NANO-OPTICS

Plasmonic hot carriers skip out in femtoseconds

Plasmonic antennas store energy by localizing light to nanoscale volumes. A plasmon's oscillating electrons can scatter directly into a semiconductor, transferring the captured energy in less than ten femtoseconds.

S. K. Cushing

Plasmonics enables metal nanoparticles to act as antennas, capturing light from around the particle with an optical cross-section that is orders of magnitude larger than the physical size of the particle. The strong localization of incident light should make plasmonics ideal for enhancing photoconversion in photovoltaics, photocatalysis and optoelectronic devices[1]. Plasmonic devices, however, have yet to routinely match or exceed the efficiencies of traditional semiconductor devices[2]. The problem is not in creating appropriate antennas — tunability is where plasmonics excels — but rather in extracting the energy captured by the plasmon before it is dissipated via intrinsic losses into, essentially, heat. Means of extracting the captured energy from plasmons before thermalization are needed.

Now, writing in *Nature Photonics*, Shijing Tan and co-workers report that a plasmon can create hot carriers in a semiconductor by directly scattering into interface states or coupling with an exciton[3]. The hot-carrier transfer is measured to occur in less than 10 fs, which is before the energy captured in the plasmon is otherwise dissipated to intrinsic losses as heat. The findings of Tan et al. give new insight into how a plasmon's energy may be efficiently harvested.

A plasmon is a collective oscillation of a metal's conduction electrons during electromagnetic excitation (Fig. 1a). After excitation, the individual electrons in the plasmon lose their collective phase by scattering off of other electrons and the nanoparticle's surface. This process, known as dephasing, occurs in less than 20 fs and leaves behind a continuum of non-thermal electrons, some with energy several electronvolts above the Fermi level[4–6]. These are the 'hot' carriers in plasmonic hot-carrier devices. The hot carriers thermalize on a longer timescale of picoseconds, releasing their excess energy by heating the lattice through electron–phonon scattering. The short, picosecond lifetime makes capturing and harvesting hot carriers a difficult premise. For comparison, photoexcited carriers in a semiconductor like silicon exist for at least one million times longer before recombination.

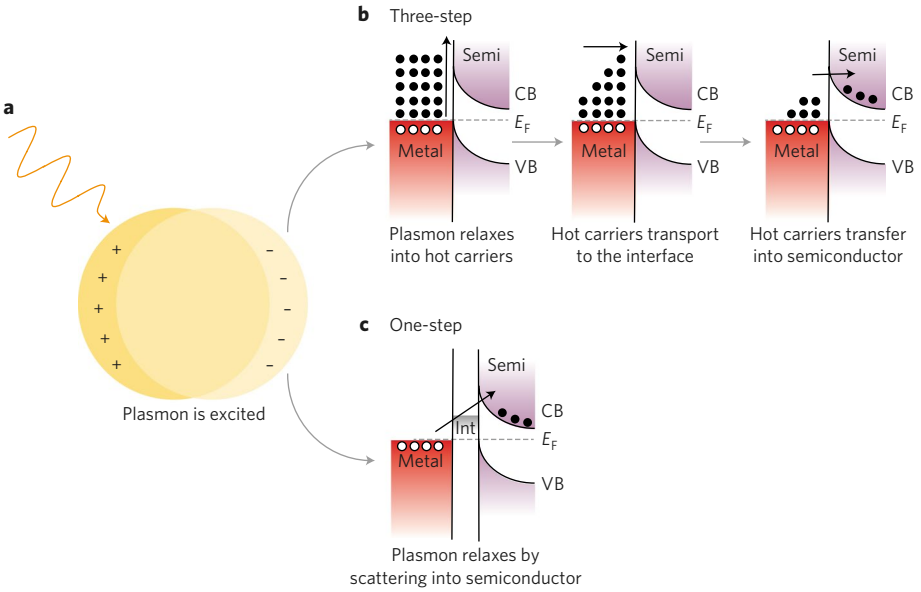

Fig. 1 | Hot-carrier capture from a plasmonic nanoparticle. a, A plasmon is the collective oscillation of conduction electrons during electromagnetic excitation. **b**, When the oscillating electrons scatter and lose their collective phase, a hot-carrier distribution is created with energy up to the plasmon frequency above the Fermi level (E_F). The hot carriers can transfer over a metal–semiconductor Schottky barrier, capturing and storing the energy of the plasmon in the semiconductor (Semi) (CB, conduction band; VB, valence band). The overall extraction efficiency is usually <1%. **c**, Tan and co-workers report[3] that a plasmon can be de-excited by directly scattering the oscillating electrons into a semiconductor, avoiding the three steps of excitation, transport and transfer shown in **b**. By scattering with an interface state (Int) or interacting with an exciton, a non-thermal hot-carrier distribution is created in the semiconductor in <10 fs. This timescale is shorter than the time it takes for the plasmon's energy to be lost to heat in the metal, and could therefore lead to higher extraction efficiencies.

To overcome their short lifetime, plasmonic hot carriers are usually captured using the Schottky barrier that exists between a metal and a semiconductor (Fig. 1b). Hot carriers with energy larger than the Schottky barrier are transferred to the semiconductor. Once transferred, the internal field of the junction prevents recombination of the photoexcited electron and hole. If a band offset exists between the metal and semiconductor, the hot carriers are preserved at a higher energy (Fig. 1b). The Schottky barrier therefore acts as a filter, effectively separating and storing the hot carriers' energy for later use. The downside of Schottky barrier-based devices is that, consistent with thermionic emission theory, the transfer efficiency is usually limited to <1% (ref. [7]). The low efficiency originates in the three competing steps of hot-carrier extraction: thermalization, transport and transfer (Fig. 1b).

Recently, an alternative approach for extracting plasmonic hot carriers has garnered attention. Instead of relying on a three-step charge transfer process with a Schottky barrier, the oscillating electrons of the plasmon are directly scattered into an interfacial state before other intrinsic losses can occur (Fig. 1c). This type of plasmon damping is usually referred to as chemical interface damping and it dominates in small (<10 nm) metal nanoparticles[8]. Chemical interface damping achieves the same

goal as the Schottky barrier device. Non-thermal carriers are again injected into the semiconductor at a higher energy. Only now, the plasmon's energy is captured in one step on a few-femtosecond timescale, or in other words, the plasmon's energy is captured before heating losses can occur. Such a one-step charge-transfer process has already been reported to result in a >20% plasmonic hot-carrier extraction efficiency[9]. This is to be compared with the <1% efficiency usually reported for the three-step process[7]. However, despite this proven potential, the timescale of the one-step charge-transfer process and the hot-carrier distribution that is created in the semiconductor have yet to be directly measured.

In their study, Tan and colleagues use ultrafast two-photon photoemission spectroscopy to quantify the direct-scattering charge-transfer process in plasmonic Ag nanoparticles on TiO_2, similar to previous work by one of the authors on one- versus three-step charge transfer in metal–molecule systems[10]. The Ag nanoparticles are on average 4 nm in diameter and 1 nm in height as grown on rutile TiO_2. The hot-carrier distribution in the semiconductor is measured by two-photon photoemission following excitation of the Ag by a visible light pulse. The excitation wavelength is below the bandgap of the TiO_2, isolating the contributions of the plasmonically excited electrons. When a plasmon is excited with polarization parallel to the TiO_2 surface, a hot-carrier distribution is created in the TiO_2 in less than 10 fs. The hot-carrier distribution has a significant non-thermal contribution only when the plasmon is polarized along the [110] axis of the TiO_2. When the plasmon is polarized perpendicular to the interface, hot carriers are still measured in the TiO_2, but without a significant non-thermal component. In both cases, a surface state between the metal and semiconductor is measured to be occupied after photoexcitation. The hot-carrier distribution is measured in the TiO_2 on an instrument-limited 10 fs timescale with no contribution from hot electrons in the Ag alone. Combined, these data suggest a three-step transfer process is not present, but rather the carriers are being directly excited into the TiO_2.

The measurements of Tan et al. provide confirmation that the plasmon's energy can be transferred to the TiO_2 before the plasmon's intrinsic losses begin. The energy transfer is suggested to occur through excitation of a coupled interface state between the metal and semiconductor or through hybridization with a dark exciton in the TiO_2. The hot-carrier distribution is only highly non-thermal when excited by coupling with the dark exciton along the [110] axis. This correlation is suggested to exist because of the dielectric anisotropy of the TiO_2, but further investigation is needed to understand how anisotropy controls the non-thermal carrier distribution. The results are also for <5 nm nanoparticles, for which the damping process is known to be controlled by surface states[8]. It will be interesting to see whether this mechanistic picture holds over a range of nanoparticle sizes where other damping mechanisms are more dominant. In the future, an attosecond or single-cycle probing pulse could also reveal the plasmon's excitation and de-excitation process at times shorter than the 10 fs instrument resolution reported here.

Even within these limitations, the results of Tan and colleagues provide an important confirmation of the hot-carrier transfer process in small metal nanoparticles. Tuning interface states or excitons to effectively 'quench' the plasmon into a semiconductor or molecule is a promising direction in plasmonics. Devices based on this principle may allow the plasmon to better enhance photoconversion, and will surely complement current efforts to geometrically engineer hot-carrier distributions[4–6]. It will also be interesting to see these studies expanded to the hot electron versus hole distributions from inter- and intraband excitation in the metal[4–6]. Either way, the amount of electromagnetic energy localized by plasmonic nanoparticles remains a tantalizing promise, and the results of Tan et al. give a strong indication as to how this energy can be unlocked. ❐

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Machine learning under the spotlight

The field of machine learning potentially brings a new set of powerful tools to optical communications and photonics. However, to separate hype from reality it is vital that such tools are evaluated properly and used judiciously.

Darko Zibar, Henk Wymeersch and Ilya Lyubomirsky

Recently, there has been an increasing amount of research that applies machine-learning techniques to tasks in optical communication. Specific applications have varied from optoelectronic component characterization, performance prediction and system optimization, to, more recently, quantum communication. The question that remains to be answered, however, is whether the application of such schemes is simply hype with limited real impact or whether it can truly bring significant advantages with orders of magnitude improvement and reduced human involvement compared with conventional methods.