

# Pushing upconversion to device-relevant efficiency

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In the past decade, there has been progress made in the application of upconversion to solar cells.[1-7] The applications of photochemical upconversion (PUC) have been confined to high-threshold solar cells such as amorphous silicon,[1-4] bulk heterojunction,[3] and dye-sensitized cells.[4,7] The prevailing figure-of-merit for such devices is the short-circuit current increase, due to upconversion, under one-sun illumination. Or, in the case that the conditions are greater than one-sun, the current is to be divided by the square of the concentration factor to reflect the quadratic dependence of the process. The progress of PUC as applied to solar cells is summarized in the Figure below. The highest recorded figure-of-merit (FoM) is  $4.5(5) \times 10^{-3} \text{ mAcm}^{-2}$ , measured at one-sun.[7] This well below a device-relevant figure of  $0.1 \text{ mAcm}^{-2}$ .

The measured FoM can be improved by many strategies. In this talk, I unfold a roadmap of the route towards an efficient PUC-solar cell by use of a stochastic upconverter simulator. We address each of the above factors to estimate the effect on the FoM.

## **Simple deep upconvertors**

We first model a rubrene upconverter sensitized with the PQ<sub>4</sub>PdNA porphyrin previously reported. The emitter and sensitizer are matched reasonably well spectrally. Rubrene emission largely occurs in the transmission window afforded by the gap between the Q- and Soret-bands of the porphyrin species. With a 600 nm long-pass filter and a porphyrin concentration of  $N_S = 1 \times 10^{-3} \text{ M}$ , we calculate that the rate of excitation per sensitizer molecule is about  $6 \text{ s}^{-1}$ . At the front of the sample, the efficiency of the upconverter may be estimated by solving firstly a quadratic equation describing the steady-state kinetics of the photochemistry,

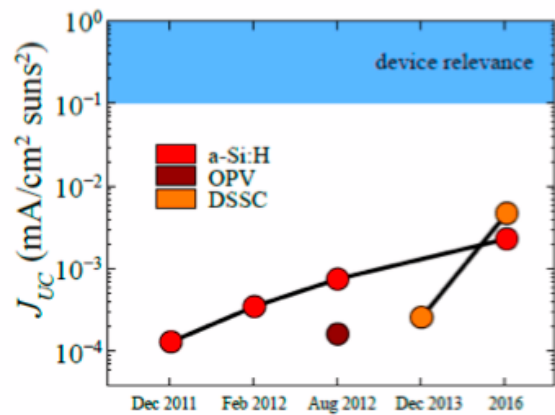
$$N_T = k_\phi N_S - k_1 N_T - k_2 N_T^2$$

assuming quantitative and rapid intersystem crossing and subsequent triplet energy transfer. Choosing realistic figures, we arrive at a triplet concentration of  $N_T = 3.27 \times 10^{14} \text{ cm}^{-3}$ . The maximum photon production rate at the front of the upconverter is thus  $W_{UC} = \Phi_F \eta / 2 k_2 N_T^2$

where  $f_2$  is the proportion of triplet decay due to second order events. For realistic emitters, this value can be reduced by a factor  $\eta$ , which accounts for the proportion of annihilation events which give rise to the desired singlet channel. For rubrene, this is 0.6. The quantity  $\Phi_F$  is the fluorescence quantum yield of the emitter and is taken as unity. At the front of the cuvette,  $f_2$  is estimated to be just 0.0055, and thus this device is operating far from optimally, where  $f_2$  approaches unity.

To model the device in detail, we propagate the incoming photons into the sample to generate a function  $k\phi(z) N_S$ . From this,  $W_{UC}(z)$  is calculated in a self-consistent manner, taking account of the recycling of upconverted photons due to reabsorption by the sensitizer.

Despite the inefficiencies, the calculated total current passing through the front of the sample is  $2.6 \times 10^{-3} \text{ mAcm}^{-2}$ , (assuming one electron generated per emitted photon). If the transmission of the solar cell in the spectral region of interest is as low as  $T = 0.4$ , as in Reference 3, then the photon current emitted by the

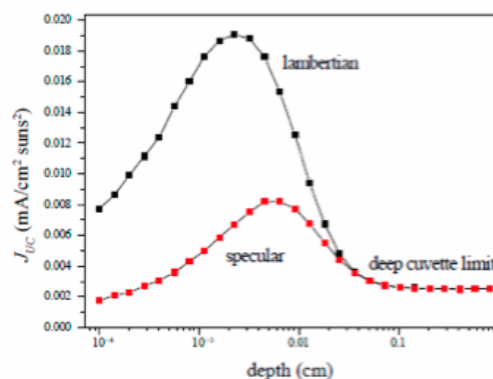


upconverter is calculated to be just  $4.0 \times 10^{-4} \text{ mAcm}^{-2}$ . When the efficiency with which the attached solar cell converts the upconverted light to current is taken into account, an FoM of the order of those first reported by our group is obtained (Figure 1). The ray-tracing model can thus be taken as physically reasonable, and a roadmap towards much higher efficiencies can be drawn.

### Device factors

If the transmission of the solar cell is increased to 1.0 below its absorption threshold,  $J_{UC}$ , is increased to  $2.6 \times 10^{-3} \text{ mAcm}^{-2}$ .

The performance of the device is plotted as a function of the device thickness in the Figure. The lambertian back reflector outperforms the specular back reflector. The lambertian back reflector aids the absorption of incoming photons. Those photons not absorbed on the first pass are scattered into paths away from the normal, thus increasing the chance of reabsorption. As such, the optimal device thickness is smaller for a lambertian back reflector than the specular reflector, effectively concentrating the absorbed photons and allowing more efficient upconversion to take place. Secondly, the isotropic upconversion emission is also out-coupled more effectively with a lambertian back reflector than a specular reflector.



### Photochemical Factors

The above calculations have all been performed for a rubrene annihilator, which exhibits rather slow triplet-triplet annihilation and triplet energy transfer kinetics. There are many others, particularly with blue emission, which have triplet-triplet annihilation rate constants an order of magnitude or more higher than rubrene. By increasing the parameter  $k_2$  by a factor of 10, to  $1.7 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ , the  $J_{UC}$  is increased to  $0.14 \text{ mAcm}^{-2}$  at a thickness of  $32 \mu\text{m}$  with a lambertian back reflector.

The value  $\eta$  is related to the efficiency with which triplet pairs annihilate to singlet states. In rubrene, this was determined to be about 0.6, which was rationalized by considering a thermally activated triplet channel. But, there is no *a priori* reason that an annihilator with similar spectral properties to rubrene cannot also exhibit  $\eta$  approaching unity. It shall not surprise anybody that the  $J_{UC}$  increases by the expected ratio  $1.0/0.6$  to  $0.24 \text{ mAcm}^{-2}$  upon relaxing this condition.

Increasing the concentration of sensitizer above about 1 mM in solution has not been found to be beneficial. While the precise reason for this has not been elucidated, it is likely to be due to aggregation, or the external heavy atom effect foreshortening the lifetimes of emitter triplets. Nevertheless, should it be possible to increase  $N_S$  by a factor of 10 or more,  $0.93 \text{ mAcm}^{-2}$  should be realisable at a film thickness of just  $5.6 \mu\text{m}$ .

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