Quantifying the role of surface plasmon excitation and hot carrier transport in plasmonic devices

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Harnessing photoexcited “hot” carriers in metallic nanostructures could define a new phase of non-equilibrium optoelectronics for photodetection and photocatalysis. Surface plasmons are considered pivotal for enabling efficient operation of hot carrier devices. Clarifying the fundamental role of plasmon excitation is therefore critical for exploiting their full potential. Here, we measure the internal quantum efficiency in photoexcited gold (Au)–gallium nitride (GaN) Schottky diodes to elucidate and quantify the distinct roles of surface plasmon excitation, hot carrier transport, and carrier injection in device performance. We show that plasmon excitation does not influence the electronic processes occurring within the hot carrier device. Instead, the metal band structure and carrier transport processes dictate the observed hot carrier photocurrent distribution. The excellent agreement with parameter-free calculations indicates that photoexcited electrons generated in ultra-thin Au nanostructures impinge ballistically on the Au–GaN interface, suggesting the possibility for hot carrier collection without substantial energy losses via thermalization.
Efficient collection of photoexcited, non-equilibrium “hot” carriers within metallic nanostructures offers considerable promise for band gap-free photodetection and selective photocatalysis. However, practical applications require significant improvements in the performance of hot carrier devices relative to current performance. Excitation of surface plasmon polaritons—hybrid light-matter states localized at a metallic interface—is commonly viewed as a promising pathway for boosting the efficiency of these systems. Indeed, numerous experimental studies based on internal photoemission have shown a close correlation between the plasmonic resonance of the nanoantenna and the device responsivity (i.e., light-to-current conversion) with the subsequent electronic relaxation and transport processes that occur within the device. While surface plasmons are well known to enhance light absorption (Fig. 1b), deeper insight into their fundamental role in the physics of hot carrier devices requires a careful analysis of the internal quantum efficiency (IQE, Fig. 1c), which deconvolutes absorption and transport. Indeed, IQE is an established measure for evaluating interband processes in semiconductor optoelectronic devices. Yet, experimental studies of IQE in plasmonic hot carrier systems to date have provided limited understanding of plasmon-mediated hot carrier transport and injection. In particular, previous work has relied on a semi-classical Fowler theory for interpreting the experimental IQE spectra, deeper insight into their fundamental role in the physics of hot carrier devices requires a careful analysis of the internal quantum efficiency (IQE, Fig. 1c), which deconvolutes absorption and transport. Indeed, IQE is an established measure for evaluating interband processes in semiconductor optoelectronic devices. Yet, experimental studies of IQE in plasmonic hot carrier systems to date have provided limited understanding of plasmon-mediated hot carrier transport and injection. In particular, previous work has relied on a semi-classical Fowler theory for interpreting the experimental IQE spectra, in contrast with results of recent ab initio calculations. Furthermore, a deeper experimental analysis of plasmonic hot carrier transport has so far been obscured by parasitic optical losses present in the plasmonic structures (e.g., from use of adhesion layers and by parasitic hot carrier relaxation and absorption away from the junction in nanostructures thicker than the hot carrier mean free path). Overall, a lack of systematic experimental measurements together with limited model fidelity have prevented a clear assessment of the physics underlying plasmon-derived hot carrier transport and collection.

In this work, we perform an experimental study to elucidate and quantify the role of plasmons in hot carrier devices. We assess the IQE of several hot carrier devices with distinct plasmonic resonances, which were designed to minimize parasitic effects, including optical loss and carrier relaxation. Our studies indicate that transport—as characterized by the IQE—is a distinct and independent process from carrier generation by plasmon excitation. With direct measurements, we deterministically conclude that plasmons solely affect the optical properties of the device without modifying the internal processes associated with hot carrier transport and collection. We also show that the metal electronic band structure and the metal–semiconductor interface influence device performance, particularly at photon energies above the interband absorption threshold. We further provide insight into hot carrier generation, transport, and collection in plasmonic-metal/semiconductor Schottky junctions by coupling spectrally resolved measurements of hot electron collection across Au/n-GaN heterojunctions with a recently developed parameter-free hot carrier transport model. Going beyond a description of individual electronic processes, this combination of theory and experiment enables an accurate depiction of the complex interplay between hot carrier generation and transport in realistic experimental structures without ad hoc assumptions. In particular, our analysis reveals that the measured photocurrents arise from ballistically injected hot electrons at photon energies below the threshold for interband transitions (~2 eV).

Results

Experimental evaluation of IQE and the role of plasmon excitation. To experimentally assess the role of plasmon excitation on hot electron device performance, it is necessary to decouple optical excitation from subsequent electronic transport and collection. For this purpose we experimentally compared several Au/n-GaN photodetector devices with distinct plasmonic resonances but identical metal–semiconductor Schottky junctions. An abrupt plasmonic metal/semiconductor interface and plasmonic nanoantennas with thickness smaller than the hot carrier mean free path are necessary to ensure maximal sensitivity to ballistically harvested carriers. Accordingly, our experimental platform consists of planar Au plasmonic photodiodes on an optically transparent yet highly electrically conductive n-type GaN substrate, that we have identified as an optimal support (see Methods) to enable coupled electrical and optical (both transmission and reflection) characterization throughout the entire ultraviolet/visible/near infrared spectral range. Each heterostructure consists of a large Au contact pad connected to an array of electrically conductive Au stripes, which serve as nanoantennas that support plasmon resonances in the Vis-NIR regime. For a fixed period (P) of 230 nm, specifically chosen to suppress diffraction orders in the wavelength (λ) range of interest, the spectral position of the dipolar plasmon mode is controlled by adjusting the stripe width (W). Three hot carrier heterostructures were constructed with W of 61, 70, and 85 nm to achieve plasmon resonances located at ca. 1.9, 1.85, and 1.72 eV. The Au nanoantenna thickness (tAu = 20 nm) approaches the expected average mean free path for hot carriers (ca. 10–20 nm at 2 eV) and was chosen to maximize the collection of ballistic hot electrons without sacrificing optical absorption. A titanium (Ti) Ohmic contact completes the planar plasmonic diode so that photocurrent can be collected while illuminating the sample through the transparent sapphire substrate.

The formation of a Schottky barrier (ΦJ ~1.2 eV) at the Au/n-GaN interface ensures that electron-hole pair separation occurs even in the absence of an external bias. As expected, we observed a linear relationship between the short-circuit photocurrent, Isc, and incident laser power (Fig. 2b) when using a 633 nm diode laser to irradiate a stripe array (W = 61 nm). We attribute the linear photoresponse to the injection of hot electrons from the Au nanoantennas into the n-GaN conduction band, since the incident photon energy is much less that the bandgap of GaN (~3.4 eV). Furthermore, the large barrier for hot hole injection from the metal into the semiconductor valence band (ΦH, Hole > 3 eV) allows us to exclude any potential contribution from hot holes to the device photocurrent in the studied photon energy range.

For each heterostructure, steady-state EQE and absorption spectra are determined experimentally by measuring both the wavelength-dependent photocurrent as well as transmission and reflection spectra under the same illumination conditions of tunable, monochromatic light polarized perpendicular to the
engineered through photonic design. Plasmon excitation indeed yields high absorption in metallic nanostructures with characteristic dimension smaller than the wavelength of the incident photon; i.e., generation of carriers through intraband and interband transitions, propagation, and scattering of the hot carriers with energy-dependent mean free path ($l_{mfp}$), and injection of hot carriers with adequate kinetic energy ($E_{kin}$) and momentum ($k$) across the Schottky barrier, $\Phi_B$.

Fig. 1 Carrier generation and transport in photoexcited metal nanostructures. a Schematic representation of carrier generation and transport via internal photoemission (IPE) in a plasmonic metal–semiconductor heterostructure: charge carriers created in the metal upon illumination are separated across the metal–semiconductor interface generating a photocurrent at sub-bandgap photon energies. The external quantum efficiency (EQE) spectrum represents the wavelength ($\lambda$)-dependent photon-to-electron conversion probability. As shown in b and c, the EQE can be decomposed into the product of absorption and internal quantum efficiency (IQE). b Illustrative absorption spectrum of a metal nanostructure displaying a resonant plasmonic feature which can be engineered through photonic design. Plasmon excitation indeed yields high absorption in metallic nanostructures with characteristic dimension $L$ much smaller than the wavelength $\lambda$ of the incident photon; c Illustrative IQE spectrum and schematic representation of the electronic processes which contribute to it, i.e., generation of carriers through intraband and interband transitions, propagation, and scattering of the hot carriers with energy-dependent mean free path ($l_{mfp}$), and injection of hot carriers with adequate kinetic energy ($E_{kin}$) and momentum ($k$) across the Schottky barrier, $\Phi_B$.

stripes (see Methods). For the heterostructure with $W = 61$ nm, a resonance peak at $\lambda_{peak} = 650$ nm can be observed in both spectra (Fig. 2c, e), absorption being in excellent agreement with numerical simulations (Fig. 2d, dashed line). Spatial maps of absorption in the photoelectrode were collected off-resonance above the interband threshold of Au ($\lambda \approx \lambda_{IB} \approx 688$ nm) and as on-resonance ($\lambda_{peak} = 650$ nm). In the first case, the unpatterned Au pad exhibits larger absorption than the array of nanoantennas (Fig. 2d, $\lambda = 514$ nm). Instead, on resonance (Fig. 2d, $\lambda = 650$ nm), absorption in the plasmonic stripe array ($\approx 60\%$) greatly exceeds that of the Au film. It is noted that this feature disappears upon rotating the incident light polarization by 90° (Supplementary Notes 1 and 2). Such behavior confirms that the photocurrent originates from optical excitation of the dipolar plasmon mode in the nanoantennas. It is interesting to note that not only the plasmon resonance, but also the fringes present in the absorption spectrum (Fig. 2e), which are due to Fabry–Perot interference in the planar GaN/sapphire substrate structure (Supplementary Note 7), cause a modulation in the photocurrent response that is reproduced in the EQE spectrum (Fig. 2c).

Comparing the optical (absorption) and electrical (EQE) performance of three hot carrier heterostructures with varying stripe width, we find a close correlation between the plasmon excitation wavelength and the EQE peak response (Fig. 2f). Increasing $W$ from 61 to 85 nm red shifts both absorption and EQE peak positions ($\lambda_{peak}$) to a commensurate amount (Supplementary Note 2). In contrast, the IQE spectra, determined by taking the ratio of EQE and absorption (Fig. 2g), do not exhibit any spectral features that are associated with the characteristic peak wavelength for plasmonic absorption in each device (see Supplementary Note 7 regarding the residual Fabry–Perot fringes). The striking similarity of the three IQE curves indicates that the carrier transport and collection processes are the same in all three devices, even though the absorption spectra are different, suggesting that the role of plasmon excitation is primarily associated with optical absorption and not transport. That is, tunable plasmon resonances efficiently couple far-field radiation into nanoscale volumes and this mechanism dominates the EQE across a range of wavelengths. This observation implies that the intrinsic material properties of the metal and the interface barrier height dictate the transport characteristics of the heterostructure. Thus, plasmon excitation does not play a priori selectively enhance the rate of any particular decay process or transport mechanism. Interestingly, as also remarked in previous studies, we observed that all three IQE curves were characterized by a broad, asymmetric feature peaking around 560–565 nm (~2.2 eV), which cannot be described by conventional Fowler models for IPE. Contrary to previous speculations about the role of indirect bandgap materials, our results on a direct bandgap semiconductor (n-GaN) indicate that it is the electronic band structure of the metal that determines the energy dependence of the IQE.

Ab initio modeling of electronic processes and IQE. For hot carriers, IQE is comprised of three distinct processes (Fig. 1c): (i) generation of a non-equilibrium distribution of “hot” electrons...
and holes in the metal nanostructure upon plasmon decay via intraband (sp-sp) and interband (d-sp) optical transitions. (ii) transport of these hot carriers to an interface either ballistically or via electron–electron and electron–phonon scattering and relaxation. (iii) injection of carriers with appropriate momenta and sufficient kinetic energy above the interfacial Schottky barrier ($\Phi_B$). We can relate the specific shape of the IQE curves to the interplay between the two hot carrier generation mechanisms, namely, intraband and interband transitions, as well as their corresponding hot carrier distributions relative to the Schottky barrier height present at the metal–semiconductor interface. The interband and intraband decay rates are determined from density functional theory (DFT) calculations, which generate the prompt hot electron energy distribution. For antennas with sizes of the order of tens of nanometers as in our study, quantization effects of the electronic levels of the metal can be neglected and the bulk properties of gold can be used. Devices employing metallic nanocrystals with dimensions smaller than a couple of nanometers would need to take this aspect into account. The decay rate is dependent on both incident photon energy and the electronic band structure of the metal. For photon energies below the interband threshold of Au ($h\nu_{IB}$), hot electrons generated via intraband transitions have a nearly uniform probability at all energies from the Fermi level up to the photon energy (Fig. 3a, solid red curve). As a result, intraband excitation accounts for a sizable fraction of the hot electron distribution at energies above the Schottky barrier height (gray shaded area in Fig. 3a). In this low photon energy regime there is very good agreement between the Fowler model, based on the parabolic band approximation, and full DFT calculations (compare solid red curve with dashed red curve in Fig. 3a). On the other hand, above $h\nu_{IB}$ (Fig. 3b, solid turquoise curve), a much higher probability distribution is observed for low-energy carriers, since hot electrons originate from d-band levels deep below the Au Fermi level. Consequently, there is a substantial reduction in the fraction of high-energy electrons created from intraband transitions compared to that predicted for the case of a purely parabolic band (Fig. 3b, dashed turquoise curve). This interplay, combined
intraband case and therefore IQE could preserve the quadratic dependence on the photon energy even above the interband threshold (~1.6 eV).

A microscopic understanding of hot carrier transport in Au/n-GaN heterostructures is obtained by comparing experimental measurements to results of a recently developed theoretical framework that combines electromagnetic simulations, ab initio DFT calculations, and Boltzmann transport methods to compute the generation and transport of hot carriers within realistically scaled (ca. 10–100 nm) metallic structures\(^{33}\) (see Methods). From electromagnetic simulations, we first determine the electric field profile in a single Au nanoantenna (\(W = 61\) nm, Fig. 4a and Supplementary Note 8). The initial energy and momentum distribution of the hot carriers are obtained from plasmon decay rates and electronic optical excitations derived from DFT calculations\(^{32,35}\), which account for the anisotropies associated with these quantities in the interband regime as well as resistive contributions in the intraband regime. Energy-dependent lifetimes and mean free paths \((l_{\text{mfp}})\) are also calculated with ab initio methods accounting for both electron–electron and electron–phonon scattering processes and have been shown previously to agree well with experimental results\(^{34,42}\). All the calculated quantities are averaged over different crystalline orientations to reflect the polycrystalline nature of the fabricated structures. This information is combined in a Boltzmann transport calculation\(^{33}\) where we compute the propagation of carriers across the Au nanostructure, determining changes to their energy distribution as well as the number of scattering events they experience. For each photon energy, our calculations yield the energy-resolved flux \(F_\text{es}(E)\) of hot electrons with energy \(E\) above the metal Fermi level that reach the Au/n-GaN interface after up to \(N\) scattering events. Attesting to the validity of our computational approach, the energy-resolved flux of hot electrons that reach the interface ballistically, \(F_\text{b}\), shown in Fig. 4b retains the key features described in Fig. 3a. The model also shows that scattering processes serve to homogenize the hot carrier distributions by smoothing the transition between the intraband and interband generated carriers that reach the interface (Fig. 4c).

Estimating the injection probability, \(P_{\text{inj}}(E)\), across the Schottky barrier based on the assumption of tangential momentum conservation (Supplementary Note 4)\(^{21}\), we then calculate IQE as \(\Phi_\text{b}\):

\[
\text{IQE} = \sum_{\Phi_\text{b}} F_\text{es}(E) \cdot P_{\text{inj}}(E) dE \quad \text{for} \quad N = 0, 1, \ldots
\]

The blue solid curve in Fig. 4d represents the IQE spectrum predicted from \(F_\text{es}(E)\) and the blue dashed curve is the predicted IQE obtained for \(F_\text{b}\). Including additional scattering events only changes the IQE by 0.01%, indicating that the vast majority of hot electrons undergo no more than three scattering events before being collected. Significantly, our parameter-free model of hot carrier generation, transport, and injection is in excellent quantitative agreement with the experimental data (gray solid curve).

**Discussion**

This result shows that a detailed description of material properties and device geometry can precisely capture the details of plasmonic hot carrier transport under illumination, both on and off resonance. Strikingly, the results of our model indicate that more than 90% of the hot carriers are collected ballistically at photon energies below 2 eV \((\lambda > 620\) nm\), implying that hot carrier transport in our Au nanoantennas occurs in the ballistic regime at the plasmon peak position. This result retrospectively
higher photon energies; those carriers created at lower photon energies would likely have insufficient energy to overcome the Schottky barrier. Nonetheless, in the studied configuration, which is very common for plasmonic photodetectors, the plasmonic antenna sits on a high-index GaN substrate, and therefore the electric field is localized close to the metal–semiconductor interface upon excitation of the fundamental plasmon mode (Fig. 4a). The largest hot carrier generation thus occurs close to the interface, and as a result, the non-uniform field profile inside the antenna favors ballistic collection, mitigating the effect of increasing antenna thickness. Therefore, by enabling strong light localization in metallic nanostructures (Fig. 4a) plasmonic excitation may be able to realize optoelectronic systems that operate in the truly ballistic regime despite the short, energy-dependent $l_{\text{diff}}$ of hot electrons in metals.

We also observe that our experimental IQE values agree quantitatively with theoretical results based on metal electronic structure, suggesting that the collection efficiency is limited by fundamental electronic structures characteristics of the metal and interface. To summarize, the key aspects influencing IQE are: (i) the metal band structure; (ii) the transport processes to the interface, (iii) the Schottky barrier height, and (iv) the momentum matching condition for injection across the interface. We note that the momentum matching factor has profound consequences for the overall magnitude of the IQE. Indeed, the low effective electron mass in GaN and the smooth metal–semiconductor interface in our devices, which imposes tangential momentum conservation, account for a reduction in IQE by nearly four orders of magnitude (Supplementary Note 5). Use of semiconductors with heavy electrons or large density of states in the conduction band (e.g., TiO$_2$) as well as nanoscopically roughened metal–semiconductor interfaces could thus be beneficial to boost the IQE and performance of hot carriers IPE devices. Irrespective of the Schottky barrier height, momentum matching conditions also cause a disproportionate suppression in the collection of low-energy electrons originating from either interband transitions or scattering of high-energy carriers generated by intraband transitions. Therefore the metal–semiconductor interface plays a significant role in the ultimate efficiency of plasmonic hot carrier IPE devices. We also note here that plasmon-mediated interfacial hot carrier excitation has been observed in selected systems employing small metallic nanocrystals and constitutes a different mechanism for harnessing hot carriers beyond IPE$^{44,45}$. In fact, in the case of interfacial plasmon excitation the quantum efficiency has been shown to exhibit a stepwise efficiency spectrum with a system-specific threshold energy$^{44}$. However, in the studied systems, which have dimensions of several tens of nanometers, we can entirely ascribe the IQE spectral features to the metal properties and we do not observe any deviations that could be attributed to a competing contribution from interfacial plasmon excitation. Transport of carriers from their point of generation to the interface, where they are filtered by the presence of a sizeable Schottky barrier ($\Phi_s \sim 1.2$ eV), accounts for the remaining one to two orders of magnitude reduction in IQE. It is worth noting that even assuming a 50 meV Schottky barrier, values of IQE $\sim 10^{-4}$ are expected for this system (Supplementary Note 5). Considering these factors, we suggest that a potentially promising strategy for increasing the IQE value is to identify metals with a high density of states close to the Fermi level, which would enable the efficient creation of hot electrons with high energies and offer an interesting path toward high-performance hot carrier devices. Simultaneously, careful design of the device geometry$^{19,30,46}$ and further engineering of the spatial hot carrier generation profile could promote ballistic collection, and hence improve device efficiency.

To summarize, our experimental analysis of IQE in ultrathin plasmonic nanoantennas with abrupt metal/semiconductor...
interfaces reveals that plasmon excitation enables the efficient coupling of far-field radiation into nanoscale volumes, but does not dictate the transport physics governing the performance of hot carrier photoemission devices. Instead, analysis of the IQE spectra emphasizes the role of interband and intraband decay processes, as well as carrier transport over nanometer scale distance in the metal, in determining the distribution of hot carriers that are collected via IPE. Our observation of ballistic electrons is encouraging for efforts to use ballistic hot carrier collection for ultrafast photodetection and excited-state photocatalysis. Our results reveal mechanisms important to the design of efficient hot carrier devices, and they suggest that new materials with tailored band structure and transport properties will be crucial for the realization of efficient hot carrier-driven devices. Future experiments using ultrafast spectroscopy techniques and time-resolved IQE measurements may expand our understanding of hot carrier transport, and allow for more comprehensive comparison with theoretical predictions. As an outlook, the agreement between our experimental data and detailed, parameter-free theoretical hot carrier transport model suggests that this combined approach can be a powerful tool to guide the design of future hot carrier optoelectronic devices.

Methods

Sample fabrication. In order to perform coupled optical and electrical measurements of a plasmonic IPE device for experimental assessment of its IQE, it is necessary to have a semiconducting substrate which: (i) does not absorb light in the wavelength range of interest in order to prevent interband photogeneration of carriers within the semiconductor and also does not scatter light (optically transparent); (ii) has high electrical conductivity to enable transport of hot carriers; and (iii) forms a Schottky barrier with the metal to favor separation of the hot electrons and holes to prevent their recombination. The n-GaN substrate employed here satisfies all of these requirements: (i) it has a wide bandgap (3.4 eV), and is optically transparent, with no light scattering centers; (ii) due to its widespread use in optoelectronics, it is commercially available with various doping levels, in the form of highly doped low electrical resistance, crystalline substrates; (iii) its band alignment leads to the formation of a sizable Schottky barrier of ~1.2 eV with Au.

Photocurrent measurements. A planar laser (2 W) was used as the light source for plasmonic excitation. The beam was monochromated (slit width 200 μm), collimated, and focused onto the sample with a long working distance, low NA objective (Mitutoyo 5×, NA = 0.14). A Si photodetector was used to measure the transmitted power or, using a beam splitter, the reflected power incident on the sample. A silver mirror (M, Thorlabs) was used to normalize the reflection and the background (BG) was subtracted from all the measurements. A tilted glass slide was used to deflect a small amount of incident power from the laser onto a reference photodiode for coincident recording of the laser power incident on the sample. A chopped, typically at a frequency of ~100 Hz, was used to modulate the incident power and thus the photocurrent signal, which was subsequently processed with a lock-in amplifier. An external, low-noise current-to-voltage amplifier was used to convert the signal to the lock-in. Piezoelectric micro-probes (Mibotech) are utilized to electrically contact the sample and perform all of the photocurrent measurements.

Numerical simulations. A commercial finite element method software (COMSOL) is used to perform the electromagnetic simulations. The 3D simulations are performed to estimate absolute absorption values as well as 3D internal electric field distributions to be used in the subsequent hot carrier generation and transport code. The scattered field formulation is utilized. For the background field calculation, a port boundary condition with excitation "ON" is used to launch a plane wave with normal incidence and variable wavelength as well as for the recording of the reflected wave. A second port boundary condition without excitation is used to record the transmitted wave. Perfect magnetic conductor and periodic boundary conditions are used on the side walls (width of the unit cell equal to the array pitch, P = 230 nm, length of the cell equal to 50 nm). For the calculation of the scattered field, perfect-matched layers are used in place of the port boundary conditions.

Hot carrier generation and transport predictions. The hot carrier flux is computed by iteratively evaluating the effects of transport and scattering. In each iteration, transport effects are computed using the 1D Green’s function (exp(-x/l_mfp)), where l_mfp is the mean free path) on a tetrahedral mesh. Multiple different directions are integrated via Monte Carlo sampling. This results in a deposition of transported carriers at the surface and scattered carriers in the interior. The scattered carriers are then transformed via the scattering matrix elements to produce a new energy distribution at each point in the mesh, which is used as the input to the next round of transport calculations. The initial input distribution is obtained using the carrier energy-resolved dielectric function Im(ω, E) and the input electromagnetic field from COMSOL, evaluated on the same tetrahedral mesh. Im(ω, E) and the energy-dependent mean free path l_mfp(E) are obtained using Fermi’s golden rule, with electron–phonon and electron–photon matrix elements calculated using the DFT software JDFTx® (see ref. 13 for further details).

Code availability. First principle methodologies available through open-source software, JDFTx, and post-processing scripts available from authors upon request.

Data availability. All relevant data are available from the authors upon request.

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Author contributions
G.T. performed experiments, numerical simulations, and IQE calculations of devices. A.
S.I., R.S., and P.N. performed ab initio hot carrier generation and transport calculations.
A.J.W., J.S.D., R.P., and A.R.D. contributed to experiments and data analysis. All authors
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