Improving the light-harvesting of thin-film solar cells with photochemical upconversion

1) Intermediate band SC

Restructuring of electronic bands, → Re-engineering of solar cell

2) Photon Upconversion (UC)

Spectral conversion by add-on unit → Augmentation of existing solar cell technology
Options for photon upconversion

**Coherent UC**

- Two-photon absorption
- Coherent effect
  - Extremely high light intensity
  - $\Rightarrow$ MWcm$^{-2}$ – GWcm$^{-2}$
  - $\Rightarrow$ $10^7$ suns

**Incoherent UC**

- Energy Transfer Upconversion (ETU)
  - QE of a few % is useful
  - Lanthanide-doped crystals and glasses
  - Applicable in a solid state concept
- Photochemical Upconversion (UC)
- Triplet-Triplet Annihilation (TTA)
  - Non-coherent UC
  - Potential at one sun?
1. Efficiency gains by upconversion
2. What is triplet-triplet annihilation?
3. Spin physics and rate equations
4. State-of-the-art in device application
5. How to further improve $\Delta J_{SC}$
6. Outlook
Efficiency limits of single-threshold solar cells

L. Hirst and N. Ekins-Daukes, Prog PV 19, 286 (2011)
Efficiency limits of single-threshold solar cells

Triplet-triplet annihilation upconversion

- **Sensitizer**
- **Emitter**
- **S**
- **T**
- **ISC**
- **TTA**
- **TET**
- **Solar cell**
- **Glass substrate**
- **UC medium**
- **BR**
0.96 eV upconversion margin
TTA efficiency: Spin statistics

TTA efficiency: Spin statistics

\[ S_0 \quad \text{h} \quad S_0 \]
TTA efficiency: Spin statistics

Simple reasoning: Only 1 out of 9 collisions statistically gives a singlet!
=> 11% conversion efficiency

Experiment: 60% conversion eff.
Quintet states cannot be populated!
Triplet channel barely open, one T* recovered!

TTA dynamics: Rate equations

Non-radiative decay
Loss mechanism
TTA dynamics: Rate equations

Rate equations

\[
0 = \frac{dN_T}{dt} = k_\phi N_S - k_1 N_T - k_{TTA} N_T^2
\]

\[
f = \frac{k_{TTA} N_T}{k_1 + k_{TTA} N_T}
\]

\[
N_T = \frac{k_\phi N_S}{k_1}
\]

Fraction of emitters undergoing TTA
Emitter triplet concentration

Concentrate light!
Back-reflectors
Micro-focussing
Near-field effects,...

Concentrate sensitizers!
Solid-state approaches
Adsorbates,...

TTA conversion eff: 60 %

Exp. TTA conversion eff: < 1 %

Auckett et al., J. Physics: Conference Series 185, 012002 (2009)
Bifacial, transparent a-Si:H pin solar cell prepared at HZB’s Photovoltaic Competence Center Berlin (PVcomB), conversion efficiency = 7.5%.
\[ \eta_\downarrow = 3.9\% \]
\[ \eta_\uparrow = 7.5\% \text{ (w. reflector)} \]

a-Si:H pin cell w. back reflector (Ag-coated beads)

19 suns: ΔEQE = 3% 
ΔJ_{sc} = 0.28 mA/cm²

Lines are model fits for UC effect in EQE:

\[
\frac{EQE_{UC}(\lambda)}{EQE_0(\lambda)} = 1 + \chi \times \frac{T_{SC}(\lambda)}{EQE_0(\lambda)} \frac{\sigma(\lambda)\sigma_b}{\sigma(\lambda) + \sigma_b}
\]

Schulze et al., J. Phys. Chem. C, online (2012)
...as compared to very first results

Experimental results on OPV

UC signal in EQE of OPV cells

Eff. solar conc.: 29 suns

η↓ = 3.1%
η↑ = 1.7%

η↓ = 3.6%
η↑ = 2.3%

Cells designed & produced by J. Czolk & A. Colsmann at KIT

Schulze et al., J. Phys. Chem. C, online (2012)
Prospects for TTA-upconversion

Analyzing the figure of merit: Current enhancement at 1 sun for a-Si:H cells

\[ \text{FOM} = \frac{\Delta j_{SC}}{C^2} \]

Yield at maximum \( \eta_{UC} \)

100 x \( C_{\text{sensitizer}} \)

optimized optics

current concentrations, optimized optics

Crucial quantities for optimization

Rate equations

\[ 0 = \frac{dN_T}{dt} = k_\phi N_S - k_1 N_T - k_{TTA} N_T^2 \]

\[ f = \frac{k_{TTA} N_T}{k_1 + k_{TTA} N_T} \]

Fraction of emitters undergoing TTA

\[ N_T = \frac{k_\phi N_S}{k_1} \]

Emitter triplet concentration

Concentrate light!
High transmission of SC back-reflector near-field effects?

Concentrate sensitizers!
Solid-state approaches Adsorbates,...

Exp. TTA conversion eff: 60 %

Exp. TTA conversion eff: < 1 %

Auckett et al., J. Physics: Conference Series 185, 012002 (2009)
Thickness variation of UC layer with reflector

Step 1: Tuning $k_{\Phi}$ – local focussing of light

Exploiting the nonlinearity of UC response

Nonlinearity $\rightarrow$ gain by focussing
• Hot embossing of PTFE foil with silica beads
• Successively Al coating for reflectance
• Measurement in the half cuvette
Step 1: Tuning $k_\Phi$ – local focusing of light

**Results:**
- Moderate gain (25%)
- Factor of up to 9 promised for optimized conditions (fill factor, reflectance)

Prospects for TTA-upconversion

Analyzing the figure of merit: Current enhancement at 1 sun for a-Si:H cells

Yield at maximum $\eta_{UC}$

- 100 x $C_{Sensitizer}$
- optimized optics

...with micro-focussing

current concentrations,

optimized optics

$FOM = \Delta j_{sc} / C^2$

Step 2: Increasing $C_{\text{Sens}}$ – All solid upconverter

Energy Upconversion via Triplet Fusion in Super Yellow PPV Films Doped with Palladium Tetraphenyltetrabenzoporphyrin: a Comprehensive Investigation of Exciton Dynamics

Vygintas Jankus,* Edward W. Snedden, Daniel W. Bright, Victoria L. Whittle, J. A. G. Williams, and Andy Monkman

SY before energy transfer can occur. It has been shown that during this migration in PdTPBP aggregates, 76-99% triplets in PdTPBP are lost due to triplet annihilation in PdTPBP.
Toward high-efficiency solar upconversion with plasmonic nanostructures

Ashwin C Atre\textsuperscript{1}, Alitzol Garcia-Etxarri\textsuperscript{1,2}, Hadiseh Alaeian\textsuperscript{3} and Jennifer A Dionne\textsuperscript{1}

\textsuperscript{1} Department of Materials Science, Stanford University, Stanford, CA 94305, USA
\textsuperscript{2} IKERBASQUE, Basque Foundation for Science, 48011, Bilbao, Spain
\textsuperscript{3} Department of Electrical Engineering, Stanford University, Stanford, CA 94305, USA

Figure 1. (a) Schematic diagram of the solar cell–upconverter system. Above-bandgap light is absorbed by the solar cell, while sub-bandgap light is absorbed in the upconverter layer. The upconverter consists of metal–dielectric core–shell nanocrescents, in which the core is doped with the upconverting material. (b) An upconverter (UC) can significantly increase the efficiency of an ideal single-junction solar cell. This relative increase is greatest when the upconverter absorption efficiency and cell bandgap are high. The inset shows the absolute efficiency for an ideal solar cell both with and without an ideal upconverter.
Tuning the absorption range → molecular engineering & multiple sensitizers

Baluschev et al., APL 90, 181103 (2007)

World Map

T. F. Schulze
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On my own behalf... introducing the Energy Materials In-situ Lab Berlin (EMIL)
What is the impact of structure, stoichiometry and electronic properties on material quality and device performance?

- Stoichiometry, interdiffusion
- Homogeneity
- Oxidation, contamination
- Structure, grain boundaries
- Interface passivation
- Light harvesting

→ Elucidate chemical/electronic structure:

A knowledge-based solar cell improvement requires...
- Fast measurements on large sample series
- Material properties must relate to device
- *In-situ* deposition/preparation/manipulation on sample areas 100 cm² (boundary effects, compatibility to industrial processes)
PES – Photoelectron spectroscopy
PEEM – Photoemission electron microscopy
HAXPES – Hard X-ray PES
XES – X-ray emission spectroscopy

XAS – X-ray absorption spec.
XRF – X-ray fluorescence spec.
XRD – X-ray diffraction spec.

Wide X-ray energy range needed (80 eV - 10keV)
EMIL: Energy research at the synchrotron BESSY II

BESSY II: 3rd-gen storage ring (d=80m, 1.7GeV), operating since 1998
EMIL’s Building: An Extension to BESSY II

Available Lab Space at EMIL > 600 m²
DEPOSITION and UHV- TRANSPORT

Samples:
Cluster/ UHV Transfer : 10*10 cm²
Analytics: 2.5*2.5 cm²

4-8 UHV deposition chambers, STM/KPFM
• Research alliance between HZB and Max-Planck Society
• Total funding secured: 26.6 Mio EUR
• First beam: End of 2014, fully operational by mid-2015.
• **Will be a user facility!**
• Stay tuned: EMIL website to be launched soon...
Thank you for your attention!