COMMENTARY

PHOTONICS INSIGHTS

Photophysical and photochemical process after light absorption in metals

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The absorption of light by metallic nanostructures significantly increases at surface plasmon resonances, attributed to the coherent oscillation of large amounts of free electrons in the metal. The dephasing of surface plasmon oscillation releases energy through radiative processes (via photon emission) or nonradiative processes (via ohmic heating). The nonradiative dissipation generates energetic electrons or holes and then goes through thermal relaxation via lattice vibration (phonons)[1,2]. Eventually, the thermalization produces intense local heating inside the metal, leading to a temporal increase in the lattice temperature after the light absorption. These processes enable efficient light harvesting via the nonradiative decay of plasmons, typically regarded as an undesirable characteristic for many plasmonic applications, such as circuitries, enhanced light–matter interaction, etc. It therefore turns the waste heat into usage and creates new directions for growth in the discipline of solar energy collection or other photothermal applications.

The formation of plasmon-induced energetic carriers, known as hot carriers, is garnering increasing research interest due to their potential applications in photocatalysis[3–5], photodetection[6], and solar energy harvesting[7,8]. Compared with traditional photocatalysis or photodetection, the involvement of plasmon significantly improves the efficiency of the generation or collection of hot carriers. Therefore, it enables unprecedented photophysical processes or photochemical reactions on metal surfaces. Unlike in traditional plasmonic applications, in which people usually try to avoid plasmon damping, hot carrier generation efficiency is proportional to the amount of light absorption in metals. Therefore, to maximize hot carrier generation efficiency, it is desirable to use noble metals with large imaginary parts in the permittivity (like Al, Cu, etc.) and to design specific photonic/plasmonic modes that maximize the proportion of light inside the metals. Optical blacking surfaces that are capable of broadband light trapping are in principle the best candidates for light harvesting and hot carrier generation[9]. Hence, it is of paramount importance for both fundamental research and realistic applications to elucidate the dynamic process of hot carriers after plasmon decay, including the timescale of relaxation processes, the probability of various dissipation channels, and the strategies to increase efficiency[10].

Recently published in *Photonics Insights*, Zhu *et al.*[11] present a comprehensive review of plasmon-induced hot carriers, encompassing their dynamics, utilization, and applications. The authors begin by discussing the mechanisms of plasmon decay and hot electron generation. They delve into the principles and techniques for measuring plasmon dephasing time, along with the initial energy distribution of hot carriers. The efficiency of hot carrier generation is the key parameter that directly influences its usage in photocatalysis, photodetection, or other photothermal applications. Regrettably, the photon-to-current conversion efficiency is typically quite low, being less than 2.5%, primarily attributed to the presence of radiation damping and electron–electron scattering processes. The former lowers the probability of nonradiative decay, while the latter prevents the generated hot carriers from reaching the metal surfaces. Also, these two processes occur within a brief time frame of 100 fs and are in principle not easy to eliminate. Additionally, the carriers generated by nonradiative surface plasmon damping tend to distribute near the Fermi energy (E_F), resulting in diminished kinetic energies. Two schemes to enhance efficiency are summarized in the review, i.e., hot spot effect and modulation of electron distribution. In general, hot electrons, having a much longer mean free path than hot holes, find a broader range of applications. Besides generation efficiency, the extraction of hot electrons from metals is critical. Two common mechanisms, plasmon-induced indirect electron transfer (PIIET) and plasmon-induced direct electron transfer (PIDET), are thoroughly discussed. The PIDET is in principle more efficient, but it is prone to rapid recombination at the interfaces. In order to reduce the electron–hole recombination in the metal/semiconductors interfaces, traditional schemes in photocatalytic semiconductors are summarized to guide the community. Strategies to improve hot carrier utilization efficiency are also listed, including interface engineering and the promotion of hot electron utilization by external forces.

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The review also incorporates various applications related to hot carriers, including photocatalysis, photovoltaics, photodetectors, and ultrafast optical modulation. These applications are the major driving force for the field. The study of hot carrier dynamic processes can also spur the development of experimental characterization methods with high temporal and spatial resolution. To explore the exact timescale and energy distribution, more accurate experimental and theoretical methods are needed, benefiting related fields such as femtochemistry, ultrafast spectroscopy, and extreme nanophotonics[1,12–15]. Systematically exploring interfacial electronic structures at the nanometer scale[16], relying on their capability to determine the probability of electron forward and backward transfer events, would further enhance hot carrier utilization efficiency. Finally, Zhu *et al.* listed three prioritized issues to accelerate the development of plasmon-induced hot carrier applications. These include: (1) direct characterization of the plasmon dephasing dynamics by transient spectroscopy instead of measuring the homogenous linewidth, since the latter only reflects the averaged dephasing time but is blind to exact dynamics of the dephasing; (2) experimental determination of the initial carrier energy distribution, since the current knowledge of the carrier energy distribution mostly comes from theoretical models where approximations are often used; (3) exploring the interfacial electronic structures that determine the probability of electron forward and backward transfer events. The last issue is to find a solution to maximize the collection of hot carriers across the interface.

In conclusion, the review is timely and comprehensive, delving into a broad spectrum of intriguing topics within the realm of plasmon-induced hot carriers. It provides a systematic summary of the process of plasmon decay, hot carrier dynamics, and the strategies to enhance hot carrier generation, carrier injection, separation, and transportation. We posit that this endeavor will significantly facilitate the entry of young researchers into this captivating field.

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