

respectively. Writing the reciprocity relation explicitly yields equation (2) in Box 1. The first term describes the radiative open-circuit voltage $V_{oc}^{rad,f}$ (at full angular restriction) by integrating the cell's absorptance A over the Sun's spectrum ϕ_{sun} or the black-body spectrum ϕ_{bb} (photons per unit area and unit solid angle at the cell's temperature T). When assuming that the absorptance A of the solar cell is a perfect step function at E_g , as in the classical Shockley–Queisser paper⁵, this term corresponds roughly to the reference value $E_g(1 - T/T_{sun})$ given in equation (1). (However, an additional term $kT\ln(T_{sun}/T)$ should be added for more accuracy, see ref. 6.) The second term in equation (2) accounts for the etendue expansion between the incident and emitted photons (ϵ_{out} and ϵ_{in} being the etendues of the incoming and outgoing photons⁶). Thus, the first two terms combined yield V_{oc}^{rad} for any etendue ratio, caused by angular restriction or geometrical concentration. For the third term (in the first line) of equation (2) we have used the definition of Q_c^{LED} . Overall recombination is described by the rate $R = R_{nrad} + (1 - p_r)R_{rad}$ multiplied by the cell's thickness w and surface area S_{cell} taking into account a finite probability p_r of photon recycling. Note that the conservation of emitted photons implies $(1 - p_r)R_{rad}wS_{cell} = \epsilon_{out}\int A\phi_{bb}dE$. The ratio $\epsilon_{out}/\pi S_{cell} = \epsilon_{out}/\epsilon_{cell}$ in equation (2) takes care of geometrical concentration. In the second line of equation (2) this term is split into two using the standard expression

$R_{rad} = 4\pi n^2\int\alpha\phi_{bb}dE$ (ref. 7) with α as the absorption coefficient of the photovoltaic absorber. The resulting two terms have their correspondence in terms 3 and 4 of equation (1).

Let us first compare the two approaches in the radiative limit (QE = 1) where in equation (1) term 4 vanishes whereas in equation (2) term 3 and 4 cancel out to yield $qV_{oc} = qV_{oc}^{rad,f} + kT\ln(\epsilon_{in}/\epsilon_{out})$, that is, the Shockley–Queisser limit. Here, the second term is compatible with its correspondence in equation (1). However, $qV_{oc}^{rad,f}$ is compatible with the first term in equation (1) only in the full absorption limit, because in the limit of weak absorption we obtain $V_{oc}^{rad,f} = w_{eff}\int\alpha\phi_{sun}dE/(w_{eff}\int\alpha\phi_{bb}dE)$ with $w_{eff} = dA/d\alpha|_{\alpha=\phi}$. Term 3 of equation (1) is entirely erroneous in the radiative limit leading to false predictions for the influence of light trapping. The only tendency that equation (1) describes correctly is the influence of angular restriction in term 2 but with respect to the wrong reference values. A similar pattern shows up in the non-radiative limit. In this case (QE \ll 1), terms 4 in equations (1) and (2) are equal and because the concentration factor I is not defined in ref. 1, we may presume $I := \epsilon_{out}\int A\phi_{bb}dE/(S_{cell}\pi w\int\alpha\phi_{bb}dE)$. This would equalize three out of four terms of both equations for an arbitrary absorptance A and all terms for an ideal step-function-like absorptance. However, this agreement is only formal because it hides the fact that with the definition above, the quantity I

cannot be varied independently from the other terms: variations of I by changes of ϵ_{out} (by angular restriction) or of A (by changing light trapping) as discussed in ref. 1 are counterbalanced in the correct equation (2) by the denominators of terms 2 or 1, respectively. Therefore, we must state that finally there is no situation left where equation (1) can be operative in a physically meaningful sense. In contrast, the more complex interdependence of the different loss terms in equation (2) leads to physically correct and meaningful results in all situations and should be considered for future optimizations of light management in solar cells. \square

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Atwater and Polman reply — We are grateful to Rau and Kirchartz for their thoughtful remarks on our Commentary¹, and hope this dialog will generate clarity in the physics of high-efficiency photovoltaics. Our Commentary identified several new design approaches and architectures using photonic structures to increase photovoltaic efficiency. It was driven by thinking about the design of solar cells with (i) high radiative efficiency, (ii) 1 sun unconcentrated ($C = 1$) operation and (iii) employing a light-collimating angle restrictor element (as opposed to a geometrical concentrator).

As Rau and Kirchartz² point out in their equation (2), the various design elements such as angle restriction, light trapping and improvement of external radiative efficiency are interdependent, a point that was also made in a number of the references cited in our Commentary. We agree that their equation (2) provides a physically complete description of the variation of open-circuit

voltage with the extent of light absorption and external radiative efficiency over the entire range of radiative efficiencies ranging from QE \ll 1 to QE \sim 1. We also agree that the light-trapping effect indicated by the third term of our equation (1) is a factor that is of importance for cell design only in the non-radiative limit, and cannot provide an additional increase in open-circuit voltage in cells with very high radiative efficiency.

For cells with very high radiative efficiency, the external radiative efficiency is the central concept in minimizing voltage loss. We note that in the limit (i) of high radiative efficiency (QE \sim 1) but low photon recycling probability ($p_r \sim 0$), our expression for term 4, written in terms of internal quantum efficiency approaches their term 4 in terms of external quantum efficiency, $kT\ln(QE) \sim kT\ln[QE/(1 - QE + (1 - p_r)QE)]$, but these two expressions will differ in the case where photon recycling is significant, so writing the fourth term in terms of external

radiative efficiency produces the most general result.

In their last paragraph, Rau and Kirchartz assert that in the non-radiative limit, variations of the light-trapping factor I “by changes of ϵ_{out} (by angular restriction) or of A (by changing light trapping) as discussed in ref. 1 are counterbalanced in the correct equation (2) by denominators of terms 2 or 1, respectively.” (ϵ_{out} , the etendue of incident photons; A , the cell absorptance.) Although true, this cancellation does not however imply that angle restriction has no influence on open-circuit voltage for cells in the non-radiative limit. By contrast, for example, for thin light-trapping cells in the non-radiative limit, V_{oc} can be increased by angle restriction via a reduced cell thickness w , rather than the ϵ_{out} term. That is, angle restriction allows w to be decreased while maintaining high absorptance and thus acts as a key light-trapping factor in this case. Indeed, Campbell and Green previously showed this concept in an

analysis of silicon solar cells in the purely non-radiative limit³.

Overall, we agree that the factors affecting cell open-circuit voltage are interdependent and there are subtleties in the interplay between these interdependent factors. That these factors can be dramatically influenced by nanophotonic design to increase the cell open-circuit voltage was the essential point that motivated our Commentary, a point that remains robustly true in light of this further analysis: new approaches to light management that systematically

minimize thermodynamic losses will enable ultrahigh efficiencies previously considered impossible. This development takes advantage of recent advances in the control of light at the nanometre and micrometre length scales, coupled with emerging materials fabrication approaches. It can lead to single-junction solar cells with efficiencies >30% for silicon³ and >35% for GaAs (ref. 4), well above the Shockley–Queisser limit for conventional cell designs. Moreover, these new designs enable parallel multijunction solar cells with efficiencies above 50%. □

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