures (up to 500°C) and the expensive and scarce ITO layer on plastic was replaced by the cheap and abundant FTO layer on glass. Finally, the barrier of flexible glass is several orders of magnitude better than the best of the state of the art plastic based barrier materials existing today.

As a direct consequence of using the new flexible conductive glass substrate, we were able to manufacture 8.5 cm x 9 cm DSC cells with photonic crystals, see fig. 1 and fig. 2.

As can be seen from fig. 1 and fig. 2, the DSC-photonic crystal device is transparent. It can also be seen that the visually percieved colour on the front side differs from the percieved colour on the back side. The assymetrical visual appearance is a typical feature of DSC’s with photonic crystals. The colour asssymetry feature is used to enhance the aesthetic quality and to boost the efficiency of the DSC device.
Figure 3 shows that the measured absorbance of a dyed TiO2 with a photonic crystal is much larger compared to the reference without a photonic crystal. This is expected since the photonic crystal reflects light back into the dyed TiO2 layer thereby enhancing the light absorption.

Figure 4 shows that the DSC containing an photonic crystal exhibits the largest IPCE values compared to the reference without PC, confirming that the photonic crystal not only enhances the light absorption in the TiO2 (as observed in fig. 3) but it also increases the obtained current from the real working DSC device. Illuminating the PC- electrode and the reference electrode from the opposite side again confirms that the PC strongly reflects light since the opposite trend is observed, i.e., the current from the DSC with a photonic crystal is lowered compared to the reference, when being illuminated from the wrong side (the side opposite to the intended sun light side).
Figure 4 displays the IV-curve between a DSC with a photonic crystal and without a photonic crystal. Both the current, the voltage, the efficiency and power output are higher for the DSC containing a photonic crystal. This is mainly due to larger current current obtained because of the effect of the photonic crystal.

Figure 5 shows the conversion efficiencies of a DSC with a photonic crystal as a function of light intensity. The maximum efficiency is obtained at low light intensity levels. This is because of the large resistive losses of the transparent conductive flexible substrate; to minimize the resistive losses in these types of glasses with resistivities of 8 ohm/sq., normally a maximum distance the current should travel, is around 8-10 mm. However, our large area device has a maximum current travel distance of about 8-9 cm and therefore large resistive losses are obtained, resulting in a shift of the maximum efficiency towards low light levels.

![Figure 6. Fill factor of a 8.5 x 9 cm transparent DSC with a photonic crystal on flexible conductive glass as a function of light intensity.](image)

Figure 6. The variation in fill factor with light intensity confirms that the resistive losses in the conductive glass are dominant. In order to increase the maximum energy output at higher light intensities current collectors must be introduced in the flexible conducting glass.

Apart from introducing the new flexible conductive glass to WP2, NLAB also inquired and sourced the nanoscale building blocks and also the organic solvents and organic binders that were used in task 1, task 4 and task 5. NLAB also developed the experimental procedure in obtaining stable, non-agglomerating nanoparticle dispersions required for producing the various layers in task 1, task 4 and task 5. NLAB also inquired and sourced several of the barrier substrates that were tested in task 3.
WP3 – Multilayer construction

NLAB was mainly responsible for WP3.

Task 1: Test and refine commercial processing methods for building multilayers

Nanoparticle dispersions

- NLAB succeeded in creating screen printable non-agglomerating nanoparticle dispersions for manufacturing photonic crystal multilayers. The nanoparticle dispersions were produced using standard large batch equipment and can thus be manufactured on an industrial scale, see fig. 7.

Flash sintering

- By using a flash sintering (see figure 8) procedure the photonic crystal layers could be sintered in a few seconds on plastic substrates instead of being sintered at 400°C for tens of minutes on glass.
- The TiO2 film could also be flash sintered in a few seconds on plastic substrates.
instead of being sintered at 500°C for 30 minutes on glass substrates. However, the efficiency of such TiO2 films were maximum around 1.5%. Although 1.5% efficiency using flash sintering during a few seconds is much higher than 0.3% efficiency using 24 hour UV irradiation (see WP2/YKI), 1.5% is still not sufficient.

• The Pt layer could also be flash sintered in a few seconds on plastic substrates instead of being sintered at 400°C for ten minutes on glass. However, these Pt films showed insufficient catalytic activity for high efficiency DSC’s.

**Spin coating**

• CSIC, developed a protocol for manufacturing large area spin coated photonic crystals on NLAB’s produced TiO2 layers. The combination of these two layers was used to manufacture the DSC-photonic crystal devices described in fig. 1 – fig. 6 above.

![Flash sintering system](image)

Figure 8. Flash sintering system capable of producing up to 2000W of UV-VIS light in 1 millisecond on a 30 cm x 2 cm area. The combination of high energy input on a short time scale allows for extremely fast temperature up- and down ramping which makes it possible to sinter metals and ceramics on temperature sensitive substrates such as cellulose based paper and plastic without significantly damaging the substrate.
Task 2: To develop and test coating methods for the photonic multilayer assembly, including ink jet printing, spray processing, screen printing and dip coating

**Screen printing**

- NLAB succeeded in developing a screen printing method for cheap and fast large scale manufacturing photonic crystals. The manufactured photonic crystals were tested and characterized with very promising results.
- Screen printing is fully industrially scalable and can be applied selectively to create fine detailed patterns on very large areas (up to several square meters).
- The size of the manufactured PC’s was around 8 cm x 8 cm.
- The maximum optical reflectance of the PC was around 35%.

![9 layer sample](image)

Figure 9. SEM pictures of cross-sections at different magnifications of a screen printed porous photonic crystal consisting of a multilayer of nine alternating porous layers of TiO2 and SiO2.

As shown in fig 9, it was possible to screen print a very well-defined multilayer structure consisting of 9 alternating layers of TiO2 and SiO2. The porosity of the individual layer is observable.
As shown in fig. 10, it was possible to screen print several photonic crystals with respectable variation in optical reflectance, i.e., +/- 4%. The best sample had a reflectance of around 35%.

**Task 3: Design and test liquid and vapour barriers for sealing various electrolytes in devices, with a particular focus on barrier methods developed in commercial packaging industries**

NLAB developed a proprietary screen printable polymeric sealing material with very high water barrier properties.

- Chemically resistant to standard DSC electrolytes.
- 0.5% water absorption
- Sufficient adhesive strength in combination with secondary seal in a temperature range between -40°C to 80°C
- Screen printable
- Excellent water barrier
- Can be printed in very thin layers for maximum energy conversion efficiency

NLAB also sourced, acquired and tested a novel commercial screen printable UV-light curing sealing material.

- Chemically resistant to standard DSC electrolytes including the harsh acetonitrile based.
- <3% water absorption
- <25% loss in adhesive strength after 1000 hours at 85°C/85%RH
- Screen printable
- Excellent water and organic solvent barrier
- Can be printed in very thin layers for maximum energy conversion efficiency

Figure 10. Optical reflectance of 4 different samples of screen printed porous photonic crystals each consisting of a multilayer of nine alternating porous layers of TiO2 and SiO2.
**WP5 – System integration**

NLAB was partially responsible for WP5

During the course and until the last end of the project it was very difficult to manufacture flexible, transparent plastic based DSC solar cells with respectable efficiency. The main root cause for this is mentioned above: It is very difficult to create a high efficiency TiO2 film on plastic at low temperatures and our top efficiency results were only 1.5% and 0.3% for flash sintering and UV treatment, respectively. The market announcement of the forthcoming market introduction of conducting transparent flexible glass substrate came very late (December 2011) and we have had very little time to source and acquire such samples and outsource laser cutting and laser hole drilling to able to perform tests on such substrates at all. However, during the second half of the year 2012 we have devoted hard work on finalizing the WP 2 and WP3 in the NORDIC DSC based on such conductive flexible glass samples.

**Task 1: Combine PV devices into a system suitable for pilot testing in the lab**

**Task 2: Overall balancing of system efficiency based on device efficiency, design, and utility**

**Task 3: Testing of pilot system in real environmental conditions including testing of physical and chemical stability of system including examination of nanomaterials for physical and chemical stability**

WP5 was dependent on WP2 and WP3 which were accomplished late in the project and was not initiated because of lack of time. We know however that the life time of a DSC using glass as a barrier is expected to be long and exceeding ten years.

**WP6 – Demonstration facility**

NLAB Solar was partially responsible for WP6

**Task 1: Define considerations of scaling up**

The new commercially available flexible transparent conductive glass substrate allows us to define a realistic industrially viable scaling up procedure:

- The flexible glass comes in rolls which makes it possible to apply a continuous process for maximum speed and reproducibility in the DSC manufacturing. On the other hand it is well known that the critical continuous process conditions are best studied and elaborated by first performing tests in a batch type pilot line process. Therefore in the first stage the first construction should be a batch based pilot line aiming at building a continuous process in the second stage.
- The glass is thin and mechanically fragile and must be handled with care and precision
to avoid cracking. Standard vacuum suction cups above the substrate are used to move the substrate from one process station to another. Vacuum tables below the substrate are used to keep the substrate registered in place at each process station.

- The thin flexible glass has unique properties in that it can be subjected to thermal shock locally without cracking (which is not the case for the standard 3mm - 4mm glass that has been used during the last 20 years of DSC development). Consequently the thin glass opens up the possibility to seal the edges of the DSC devices by a laser instead of using organic thermal- or UV adhesives. Such a laser sealed glass-to-glass seal should theoretically prevent the water in-leakage and DSC component out-leakage completely and permanently and have a profound effect on the DSC the stability and DSC life time. Sourcing and testing suitable laser sealing equipment should therefore have very high priority.

- Standard process steps developed since the start of DSC in the such as screen printing, sintering at high temperature, dying, TiCl4 treatment etc, could be performed in the conventional type batch processes, however, with the advantage that the glass substrate is very thin and therefore a larger number of substrates (a larger area) can be processed in one batch compared to the conventional thick glass substrates.

- Due to the fragile nature of thin glass it is necessary to reinforce the DSC devices mechanically. This is easiest done by covering the front and back side with a polymer, preferably by lamination techniques. In conjunction with the lamination, it could be advantageous to co-laminate a glass sheet in the front on top of the polymer coated device to provide a tough weather resistant top surface and to co-laminate a stiff sheet on the back of the solar cell for providing mechanical joints and fixtures for the application of junction boxes and for integration of multiple solar panels. A laboratory lamination equipment capable of laminating A4 size DSC’s was developed during the project.

- Material suppliers for chemicals and flexible glass substrates have been identified and bulk price quotations have been acquired.

- Pilot production processing equipment for ink manufacturing, screen printing and sintering and DSC sealing have been identified and quotations have been acquired.

**Task 2: Testing and measuring at demonstration scale**

NLAB has just recently built the first large area demonstrator DSC’s with photonic crystals on the new flexible conductive glass. Thus the testing and measuring at demonstration scale has not been initiated yet.

**Task 3: Publish articles**

During the course of the NORDIC DSC project NLAB has published 2 articles in high impact journals.

- **Colonna, Daniele; Colodrero, Silvia; Lindstrom, Henrik; et al.**  
  *ENERGY & ENVIRONMENTAL SCIENCE* Volume: 5 Issue: 8 Pages: 8238-8243  
  Impact factor 9.6 (2012),  
  *ENERGY & ENVIRONMENTAL SCIENCE* is the #1 journal in its ISI cathegory.

- **Lopez-Lopez, Carmen; Colodrero, Silvia; Raga, Sonia R.; et al.**  
  *JOURNAL OF MATERIALS CHEMISTRY* Volume: 22 Issue: 5 Pages: 1751-1757  
  Impact factor 6.0 (2012)
Task 4: Define manufacturing methods
A detailed specification of the manufacturing methods including the newly found flexible conductive glass has not been initiated yet because of lack of time.

Dissemination of project results
During the course of the NORDIC DSC project NLAB has published 2 articles in high impact journals.

- Colonna, Daniele; Colodrero, Silvia; Lindstrom, Henrik; et al. ENERGY & ENVIRONMENTAL SCIENCE Volume: 5 Issue: 8 Pages: 8238-8243
- Lopez-Lopez, Carmen; Colodrero, Silvia; Raga, Sonia R.; et al. JOURNAL OF MATERIALS CHEMISTRY Volume: 22 Issue: 5 Pages: 1751-1757

Future outlook
The work on flexible glass is the foundation for a future arena for NLAB Solar. Machines and equipment for processing this new type of glass will be tested, acquired and installed. Demonstrated pilot production of flexible transparent DSC with photonic crystals is scheduled to the end of 2013.

Deviations from original milestone plan and rationale for deviation
The intended output from WP1 was the basic foundation and input for all other WP’s. WP1 was designed to feed in DTI’s, at that time, existing basic input and basic market driven boundary conditions to all other WP’s. However, due to the initial competency loss in WP1, the realistic frame work and realistic boundary conditions for all other WP’s were also lost. Accordingly, WP1 was modified: DTI with its vast experience on polymers was redirected to work in WP3 and coassist NLAB in the development of a printable polymer seal, -one of the crucial key areas in the NORDIC DSC project.

Furthermore, the during almost the whole NORDIC DSC project, the results from WP2 to WP3 were not sufficient to be able to actually build a large area working device consisting flexible plastic based DSC’s with photonic crystals. The main reason was simply that plastic cannot be subjected to high heat and that the results from the development of low temperature materials and low temperature processes were simply not sufficiently adquate. The market introduction of flexible transparent conductive glass (solving the temperature and barrier problems) came close to the end of the NORDIC DSC project and accordingly a few tasks have not been performed because of lack of time: WP5 was not performed and Task 2 and Task 4 in WP6 were not performed.

Conclusions
NLAB Solars work in WP2 and WP3 succeeded to meet the tangible objective of the NORDIC DSC project: A real large area working device consisting of a transparent DSC solar cell with an incorporated photonic crystal.

The work on conducting flexible glass substrates will greatly impact the future of NLAB Solar’s production of transparent solar cells with photonic crystals.
YKI, YTKEMISKA INSTITUTET

Technical results related to the national and transnational project descriptions

Summary

During the project YKI have had the responsibility to lead activities within WP2, a work package which targets different aspects of the design and integration of nanomaterials into new types of DSC. Specifically, YKI’s research efforts have been focused on:

1. the formulation of non-agglomerating nanoparticle dispersions (“inks) required for the various layers in the DSC and their deposition by means of well-established printing technologies
2. the improvement of moisture and oxygen barrier properties of the carrier films in the DSC structure (poly(ethylene terphthalate) (PET) and poly(ethylene naphthalate) (PEN) and on
3. the designing of new conductive materials.

The work carried out within the first of these aspects represent an important step towards the large-scale production of the DSCs in question while the research performed on improving barrier properties has a direct bearing on the overall lifetime of the DSC devices to be produced.

On the formulation front, ink formulations that target the deposition of transparent DSC onto flexible substrates (no calcination steps required) were investigated. Formulations making use of UV radiation to induce degradation of organic materials incorporated in the DSC deposited layers (ink additives) were developed. The concept has been tested in lab-scale prototypes of plastic and glass-based solar cells, where despite the relatively low efficiencies obtained, the concept proved to have potential. Additionally, in collaboration with the ink-jet printing company Ceradrop, several attempts were made to deposit multilayered structures of SiO2 and TiO2 particles fulfilling the requirements (approximate thickness, smoothness, homogeneity) of those that are required for the preparation of a photonic crystal (PC). Although only partially successful, these attempts provided information about key formulation strategies that will guarantee a successful outcome in future work to be carried out outside the framework of this project.

For the barrier materials development we can draw the following conclusions so far:

• The new, thinner ALD coatings have a significantly improved barrier performance
• Protective layer on top of the ALD coatings improves the performance further
• ITO + ALD layers are a very powerful combination. Results often below detection limit of the instruments
• The commercial films from 3M and Kimoto are good but not as good as the ALD-coated films
• The organic poly(oxetane) coatings look promising.
Furthermore, interesting features of conductive coatings of graphite/graphene have been observed using the AFM Peak Force TUNA instrument at YKI.

WP2 - Designed nanomaterials

Task 1: Develop and characterize basic nanoscale building blocks..., 

Task 4: Develop nanostructures with well designed interfacial architectures..., 

Task 5: Construct well integrated and interfaced multilayer assemblies of layered nanomaterials....

During the project YKI have had the responsibility to lead activities within WP2, a work package which targets different aspects of the design and integration of nanomaterials into new types of DSC. YKI’s research efforts within WP2 are focused on the formulation of non-agglomerating nanoparticle dispersions required for the various layers in the DSC (Task 1) as well as on the methods used for the deposition of these dispersions to form multilayered structures with well-defined interfacial architectures (Tasks 4 and 5). The ambition of a large scale production makes the use of different well-established printing technologies a very attractive alternative for the deposition of the very thin layers that make up the DSC device. Thus, the production of printable nanoparticle formulations (“inks”) has become the specific target of YKI’s formulation work. On this front, the work has been divided into the two parts described below:

1. Formulation of a screen printable, transparent TiO2 layer that does not require elimination of organic materials by calcination.

One very specific objective of the project as a whole is the fabrication of transparent DSCs deposited on flexible (plastic) substrates. The requirement of using a plastic substrate precludes the use of high-temperature calcination. Calcination of the TiO2-layer improves the performance of the transparent solar cell by sintering of the TiO2 network and allows the removal of the organic additive. Organic additives are commonly added to the nanoparticle dispersions as viscosity modifiers, which aids the printing process and also have a positive effect on the homogeneity of the printed layer. Furthermore, the removal of the organic additive creates a high porosity in the TiO2 layer, which is beneficial for a high amount of dye adsorption.

The elimination of all organic materials (typically polymeric additives) from the TiO2 without the use of a calcination process is not a trivial task. For this purpose, several options were under consideration. In the project it was decided to explore the use of UV treatment for the TiO2 photocatalyzed decomposition of the polymer additive in a TiO2 screen printing (SP) ink. UV/O3 treatment 1 and long wave UV treatment 2 has previously shown to be promising methods for removal of the organic binder within DSC applications. Initial analysis of model TiO2 screen printing pastes indicated that UV treatment could successfully decompose the

polymer additive in the pastes. It was thus decided, based on these promising results, to test the performance of the pastes in plastic solar cell prototypes.

Initial analysis of model TiO2 SP pastes with UV-treatment

TiO2 pastes were formulated using commercially available TiO2 nanoparticles (7.5 wt%), ethyl cellulose (3 wt%) as the organic binder and terpineol as the solvent. The TiO2 paste was coated on glass slides and ITO coated PET and PEN substrates with a film coater (120 µm wet film thickness). After film deposition, the films were dried at 120°C for 30 min. The resulting dry film thicknesses were determined with a profilometer (Dektak, Veeco). In order to decompose the ethyl cellulose, the films were irradiated with short wave UV light ($\lambda=254$ nm) for time frames ranging between 2 and 17 hours. After the UV treatment, some of the films were further heat treated at 130°C for 30 min. The UV treated and untreated reference samples were characterized with ATR-IR, TGA, and by visual observation during calcination on a heating plate. The stability of the coated layers was evaluated by rinsing with a series of common solvents used in DSC fabrication.

The dry film thickness of the coated TiO2 layers was determined to 4-5 µm. The thickness of the UV-treated films was generally slightly lower, indicating that ethyl cellulose is decomposed during UV irradiation.

Attenuated Total Reflectance Infrared (ATR-IR) spectra for a series of TiO2 coatings on glass slides are given in Figure 1. The characteristic peaks originating from ethyl cellulose are observed for the untreated film, and films irradiated for 2h and 4h with short wave UV light, respectively. However, for the film that was irradiated for 17h a significant decrease in the signal originating from ethyl cellulose can be observed.

![Figure 1. ATR-IR spectra for a series of TiO2 coatings.](image-url)
In order to study the degree of remaining organics in the UV treated TiO$_2$ coatings, a series of films were heated on a hot plate. During heating, the coatings turn brownish due to the decomposition of the ethyl cellulose. However, the films that were UV-treated for 17h (the two most to the right) become transparent faster than the other films, which indicates that the amount of ethyl cellulose left in the films is less. However, 17h of UV treatment does not seem to decompose all of the organic binder.
The stability of the coated TiO$_2$ layers was evaluated by rinsing with common solvents used in DSC fabrication. On glass slides, the TiO$_2$ layer could be removed by rinsing with ethanol and acetone. However, on ITO-PET and ITO-PEN the coating could resist rinsing with ethanol, acetone, acetonitrile, tert-butyl alcohol, and electrolyte solution.

**Preparation of plastic-based solar cells:**

In collaboration with NLAB Solar, plastic solar cells have been prepared based on our TiO$_2$ paste and UV-degradation method. The efficiency of these cells has been compared with standard cells prepared on conductive glass and where the organic binder is removed by calcination.

TiO$_2$ pastes were formulated using commercially available TiO$_2$ nanoparticles (7.5 wt%), ethyl cellulose (3 wt%) as the organic binder and terpineol as the solvent. The TiO$_2$ paste was screen printed on FTO-coated glass slides (resistance 10 Ohm/sq) and ITO-coated PEN substrates (resistance 15 Ohm/sq) with a 36 mesh screen with an area of 0.16 cm$^2$. After printing, the films were dried at 150°C for 30 min. In order to decompose the ethyl cellulose, the films were irradiated with short wave UV light ($\lambda$=254 nm) for 24 hours. Reference cells
on glass were prepared by standard sintering at 500°C. The devices were assembled according to standard procedure by NLAB Solar using N719 dye. The performance of the devices was determined with photocurrent-voltage (I-V) measurements (AM 1.5) under 1000 W/m² illuminations.

Devices on FTO-glass:
- Standard sintering: Conversion efficiency 1.6%, fill factor > 0.7, voltage > 0.7 V
- 24 hours UV irradiation: Conversion efficiency 0.3%, current < 1 mA, fill factor (< 0.6)

Devices on ITO-PET
- 24 hours UV irradiation: The film detached during dye immersion

UV irradiation of the TiO₂ layer decomposes the organic binder, but the adhesion to the substrate and the connectivity between the particles is poor when no sintering is conducted. This is seen in the low conversion efficiency and that the TiO₂ film detaches from the ITO-PEN substrate during dye immersion. However, the conversion efficiency of 1.6% for the sintered reference cell on glass is promising considering a film thickness of only 1.8 µm. It can thus be concluded that the formulated ink show promising properties.

Further research work along this track would involve pretreatment of the substrate (e.g. with TiCl₄) before printing in order to increase the adhesion of the deposited layer to the substrate. Additionally, the overall efficiency of the UV treatment could be tried to be increased by e.g. exposing the deposited layer to long wave UV radiation and/or using different exposure times.

2. Deposition of a photonic crystal (PC) (alternating layers of TiO₂ and SiO₂) by means of well-established printing techniques

Deposition of the photonic crystal (PC), a central part of the DSCs under development, had up to now been done by means of lab scale coating devices which are not well suited for large scale production. In this respect, well-established printing techniques represent an attractive option for controlled, large-scale deposition of thin layers of material. However, if a conventional printing technique is to be used for the deposition of the extremely thin layers that conform the PC, the nanoparticle dispersions need to formulated into “inks” that match the requirements of that specific printing technique. The challenge is then to achieve good printability of the dispersions while depositing a coated layer that fulfills the requirements (thickness, homogeneity and smoothness) of those needed for the preparation of a PC. In this respect, the possibility to use the screen printing technology for the deposition of a PC has already been evaluated by NLAB Solar with success. Among the other different possible printing techniques, inkjet printing represent the second most attractive alternative due to its compactness, flexibility and the clear advantages associated with the non-contact printing technology. This is the printing technology that YKI has focused their efforts on. For the sake of simplicity, it was decided to deposit the prototypes on glass, which would allow using calcination after deposition for the sintering of the layers. Initially, the rheology of the inks were characterized.

Ink characterization: Rheology

The formulation work to be carried out requires as a first step a thorough characterization of the existing DSC printing inks (commercially available and previously developed by NLAB
Solar) in terms of their rheological properties, wetting and spreading performance and colloidal stability. This work allows the identification of the target behavior and requirements that new ink formulations should fulfill. A few selected results from the rheological characterization of these inks are presented in Figures 3 and 4.

Figure 3. Flow curves for commercial TiO2 screen printing paste Solaronix (a) and TiO2 and SiO2 screen printing inks formulated for the production PC (b). Screen printing inks: TiO2 (STS-01) nanoparticles (2.7 wt%) and ethyl cellulose (1.9 wt%) dispersed in terpineol; SiO2 (Ludox CL) nanoparticles (2.6 wt%) and ethyl cellulose (2.3 wt%) dispersed in terpineol. The rheological characterization was conducted with a Bohlin rheometer using a plate-plate geometry (100 µm gap) under controlled shear stress mode.

Figure 4. Flow curve of a prototype TiO2 ink jet ink meant to be used for the production of a PC. Inkjet ink composition: TiO2 (STS-01) and SiO2 (Ludox CL) nanoparticles (2 vol%) dispersed in ethylene glycol butyl ether (EGBE). Surface tension determined with the pendant drop method: 26-27 mN/m.

The flow curve of a commercially available screen printing paste (Solaronix) is presented in Figure 3.a. The SP paste was found to be highly viscous at low shear rates, but shows a very strong shear-thinning behavior. Flow curves of the formulated SP inks are presented in Figure 3.b. The SiO2 ink appears more viscous at low shear rates while at higher shear rates both inks show similar apparent viscosity.

The flow curve for the TiO2-ink-jet printing ink is given in Figure 4. With the plate-plate geometry and a small gap distance it was possible to reach relatively high shear rates without
creating too much turbulence, which was not the case for the other measuring geometries. A moderate shear-thinning behavior was observed for the studied inkjet inks.

Ink characterization: Spreading of SP TiO2 and SiO2 inks on glass, PET, and PEN substrates

The spreading of TiO2 and SiO2 screen printing inks on glass, PET, and PEN substrates were studied by dynamic contact angle measurements using a Dataphysics OCA 40 instrument. The spreading behavior on the different substrates was very similar, suggesting that the spreading is mainly governed by viscous forces (data not shown).

The next steps to be taken as part of the formulation work include:

- Characterization of the deposited TiO2 layers (SEM, ATR-IR, confocal Raman).
- Further characterization of the formulated inkjet- and screen printing inks including determination of viscoelastic properties by means of extensional rheology and oscillation.
- Formulation of flexography inks (PC).
- Test printing of PC at different ink-jet and flexo-printing facilities (pre-agreements have been made).

Production of a PC prototype by means of ink-jet printing

This works targets the ink-jet printing of a multilayer device (up to 6-8 stacked layers) consisting of alternating layers of TiO2 and SiO2 nanoparticles as shown in the schematic below.

Ink-jet printed single layers of tailor-made inks of TiO2 and SiO2 nanoparticles formulated earlier in the project, lacked homogeneity and smoothness due to apparent de-wetting/ink migration problems taking place upon deposition of ink drops onto the glass substrate. In an attempt to overcome this problem, while introducing no changes in the current ink formulations, it was decided to modify the ink/substrate interactions by changing the properties of the printing substrates. This was done by effecting surface modifications of clean microscope slides by means of silanization reactions which would alter the surface energy and nano-scale roughness of the substrate. The properties of the conventional glass slides were thus modified by reacting them with Aminopropyl-triethoxysilane (APTES) and Octyltrichlorosilane (OTS). The surface properties of the resulted modified glass surfaces are summarized in Table 1 below.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Description</th>
<th>Ink contact</th>
<th>Water contact</th>
</tr>
</thead>
</table>

Table 1. Surface properties of the modified and unmodified glass printing substrates.
A second set of printing trials using the modified glass substrates was performed at Ceradrop (www.ceradrop.fr). The suggested printing resolution and drop volume for those trials was 309 dpi and 25 pL, respectively (estimated dry film thickness ca. 40 nm/per printing pass). Different printing strategies (filling patterns, positioning of the drops, variable printing resolution) are possible at Ceradrop printers and were tried during the trials. A number of different samples were however produced and sent to YKI for analysis:

(a) 1 printing pass of SiO$_2$ on glass  
(b) 1 printing pass of TiO$_2$ on glass  
(c) 1 printing pass of SiO$_2$ + 1 printing pass of TiO$_2$ on glass  
(d) 1 printing pass of SiO$_2$ on APTES-modified glass  
(e) 1 printing pass of SiO$_2$ on OTS-modified glass  
(f) 1 printing pass of TiO$_2$ on OTS-modified glass

Characterization of ink-jet printed single layers of SiO$_2$ and TiO$_2$

Simple visual inspection on samples printed on OTS-modified glass, the more hydrophobic surface, indicated the existence of very irregular, inhomogeneous layers, likely associated to the poor wetting and limited spreading of the inks on this substrate. Layers printed on APTES-modified glass, a substrate slightly less hydrophilic than untreated glass, appeared much more homogeneous and essentially defect-free. Thus homogeneity and thickness of such samples was further analyzed on different length scales by means of Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and profilometry. Figures 5 to 7 show the results from the microscopic analysis of such samples, where appearance of SiO$_2$ layers printed on APTES-modified glass is compared to that of SiO$_2$ and TiO$_2$ layers printed on untreated glass. Overall, microscopic analysis of layers of SiO$_2$ nanoparticles printed on APTES-modified glass confirmed the existence of a very homogeneous and smooth layer with no apparent defects. Profilometric analysis of the samples indicated that the approximate thickness of the printed layers ranged between 35 and 135 nm. Apart from inherent inaccuracies of the profilometric analysis, the actual film thickness of layers produced upon 1 printing pass may differ depending on the specific filling pattern used upon printing. Regardless, the results indicate that the thickness of the ink-jet printed layers is within the length scale required to create a PC.

AFM analysis of the printed SiO$_2$ and TiO$_2$ layers revealed that, on a nanoscale, the deposited layers of SiO$_2$ are less regular than those of TiO$_2$. This is indicated by the fact that, regardless of the substrate they are deposited on (APTES-modified or untreated glass), the roughness (RMS) of the layer is seen to decrease upon reduction of the scanned area (see RMS roughness values in Figure 6).
Overall, results presented in this section indicate that single, ink-jet printed layers of SiO$_2$ and TiO$_2$ particles, in particular when deposited on an APTES-modified glass substrate, fulfill the requirements (approximate thickness, smoothness, homogeneity) of those that are required for the preparation of a PC.
Figure 5. SEM micrographs of SiO$_2$ and/or TiO$_2$ layers printed on untreated-glass and APTES-glass.
Figure 6. AFM images (scanned areas of 50x50 µm, 10x10µm and 3x3 µm) of SiO2 and/or TiO2 layers printed on untreated-glass and APTES. The root mean square (RMS) value of the roughness is indicated at the bottom of each image.

Estimated thickness:

<table>
<thead>
<tr>
<th>Layer</th>
<th>Estimated Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2 on glass</td>
<td>≈ 35 nm</td>
</tr>
<tr>
<td>SiO2 on glass</td>
<td>≈ 75 nm</td>
</tr>
<tr>
<td>SiO2 on APTES</td>
<td>≈ 151 nm</td>
</tr>
</tbody>
</table>

Figure 7. Profilometry images of SiO2 and/or TiO2 layers printed on untreated-glass and APTES-glass. The estimated thickness of the layers (based on analysis of the profilometry images) is presented at the bottom of the images.

A final set of printing trials at Ceradrop was scheduled for the first quarter of 2012 for the production of the targeted multilayer structure (with the current ink formulations and APTES-modified glass as the printing substrate).
To increase the chances of success, both YKI and NLAB Solar project partners were present at the Ceradrop facilities (Limoges, France) for this trial. A new set of TiO₂ and SiO₂ inks and modified glass substrates was sent to Ceradrop a few weeks before the trials for preliminary optimization of the printing parameters (jetting, filling patterns and drying conditions) by Ceradrop.

Optimization work performed at Ceradrop before the trials, revealed that although the new set of inks exhibited the same bulk properties and jetting behavior as earlier batches, the wetting and spreading of the inks onto the modified glass substrate was not as good. This resulted in the production of rather in homogeneous single printed layers of TiO₂ and SiO₂.

The spreading problems of the inks are related to a tendency to accumulate at the center of the printed area once printed (opposite phenomena to the well-known “coffee stain” effect). This behavior is very atypical for water based inks, and it is believed to be associated with the low vapour pressures of the solvents used in the current inks (Tb between 188 and 230°C).

Despite the relative inhomogeneity of the printed single layers, attempts were made to construct a multilayer structure consisting of 4 alternating layers of TiO₂ and SiO₂. During the deposition of each layer, the printed substrate was subjected to up to 10 flashes of IR radiation and oven drying at 200°C for ca. 2 min in order to get the printed later to dry. The overall resulting multilayer structure was inhomogeneous, with defects and craters visible to the naked eye. Clearly, even the extensive exposure to heat sources was not able to allow for a homogeneous and uniform drying of the deposited layers. Further, the printed multilayer structure did not exhibit any of the characteristic features of a photonic crystal (PC).

The unsuccessful results from this third and final printing trial indicated that the use of water-based inks instead of solvent-based inks would increase the chances for success with the ink-jet printing approach. The use of water-based inks was ruled out by NLAB Solar at the beginning of the project based on misleading indications from an ink-jet print head producer. Changing to water based inks not only would eliminate the drying problem but also would greatly simplify the formulation of the inks as it would eliminate the need for a solvent exchange process. As a consequence of this, all involved project partners are interested in continuing this work outside the framework of this project.

**Task 3: Designing of barrier materials**

YKI’s work within WP2, task 2.3, on improvement of moisture and oxygen barrier properties of the carrier films in the DSC structure, poly(ethylene terphthalate) (PET) and poly(ethylene naphthalate) (PEN) has consisted of the following parts:

1. Plasma coatings
2. ALD (Atomic Layer Deposition) coatings from Beneq
3. ALD (Atomic Layer Deposition) coatings from Lotus Applied Technologoes (USA)
4. Evaluation of commercial barrier films from 3M and Kimoto
5. Development of a transparent organic coating aimed for multilayer barrier structures
**Plasma coatings**

YKI has used a plasma process for deposition of ultrathin, glass-like SiOx layers on PET surfaces. However, even though some optimization of the process has been carried out the barrier properties of these coatings are not satisfactory. The results obtained are summarized in Table 2. These values are unfortunately still far away from the targets.

### Table 2: Results from plasma deposition trials on 12 µm PET film substrates with respect to oxygen transmission rate (OTR), oxygen Barrier Improvement Factor (O2-BIF), water vapor transmission rate (WVTR) and water vapor Barrier Improvement Factor (WV-BIF),

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate thickness (µm)</th>
<th>OTR (cm³/m²·day)</th>
<th>O₂-BIF</th>
<th>WVTR (g/m²·day)</th>
<th>WV-BIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET, Ref</td>
<td>12</td>
<td>91.0</td>
<td>1.0</td>
<td>9.4</td>
<td>1.0</td>
</tr>
<tr>
<td>PET-SiOx – 70 W</td>
<td>12</td>
<td>40.0</td>
<td>2.3</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PET-SiOx – 100 W</td>
<td>12</td>
<td>27.3</td>
<td>3.3</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PET-SiOx – 140 W</td>
<td>12</td>
<td>2.7</td>
<td>33.7</td>
<td>10.6</td>
<td>0.9</td>
</tr>
<tr>
<td>PET-HMDSO, 30 W + SiOx 140 W</td>
<td>12</td>
<td>---</td>
<td>---</td>
<td>8.6</td>
<td>1.1</td>
</tr>
<tr>
<td>HMDSO, 100 W + SiOx 150 W</td>
<td>12</td>
<td>3.1</td>
<td>29.4</td>
<td>3.8</td>
<td>2.5</td>
</tr>
<tr>
<td>HMDSO/SiOx 100 W+150 W-multilayer</td>
<td>12</td>
<td>15.2</td>
<td>6.0</td>
<td>3.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

**ALD (Atomic Layer Deposition) coatings from Beneq**

Coatings from two different ALD producing companies have been evaluated: Beneq Oy in Finland and Lotus Applied Technologies in USA.

The principle of ALD is based on sequential pulsing of chemical precursor vapors, forming one atomic layer during each pulse sequence. This generates pinhole free coatings that are extremely uniform in thickness. Beneq’s nCLEAR inorganic barrier films are based on proprietary nanolaminates, deposited with the ALD technique. Two types of ALD coatings have been tested; OLD and NEW. The main difference between the NEW ALD coatings deposited on PET and ITO-coated PET films and the OLD coatings, is that it is only made of Al₂O₃ and the thickness is only approximately 30 nm. The OLD coating was a multilaminate composed of alternating Al₂O₃ and TiO₂ layers, with a total thickness of approx. 100 nm.

The surface chemical composition of a typical OLD ALD coating on PET and PEN substrates has been determined by XPS (X-ray Photoelectron Spectroscopy). The results from the XPS analyses are shown in Tables 3 and 4 as well as Figure 8.
Table 3: Relative surface composition of OLD ALD coatings in atomic %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
<th>N</th>
<th>Al</th>
<th>Si</th>
<th>Cl</th>
<th>Ti/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLD ALD on PET (as received)</td>
<td>14.2</td>
<td>55.6</td>
<td>22.8</td>
<td>0.3</td>
<td>5.4</td>
<td>0.6</td>
<td>1.0</td>
<td>4.2</td>
</tr>
<tr>
<td>OLD ALD on PET (after Ar sputtering)</td>
<td>0.9</td>
<td>59.2</td>
<td>12.2</td>
<td>0.7</td>
<td>23.1</td>
<td>0</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>OLD ALD on PEN</td>
<td>20.5</td>
<td>51.3</td>
<td>21.6</td>
<td>0.3</td>
<td>5.2</td>
<td>0.2</td>
<td>0.9</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Ar sputtering: 1 min 500 V (training) + 30 sec 4 kV general + 30 sec 4 kV general

Table 4: Chemical shifts in high-resolution carbon (C1s) spectra of the OLD ALD coatings Value from curve fitting of different carbon peaks with total amount of carbon = 100 %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>285.0 eV</td>
<td>286.5-6 eV</td>
<td>287.7-9 eV</td>
<td>289.2-6 eV</td>
</tr>
<tr>
<td>OLD ALD on PET (as received)</td>
<td>74.5</td>
<td>14.7</td>
<td>---</td>
<td>10.8</td>
</tr>
<tr>
<td>OLD ALD on PEN</td>
<td>80.9</td>
<td>10.8</td>
<td>---</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Figure 8: C1s peaks of a typical OLD ALD coating. Left: on PET substrate; Right: on PEN substrate.

The XPS result shows the OLD ALD layer consists of two different sublayers, Al₂O₃ and TiO₂ in a multilayer structure, with the latter on top. Ar sputtering in the XPS instrument exposes the underlying Al₂O₃ layer. The C 1s high resolution spectra are very similar to those of the bare PET and PEN substrates.

The oxygen and water vapor barrier results obtained are presented in Tables below. The OTR results of ALD- and ITO-(Indium Tin Oxide)-coated PET films are shown in Table 5.
Table 5: Results from oxygen transmission rate (OTR) measurements of OLD ALD-coated PET films, with oxygen Barrier Improvement Factor (O2-BIF) and normalized OTR data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate thickness (µm)</th>
<th>OTR (cm³/m²,day)</th>
<th>O2-BIF</th>
<th>Normalized OTR (cm³µm/m²,day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET, Ref.</td>
<td>175</td>
<td>7.16</td>
<td>1.0</td>
<td>1253</td>
</tr>
<tr>
<td>PET-OLD ALD-1 side</td>
<td>175</td>
<td>0.375</td>
<td>19.1</td>
<td>65.6</td>
</tr>
<tr>
<td>PET-OLD ALD-2 side</td>
<td>175</td>
<td>0.059</td>
<td>121.4</td>
<td>10.3</td>
</tr>
<tr>
<td>PET/ITO</td>
<td>175</td>
<td>0.175</td>
<td>40.9</td>
<td>30.6</td>
</tr>
<tr>
<td>PET/ITO-OLD ALD</td>
<td>175</td>
<td>0.013</td>
<td>551</td>
<td>2.28</td>
</tr>
</tbody>
</table>

It is shown that the ITO coating also gives a good oxygen barrier and its O2-BIF (40.9) is twice as high as the BIF for the PET film with OLD ALD coating on one side (19.1). Combining ITO and OLD ALD coatings gives the best barrier performance (O2-BIF = 551).

The OTR results of OLD ALD- and ITO-(Indium Tin Oxide)-coated PEN films are shown in Table 6.

Table 6: Results from oxygen transmission rate (OTR) measurements of OLD ALD-coated PEN films, with oxygen Barrier Improvement Factor (O2-BIF) and normalized OTR data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate thickness (µm)</th>
<th>OTR (cm³/m²,day)</th>
<th>Normalized OTR (cm³µm/m²,day)</th>
<th>O2-BIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN, Ref.</td>
<td>130</td>
<td>2.38</td>
<td>309.4</td>
<td>1.0</td>
</tr>
<tr>
<td>PEN-OLD ALD-1 side</td>
<td>130</td>
<td>0.080</td>
<td>10.4</td>
<td>29.8</td>
</tr>
<tr>
<td>PEN-OLD ALD-2 side</td>
<td>130</td>
<td>0.018</td>
<td>2.34</td>
<td>132</td>
</tr>
<tr>
<td>PEN/ITO</td>
<td>205</td>
<td>0.069</td>
<td>14.1</td>
<td>21.9</td>
</tr>
<tr>
<td>PEN/ITO-OLD ALD</td>
<td>205</td>
<td>0.0069</td>
<td>1.41</td>
<td>219</td>
</tr>
<tr>
<td>Kimoto</td>
<td>220</td>
<td>0.0068</td>
<td>1.50</td>
<td>----</td>
</tr>
</tbody>
</table>
It is shown that the uncoated PEN film has approximately four times lower OTR than has the uncoated PET film at comparable film thicknesses. Also the coated PEN films have lower OTR-values than the coated PET films. Again, the combination of ITO and OLD ALD coating gives the best barrier properties. Kimoto, a Japanese barrier film, was also tested for comparison and its oxygen barrier properties were found to be just as good as the PEN/ITO-OLD ALD sample.

The two types of ALD coatings (OLD and NEW) are compared in Table 7 and 8. The ALD coating was always deposited on one side. The PET/ITO and PEN/ITO films were coated on the opposite side of the ITO coating. The water vapor barrier results obtained for the NEW coatings are presented in Tables 7 and 8 together with the results from the OLD coating. As shown in the Tables, it is very clear that the NEW coatings are superior to the OLD ones and the Barrier Improvement Factors are significantly higher. This is true for both PET and PEN substrates. As before, the films already coated with ITO obtain significantly lower transmission rates, which again confirm the ITO layer is a potent barrier coating as well as an excellent conductive coating.

**Table 7: Results from water vapor transmission rate (WVTR) measurements of ALD-coated PET films, with WV Barrier Improvement Factor (WV-BIF) and normalized WVTR data.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate thickness (µm)</th>
<th>WVTR (g/m²,day)</th>
<th>Normalized WVTR (gµm/m²,day)</th>
<th>WV-BIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET, Ref.</td>
<td>175</td>
<td>0.69</td>
<td>120.8</td>
<td>1.0</td>
</tr>
<tr>
<td>PET-ALD-1, old</td>
<td>175</td>
<td>0.099</td>
<td>65.6</td>
<td>19</td>
</tr>
<tr>
<td><strong>PET-ALD-1, NEW</strong></td>
<td><strong>175</strong></td>
<td><strong>0.004</strong></td>
<td><strong>0.7</strong></td>
<td><strong>173</strong></td>
</tr>
<tr>
<td>PET/ITO-ALD, old</td>
<td>175</td>
<td>0.013</td>
<td>2.28</td>
<td>53</td>
</tr>
<tr>
<td><strong>PET/ITO-ALD, NEW</strong></td>
<td><strong>175</strong></td>
<td><strong>0.002</strong></td>
<td><strong>0.35</strong></td>
<td><strong>345</strong></td>
</tr>
</tbody>
</table>

**Table 8: Results from water vapor transmission rate (WVTR) measurements of ALD-coated PEN films, with WV Barrier Improvement Factor (WV-BIF) and normalized WVTR data.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate thickness (µm)</th>
<th>WVTR (g/m²,day)</th>
<th>Normalized WVTR (gµm/m²,day)</th>
<th>WV-BIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN, Ref.</td>
<td>130</td>
<td>0.24</td>
<td>31.2</td>
<td>1.0</td>
</tr>
<tr>
<td>PEN-ALD-1, old</td>
<td>130</td>
<td>0.060</td>
<td>7.8</td>
<td>4</td>
</tr>
</tbody>
</table>
It is thus clear that the thickness of the ALD coating is a very critical factor. The coatings must not be too thick, as this will create internal stress in the coating and it will cause cracks, leading to deteriorated barrier properties.

Beneq Oy has now launched the first its roll–to–roll ALD coater for flexible webs up to 500 mm in width, as shown in Figure 9.

Figure 9: A schematics of Beneq’s first roll to roll ALD coater for flexible films

*ALD (Atomic Layer Deposition) coatings from Lotus Applied Technologoes (USA)*

Lotus Applied Technology develops and licenses thin film technology for application to a wide variety of end uses and markets. They have expertise and capabilities in a wide array of methods for depositing and processing thin films, including unique experience and capabilities in the field of Atomic Layer Deposition (ALD). The Lotus technology also allows the deposition of ALD films on flexible substrates in a true Roll-to-Roll systems with web speeds up to meters per second. A schematic drawing of the process is shown in Figure 10.
In Lotus’ ALD Roll to Roll process, the substrate is passed back and forth between separate precursor zones, eliminating the time required for pulsing and purging precursors from a shared volume. In addition to processing speed, this approach provides several distinct advantages, including the fact that all coating is limited to the surface of the web itself, as it is the only surface that is exposed to both precursors. All surfaces within the machine itself remain clean and coating-free.

The following film samples have been prepared by Lotus AT and sent to YKI:

- 2 PET films with ALD (TiO₂) coating on one side, without protective layer. The PET films were cut to fit our WVTR cups prior to deposition of the ALD coating
- 2 PET films with ALD (TiO₂) coating on one side, with protective layer (1 μm acrylic topcoat). The PET films were cut to fit our WVTR cups prior to deposition of the ALD coating
- 2 PET films with ALD (TiO₂) coating on one side, without protective layer. The PET films were cut to fit a Mocon Aquatran cell prior to deposition of the ALD coating

The thickness of the ALD (TiO₂) coating was only between 13 – 17 nm. The thickness of the PET film was not given, but was estimated to be 150-200 μm.

The results from the WVTR measurement according to the Cup Method are presented in Table 9.

Table 9: Results from water vapor transmission rate (WVTR) measurements of ALD-coated PET films from Lotus AT, with WV Barrier Improvement Factor (WV-BIF) and normalized WVTR data. Measurements were performed according to the WVTR Cup Method. *) ALD coating exposed to a small water droplet
The results in Table 9 illustrate the importance of protecting the ALD coating. Negative transmission rates (i.e. absolutely no water uptake whatsoever) are reported when a 1 µm protective acrylic topcoat was used! ALD-coated PET films without a protective topcoat also obtained very low WV transmission rates, but it is also shown that a small water droplet placed (by accident) on the ALD coating can result in a significant decrease in the barrier performance.

The ALD-coated PET films without any protective topcoat were measured both according to the Cup Method and in a new Mocon Aquatran instrument. This instrument can measure WVTRs down to $5 \times 10^{-4}$ g/m²,day. The Mocon Aquatran measurements were performed at Innventia AB The WVTR results are compared in Table 10.

Table 10: Comparison between WVTR measurement methods: Mocon Aquatran and Cup method.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>WVTR Mocon Aquatran (g/m², day)</th>
<th>WVTR Cup Method (g/m², day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET-ALD without protective topcoat - 1</td>
<td>0.0017</td>
<td>0.0006</td>
</tr>
<tr>
<td>PET-ALD without protective topcoat - 2</td>
<td>0.019</td>
<td>0.0057 *</td>
</tr>
</tbody>
</table>
As shown in Table 10, both sets of samples show a factor of 10 difference in WVTR, which is quite significant. This is ascribed the sensitivity of the coatings towards damage during handling of the films. It would have been interesting to measure the ALD-coated PET films with a protective topcoat also in the Aquatran instrument.

To summarize, the ALD coatings have a high potential to provide very good oxygen and water vapor barriers on plastic substrates such as PET and PEN, especially in combination with sputtered ITO coatings. However, it is now well known that the ALD coatings are very sensitive and are easily damaged during handling of the films. Further development work must therefore focus on how to protect the coatings.

**Evaluation of commercial barrier films from 3M and Kimoto**

Two different commercial films have been evaluated:

1. 3M<sup>TM</sup> Solar Ultra Barrier Film from 3M
2. Barrier Film-2 from Kimoto, Japan

The WVTR of the commercial films have been measured according to the Cup Method and the results are shown in Table 11. According to 3M, their film should have a WVTR-value around 5x10<sup>-4</sup> g/m<sup>2</sup>·day. However, as shown in Table 11, the obtained WVTR value is 10-100 times higher.

The film from Kimoto has a WVTR value which is approximately 10 times higher than the 3M film and the ALD-coated samples

Table 11: Results from water vapor transmission rate (WVTR) measurements of ALD-coated PET films from Lotus AT, with WV Barrier Improvement Factor (WV-BIF) and normalized WVTR data. Measurements were performed according to the WVTR Cup Method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate thickness (µm)</th>
<th>WVTR (g/m&lt;sup&gt;2&lt;/sup&gt;·day)</th>
<th>Normalized WVTR (gµm/m&lt;sup&gt;2&lt;/sup&gt;·day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3M - 1</td>
<td>230</td>
<td>0.0001</td>
<td>0.023</td>
</tr>
<tr>
<td>3M - 2</td>
<td>230</td>
<td>0.0014</td>
<td>0.32</td>
</tr>
<tr>
<td>Kimoto 2 - 1</td>
<td>140</td>
<td>0.0031</td>
<td>0.434</td>
</tr>
<tr>
<td>Kimoto 2 - 2</td>
<td>140</td>
<td>0.0050</td>
<td>0.70</td>
</tr>
</tbody>
</table>

The 3M samples were also measured in the Mocon Aquatran instrument, and the results are compared with the Cup Method results in Table 12.

Table 12: Comparison between WVTR measurement methods: Mocon Aquatran and Cup method.
As shown in Table 12, the agreement between the two methods is quite good.

**Development of a transparent organic coating aimed for multilayer barrier structures**

A transparent organic coating aimed for a multilayer barrier structure based glass-like SiOₓ coatings has been developed. The coating is based on Trimethylol propane oxetane (TMPO) and 3,4-epoxycyclohexyl-methyl 3,4 epoxy-cyclohexane-carboxylate (ECC). This mixture is cured under UV, i.e. there are no solvents involved. Other advantages are that highly branched polymer networks can be achieved and the degree of cross-linking variable. The polymer solution can be either spin-coated, dip-coated or spray-coated on the polymer (PET) substrate.

The idea is that this crosslinked and hyperbranched poly(oxetane) (POₓ) coating and a plasma-deposited SiOₓ coating should be alternately deposited on PET. So far, the POₓ coating has been deposited on a PET film substrate (same substrate as in the ALD coating trials in chapter 1.1.) and the WVTR has been measured. See Table 13.

Table 13: Results from water vapor transmission rate (WVTR) measurements of poly(oxetane)-coated PET films with WV Barrier Improvement Factor (WV-BIF) and normalized WVTR data. Measurements were performed according to the WVTR Cup Method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate thickness (µm)</th>
<th>WVTR (g/m²,day)</th>
<th>Normalized WVTR (gµm/m²,day)</th>
<th>WV-BIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET, Ref.</td>
<td>175</td>
<td>0.69</td>
<td>120.8</td>
<td>1.0</td>
</tr>
<tr>
<td>PET with organic poly(oxetane) coating.</td>
<td>175</td>
<td>0.12</td>
<td>21</td>
<td>5.8</td>
</tr>
</tbody>
</table>

As shown in Table 13, the deposition of the POₓ coating does improve the water vapor barrier properties of PET by a factor of almost 6.
Next step will be to deposit the SiO\textsubscript{x} coatings and the POx coatings alternately and measure the WVTR between each step.

**Conclusions**

The following conclusions can be made so far:

- The new, thinner ALD coatings have a significantly improved barrier performance compared to the old thicker one
- Protective layer on top of the ALD coatings improves the performance further
- ITO + ALD layers are a very powerful combination. Results often below detection limit of the instruments
- The commercial films from 3M and Kimoto are good but not as good as the ALD-coated films
- The organic poly(oxetane) coatings look promising.

**Task 2: Designing of conductive substrate materials**

The conductivity of the conducting layer is very important for the final product, in this task YKI has studied how new conductive substrates can be used as alternatives to the ITO coatings used today. For example, graphene is an interesting material for conductive coatings and YKI has investigated new graphene-based coatings using AFM Peak Force TUNA.

**Graphite steps – mapping of interactions with graphite colloidal probe and conductive AFM tip in PeakForce TUNA**

A cantilever with a glued carbon colloidal probe was used to measure the interaction with stepped graphite. Fig. 11 displays the obtained topography, where the steps range from 10 nm up to 30 nm, with step lengths from 20 nm to 150 nm. The rounded shapes are due to the probes inability to measure sharp features. In that case, the image become “reverse”, i.e. an image of the probe itself.

![Graphite steps](image)

**Fig. 11: 500 nm x 500 nm topography image of stepped graphite obtained with a carbon colloidal probe. Where brown<yellow<pink ranging from 0 nm (black) to 90 nm (white).**

The material parameters can be evaluated from different parts (peaks, slopes, areas, distances) of the force curves according to Fig. 12. Every channel can be individually plotted or applied as a “skin” on the 3D structure of another channel.
Fig. 12 Force curve evaluation.

For a diagonal line across the figure, perpendicular to the steps, there are 1021 data points for each of the channels. An evaluation of four material parameters in this line together with the topography is displayed in Fig. 13. Largest variation in the material parameter channels can be seen between 200 and 460 nm. Part of this variation could be explained by the fact that the topography is adjacent to a steeper slope which can have caused double contact with the probe. However at 600 nm there is approximately the same situation and although there is a small variation in the adhesion channel, it cannot be compared to the large values in the 200-460 nm region. This suggests that the measured materials parameters are more of chemical origin than geometrical, likely due to differences between basal and edge plane sites.

Fig. 13 Absolute values for height, adhesion, modulus, dissipation and deformation over one diagonal line perpendicular to the steps.

In order to investigate the material properties together with conductive properties, the cantilever with the colloidal probe was changed to a cantilever with a conductive tip with an applied voltage of 1 V. An image of 5 µm x 5 µm is displayed in fig. 14. It can be noted that here the selected step appears less rounded than in the case with the colloidal probe. The step height is 220 nm and the step length is 0.9 µm. In the 3D-image some lines are visible on the lower flat plane. These lines which have a height between 1 nm and 4 nm and a width of 40
nm – 130 nm, are not tip-induced since the applied force is constant over the area and no “scraping” occurs, just z-movement individual touching in every point. A probable origin of the features is stresses induced during the micromechanical cleaving.

Fig. 14. 5 µm x 5 µm topography image of stepped graphite obtained with a conductive tip. Where brown-yellow-pink ranging from 0 nm (black) to 350 nm (white). Left: 2D, right: 3D.

Fig. 15 displays the same topography images as in fig. 14, but with applied skins from the modulus and adhesion channels. The striped patterns across these images are likely due to interference. The lines previously observed in fig. 14 are visible in both these channels, but the adhesion channel also displays some circular features within the step/slope area.

Fig. 15 Left: 5 µm x 5 µm topography image with relative modulus skin of stepped graphite obtained with a conductive tip. Right: 5 µm x 5 µm topography image with relative adhesion skin of stepped graphite obtained with a conductive tip.

In fig. 16, where the deformation and current images are displayed, these features are more apparent. Especially the current channel is intriguing, showing highly conductive filled and unfilled circular features located on the step and low-conductive larger “poodles” on the flat parts. Since we earlier argued adhesion variations as being due to differences between basal and edge plane sites and since we here don’t have any large adhesion difference, the origin of the circular features might be something else, like metallic impurities in the material. The high conductivity of the features supports this theory. Concerning the low conductivity poodles, they were first assumed to be glue from the micromechanical cleaving process. However, firstly it is unlikely to have any glue residues on the surface since it is more likely to cleave when pulled apart by glue. Secondly, glue should appear much more adhesive than graphite on the adhesion channel, where they are totally invisible. This suggests that also the poodles are of chemical origin within the basal plane of the graphite.
Fig. 16 Left: 5 µm x 5 µm topography image with deformation skin of stepped graphite obtained with a conductive tip. Right: 5 µm x 5 µm topography image with relative current skin of stepped graphite obtained with a conductive tip.

**Distribution of conductivity and mechanical properties over graphene-nano platelets measured by AFM PeakForce TUNA**

AFM PeakForce Tuna was used to image commercial graphene platelets deposited onto a metal disc. On a 3-D, unflattened representation of the height (fig. 17) stacked platelets are visible. Since the surface is not molecularly smooth, some of its underlaying roughness is contributing to the overall level differences. The size of the platelets in the image is in the order of 40-100 nm in X-Y and 10-20 nm in Z direction. The tip broadening in this Z region is only 2-4 nm and can be neglected. Interestingly the platelets all display a somewhat convex shape, which could be due to gas trapped beneath the platelets during the drying, surface chemical interactions with the underlying material or variation in thickness between the platelet center and perimeter. Worth noticing is also the island shapes of the stacks – implying a strong adhesion between the platelets, probably partly originating from the insolubility in the water phase.

Fig. 17 Topographic 3003 nm 3-D representation of graphene platelets.
An interesting aspect is also that geometrical differences are predicted by the presence of different amount of atoms in the carbon rings. Generally, more five- than seven-rings give spherical shapes – like parts of fullerenes, while more seven- than five-rings give saddle shapes\textsuperscript{1}. A closer look at the curvatures (fig. 18) relieves that for the circular platelets, the curvature is regular in both directions, but for larger, more elliptical platelets, the curvature is varying depending on direction. Considering the curvature of fullerenes, i.e. C\textsubscript{60} (1/R=1.96 nm\textsuperscript{-1})\textsuperscript{2}, it can be noted that the observed curvatures are much smaller. Consequently, the ratio five-ring/seven-ring should be larger for fullerenes than for the observed geometry, assuming ring-structure origin. It can also be noted that the geometry of some fullerenes is more ellipsoidal than spherical (fig. 19) and that a large ellipse with open ends form a sort of nanotube-fullere intermediate.

\begin{center}
\begin{tabular}{c}
Arc height: 6 nm \\
Arc Full length: 41 nm \\
Radius of circle: 38 nm \\
1/R= 0.026 nm\textsuperscript{-1} \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{c}
Arc height: 4.5 nm \\
Arc Full length: 22.5 nm \\
Radius of circle: 16 nm \\
1/R= 0.063 nm\textsuperscript{-1} \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{c}
Arc height 1: 4.5 nm \\
Arc Full length 1: 27 nm \\
Radius of circle 1: 22.5 nm \\
1/R=0.044 nm\textsuperscript{-1} \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{c}
Arc height 2: 1.7 nm \\
Arc Full length 2: 27nm \\
Radius of circle 2: 54 nm \\
1/R=0.018 nm\textsuperscript{-1} \\
\end{tabular}
\end{center}

Fig. 18 Curvatures of graphene platelets.
Fig. 19 The major isomers of fullerenes C60, C70, C76, C78, C80, C82, and C843.

Fig. 20 displays a relative representation of the modulus. In this image can be noted that the platelets are softer than the underlying medium, also smaller platelets are generally softer than larger and the softness is greater closer to platelet perimeter than center.

Fig. 20 Left: relative DMT Modulus map where black<red<white. Right topographic 300 nm3 3-D representation with modulus overlay.

Fig. 21 shows that most adhesive parts are found in between the platelets and the lowest adhesion is generally found on the platelet edges. Generally smaller platelets have lower adhesion than larger.
Fig. 21 Left: relative adhesion map where black→purple→pink→white. Right: topographic 300 nm 3-D representation with adhesion overlay.

In Fig. 22, where the deformation values are calculated as the difference in the constant compliance regions of the trace and retrace curves, it can be noted that the edges of the platelets deform more than the centers. Also smaller platelets deform more easily than the larger. In order to obtain correct values for modulus and adhesion it is important that the sample deforms, which the deformation map clearly displays, hence the cantilever stiffness chosen for the image is adequate.

Fig. 22 Left: absolute deformation map ranging from 0 to 10 nm where brown→yellow→pink. Right: topographic 300 nm 3-D representation with deformation overlay.

In the current map (Fig. 23) it is shown that the graphene platelets are heterogeneously conductive and that local conductivities can reach high values at the very low applied voltage of 200 mV through the 20 nm tip. Conductivity is generally larger for smaller platelets and larger at platelet perimeter than center.
Fig. 23 Left: absolute current map ranging from 0 to 240 pA where green<yellow<blue<white. Right: topographic 300 nm³ 3-D representation with current overlay.

References:

**Collaboration with other national and international projects and programs**
No such collaborations have been established.

**Dissemination of project results**
Presentation by Kenth Johansson:
General meeting DTI, Taastrup, Denmark- September 1-2, 2011

**Future outlook**
YKI has established collaboration with important partners in the area of DSC within the project. Future cooperation with these partners in new projects and proposals is envisages, together with YKI and other parts of the SP Group.

**Deviations from original milestone plan and rationale for deviation**
No deviations

**Conclusions**
During the project YKI have had the responsibility to lead activities within WP2, a work package which targets different aspects of the design and integration of nanomaterials into new types of DSC. Specifically, YKI’s research efforts have been focused on:
1. the formulation of non-agglomerating nanoparticle dispersions ("inks") required for the various layers in the DSC and their deposition by means of well-established printing technologies
2. the improvement of moisture and oxygen barrier properties of the carrier films in the DSC structure (poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) and on
3. the designing of new conductive materials.

The following developments were achieved:

- On the formulation front, ink formulations that target the deposition of transparent DSC onto flexible substrates (no calcination steps required) were investigated. Formulations making use of UV radiation to induce degradation of organic materials incorporated in the DSC deposited layers (ink additives) were developed. The concept has been tested in lab-scale prototypes of plastic and glass-based solar cells, where despite the relatively low efficiencies obtained, the concept proved to have potential.
- In collaboration with the ink-jet printing company Ceradrop, several attempts were made to deposit multilayered structures of SiO\textsubscript{2} and TiO\textsubscript{2} particles fulfilling the requirements (approximate thickness, smoothness, homogeneity) of those that are required for the preparation of a photonic crystal (PC). Although only partially successful, these attempts provided information about key formulation strategies that will guarantee a successful outcome in future work to be carried out outside the framework of this project.
- For the barrier materials development we can draw the following conclusions:
  1) The new, thinner ALD coatings have a significantly improved barrier performance
  2) Protective layer on top of the ALD coatings improves the performance further
  3) ITO + ALD layers are a very powerful combination. Results often below detection limit of the instruments
  4) The commercial films from 3M and Kimoto are good but not as good as the ALD-coated films
  5) The organic poly(oxetane) coatings look promising.
- Furthermore, interesting features of conductive coatings of graphite/graphene have been observed using the AFM Peak Force TUNA instrument.
AALTO UNIVERSITY SCHOOL OF SCIENCE AND TECHNOLOGY (AALTO)

Introduction

The actions of AALTO, reported below, took place under WP 4: Device component integration and testing of photovoltaic devices. The aim of this work package was to assemble the components into a device, analyze the behavior of such and optimize the production method for such a device, with objectives to 1) refine general construction of PV devices, 2) refine overall device structure, multilayer development, dye and electrolyte incorporation, physical and chemical stability, 3) develop testing model(s) for overall DSC devices, and 4) provide an additional feedback loop to WP2 and WP3. The deliverables were specified to be optimized devices, methods to produce such devices and quality control tool.

The practical project execution under WP4 was organized mainly between AALTO, CSIC and NLAB on experimental related work and between AALTO and CSIC on theoretical modeling. The experimental work involved testing one-dimensional photonic crystal (1DFC) layers made by NLAB Solar and CSIC in the solar cells constructed by AALTO with the aim in meeting WP4 objectives 1) and 2). The modeling work done in collaboration of AALTO and CSIC supported meeting the objective 3). Both actions supported objective 4).

The main results over the entire project lifetime can be summarized as follows. For more details, the reader is referred to the Status Reports.

Experimental testing and refining of 1DPC DSC device structure

First batch of TiO₂ films were sent to NLAB Solar for 1DFC deposition in September 2010 and a second batch on 28th January, 2011. As a result of discussions between AALTO and NLAB Solar the thickness and smoothness of the films was optimized in AALTO through manipulation of the screen printing settings. In the end it was possible produce ca. 5.2 ± 0.2 μm thick (after sintering) smooth and transparent TiO₂ films at the in-house standard size of 8 mm x 5 mm (film area). 30 films could be printed at once on a 100 cm² glass substrate, which allowed selecting the smoothest ones for the 1DPC application (Figure 1). The quality of the films was concluded adequate for 1DPC deposition and samples were sent both to NLAB and CSIC.
Tests using 1DPC layers prepared by NLAB and typical DSC construction by AALTO (Table 1) showed that ca. 4.5 % cell efficiency could be obtained without significant problems due obstructed ion diffusion though the 1DPC layer, although such effect could be seen to some extent with electrochemical impedance spectroscopy (EIS) measurements of the solar cells. However, based on other results by the project partners, ion diffusion through the 1DPC layer was considered a general problem that deserved further attention. Part of the work in the project was thus devoted to its theoretical understanding and modeling, as discussed below.

Table 1. Materials used in the preparation of 1DPC-DSC sample solar cells yielding typical 4.5 % efficiency (M = mol/dm3)

<table>
<thead>
<tr>
<th>Material</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass (TCO, CE)</td>
<td>Pilkington TEC-15 fluoride doped tin oxide (FTO) glass</td>
</tr>
<tr>
<td>Sealing</td>
<td>Surlyn 1702, 25 μm thick</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>I2: 0.05 M, NMBI: 0.5 M, GuNCS: 0.1 M, PMII: 0.5 M</td>
</tr>
<tr>
<td>Solvent</td>
<td>3-methypropionitrile (3-MPN)</td>
</tr>
<tr>
<td>TiO2 Dyesol</td>
<td>Dyesol: DSL 18 NR-T</td>
</tr>
<tr>
<td>Dye N719-dye</td>
<td></td>
</tr>
</tbody>
</table>

Electrical modeling ion diffusion through the porous 1DPC layer in DSCs

An mentioned above, one of the possible negative side-effect of the 1DPC on DSC operation is that the nanoporous structure of the 1DPC layer can obstruct current transport in the electrolyte by impeding the diffusion of the tri-iodide in the electrolyte between the photoelectrode and the counter electrode. To clarify the significance of the 1DPC layer on the electrolyte diffusion and to aid in the optimization of the 1DPC properties with this respect, a study involving numerical simulations of the coupled mass-transport and light absorption in the 1DPC DSCs was initiated as a joint work between AALTO and CSIC. This work involved a 1 month visit of Mr. Francisco Enrique Gálvez (CSIC) in Aalto University in August 2011, during which a simulation code were written by Mr. Gálvez and Mr. Erno Kemppainen (AALTO) under the instruction of Dr. Janne Halme. The simulation code takes experimental optical data of the DSC and the 1DPC layers as an input and calculates the light absorption profile in the TiO2 photoelectrode film. This is used as the spatially dependent current source term for solving differential equations describing electrolyte diffusion in the whole solar cell structure.
In addition to porosity (pore volume per total film volume) and tortuosity (average path length of diffusion though the porous film compared to the thickness of the film) a critical parameter was found to be the constrictivity of the 1DPC film. Constrictivity is defined a parameter that tells how much slower the ion diffusion in the pores of the film is compared to diffusion in the bulk electrolyte, the diffusion being slowed down by the constrictions ("bottle necks") between the pores and due to electrostatic or chemical interaction with the pore walls. Comparing the so-called limiting current density (due to electrolyte diffusion) with the experimentally observed short circuit current densities of the 1DPC solar cells, we found that in order to cause problems on the solar cell performance, the constrictivity would need to take values that are surprisingly low: less than ca. 0.01 for a 1 \( \mu \)m thick 1DPC that the diffusion coefficient of tri-iodide would need to be 1% or less compared to its free electrolyte value. Whether such a low values for the constrictivity are physically realistic, and thus explain the experimental observations of diffusion limited currents in 1DPC DSCs in some cases, remains to be studied experimentally.

The results of from these investigations are under preparation for a manuscript to be submitted to a peer-review scientific journal [1].

**Optical – electrical modeling of light scattering designs for DSCs**

The collaboration between AALTO and CSIC on theoretical of DSCs started with a study on the effect of different light scattering design on the optical – electrical performance of DSCs. The purpose was in one hand to get deep understanding of the advantages and limitations of the competing optical designs to 1DPCs, namely light scattering particles and diffuse back scattering layers, and on the other hand, to lay grounds to performing similar analysis in the case of 1DPC and reflecting mirrors later on. A specific research question was how non-uniform electron generation, caused by back-reflection of light from diffuse scattering layer (alike 1DFC layer), influences electron collection efficiency from the nanostructured TiO\( _2 \) film. This work involved numerical optical modeling and simulations by CSIC coupled to electrical solar cell device modeling by AALTO.

As a background for this study it was known that light scattering can be used to boost short circuit current in DSCs. However, it also affects light absorption profile in the film, which could be important for the performance of the solar cell when its electron collection efficiency is low, as is a typical the case with flexible cells that were the target in this project. We studied through the above mentioned combined optical – electrical simulations what would be the best optical design for flexible DSCs, and how big the gain in efficiency could be from localizing light absorption close to the substrate contact through which the electrons are collected form the film. As a result from the simulation we concluded that significant efficiency gains by the contact-localized absorption can be obtained only at the case of relatively low collection efficiency, in practice only when the cell efficiency is quite poor (1-2 %), and that the diffuse back scattering layer is always optically superior compared to scattering particles mixed to the absorbing layer. The results were published as a peer-reviewed journal paper in Journal of Physical Chemistry C [2] and presented as an oral presentation by Dr. Hernán Miguez in The International Conference on Simulation of Organic Electronics and Photovoltaics (SimOEP12), Oliva, Valencia, Spain, 10th - 14th June 2012 [6].
Modeling of transparency, color and photovoltaic performance of DSCs from optical properties of the solar cell materials and components

The 1DPC DSCs developed in the project are particularly interesting from the point of view of glass façade applications since their transparency and color appearance can be modified to increase their photovoltaic energy conversion efficiency. Different color and transparencies can be obtained depending on the choice for the light absorbing dye and the wavelength range of 1DPC reflection spectrum that is tunable by its layer structure. The depth of color and transparency can be further tuned by the photoelectrode film thickness. The color is also different when viewing the reflected light than the transmitted light. The overlap of the 1DPC reflection and dye absorption spectra determine the photovoltaic efficiency and transparency of the solar cell. While these relationships have been previously known to exist, it has not been possible to reliably predict and design the color of the DSC using real experimental data of the DSC materials. A separate research task was initiated by AALTO to develop a method for this purpose. As a result, a design methodology was developed for goal oriented design of 1DPC DSCs for façade applications.

In the method, we take experimental optical data of the actual DSC materials used in the lab as input, including different options for the dyes and 1DPCs. These data are applied to an optical model of the complete solar cell structure to calculate its optical reflection and transmission spectra, as well as its visual transparency of solar light and color of the complete solar cell under a given source light spectrum, here sunlight. Moreover, using a simple electrical model, we calculate also the photovoltaic energy efficiency of the cell, as well as other parameters of its current voltage curve (Figure 2).

The methodology was verified experimentally by comparing predicted color and transparency of complete DSCs with calibrated (color and white balanced) color photography of real experimental DSC samples. Figure 3 shows that when the dye concentration, that was not controlled experimentally, is adjusted in the simulations an excellent match between the predicted and photographed color is obtained, while the visible transparency ranges between 20 – 30 % depending on the 1DPC used.
Figure 4 demonstrates application of the methodology by showing results from a case study where the amount of dye adsorbed in the TiO$_2$ film was hypothetically varied to meet a specific design criterion, namely 30 % visible transparency, in typical DSCs with experimentally determined optical properties. The results show how the design criterion can be met with a range of combinations of different dyes and 1DPC layers, each giving somewhat different color and photovoltaic performance at the fixed predetermined transparency. The results demonstrate that a compromise has to always be made between photovoltaic efficiency, device transparency and visual esthetics of the DSC solar panel. This decision is fundamental in designing semitransparent 1DPC DSCs for example to building integrated photovoltaic (BIPV) applications. The simulation model combined with the experimental methodology developed in this project and described briefly above is expected to be an important tool in designing DSCs for BIPV facade applications in the future.

This work was accepted as an oral presentation to the international conference Energy Forum on Solar Building Skins, to be held 06-07 December 2012 in Bressanone, Italy to be presented by Janne Halme [5]
Figure 4. The color of light transmitted through or reflected from a DSCs with different dye-1DPC – combinations when the incoming light in solar light according to the AM1.5G standard spectrum. On the left are shown estimated photovoltaic energy conversion efficiencies of the corresponding cases. N719 is a common commercial Ru-dye and D205, D149, and D102 are three commercial indoline dyes from Mitsubishi Paper Chemicals. The 1DPC layers were prepared by NLAB Solar and CSIC and characterized optically by AALTO, along with all other cell materials and components used in the simulation.

Angular optical modeling of 1DPC DSCs

A particular feature of the 1DPC layer is that, being essentially a Bragg reflector, its optical reflectance spectrum depends on the angle of incidence of the light. For example, the 1DPC dye solar cell appears to have different color when viewed from different angles. Although important for the designing of the 1DPC DSCs, it had not been possible to predict this angle-dependence theoretically before for DSC application. To resolve this situation, work on angular-optical modeling of 1DPC DSCs was carried out in spring 2012, when Dr. José Miguel Luque Raigón from CSIC joined AALTO group for a post-doctoral research funded by the project. In this study, theoretical modeling work initiated in 2011 in CISC by Dr. Luque Raigón et al. was continued at AALTO and resulted in a joint paper by the two groups in 2012 [3]. The optical model developed is a full vectorial electro-magnetic model that solves the Maxwell’s equations in an arbitrary one-dimensional optical multilayer (here 1DPC DSC, Figure 5) using transfer matrix method (TMM) as a function of the incident angle of light. Successful implementation of the theory as a numerical code in Matlab software was made possible by careful handling of numerical instabilities that occurs near total internal reflection (TIR) and strongly absorbing (dyed layer) or thick (glass substrates) films. In conclusion, a multi-scale optical model was developed that is particularly suitable for modeling and design of 1DPC DSCs.

In addition to the optical properties and the photovoltaic performance of 1DPC DSC being angle-dependent the visually observed color of the solar cell depends on the viewing angle. We therefore combined the color modeling developed in AALTO (discussed above) with the angular optical model, with the result that the angle-dependent color appearance of 1DPC DSC solar panels can be predicted (Figure 5).
Research is planned to continue this work by verifying the angle dependent simulation results by experiments, with the objective to submit a paper on the results by the end of 2012 [4].

Figure 5. A multiscale angular model of a one-dimensional non-periodic optical multi-layer was developed which is particularly suitable for angular modeling of 1DPC dye solar cells. On the left: typical multi-layer structure of a 1DPC DSC. On the right: simulated color and intensity of sunlight transmitted through (top) or reflected from (bottom) of a typical 1DPC DSC. Not that at large angles (close to 90 degrees) most light is reflected and practically none is transmitted, as expected.
**Dissemination of project results**

Following publications, conference contributions and academic theses resulted directly from the project.

**Publications from the project**

[http://dx.doi.org/10.1021/jp2092708](http://dx.doi.org/10.1021/jp2092708)


[4] Halme, J., Kemppainen, E., Gálvez, F.E., Míguez, H., Effect of porous layer constrictivity on electrolyte diffusion and photovoltaic performance in dye solar cells employing porous one-dimensional photonic crystal layers (Manuscript in preparation)


**Conference contributions from the project**


**Theses from the project**

**Future outlook**

The methodology for simultaneous optical and electrical modeling of DSCs including visual color and transparency as a function of incident light and viewing angle is unique in this field and anticipated to create attention and prospects for collaborations and further research to the directions of simulations and technical performance studies of DSCs for BIPV applications.

Fruitful and active collaboration between AALTO (Dr, Halme) and CSIC (Dr. Miquez) was initiated within this project and is expected to continue in the future with several new joint research topics planned already on the electrical and optical modeling of DSCs, partially indicated by the papers in preparation (see publication list).

**Conclusions**

The work in WP4 overall succeeded to meet the objectives defined in the project plan. Both practical results and theoretical simulations tools were developed to support the overall project goals that are anticipated useful for the project partners also later on.
Because of changes in personnel at DTI and reprioritizing in the project the work tasks of DTI were changed to work on a polymer based printable sealant system for use in DSCs. This activity was not included in the original work plan and thus has no workpackage.

In order to harvest the energy from the sun the chemical system inside a DSC must remain intact. Careful design of the chemical system inside the DSC can make the system more robust but no matter how robust the chemistry inside is, it must still be protected against the elements when the DSC is installed for electricity production. The first and foremost protection is a physical barrier consisting of the DSC substrate and an edge sealant which together produce a cavity wherein the chemistry of light harvesting can take place. This physical barrier serves two purposes. Firstly, it must keep the materials, most notably the electrolyte, within the DSC and secondly it must keep out unwanted materials. One of the key materials to keep out of the cell is water as it has been shown to degrade cell performance rapidly via hydrolytic and photocatalytic reactions.

Many methods have been used for DSC edge sealing. One method used widely in laboratories around the world is by sealing with the thermoplastic polymer film Surlyn 1702. This method has the advantage that it is easy to apply as the film can be cut to shape and low temperatures are used for the sealing. However, the barrier properties of Surlyn 1702 are inadequate to ensure long term stability of the DSC, and cutting and handling of the sealing material is difficult to automate and scale to large areas.

To overcome the problems with using Surlyn 1702 a new sealing concept based on thermoplastic polymers was developed in this work task.

The central part of the improved sealing concept is the selection of a thermoplastic polymer that has sufficient barrier properties necessary for a commercial DSC module. The parameter of interest here is the permeability of water and electrolyte through the polymer at temperatures where the DSC will operate. The temperature of a DSC in operation may be significantly higher than ambient, thus sealant permeability at temperatures ranging from 50 to 90 °C are relevant.

Besides the sealant performance, the processability of the sealant is also a key aspect. Polymers that perform well with regards to permeability generally have difficulty being processed mainly because of high melting point and very limited solubility in common solvents. This has led to the development of a new concept for printable sealant based on high performance thermoplastic polymers.

This concept involves milling the polymer to a fine powder, mixing this powder into a suspending liquid, printing the suspension, removing the liquid phase and finally obtaining a solid polymer seal by heat treatment. The application of the sealing concept applied for the protection of a silver conductor in a DSC is illustrated in Figure 6.

Figure 6: Protecting a silver conductor on glass within a DSC using new sealing concept. Left: suspension of thermoplastic polymer printed on top of silver (grey). Middle: liquid of suspension is removed by
evaporation. Right: Particles of polymer are transformed to solid polymer by heat treatment. Illustration is not to scale

Testing water and electrolyte permeation through candidate polymers

Screening of materials was performed in order to find suitable polymers. Several properties of the materials were considered, among these the permeability to water, chemical resistance to electrolyte components, and an operating range from -20 to 85 °C. The screening was based on information obtained from literature and materials suppliers. Based on this screening, four candidates were chosen: three thermoplastics and a single thermoset. These candidates were polyvinylidene chloride (PVDC), polychlorotrifluoroethylene (PCTFE), vinylester (VE), and liquid crystal polymer (LCP). In order to test the polymer permeability, film form of the polymers were required. PCTFE and PVDC were readily available in film form with uniform thickness, while thin films of LCP were produced by hot pressing and thin films were vacuum cast from VE. These thin films were used for testing permeation of water and typical DSC electrolyte through the polymers. In the case of water, the test was set up to test water vapour transmission, while for electrolyte the transmission for the film in contact with liquid electrolyte was tested. This represents most accurately the circumstances of an actual DSC. For simplicity only the normalized transmission rates (NTR) are considered. This is the transmission of water vapour or electrolyte through the polymer normalized according to the polymer film thickness. The partial pressure difference over the material is thus not considered.

Two different tests were set up. Both applied glass containers containing either electrolyte or water. These containers were then tightly closed using the candidate polymer.

In one test, multiple tests were run in parallel. In this case the containers were placed in a heating cabinet at the desired temperature and then regularly removed and weighed to determine the rate of either water or electrolyte loss. This method can only be done at temperatures slightly above room temperature (25 – 45 °C), as otherwise the change in temperature and hence volume inside the test containers will disturb the measurement. In the case of electrolyte, the containers are placed in a desiccator in addition to the heating cabinet. This was to avoid water ingress into the container that would otherwise distort the mass loss result. Figure 7 shows a collection of test containers in the heating cabinet.

![Figure 7: Parallel test with water vapour and liquid electrolyte](image)

The other setup that was used allowed testing at higher temperatures. This was necessary because mass loss associated with permeation through the best performing polymers was small at lower temperatures to be reliably measured. In this case, the mass loss of only a single container at the time was measured. The container was suspended in a heating cabinet.
under a balance placed outside. Continually, the balance measured the mass of the suspended container and thus allowed the measurement of mass loss. Figure 8 shows this setup.

![Figure 8: Setup using continuous weighing of suspended container](image)

Using the parallel test measurements were performed at 25, 30, 35, 40, and 45 °C. For reference a film of Surlyn 1702 was also tested. The bar chart in Figure 9 shows the measured water vapour NTR using the parallel test for Surlyn 1702, PVDC and VE. It is seen from the figure that PVDC has lower water vapour NTR than Surlyn 1702 at all temperatures, while VE has a higher NTR. No results are shown for PCTFE or LCP as reliable measurements were not obtained.

![Figure 9: Bar chart showing calculated NTR of water vapour through Surlyn 1702, PVDC, and VE based on parallel permeability test](image)

Figure 10 shows a bar chart similar to Figure 9 but for the NTR of liquid electrolyte. Again, PVDC has lower NTR than Surlyn 1702 and VE has higher NTR. However, the difference between PVDC and Surlyn 1702 is less pronounced than for water vapour. Reliable measurements for PCTFE and LCP were also not obtained in this case.
In Table 2, NTR of water vapour through PCTFE and LCP are shown. Because of time constraints only few measurements were conducted. At 90 °C the two polymers have comparable NTR.

Table 2: Measured NTR of water vapour through PVDC and LCP using the continuous method in units of g*µm/(day*m²).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>80 °C</th>
<th>90 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCTFE</td>
<td>480</td>
<td>771</td>
</tr>
<tr>
<td>LCP</td>
<td>689</td>
<td></td>
</tr>
</tbody>
</table>

Prediction of performance improvement

Based on the measured NTR of liquid electrolyte and water vapour at low temperatures, a prediction of the lifetime improvement of changing sealant from Surlyn 1702 to PVDC can be made. First, the NTR at elevated temperatures is predicted by estimating the temperature dependence of NTR (Q) with an Arrhenius type expression:

\[ Q(T) = Q_0 e^{\frac{E_Q}{RT}} \]

Where T is the absolute temperature, R is the universal gas constant and Q₀ and E_Q are suitable constants.
Figure 11: NTR of water vapour through Surlyn 1702 as a function of temperature. Red diamonds show measurements. Solid black line shows Arrhenius type fit to data

By taking the ratio of NTR calculated in this manner for PVDC to the value for Surlyn 1702, an improvement factor is obtained. This factor gives an estimate of the increase in lifetime by changing the sealant material from Surlyn 1702 to PVDC and keeping the other properties constant. Factors are calculated both for failure for via water ingress and electrolyte loss. This is because no information on the failure modes and tolerances are available for the DSC. Table 3 shows the calculated enhancement factors for use of PVDC as sealant material over Surlyn 1702.

Table 3: PVDC sealant enhancement on DSC lifetime over Surlyn 1702 sealant for failure via water ingress or electrolyte loss.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>PVDC enhancement factor (water ingress)</th>
<th>PVDC enhancement factor (electrolyte loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>11</td>
<td>2,2</td>
</tr>
<tr>
<td>60</td>
<td>14</td>
<td>2,8</td>
</tr>
<tr>
<td>70</td>
<td>19</td>
<td>3,6</td>
</tr>
<tr>
<td>80</td>
<td>24</td>
<td>4,5</td>
</tr>
</tbody>
</table>

Care must be taken using these values as they only reflect the performance of the isolated polymer. No information on the bonding to e.g. glass is included in these calculations. Also the factors are based on predicted values for NTR that may not be accurate due to the model being incorrect at the elevated temperatures. Similarly, enhancement factors for LCP and PCTFE can be calculated but here the measured NTR at elevated temperatures are compared to calculated NTR for Surlyn, instead of values predicted from the Arrhenius model. Also only failure via water ingress can be considered as no NTR for electrolyte through PCTFE and LCP are available.
Table 4: PCTFE and LCP enhancement on DSC lifetime over Surlyn 1702 sealant for failure via water ingress.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>PCTFE enhancement factor (water ingress)</th>
<th>LCP enhancement factor (water ingress)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>266</td>
<td>-</td>
</tr>
<tr>
<td>85</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>513</td>
<td>574</td>
</tr>
</tbody>
</table>

Milling of polymers for printable sealant

In order to be able to print the sealing material, the polymers must be milled down to a small particle size. Based on the work described above, PCTFE and LCP were selected for further testing with milling. Preliminary milling attempts were unsuccessful resulting in either too large particles or particles in fibrous form. The fibrous particles tangle together during printing of these resulting in uneven distribution of polymer and unsuccessful sealing.

![Figure 12: Left: Unsuccessful milling of PCTFE resulting in large particles. Right: Unsuccessful milling of LCP resulting in fibrous particles](image)

A successful milling procedure was developed and was combined with size separation for the production of particles suited for sealant production. Milling was done by a combination of a rotating knife mill followed by prolonged milling in a tumbling bill mill. This milling procedure was effective in producing small particles but with a very wide particle size distribution. In order to extract the particles with suitable size sedimentation, particle separation was applied using water with added surfactant. Examples of the resulting particles are shown in Figure 13.

![Figure 13: Left: Fine PCTFE particles ready for sealant use. Right: Fine LCP particles ready for sealant use](image)
The finished particles were then mixed with suspending liquid to produce a printable sealant ready for further testing.

**Collaboration with other national and international projects and programs**
Collaboration with Professor Torben Lund at Roskilde University regarding the PhD thesis on dye stability in DSCs has been running during the project.

Additionally, during the first year of the project collaboration with the Danish company Meko Print on the printing of DSC modules was done in a project under the Danish ForskEL program.

Education of the PhD student Anders Rand Andersen under the Nordic Center of Excellence. Thesis title: Life-Time Studies for Dye-Sensitized Nanostructured Solar Cells

**Dissemination of project results**

**Future outlook**
No future activities are planned at the moment of reporting.

**Deviations from original milestone plan and rationale for deviation**
Overall the work of DTI was reallocated from the original tasks to the task of developing a polymer based printable sealing system. This decision was grounded in mainly two aspects.

Due to personnel changes the competences for solving the original task were limited and would therefore not lead to a satisfactory completion of the task. The substituted task was within an area of strong competence of DTI together with it not originally being addressed in the project.

**Conclusions**
Two printable sealants have been produced within the project. The polymers used for these sealants show very promising barrier properties at elevated temperature. These two polymer sealants will be supplied to NLab Solar for further testing.
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Technical results related to the national and transnational descriptions
Collaboration with the group of Janne Halme in Helsinki was been established, aiming at evaluating and comparing the magnitude of the photocurrent enhancement effect of the different optical materials employed today to improve the efficiency of DSSC in laboratories and industries. These include:
1. The use of diffuse scattering layers, commercialized by Dyesol and Solaronix
2. The mix of scattering particles of different sort, as utilized by companies like G24 Innovations
3. The coupling to a highly reflecting porous photonic crystal mirror, which is the key component of the DSSC developed in the NICe project.

As a result of this collaboration, we have carried out an integral computational approach in which both the optical and electrical aspects of the cell are included for the first time, which might give rise to a software of potential commercial value. Also, we have an unprecedented tool to evaluate the different possible approaches to efficiency enhancement through optical design.

Analysis of the optical performance and structural quality of the different types of large-area photonic crystals that are being developed by NLAB Solar in Stockholm is also being performed at CSIC laboratories. High resolution FESEM characterization of the cross sections of a large number of samples (>50) have been performed, as well as surface maps of the optical reflectance measured from these samples to evaluate the uniformity of the response. Multilayers deposited by screen printing, spin coating and spray coating have been evaluated and results are very promising.

CSIC developed a spin coating protocol for depositing large area photonic crystals onto NLAB’s TiO2 films. These layers were then assembled into transparent flexible solar cells.

CSIC were responsible for optical- and SEM characterization of NLAB’s screen printed photonic crystals.

Dissemination of project result
Publications as described in NLAB Solar section and Aalto section above.

Future outlook
Not applicable

Deviations
Not applicable

Conclusions
Not applicable
Technical results related to the national and transnational project descriptions

We have created a prototype using vacuum lamination in order to check if the printed material survives the lamination process, see fig. 1. The result is 100% satisfactory, and the printed material is fully compatible under these lamination process conditions.

![Laminated glass sheets with an ink-jetted image printed directly on glass. A sheet of lamination material is placed on top of the ink-jetted image and a second glass sheet is positioned on top of the lamination material. The sandwich structure is sealed under vacuum in combination with heat. The lamination material improves glass breaking security features and preserves and enhances the quality of printed image.](image)

We have continuously supplied NLAB with glass, glass cutting service and lamination service, and lamination materials.

Collaboration with other national and international projects and programs

Participation in the so called klimatpakten in Stockholm,
Participation in 100Hus, a clean tech show case in the south of Stockholm city center.

Dissemination of project results

Bench marking of existing solar panel systems and bench marking of world-wide architecture concerning the artistic expression of solar panels, resulted in a full-scale mock-up of DSC solar panels for the ”100 house”-exhibition for a sustainable society. Additionally Fasadglas together with SSARK performed an internal project study on the commercial possibilities for using solar panels in buildings from a technical- and energy producing point of view.
Future outlook
Installation of prototypes
Product development

Deviations
None

Conclusions
Façade and building integrated solar cells hold a very promising future and during the spring of 2013 the installation of a prototype system will be undertaken. Although the project in itself has finished the work continues together with NLAB and SSARK mainly.
Technical results related to the national and transnational descriptions

- Pre-studies with possible patterns for the DCS from an architectural point of view. This was resulting in a prototype together with Fasadglas.
- Benchmarking of existing systems concerning solar panels
- Benchmarking of worldwide architecture concerning the expression and technique of solar panels

Collaboration with other national and international projects and programs

- Collaboration with Fasadglas and NLAB Solar in the project
- Seminar arranged by SSARK in April 2010 together with Sven Werner from the University in Halmstad concerning Europe’s new energy systems and the interface between architecture and technique
- Preparing for another seminar to be arranged by SSARK in November 2010 together with NLAB Solar and Björn Stigson, WBCSD
- An internal project study concerning the integration of architecture and energy in future buildings with the parameters transparency, views and sun protection.
- Collaboration with an entrepreneur concerning the commercial possibilities for the use of solar panels on a building with special studies of the technical aspects as well as the possibility to use the energy for commercial purposes.

Dissemination of project result

- Meeting with the steering group
- Participation in conference at Fasadglas/Glasskolan to listen to and discuss possibilities with DSC
- Collaboration with Fasadglas to develop a full scale mock-up of DSC solar panels for the exhibition “100 houses”, an exhibition for a sustainable society

Future outlook

- Internal report with examples and participants published as a report and on our homepage
- Spreading the result in Sweden Green Building Council in which we are a member
Deviations

- None

Conclusions

- The Swedish Government has a goal of diminishing the need of energy until 2020. The solar panels are one of the components in this goal.
- During the project period 2009 12 01 – 2012 05 31 has the interest in alternative energy systems increased as well as the commercial possibilities
- It is a necessity to integrate the different sorts of energy systems with the architecture from start
- The efficiency of the nanotechnology make it possible to use smaller units, which is easier to integrate with the architecture, it gives more possibilities to make interesting solutions. That is welcomed in the commercial market.
- The investment of alternative energy systems must have a pay off time that is reasonable for the real estate owner
- The energy produced is not always optimal in time, the energy is not produced when you need it most. The legal possibilities to sell your surplus of energy as a private real estate owner is not possible. We hope that the government can solve this in a near future.
- The new residential area “Norra Djurgårdsstaden” in Stockholm is under progress. The city authorities has an environmental goal including not just energy systems but waste systems, transportation etc. We cannot yet see if the result fulfill the goal, but we know that alternative energy systems are used including solar panels.
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Nordic DSC

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