Reply to: “Thermal artefacts in two-photon solar cell experiments”

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REPLYING TO C. C. Phillips Nature Communications https://doi.org/10.1038/s41467-018-07166-1 (2019)

Two-step photon up-conversion solar cells (TPU-SCs) are among the most promising photovoltaic devices1,2. In our previous works, we demonstrated the increase in the open-circuit voltage as well as the short-circuit current induced by the additional infrared (IR) light1. Phillips suggested that this phenomenon could be attributed to the sample heating2. Here, we present additional data suggesting that photoexcitation might be the cause. In the TPU-SC, the up-conversion is achieved by a series of two-step photoexcitation. By absorbing a below-gap photon, an electron transfers from the valence band to the conduction band of the narrow bandgap semiconductor. Upon absorption of another below-gap photon, the electron is excited to the conduction band of the wide bandgap semiconductor. This TPU process, following the absorption of two below-gap photons, produces additional photocurrent and boosts the photovoltage depending on the band offset at the hetero-interface. In this Reply to Matters Arising, we discuss the excitation power dependence of the external quantum efficiency (EQE) observed in TPU-SC and the efficient intraband excitation at the hetero-interface.

We measured the change in the EQE (ΔEQE) of TPU-SCs with InAs quantum dots (QDs) as a function of interband excitation power density. Here, ΔEQE was defined as the difference between the EQE obtained with and without the 1300 nm laser diode (LD) illumination. We conducted a systematic experiment to study the excitation power density dependence of the increased short-circuit current, ΔJSC, and the ΔEQE. Detailed measurements taken at 300 K are presented in Fig. 1. We used a 784-nm continuous wave (CW) LD and a 1300-nm CW LD for the interband and the intraband excitations, respectively. With increasing interband excitation density, the ΔJSC increases sub-linearly and tends to deviate from the power law at high-excitation density above ~10 mW cm⁻². Thereby, ΔEQE significantly decreases with the interband excitation density. This set-up reproduces the results reported in our original article. Note that, in this experiment, we did not use a simulator and, indisputably, there were no artefacts of the simulator’s sensitive reference channel optical detectors with scattered laser light. Furthermore, we did not perform a signal modulation technique for the photocurrent detection, because the lifetime of electrons separated from the holes can be extended to milliseconds3.

Here, we discuss the effects of thermal artefacts on the results. If ΔJSC is produced by the sample warming under the 1300-nm LD illumination, ΔJSC is given by

\[ \Delta J_{SC} = J_{SC} \exp \left( - \frac{E_a}{k_b T + k_b \Delta T} + \frac{E_a}{k_b T} \right) - 1 \quad (1) \]

where \( k_b \) is the Boltzmann constant, \( E_a \) is the activation energy, \( T \) is the temperature, and \( \Delta T \) is proportional to the 1300-nm LD power density. This gives an almost linear relationship in the measured region, as shown in Fig. 7b of the original article. However, the measured intraband excitation power density dependence in Fig. 7b was sublinear. Therefore, ΔJSC is not necessarily caused by thermal artefacts. We considered the possibility that the sublinear dependence of Fig. 7b arises from a change in the electron density at the hetero-interface. Figure 7d of the original article illustrates the dependence of the power-law index \( n \) on the reverse-bias voltage in the relationship of the intraband excitation power density and ΔJ. As the reverse-bias voltage increases, \( n \) increases and approaches unity. The space charge reduced by the intraband excitation weakens the electric field at the hetero-interface, resulting in a sub-linear response to the excitation density caused by the weaker electric field reducing the carrier collection efficiency of the TPU. We have recently reported the bias voltage dependence of \( n \) in detail (for example, ref. 4). The result is shown in Fig. 2, which reproduces the data of Fig. 7d of the original article. It is interesting to note that \( n \) quickly returns to unity by injecting carriers at the forward bias above ~0.4 V. When enough carriers are injected, the influence of the accumulated electrons on the electric field near the hetero-interface is weakened. Thus, the sub-linear relationship between ΔJ and the interband excitation power density in Fig. 1 answers all questions. Accumulated electrons at the hetero-interface significantly influence the local electric field near the hetero-interface, which changes the carrier collection efficiency of the TPU. Therefore, ΔJ is determined by the number of intraband excited electrons.

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Bias voltage dependence of two-step photon up-conversion properties
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carriers and their collection efficiency. Detailed analysis and the
physics behind Fig. 1 will be discussed in our upcoming paper.

We next focus on the efficient intraband excitation occurring at the
hetero-interface. Free carrier absorption should be considered
at least in the TPU-SC without InAs QDs. If only the free carrier
absorption occurs in the ‘bulk’ portion, the accumulated electron
density becomes considerably high and causes a lower bound. It is
well known that the wave-function of the accumulated electrons
can generally penetrate the barrier layer. The wave-function
penetration depth depends on the electric field at the hetero-
interface. The penetrated component contributes to the transition
from the confined level to the conduction band edge of AlGaAs,
which improves the excitation cross-section and, therefore, lowers
the estimated electron sheet density. Such a mechanism can
contribute to the improvement of the intraband excitation at the
hetero-interface. Further experiments and theoretical work are
necessary to unveil the efficient photoexcitation at the hetero-
interface, which is the most important and interesting mechanism
in TPU-SC.

The intermediate-band SC includes intermediate states in the
bandgap. By absorbing a below-gap photon, an electron transits from the valence band to the intermediate band. Upon
absorption of another below-gap photon, the electron is further
excited into the conduction band. This ideal TPU process, fol-
lowing the absorption of two below-gap photons, produces
additional photocurrent without degrading the photovoltage.
However, it is well known that thermal coupling between the
conduction band and the intermediate band gives rise to a
reduction of \( V_{OC} \). Many studies discussing the \( V_{OC} \) reduction
have been published\(^5\). Similar processes occur at the hetero-
interface of the TPU-SC. The photo-carrier generation of the
TPU-SC without IR illumination indicates that the conduction
bands of AlGaAs and GaAs are thermally coupled. The thermal
coupling becomes stronger with rising temperature, which causes
the change in \( V_{OC} \) according to Eq. (4) of the original article. This
analytical model suggests that \( \Delta V_{OC} \) depends on the intraband
carrier density. We recently confirmed the strong dependence
of the change in \( V_{OC} \) on the intraband excitation density. The
different trends, compared in Fig. 7e of the original article, are
essential to demonstrate the contribution of the optical excitation
process.

Finally, we would like to comment on the data error of the
current–voltage (J–V) curve shown in Fig. 7a of the original
article. The J–V curve was drawn by smoothly connecting current
density measured at discrete voltages at a step of every 0.02 V (see
Fig. 3), and there is no real data point in the area magnified in the
inset of the original Figure 7a. To better demonstrate the preci-
sion of J–V curve and thus \( V_{OC} \) that can be extracted from our
original measurements, we replotted the magnification of J–V curve
around a zero current density in the inset of Fig. 3 here by
highlighting the uncertainty induced by the errors in the original
data. The shaded areas around the J–V curve represent the
standard error of the current density. It is clear that the uncer-
tainty in our \( V_{OC} \) measurements is substantially smaller than the
difference between \( V_{OCs} \) that can be extracted from the raw data
at three irradiation conditions.

![Fig. 1](image1.png)

**Fig. 1** Interband excitation power density dependence of two-step photon up-conversion current at 300 K. a Change in the short-circuit current density \((\Delta J_{SC})\). b Change in the external quantum efficiency \((\Delta EQE)\); the wavelength and excitation power density of the second intraband excitation light were 1300 nm and 300 mW cm\(^{-2}\), respectively.

![Fig. 2](image2.png)

**Fig. 2** Bias voltage dependence of two-step photon up-conversion properties at 297 K. a Short-circuit current density (JSC), b n value of \( \Delta J_{SC} \propto P_n \), where \( \Delta J_{SC} \) is the change in the short-circuit current density, and \( P_n \) is the 1300 nm excitation power density. The wavelength and excitation power density of the first interband excitation light were 780 nm and 110 mW cm\(^{-2}\), respectively. \( P_n \) was varied in the range 1-320 mW cm\(^{-2}\).
Data availability
The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions
S.A. carried out experiments, performed modelling and data analysis, and wrote the manuscript. T.K. co-wrote the manuscript and was in charge of overall direction and planning.

Additional information

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