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Localized surface plasmons and hot electrons

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ABSTRACT

The ability of plasmonic devices to generate hot electrons has the potential to move chemical manufacturing outdoors by harnessing photon energy and converting it to useful chemical energy. By using localized surface plasmons to generate hot carriers in noble metal nanostructures, visible light can produce energetic electrons (or holes) which drive chemical reactions or create a light-induced photocurrent. Within this Perspective, we look into recent theory of plasmonic hot electron generation and how the underlying nanoparticle structure influences both the number and energy of the hot carriers produced. Applications in photodiodes and photocatalysis are highlighted to demonstrate potential device opportunities for plasmon-generated hot electrons. Super-resolution imaging studies, in which the location of hot carrier production in hybrid plasmonic-semiconductor devices is spatially localized to <10 nm, are also presented.

1. Introduction

The collective oscillation of surface conduction electrons in metallic nanoparticles and nanostructures induced by the electric field component of light, known as a localized surface plasmon [1], has led to a variety of applications in areas such as biological imaging [2], chemical sensing [3], and enhanced surface-detection techniques including surface-enhanced Raman scattering (SERS) [4] and metal-enhanced fluorescence (MEF) [5]. The localized surface plasmon resonance of these nanoparticles is dependent upon the size, shape, and material that comprise the particles and is tunable across the visible and near-infrared spectrum [6]. Surface plasmon properties have been utilized in many devices and applications including biosensing and nanomedicine [7–15], plasmon rulers [16–20], steam generation [21–23], photovoltaics [24,25], small molecule gas sensing [26–29], single molecule detection [30–32], tip-enhanced spectroscopies [33–36], and waveguiding [37].

Upon excitation, surface plasmons can either decay radiatively as re-emitted photons [38] or nonradiatively, leading to local heating [39,40] and/or energetic electrons [41]. In most applications related to sensing and spectroscopy, the nonradiative decay of plasmons has been considered a hindrance that negatively affects the performance of plasmonic devices by limiting the plasmon lifetime and thus the strength of the enhanced fields at the nanoparticle surface [42]. Recently it has been shown that energetic electrons, referred to as "hot" electrons, can be useful in a variety of applications including photodetection/photovoltaic devices [24,43], photocatalysis [43,44], and surface imaging [45]. In the most straightforward definition, a hot electron has energy that is above the distribution of available electron energies in the material as described by Fermi–Dirac statistics; put another way, the electron appears to have a higher effective temperature than is expected based on thermal equilibrium, which renders it "hot" [46]. A simplified view of hot electron excitation by a photon with energy $\hbar\omega_p$ is depicted in Fig. 1. Hot electrons with varying energies relative to the Fermi level E_F can be produced in this scheme, with the maximum hot electron energy given by $E_{max} = E_F + \hbar\omega_p$.

Recent experimental and theoretical work has shown that plasmon excitation can promote enhanced formation of hot electrons in noble metal nanoparticles [47–51]. As such, significant interest in characterizing the relationship between plasmon excitation and hot electron generation in metallic nanoparticles has arisen within the field, as demonstrated by the recent reviews by Clavero [43], Baffou and Quidant [52], and Kale et al. [53], with new device geometries and materials being explored in order to favor hot electron production. Within this Perspective, we will focus on describing the processes, applications, and challenges that arise from harnessing hot electrons generated by the decay of surface plasmons on metal nanoparticles.

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2. How "hot" is hot? Predicting hot carrier energy distributions

The picture of hot electron excitation shown in Fig. 1 implies that electron energies can be accessed over a wide range from E_F to $E_{max} = E_F + \hbar\omega_p$. However, in reality, the actual available energies of hot electrons (and hot holes) that can be generated depend on many parameters, including the size of the nanoparticle and the hot carrier lifetime. To understand the distribution of hot carriers (both electrons and holes) that can be produced by photon excitation, Govorov and coworkers performed calculations in which both bulk plasmon excitation in a gold film and localized plasmon excitation in a 10 nm gold nanocube are compared, as shown in Fig. 2A and B, respectively [50]. In both figures, dashed lines show the distribution of electron energies at thermal equilibrium, as described by Fermi–Dirac statistics, while solid lines illustrate the change in the electron (and hole) populations as a function of energy upon photon excitation. In the case of bulk plasmon excitation (Fig. 2A), momentum conservation limits the energies that can be accessed by the hot carriers, resulting in a cluster of hot electron and hole energies around the Fermi energy of the metal. On the other hand, hot electrons generated by localized surface plasmon excitation can access the full range of energies from E_F to E_{max}. In this case, the electrons can interact with the walls of the nanoparticle, which relaxes the momentum conservation rules, and allows electrons to access higher energies relative to the Fermi level. Based on this argument, the size of the nanoparticle becomes important, with smaller nanoparticles favoring production of more *high energy* hot electrons, despite the fact that larger nanoparticles will produce more hot electrons (e.g. electrons with energy above E_F) overall [50,51].

To illustrate this last point, Fig. 3 shows recent work from Nordlander and coworkers in which the distribution of hot carrier energies in silver nanospheres is plotted as a function of both the lifetime of the hot carrier as well as the nanoparticle size [51]. The lifetime of the hot electron (τ) collapses the time scales of the different mechanisms by which the hot electron can decay (e.g. electron–electron, electron-surface, and electron–phonon scattering) into a single value, ranging from 0.05 to 1 ps. For smaller nanospheres (15 nm diameter, Fig. 3A), more high energy hot electrons (relative to E_F) are produced, especially for longer carrier lifetimes (τ = 0.5, 1 ps). On the other hand, the overall number of hot electrons increases as the carrier lifetime gets shorter, albeit with energies clustered closer to the Fermi level. In the case of a 25 nm diameter nanosphere (Fig. 3B), the number of hot electrons is increased relative to the smaller nanosphere for a given carrier lifetime, but there are significantly fewer high energy hot electrons.

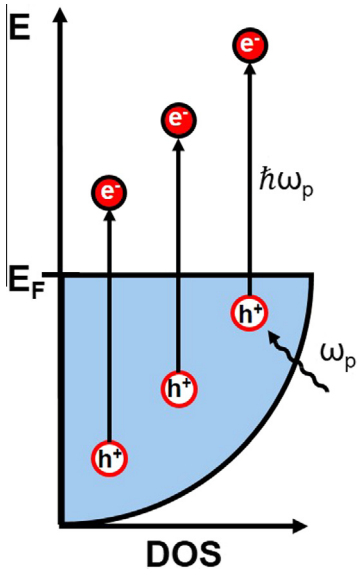

Fig. 1. Schematic of hot electron and hot hole generation by photons with energy $\hbar\omega_p$. Electrons are excited from occupied energy levels to energies above the Fermi level, E_F, leaving hot holes behind.

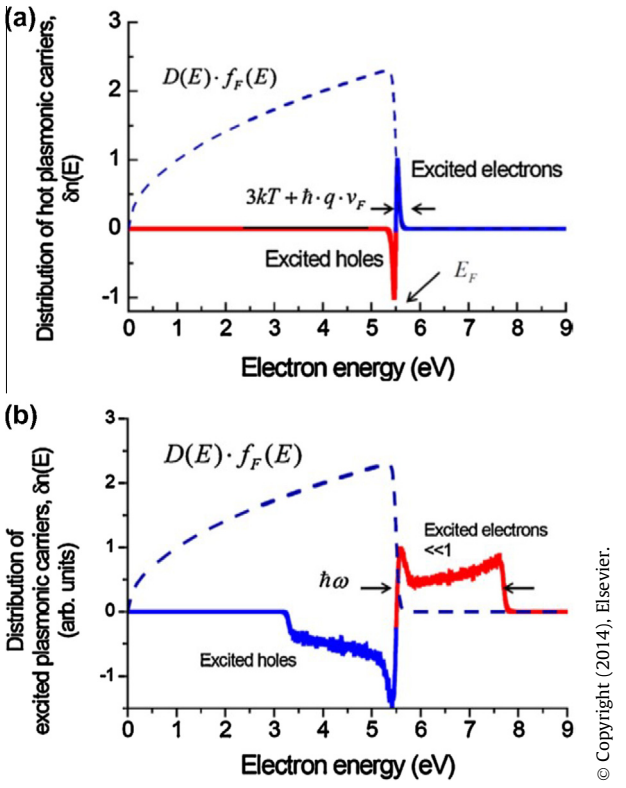

Fig. 2. (Solid lines) Plasmon-generated hot carrier distribution excited by (a) bulk plasmon in a thin gold film and (b) localized plasmon in a 10 nm gold nanocube. The dashed curve shows the equilibrium Fermi distribution of electrons at room temperature. Reprinted with permission from Ref. [50].

Both the work from Govorov and coworkers and the work from Nordlander and coworkers highlight an important point when considering plasmon-generated hot electrons: it is not just the number of hot electrons produced but also the energy (the relative "hotness" if you will) that is dictated by the properties of the underlying nanostructure. To address this, Nordlander and coworkers defined a figure of merit which represents the number of hot electrons produced per plasmon with energy above a certain threshold (typically defined relative to the energy of the plasmon excitation, $\hbar\omega_p$). Using this definition, they showed that while nanoshells produce more than twice as many hot electrons as solid nanospheres of comparable size, the figures of merit with energy thresholds set above both 20% and 50% of the original plasmon excitation energy are roughly identical between the two different structures. This balance between number and energy of hot electrons is a critical point when thinking about using plasmon excitation to enhance hot electron production and utility.

3. Hot carrier lifetimes

As described above, the non-radiative decay of plasmons gives rise to single-electron excited states, which can undergo a variety of paths to relaxation that, in turn, determine the hot carrier lifetime. The plasmon lifetime is determined by a loss of coherence in the collective electron oscillation, which can be due to electrons