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Increased upconversion performance for thin film solar cells: a trimolecular composition

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Photochemical upconversion based on triplet–triplet annihilation (TTA-UC) is employed to enhance the short-circuit currents generated by two varieties of thin-film solar cells, a hydrogenated amorphous silicon (a-Si:H) solar cell and a dye-sensitized solar cell (DSC). TTA-UC is exploited to harvest transmitted sub-bandgap photons, combine their energies and re-radiate upconverted photons back towards the solar cells. In the present study we employ a dual-emitter TTA-UC system which allows for significantly improved UC quantum yields as compared to the previously used single-emitter TTA systems. In doing so we achieve record photo-current enhancement values for both the a-Si:H device and the DSC, surpassing 10^{-3} mA cm⁻² sun⁻² for the first time for a TTA-UC system and marking a record for upconversion-enhanced solar cells in general. We discuss pertinent challenges of the TTA-UC technology which need to be addressed in order to achieve its viable device application.

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1 Introduction

All absorbers in photovoltaic (PV) cells transmit photons with energies below their respective bandgaps, and therefore they fail to harvest the low energy portion of the solar spectrum. Photon upconversion (UC) has been recognized as a method to assist photovoltaic devices to harvest this unused sub-threshold light. The UC method can theoretically expand the utilization of the solar spectrum and thus is recognized as a potential method to exceed the Shockley–Queisser efficiency limit¹ for PV conversion.^{2–5} A maximum solar power conversion efficiency of around 43% has been calculated for an upconversion-assisted solar cell assuming the AM1.5G solar spectrum.^{3,6–8}

Essential requirements for the application of UC include a broad absorption in the sub-threshold region of the PV absorber and high UC quantum yield under incoherent low-intensity illumination. UC through sequential photon absorption (SPA) using lanthanide ion-doped materials in solid-state matrices has been studied intensively.^{9,10} However, these UC systems suffer from very weak absorption due to their Laporte-forbidden optical transitions, and very narrow atomic absorption lines.¹¹ Applications of SPA-UC systems to PV devices based

on gallium arsenide,¹² crystalline silicon,^{13–18} hydrogenated amorphous silicon (a-Si:H),^{19,20} dye-sensitized solar cells (DSC)^{21–23} and organic photovoltaic materials²⁴ have been demonstrated, but in consequence they mostly require relatively high solar concentration to achieve measurable current enhancement. Recently, researchers have been able to broaden the absorption range of SPA materials through the attachment of organic dyes acting as antennae,²⁵ or to increase their absorption by exploiting plasmonic resonances in metallic nanostructures.²⁶ However, these advanced SPA concepts still await device implementation in solar energy conversion.

In contrast, UC based on triplet–triplet annihilation (TTA-UC) involves organic molecular species, which typically have broader and stronger electronic transitions as compared to lanthanide ion-doped materials. Additionally, TTA-UC exploits the large oscillator strength of singlet–singlet transitions to absorb and emit the light, in contrast to SPA-UC, which has a weak oscillator strength to absorb and emit. Moreover, in TTA-UC, the intermediate energy storage is facilitated by long-lived triplet states of the organic chromophores (>40 μs (ref. 27)), which is important for the merging of energy from two photons arriving at different times. Consequently, TTA-UC has been proven to be an efficient photon upconversion process by various research groups^{27–31} and UC yields of greater than 30% have been measured for TTA-UC under intense monochromatic illumination.^{28,32,33} However, studies have also shown that TTA-upconversion is achievable under broad-band white-light illumination.^{34–37} Based on the promising quantum yields and the spectral tunability of TTA-UC, several applications in solar energy conversion and storage have been demonstrated ranging

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Fig. 2 Solutions of the TTA rate equations for typical rate constants of presently employed single-emitter TTA systems (black curve), and for a 10-fold increased TTA rate (red curve). The blue area highlights the range of sensitizer excitation rate achievable under sunlight illumination. It can be seen that upon increasing the TTA rate, the UC quantum yield under 1 sun conditions is significantly enhanced.

similar sensitizers.^{46,52} However, the 2CBPEA fluorescence overlaps with the Soret band absorption of the sensitizers relevant to thin-film PV devices.^{40,42,44,45} Combining 2CBPEA with these relevant sensitizers in a UC system for PV cells would therefore result in severe parasitic reabsorption of the upconverted light, rendering 2CBPEA inapplicable to solar energy conversion as a solitary emitter species.

We demonstrate here that the high TTA rate constant of a compound closely similar to 2CBPEA – BPEA in our case – can indeed be exploited by *combination* with the rubrene-based flagship TTA system. We show that a synergistic action of the two emitter species leads to a significantly increased yield of the upconverted fluorescence emitted by the rubrene species, and an accordingly increased current enhancement of a-Si:H and DSC thin-film solar cells. These two devices have absorption onsets of 1.7 eV and 1.8 eV, respectively, making them ideal candidates for UC enhancement under AM1.5G illumination.^{6–8} The combination of the dual-emitter UC system and the devices leads to record current enhancements. This UC architecture is similar to the mixed system reported by Cao *et al.*,³² who observed an increased quantum yield of a dual DPBF/DPA emitter system as compared to the individual components. Importantly, as the UC emission still results from rubrene, the dual-emitter system is *not* affected by parasitic absorption. We reasoned that BPEA would rather act as a triplet shuttle, which

would assist in funneling triplet energy into the slowly moving rubrene molecules by means of its high TET and TTA rate constants.⁴⁹ Details will be given in the discussion section. We begin with the description of the solar cells and the upconversion system.

3 Experimental

3.1 Solar cell preparation

Semi-transparent hydrogenated amorphous silicon (a-Si:H) p-i-n solar cells were prepared on $30 \times 30 \text{ cm}^2$ glass sheets by the following process sequence: 1000 nm of aluminium-doped zinc oxide (ZnO:Al) was deposited as front TCO by reactive sputtering. Then, a p-doped $\mu\text{c-Si}/\mu\text{c-SiO}_x/\text{a-Si:H}$ triple layer stack with a total thickness of 26 nm, 150 nm of undoped a-Si:H as absorber layer, and 27 nm of n-doped $\mu\text{c-Si}$ were grown by plasma-enhanced chemical vapor deposition (PECVD). Finally, a 525 nm thick ZnO:Al back contact layer was sputtered. As in our previous study,⁴² the front TCO was a smooth film to achieve a sharp cutoff of the spectral response which helps the measurement of the UC effect. The increased transmittance of the newly developed p-doped layer stack⁵⁶ allowed the i-layer thickness to be increased to 150 nm, while maintaining the peak EQE and near-infrared transmittance as in our previous studies. Using this approach, semi-transparent a-Si:H cells with 7.0% conversion efficiency were realized without any backside reflector (previously: 6.7%). For combination with the UC unit, the glass substrates were cut into $10 \times 10 \text{ cm}^2$ pieces, each containing 20 individual solar cells of $1 \times 1 \text{ cm}^2$ size.

DSC devices were produced in a manner similar to previously described.^{45,57} A dense TiO_2 layer was deposited on clean F:SnO₂ glass (Hartford) by spray pyrolysis, onto which a 3 μm layer porous TiO_2 (18NR-T, Dyesol) film was screen printed. After sintering, this was placed in a dye bath containing 0.5 mM D149 (1-material) in 1 : 1 acetonitrile : *tert*-butanol. The sensitized film was sandwiched together with a platinised counter electrode (made by thermally decomposing a drop of 10 mM H_2PtCl_6 ethanolic solution on F:SnO₂ glass), using a 25 μm Surlyn spacer. Electrolyte solution (0.1 M LiI, 0.6 M DMPII, 0.05 M I₂ in methoxypropionitrile) was introduced into this cavity through a pre-drilled hole in the counter electrode, using a vacuum backfilling method. The filling port was then sealed using a small piece of Surlyn:aluminium laminate. Electrical connections were made using an ultrasonic soldering iron and Cerasolzer 186 (MBR).

3.2 TTA-UC solution preparation

The TTA-UC solution was prepared by dissolving {5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-6'-amino-7'-nitro-tetrakisquinoxalino[2,3-*b'*7,8-*b''*12,13-*b'''*17,18-*b''''*]porphyrinato}palladium(II) (PQ₄PdNA^{40,58}) with rubrene (Sigma-Aldrich) and 9,10-bisphenylethynylantracene (BPEA, Sigma-Aldrich) in toluene to concentrations of 0.8 mM, 2 mM and 5.1 mM, respectively. The TTA-UC sample was deoxygenated through three freeze-pump-thaw cycles using liquid nitrogen cooling, during which the solution was pumped down to the order of 10^{-3} mbar in





Fig. 3 The spectral properties of the two UC/device assemblies in this study: (a) absorption of PQ₄PdNA (green) and emission of rubrene (orange) and BPEA (blue). IPCE (solid) and transmittance (dash) of (b) a-Si:H, illuminated through glass substrate and (c) DSC, illuminated through working-electrode.

a custom vacuum cuvette. A concentration of 5.1 mM of BPEA was chosen as it is close to its solubility limit in toluene and does not lead to recrystallization during freeze–pump–thaw cycles. Initial investigations revealed that a 3 : 1 ratio of BPEA : rubrene provided the most significant increase to UC intensity.

Fig. 3 shows the absorption spectrum of PQ₄PdNA, emission spectra of rubrene and BPEA, as well as the IPCE and transmission curves of the two solar cells. It is clear that the sensitizer is readily able to harvest light transmitted by both devices. Although containing two emitter species, the UC solution emits exclusively at the wavelength of the lower-energy emitter S₁ state.³² This way, parasitic absorption is avoided as rubrene emits within the absorption window of the sensitizer and the emission spectrum matches well with the a-Si:H and DSC spectral responses.

3.3 Optical coupling

In previous studies we have optimized the combined optics of solar cell/UC unit assemblies.^{40,41,43} We found that the UC performance is optimal if the UC material is combined with a back reflector and its thickness chosen such that the reflector is positioned at approximately the characteristic absorption length ($1/e$ decay) of the incident light at the sensitizer peak absorption.⁴⁰ After propagating through the TTA-UC medium twice, the light at the peak absorbance of PQ₄PdNA will then attenuate to $1/e^2$ of its original intensity. This means that approximately 13% of the incident light leaves the UC medium, but the resulting effective concentration of the incident light leads to a net increase of UC photon yield due to the nonlinear response of the UC unit.⁴³ For typically achievable sensitizer concentrations the optimum thickness is in the 100 μm range. To realize such thin effective thicknesses of the UC medium, we add silver-coated glass spheres with 100 μm diameter to the 1 cm diameter cuvette. The closely packed spheres create cavities of appropriate size in which the UC medium resides and thus help to efficiently outcouple the upconverted light.⁴¹ The

concentration of PQ₄PdNA was optimized for the cavity size created by the 100 μm silver-coated spheres. The front of the 1 cm cuvette with the degassed TTA-UC sample was optically coupled to the back of the a-Si:H (ZnO:Al) and DSC (working-electrode) by means of immersion oil (Sigma-Aldrich, $n_D^{20} = 1.516$).

3.4 Measurement and data analysis

The current enhancement of solar cell devices brought about by TTA-UC is measured using a pump–probe technique.^{40–45} Since TTA-UC is a non-linear process under low excitation photon flux^{27,50,51,53} (Fig. 2), the low-intensity monochromated probe beam used to measure the incident photon-to-current efficiency (IPCE) in common measurement setups alone will not attain a significant TTA-UC effect. To yield a measurable UC response we therefore employ a continuous wave (CW) bias light in the form of a 670 nm diode laser, selectively exciting the sensitizer. The pump beam excites the TTA-UC solution behind the PV sample to provide a background concentration of emitter triplets to increase the upconverted photon yield induced by the chopped probe light, allowing comparisons to be made on the basis of excitation rates exerted by the pump beam. The monochromatic probe beam was chopped and the resulting signal (from the device) was recorded by lock-in amplification. The chopping frequencies used were 117 Hz and 23 Hz for a-Si:H and DSC respectively.

The analysis of our IPCE data relies on the comparison of IPCE curves taken with and without the UC effect. It turns out that the measurement without the UC effect is a non-trivial task. We cannot physically remove the UC unit as this will alter the optics of the semitransparent solar cell device and impede a direct comparison of the IPCEs. However, the UC response without the bias beam is negligible, and we therefore take this situation to be the baseline IPCE. The probe energy is ~ 1 order of magnitude weaker than the lowest pump intensity employed in this study and therefore the UC intensity will be $\sim 100\times$ weaker.⁴¹ Furthermore, this approach will result in an underestimation of the UC-derived current enhancement. A second issue concerns switching off the bias beam: although the bias laser energy is below the nominal bandgap of the PV absorbers employed here, their absorption tails may still absorb the bias beam. Even though an eventual DC current contribution from the bias will be filtered out by the lock-in detection technique, if the cell has a nonlinear response, artifacts might still be induced. We therefore do not turn off the bias beam, but laterally displace it on the solar cell area such that the probe beam is probing an unbiased region of the UC unit. By misaligning the pump and probe beams, TTA-UC generated by the probe beam is minimized while an eventual weak current-bias from the UC induced by the pump is maintained.

After measuring an IPCE response curve of a device under monochromatic illumination from 500 nm to 780 nm with the pump and probe beam aligned, we repeated this measurement with the pump and probe beam misaligned. For both the a-Si:H and DSC devices, 6 sets of aligned and misaligned IPCE measurements were taken and averaged. The pump intensity



was then adjusted in order to probe the UC effect at different excitation powers. Further detail on the measurement procedure can be found elsewhere.⁴⁵

The IPCE traces with UC contribution are divided by the corresponding baseline IPCE measurements to obtain IPCE enhancement curves. We found earlier that the resulting enhancement traces can be understood and modeled, taking into account the solar cell transmission and sensitizer absorption,⁴¹ confirming the enhancement to be TTA-UC related. Furthermore, integrating the measured enhancement curves over the AM1.5G spectrum, the enhancement of the solar cell photocurrent (ΔJ_{SC} , in mA cm^{-2}) under the given solar concentration factor defined by the pump beam intensity can be determined.

In order to quantify the effective solar concentration sensed by the UC unit, we calculate the rate of excitation of an individual sensitizer molecule $k_{\phi b} = \sigma(\lambda_b)T_{SC}(\lambda_b)I_b$, with the irradiation I_b of the bias beam in photons per area per time and the bias laser wavelength λ_b . We then compare this rate to the excitation rate brought about by the AM1.5 solar spectrum filtered by the solar cell transmission (k_{ϕ}). k_{ϕ} is calculated by multiplication of the AM1.5G solar spectrum, ρ_{\odot} , in photons $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ by the transmission of the solar cell, T_{SC} , and integrating the product of this with the absorption cross section of the sensitizer species, $\sigma(\lambda)$ in cm^2 ,

$$k_{\phi\odot} = \int \rho_{\odot}(\lambda)T_{SC}(\lambda)\sigma(\lambda)d\lambda. \quad (3)$$

Typical values for $k_{\phi\odot}$ are in the 2–10 s^{-1} range and depend on the solar cell transmission. The ratio $C = k_{\phi b}/k_{\phi\odot}$ then gives the effective solar concentration sensed by the upconverter. Since the two devices have different transmittances of the solar spectrum, the excitation rates from the solar spectrum are not identical even with the same TTA-UC materials and measurement conditions. As a consequence, the two devices were studied under different solar concentration ranges. ΔJ_{SC} values were normalized by dividing by the square of the concentration factor (C^2) to account for the inherently quadratic response of the TTA-UC process for low illumination densities (Fig. 2).^{40–45,59} The normalized ΔJ_{SC} values are our figures of merit (FoMs) for comparisons between UC/device pairs, and equal the current enhancement by UC that would be measured under 1 sun conditions. Further details of experimental techniques, data analysis and modeling can be found in our recent publications.^{40–42,45}

4 Experimental results

The initial experiment in this series started by studying the behaviour of the TTA-UC solutions coupled to a DSC upon changing the emitter composition. Firstly, IPCE control measurements were established with a rubrene only, a BPEA only and a dual-emitter (BPEA : rubrene = 3 : 1) UC system with the same *total* emitter concentration each, and in combination with a DSC. The short circuit current responses without UC contribution were subtracted from the responses with activated UC unit and the resulting raw current enhancement traces are

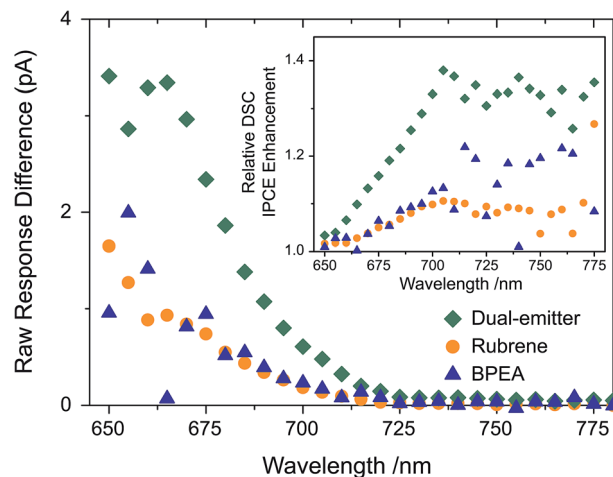


Fig. 4 Extra current generated from a DSC due to TTA-UC with dual-emitter (green), rubrene only (orange) and BPEA only (blue) UC system. The inset shows the IPCE enhancement of the DSC with the three different UC systems.

shown in Fig. 4, which represent the extra solar cell current generated due to the presence of the different TTA-UC solutions. Despite the parasitic absorption of the BPEA emission by the sensitizer, its higher TTA rate constant makes up for this, and the increased currents of BPEA and rubrene alone are near identical. We saw that in the presence of both emitter species, ~ 3 times more UC-related current was generated by the DSC, as compared to the situation where only a single emitter (either rubrene or BPEA) was employed. It is important to note that this occurs despite the total emitter concentration remaining constant, and points towards a synergistic action of rubrene and BPEA in the utilization of the sensitizer triplet density.⁴⁹

The IPCE enhancements of the two UC/device assemblies, obtained by dividing UC-assisted and baseline IPCE, are shown in Fig. 5 at an effective solar concentration for the a-Si:H cell of 1.4 \odot and for the DSC of 1.3 \odot . The error bars on the traces are

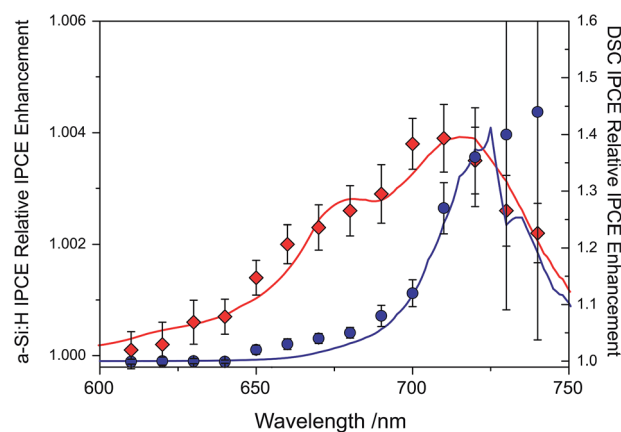


Fig. 5 Relative enhancement trace for a-Si:H device (\diamond , red trace) tested with ~ 1.4 suns equivalent illumination ($\lambda = 670 \pm 5$ nm) and a DSC (\circ , blue trace) tested with ~ 1.3 suns equivalent illumination, including the modeled traces for the two devices.^{40,41}



the standard deviations from point averaging at the respective wavelength. Since the DSC has a significantly lower IPCE in the range of $680 < \lambda < 750$ nm, it has a much more pronounced relative IPCE enhancement compared to the a-Si:H device. This shows that direct comparisons of UC/device assemblies drawn from the relative enhancements are not sensible.

The IPCE measurements and the determination of the short-circuit current increase ΔJ_{SC} as well as of the FoM were repeated as described above for a range of different effective solar concentrations (0.1 to 9 \odot). The results are shown in Fig. 6. Panel (a) reproduces the generic behavior of TTA-UC systems shown in Fig. 2 by displaying a quadratic response of the UC-related current for low excitation densities which turns into a sub-quadratic increase above ≈ 3 –5 \odot . This behavior was also seen experimentally in many studies analyzing the upconverted fluorescence intensity upon varying the pump intensity.^{2,5,50,51,60,61} The fact that ΔJ_{SC} (\odot) is sub-quadratic already beyond 3–5 \odot indicates that the TTA efficiency of the UC system is beginning to saturate.²⁷ The comparison to the simulated QY from Fig. 2 suggests that our dual-emitter UC system is indeed operating at a higher effective TTA rate than that of rubrene: the changeover to the sub-quadratic regime should not happen



Fig. 6 (a) Dependence of calculated current gain (ΔJ_{SC}) on effective solar concentration (both axes on a logarithmic scale) for the a-Si:H device (\diamond) and DSC (\circ). (b) Figure of merit (FoM) as a function of solar concentration for a-Si:H (\diamond) and DSC (\circ).

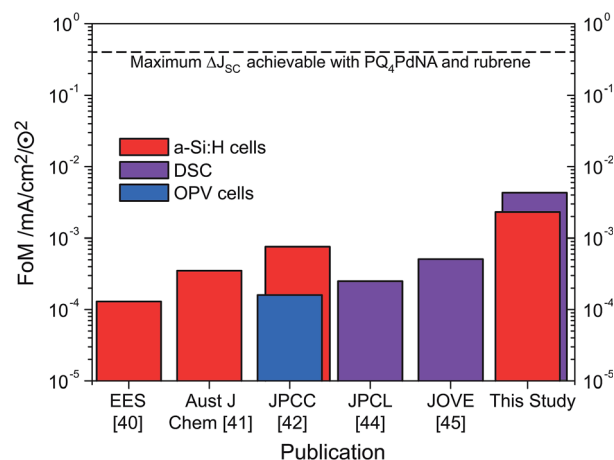


Fig. 7 The evolution of the FoM applied to a-Si:H cells (red), DSC (purple) and OPV (blue) in logarithmic scale.

below ≈ 25 \odot for a pure rubrene system (Fig. 2 taking into account that k_{ϕ} at 1 sun is 4 s^{-1} for PQ₄PdNA). The position of the changeover at ≈ 3 –5 \odot suggests a roughly 10-fold increased effective TTA rate. Although further studies are needed to substantiate this claim, we take it as a strong indication that BPEA increases the effective TTA rate of rubrene-based TTA systems.

As seen in Fig. 6b the FoM values are constant in the quadratic regime from panel (a) and decay to lower values for higher concentration factors. The FoMs can be used for meaningful comparisons between different UC/device assemblies from both the present report and previous studies. The DSC FoM was $\sim 4.5(5) \times 10^{-3}$ $mA/cm^2/\odot^2$, deviating from quadratic at illumination levels of 3 \odot , while the a-Si:H device displayed an FoM of $\sim 2.4(0.1) \times 10^{-3}$ $mA/cm^2/\odot^2$ up to 3 \odot .

Apart from the impact of the sub-quadratic response for the highest excitation densities, it seems that the DSC device outperforms the a-Si:H device also in regions where the illumination density is moderate.

Inspecting the baseline IPCE spectra in Fig. 3, it appears that the DSC can make better use of the upconverted light as it displays a constant IPCE of roughly 0.6 across the entire region of the rubrene emission, while the a-Si:H cell IPCE is reduced for $\lambda > 500$ nm. The advantage of the DSC over the a-Si:H device is that its spectral response can be readily tuned by choosing a specific dye to match the UC emission. For example, the D149 dye employed here is chosen for the DSC to provide a good spectral response to rubrene emission. The a-Si:H device on the other hand has higher transmission in the (infra)red region and results in enhancements across a broader spectral range (Fig. 5). Nonetheless, this fact does not compensate for the mismatch of a-Si:H IPCE and rubrene emission.

5 Discussion

5.1 Increase of UC quantum yield by dual-emitter system

There are, to our knowledge, two studies that have shown a beneficial effect of combining two emitter species with



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