

Energimyndighetens titel på projektet – svenska Högeffektiva och stabila perovskitsolceller genom modifiering av gränssytor	
Energimyndighetens titel på projektet – engelska Highly efficient and stable perovskite solar cells through interface modification	
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Nyckelord: 5-7 st Photovoltaics; lead halide; solution-processed; alkylamines; hole conductors;	

Introduction

This project was financed by the Swedish Energy Agency. The work was done in connection to the research consortium Center for Molecular Devices (CMD) at Uppsala University and KTH Stockholm.

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Sammanfattning

Perovskitsolceller (PSC) är en banbrytande ny solcellsteknik med potential för högeffektiva solceller till en mycket låg kostnad och med extremt kort energiåterbetalningstid. Det krävs fokuserad forskning för att förbättra den grundläggande förståelse för PSC, som kommer att ligga till grund för ytterligare ökning av effektivitet samt för förbättring av stabiliteten.

I vårt samarbetsprojekt har vi kombinerat forskning på effektiva solceller med avancerad grundforskning. Vi har tillverkat PSC med en verkningsgrad på mer än 23% (utan anti-reflektions (AR) -film), som är mycket nära världsrekordet som ligger på 25.7% (med AR-film). Innan projektet var labb-rekordet ca. 20%. Genom förbättrade tillverkningsmetoder för perovskiten och molekylär ytmodifiering kunde vi gradvis förbättra verkningsgraden.

Molekylär ytmodifiering samt nya polymera hålledare förbättrade stabiliteten av solcellerna avsevärd. Utan vidare inkapsling är cellerna stabila under 1000 timmar fullt solljus. Jonledning och metallkontaktorna är problematiska för stabiliteten i perovskitsolceller, men genom förbättrade syntesmetoder och nya kontakt material kan stabilitetsproblem lösas.

Summary

Perovskite solar cells (PSC) represent a ground-breaking new photovoltaic technology with the potential for highly efficient solar cells at very low cost and with extremely short energy payback time. Focused research is needed to improve fundamental understanding of the PSC, which will lay the foundation for further increases in efficiency as well as for improvement of stability.

In our collaborative project, we have combined research on efficient solar cells with advanced fundamental research. We have manufactured PSC with an efficiency of more than 23% (without anti-reflective (AR) film), which is very close to the world record of 25.7% (with AR film). Before the project, the lab record was approx. 20%. Through improved manufacturing methods for the perovskite and molecular surface modification, we were able to gradually improve the efficiency.

Molecular surface modification, as well as new polymeric hole conductors significantly improved the stability of the solar cells. Without further encapsulation, devices can be stable for 1000 hours of full sunlight. Ion conduction and metal contacts are problematic for the stability of perovskite solar cells, but through improved synthesis methods and new contact materials, stability problems can be solved.

Inledning/Bakgrund

Perovskite solar cells (PSC) represent a ground-breaking new photovoltaic technology with the potential for highly efficient solar cells at very low cost and with extremely short energy payback time. Focused research is needed to improve fundamental understanding of the PSC, which will lay the foundation for further increases in efficiency as well as for improvement of stability.

Both high efficiency and long lifetime are required for a viable new photovoltaic technology. This project, led by prof. Gerrit Boschloo (Uppsala University), running from end of 2017 to early 2021, was mainly focused on increasing the efficiency of PSC through molecular modifications of perovskite and contact materials. Suitable molecules can pacify defects at the perovskite / selective contact interfaces, thereby minimizing carrier recombination and improving solar cell performance. Improved perovskite synthesis methods will also lower defect density and improve long-term stability of the material.

Genomförande

Research groups:

UU-CHEM Uppsala University - Dept. of Chemistry - Ångström Laboratory: Gerrit Boschloo (PI); Hannes Michaels (PhD student); Byeong Jo Kim (Postdoc)

UU-PHYS: Uppsala University - Dept. of Physics and Astronomy: Håkan Rensmo (PI); Sebastian Svanström (PhD student)

UU-ENG: Uppsala University - Dept. of Engineering Sciences: Tomas Edvinsson (PI); Meysam Pazoki (Postdoc)

KTH: KTH Stockholm- Chemistry: Licheng Sun (PI); Fuoguo Zhang (postdoc); Linqin Wang (PhD student)

Workpackages:

1. Improved perovskite materials: UU-CHEM, KTH
2. Improved electron-selective contacts: UU-CHEM
3. Improved hole transport materials: KTH
4. Fundamental understanding / stability (methods: quantum chemical calculations; x-ray photoelectron spectroscopies): UU-PHYS; UU-ENG

Resultat

1. Improved perovskite materials

In general, there are two solution-based methods towards high-performance lead halide perovskites: the one-step method, where all components are mixed in one precursor solution, and the two-step method, where first a lead halide film is

deposited, followed by conversion to the perovskite by exposure to appropriate halide salt solutions. Both methods were explored in this project. The inherent polycrystalline nature of perovskite films leads to a high density of structural defects, especially at the grain boundaries and interfaces, representing a key challenge that impedes the performance of perovskite solar cells (PSCs).

One step method:

The addition of 20% ethylammonium chloride (EACl) to the MAPbI₃ precursor solution, in combination with a facile diethyl ether solvent bathing approach, leads to very high quality methylammonium lead iodide (MAPbI₃) films. Upon annealing (150°C) EACl is completely removed from the film, well-oriented, micron-sized grains are obtained that contribute to a long carrier lifetime and reduced trap density. The power conversion efficiency (PCE) is increased from 17.7% (no EACl) to **20.9%**, with negligible current hysteresis and enhanced stability upon dark storage (no degradation during 1000 h storage in air with relative humidity of 34% without encapsulation) [3].

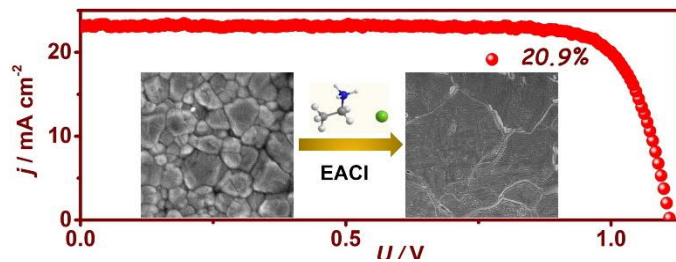


Figure 1: JV-curve of best perovskite solar cell using EACl

MAPbI₃ perovskite suspensions are prepared using a simple method without toxic solvents. A highly crystalline powder was obtained by evaporation of the solvent in a low-vacuum oven. MAPbI₃ solar cells were fabricated by dissolving the powder and applying it in a classical fabrication route. A champion efficiency of 19.9% was obtained and an average efficiency of 17% with low hysteresis effects. This method provides a more reproducible way of PSC production, since not all separate precursors have to be weighed in into the precursor solutions [12].

Two step method:

First a PbI₂ layer with Cs-acetate (CsAc) included is prepared; acetate forms a strong intermediate phase, which can help the intercalation of PbI₂ with cation halide (FAI, MAI, MACl) in the sequential process. The addition of CsAc reduces the trap density in the perovskite layer and extends the carrier lifetime. The CsAc-modified perovskite solar cells show higher efficiency: 21.3% average (1% CsAc) vs. 20.4% (0% CsAc), less hysteresis phenomena and enhanced operational-, and thermal stability. The efficiency of devices with 1% CsAc decreased by 5% (relative) after 1 hr continuous illumination, while 0% CsAc decreased by 20% (relative). The devices recover to their initial efficiency in the dark [16].

Surface modification of lead halide perovskites

Phenylammonium iodide (PAI), benzylammonium iodide (BAI), and phenylethylammonium iodide (PEAI) were used to modify the interface between MAPbI₃ perovskite and spiro-OMeTAD in solar cell devices. The formation of two-dimensional (2D) perovskite interfacial layers is found on the surface of MAPbI₃ films modified with PEA and BAI, whereas MAPbI₃ modified with PAI gives an interface layer with slightly different properties. Slower open-circuit voltage decay

and longer carrier lifetime are also observed for the modified cells, leading to a slight improvement of the photovoltaic performance [10].

In a novel approach gas-phase interface modification of perovskites was explored. Exposure of MAPbI_3 to butylamine vapor leads to significant effects: it leads to formation of the 2D perovskite BA_2PbI_4 with a yellow color, demonstrating that butylamine reacts with methylammonium (MA) to form butylammonium (BA) and methylamine gas. Initial results suggest that a short exposure can lead to surface modification with improved solar cell stability.

For the highest performing PSCs we used FAPbI_3 perovskite (2-step method) modified with n-hexyl ammonium bromide, forming a very thin 2D perovskite layer at the interface with the hole transporting material.

High bandgap perovskites

Purely inorganic CsPbI_3 perovskite has a bandgap of 1.7 eV, suitable for tandem solar cells. We found a remarkable light soaking effect in CsPbI_3 perovskite solar cells as the PCE increases from 10.8% to 18.3% after 180 s soaking under AM 1.5 G sunlight. It is revealed that the depressed dark current caused by a stronger built-in field and the decreased defects density passivated by the photogenerated electrons result in the enhanced PCE after light soaking [15].

2. Improved electron-selective contacts

KF addition to the SnO_2 colloid solution used for preparation of the electron-selective contacts gives significant positive effects: it leads to more uniform coating of the FTO substrate, and improves formation of the FAPbI_3 perovskite film. This results in PSC with higher PCE from 20.6% to 22.9% upon KF addition.

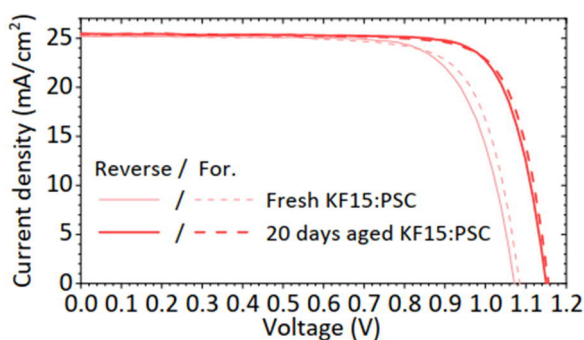


Figure 2. JV characteristics of a FAPbI_3 solar cell with KF-modified SnO_2 electron-selective contact. The PCE is 22.9% (without anti-reflective coating) after 20 days of aging in inert atmosphere.

3. Improved hole transport materials (HTM)

Several new conducting polymer HTMs were developed to replace the expensive and rather unstable standard spiro-OMeTAD. One series was based on BDT (benzo[1,2-b:4,5-b']dithiophene) and thiophene or selenophene, which featured properly tuned energy levels, good temperature and humidity resistivity, and excellent photoelectric properties. Using P3 a PCE of 20.3% was obtained [6]. The next series was new class of phenanthrocarbazole (PC) based polymers. With dopant-free PC3 a stabilized PCE of 20.8% was obtained for MAPbI_3 -based solar cells. The excellent humidity resistivity of the polymers resulted in excellent PSC device stability upon storage under ambient conditions, and upon light soaking at 40° C and 85° C, see Fig. 3. In comparison with the published state of the art, the

HTMs derived from the project are world-class. PC3 qualifies as one of the best PSCs based on dopant-free HTMs [13].

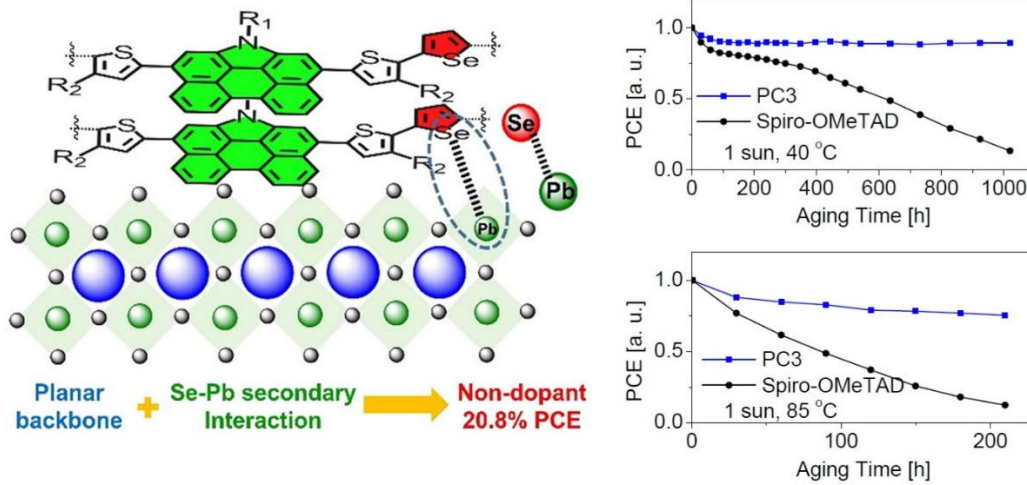


Figure 3. PC3 based dopant-free polymeric HTM for efficient perovskite solar cells and excellent device stability under long term 1 sun-illumination conditions. At 40 °C, 88% of the initial PCE is maintained after 1000 h illumination, while for PSCs with the standard HTM spiro-OMeTAD only 13% of the initial PCE is left.

Furthermore, a new crosslinked hole-transport polymer **P65** was designed and synthesized for n-i-p type PSCs. **P65** is obtained from a low-cost and easily synthesized spiro[fluorene-9,9'-xanthene]-3',6'-diol (SFX-OH)-based monomer **X65** through a free radical polymerization reaction. **P65** has good solubility and excellent film-forming properties, and PCE up to 17.7% was achieved [15].

4. Fundamental studies

Quantum chemical calculations

Ab-initio chemical calculations on the nature of the excited state have been performed to study and understand the mechanism behind the light induced trap/ion-migration that we have found experimentally. Blue light and light in the UV region create a much stronger force for lattice relaxation and an excess energy larger than the activation energy for iodide migration. This can trigger iodide vacancy movement. The activation energy for ionic conduction is by far lowest for iodide vacancies, and was found to be higher for FAPbI₃ than for MAPbI₃ and CsPbI₃, see Fig. 4 [1].

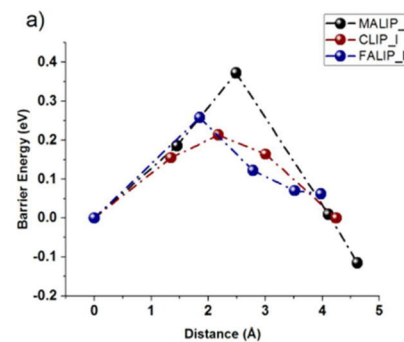


Figure 4: Calculated activation energies for iodide vacancy transport

XPS studies on perovskite stability

X-ray photoelectron spectroscopy provided insights on the chemical composition and the chemical distribution near the surface/interface of perovskite samples with improved material stability, achieved by incorporating small amounts of inorganic cations (Cs^+ and Rb^+) that partially replace the more common organic cations (e.g., methylammonium, MA, and formamidinium, FA). Rb and Cs appeared to act jointly, resulting in a different cation depth profile compared to that of the triple – cation counterparts. These findings provide significant understanding of the intricate depth-dependent chemical composition in perovskite materials using the common practice of cation mixing.

Selective contacts and electrodes influence the stability of perovskite solar cells. By adding thin contact layers by evaporation or controlled spin-coating we studied the chemistry in the interface layer and determined if the perovskite quality is degraded or improved by the addition of different contact layers. We have investigated thin metal films (Ag and Cu) directly deposited on perovskite as well as metal layers on top of a perovskite film covered with a hole-conducting material. We were able to determine that the perovskite interface is highly enriched in bromide. This suggests that a bromide-rich barrier layer forms with a thickness of a few nm in the interface, which might degrade the cell performance. Moreover, the investigation showed clear evidence for metal ion migration into the perovskite film [8].

We have also developed a sample environment that allow the use of high kinetic energy electron spectroscopy to probe buried interfaces (see Figure 5) and follow the material changes with such an element specific method. With this method we can follow how the ions move reversible in a complete device structure and how such ion movement can be affected. Moreover, from the measurements, we are also able to reconstruct the band alignment at the back contact in the solar cells during the measurements, which will help in further optimize the selection of electron and hole conducting materials [18].

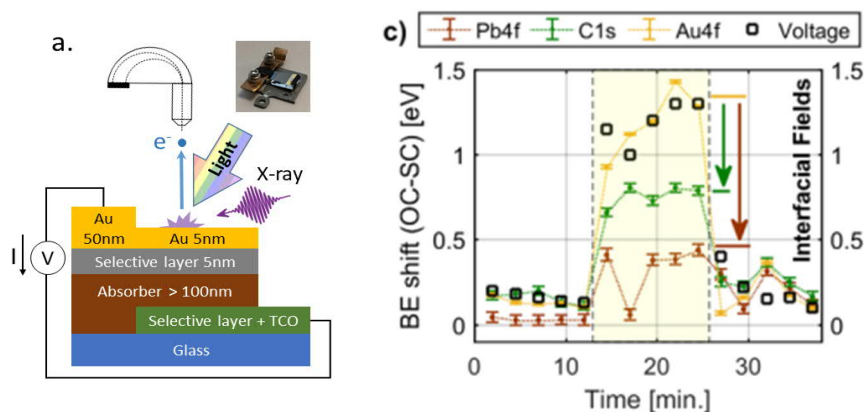


Figure 5. (a) Using hard X-rays we can study buried interfaces in the solar-cell device structure and follow material mixing and energy level alignment during operation. (b) The open circuit (OC) voltage generated by the cell and the binding energy shift between OC and short circuit in the Pb4f, C1s and Au.

Diskussion

The results from this project show that the perovskite solar cell research of the CMD consortium (UU-KTH) can compete with the rest of the world in terms on highly efficiency and fundamental insight. The high level of PSC performance is crucial for relevant research and high impact publications. The obtained know-how in the groups is important for the success of new applications and projects, and it qualifies researchers for new jobs (one researcher in the project is now employed at Evolar AB).

In a general sense, the continued improvement of PSC technology is encouraging and still on-line for a possible large-scale introduction of PSC on the PV market. There is, however, still a long way to go, especially in terms of long-term stability for PSC modules. It is noted that energy-payback time for PSC modules is calculated to be 4-5 times lower than that of silicon PV.

As for early industrial applications, perovskite – silicon tandem cells have been identified. Commercial production should start in 2022 (Oxford PV). Tandem cells take advantage of the higher bandgap of perovskites compared to silicon. A discrepancy in the long-term stabilities of the two technologies, where perovskite is the weaker link, is problematic, but seems possible to be solved soon.

Publikationslista

Scientific publication in peer-reviewed journals

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Book chapter

A book on characterization techniques for perovskite solar cell materials is under finalization, where two persons involved in this project are editors, and other (Boschloo, Rensmo) are involved as chapter contributors. (*Characterization Techniques for Perovskite Solar Cell Materials and Devices*, Elsevier, 2019, Eds. Pazoki, Hagfeldt, Edvinsson).

Referenser, källor

Bilagor

- Administrativ bilaga
- Publications (pdf format) can be send upon request