NANOPHOTONICS

Interrogating hot electrons in tunnel junctions

Electronic transport reveals excited-carrier energy distribution in plasmonic nanostructures

By **Luis Martín-Moreno**

Light impinging on a metal nanostructure can excite plasmons (collective charge-density oscillations), and if plasmons decay into electron-hole pairs, so-called hot carriers can be created (see the figure, top). These hot carriers are produced on a time scale of tens of picoseconds, and their energy distribution differs from that at equilibrium. Potential applications (*1*, *2*) include photochemistry, in which hot electrons can trigger chemical reactions in nearby molecules (*3*), and in light-harvesting in solar cells (*4*) and photodetectors (*5*), in which hot electrons from a metal can overcome the interfacial energy barrier and be injected into a semiconductor. Knowing the hot-carrier energy distribution (HCED) is critical for designing devices or planning reactions. Most studies have been theoretical, with some discrepant results (*6*–*8*). On page 423 of this issue, Reddy *et al.* (*9*) provide needed direct experimental results on the steady-state energy distribution of hot carriers by cleverly using transmission through molecular resonances.

These discrepancies in theoretical work on HCEDs are not surprising because the formation of hot carriers is a complex problem. Models have had to rely both on material parameters and, more so, on assumptions on the physical processes involved. In this regard, the direct detection principle developed by Reddy *et al.* is ingenious in that a suitable molecule serves as an electrical contact between the nanostructure and a metallic probe (see the figure, top).

In the experiment, the chosen nanostructure was a gold film either 6 or 13 nm thick on which a monolayer of appropriate molecules were adsorbed. A designed grating was used to couple light from a laser beam to the plasmon in the film, which in turn creates a steady-state hot-carrier distribution. A metal-molecule-metal break junction is then created by using a scanning tunneling microscope (STM) tip. The tip is first brought into mechanical contact with the metal film and then slowly retracted while monitoring the current through the system.

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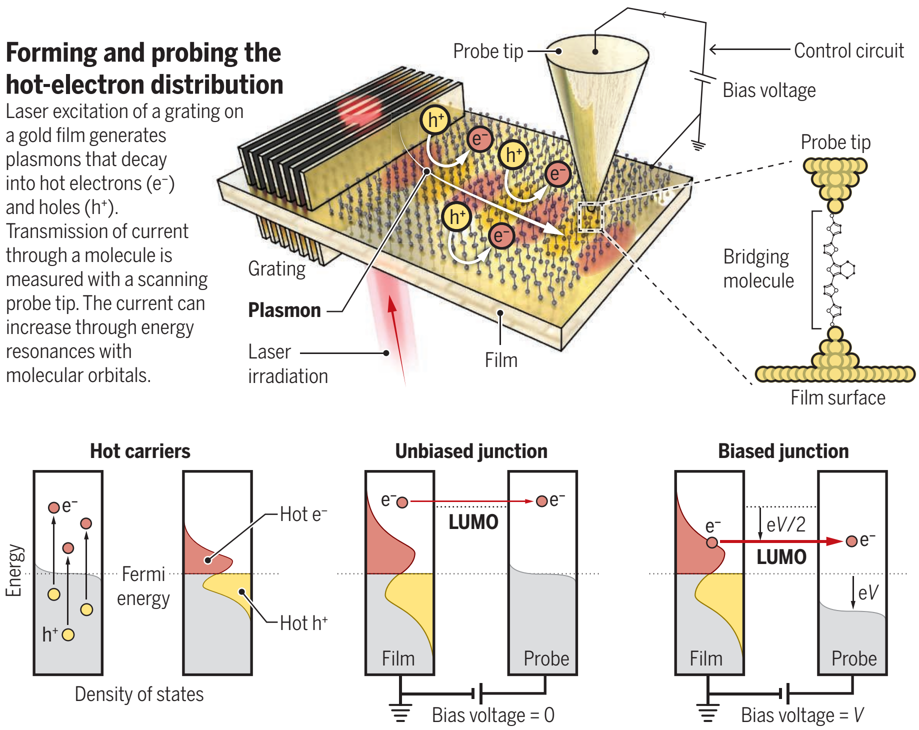
Electrical current is forced to flow through a molecular level, which thus acts as an energy filter. If this level is above the electrochemical potentials of both contacts, only hot electrons at the resonant energy contribute to the current. The HCED is then mapped by biasing the junction (see the figure, bottom). In the same way, the HCED of hot holes can also be measured by selecting a molecule with a resonant molecular level below the electrochemical potentials of the contacts.

The current monotonically decreases as the film-tip distance is increased, with some current plateaus corresponding to single or few molecules being transiently trapped between the electrodes. For each bias voltage, this process is repeated thousands of times, so that the case corresponding to single-molecule junctions (and its associated current) can be extracted from a statistical analysis. Comparing the electrical current with and without laser illumination provides the contribution from the hot carriers. Moreover, the HCED can be quantitatively determined by the experimental determination of the transmission characteristics through the molecule.

The experimental set up used by Reddy *et al.* is extremely flexible and allows for many variations of external conditions. For example, the essential role played by plasmons in the formation of hot carriers is revealed by the common dependence on laser polarization of plasmon excitation and electrical current through the device. A smaller current was measured when the grating is not present, which shows that the direct formation of hot carriers by light is less efficient than the plasmon-mediated

Assessing hot carriers

Plasmons excited in metals can decay into electrons and holes that carry much more energy relative to equilibrium distributions. Reddy *et al*. measured carrier energies using the energy levels of molecules as probes.



Bringing levels into resonance

Hot carriers from decaying plasmons have a distribution of energies above and below the Fermi level. With no bias, few hot electrons are available to transport through the lowest unoccupied molecular orbital (LUMO). Biasing the junction shifts the LUMO energy, allowing the determination of the hot-carrier energy distribution.

GRAPHIC: C. BICKEL/*SCIENCE*

one. Experiments at different tip-grating distances show a spatial dependence of the current that is consistent with the plasmon decay. In another set of experiments, Reddy *et al.* heated a nonilluminated film up to temperatures even higher than those estimated to be reached when the film was illuminated. The current-voltage characteristics strongly differ from those previously described for illuminated systems, showing that the main effect of plasmon excitation is not caused by an increase of the system temperature.

Reddy *et al.* used their experimental results to probe the physical processes involved in hot-carrier generation. Hot carriers were more abundant for a film thickness of 6 versus 13 nm, indicating that plasmon decay into electron-hole pairs mainly occurs because of the extra momentum provided by reflection with the surface (*10*). Surfaces break translational symmetry and the associated momentum conservation rules and allow this process to occur. Also, although some models have treated hot carriers as though they were in equilibrium at an effective electron temperature that differs from that of the lattice, the experimental HECD could not be fitted in this way.

The technique presented by Reddy *et al.* offers numerous possibilities for future work, including investigations of the dependence of HCED on excitation wavelength and the study of different plasmonic nanostuctures supporting hot spots, where the prospect of nanometric resolution is within the realm of STM techniques. These experimental studies are a valuable contribution to understanding how hot carriers are generated and the nature of their energy distribution. These results are likely to have important applications in the design of new light-harvesting devices. ■

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INFECTIOUS DISEASE

Was smallpox a widespread mild disease?

Ancient DNA from the Viking Age suggests a rethink about the origin and evolution of smallpox

By **Antonio Alcamí**

Smallpox—caused by variola virus (VARV), a poxvirus—was one of the most virulent diseases known to humans, killing up to 30% of infected individuals and 300 million to 500 million people in the 20th century. The year 2020 commemorates the 40th anniversary of smallpox eradication, the first human disease eradicated after a global vaccination campaign led by the World Health Organization (WHO). The last samples of VARV are kept in two high-security laboratories pending destruction, and fears about reemergence or deliberate release of VARV have not subsided (*1*). Smallpox eradication is one of the most successful stories of public health, but the origin of the deadly virus remains an enigma. On page 391 of this issue, Mühlemann *et al.* (*2*) report the identification of VARV in archaeological remains from the Viking Age (600 to 1050 CE) that reveals new information about the origin of VARV and its evolution in human populations.

The origin of modern VARV, which includes the major and minor VARV strains that caused the smallpox epidemics, is a matter of debate (*3*, *4*). Evolutionarily successful viruses replicate and transmit without causing host pathology. High virulence is often seen when viruses transmit to another animal species, as observed with the current coronavirus disease 2019 (COVID-19) pandemic. The current hypothesis is that thousands of years ago, a variola-like virus ancestor from Africa was transmitted from rodents, which are common reservoirs of poxviruses, to humans, in which it evolved to become VARV. The genetically closest relatives to modern VARV—taterapox virus that infects gerbils and camelpox virus that infects camels—also evolved from a rodent variola-like virus ancestor in Africa (*5*) (see the figure).

Once VARV transmitted to humans, it spread out of Africa and caused the epidemics of smallpox reported in numerous written records (*1*). The skin lesions seen in the mummy of Ramses V, who died in 1157 BCE, suggests that ancient Egypt was an early smallpox endemic region. The VARV genome sequences recently reported in a 17th-century Lithuanian mummy (*6*) and two Czech museum skin specimens from the 19th and 20th centuries (*7*) are related to the genomes of 47 modern VARV major and minor isolates from 1944 to 1977 (*4*).

> **"…the ancient VARV [variola virus] sequenced from Viking corpses corresponds to an extinct clade of VARV."**

The study of Mühlemann *et al.* brings a new and challenging perspective on the origin of VARV. They recovered ancient VARV DNA sequences from archaeological human remains (teeth and bones) from northern Europe, western Russia, or the United Kingdom, dated from the Viking Age. The complete viral genomes from four samples and partial genome sequences from seven samples were assembled. Analysis of the complete viral genomes showed closest relation to the taterapox viral genome (even closer than to the modern VARV genome), supporting a rodent origin of ancient VARV. Zoonotic infections (which are derived from other animals) are illustrated by current transmission events of cowpox virus—a rodent virus that sporadically infects cows—to humans in Germany, which has increased after the cessation of smallpox vaccination (*1*).

A notable feature of all modern VARV genomes is the inactivation (deletion, truncation, or mutation) of 29 genes involved in host immune evasion and in infection of a wider host range (*4*). Deletion of all these genes in VARV major and minor strains suggests that they were not required for human infection. Surrogate models of human smallpox may provide clues about the impact of

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