Ultrafast Non-Thermal Response of Plasmonic Resonance in Gold Nanoantennas

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Abstract: Ultrafast thermalization of electrons in metal nanostructures is studied by means of pump-probe spectroscopy. We track in real-time the plasmon resonsance evolution, providing a tool for understanding and controlling gold nanoantennas non-linear optical response.
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In metal nanostructures, the collective oscillations of the conduction electrons, known as Localized Surface Plasmons (LSPs), dominate the light-matter interaction. LSPs give rise to intense optical resonances which are extremely sensitive to the dielectric environment and to the size and shape of the nanostructure as well. This feature makes plasmonic nanostructures particularly suitable for sensing applications in chemistry, biology and medicine [1]. Moreover, metal nanostructures are of great interest both from a fundamental perspective and for applications in novel devices combining electronics and optical generation/detection. For example, the capability of controlling light-matter interaction at the nanoscale leads to the confinement of large quantities of energy in sub-wavelength volumes allowing to access giant optical nonlinearities. Applications that aim to extreme light concentration, such as plasmonic antennas, lenses and resonators, are indeed the most successful up to date [2]. In this framework, manipulation and control of electron dynamics immediately after photo-excitation is of major importance in the development of active nanodevices. This clearly highlights the necessity of understanding, and experimentally accessing, the primary ultrafast electron relaxation processes of metals and confined metallic nanostructures.

Upon photoexcitation, the evolution of a plasmonic antenna starts with the radiative damping of the plasmon (≈ 10fs). In parallel, an out-of equilibrium electronic energy distribution is also created. Subsequent thermalization is driven by ultrafast electron-electron scattering, which leads to a thermal distribution within few hundreds of fs, and by electron-phonon scattering processes that become dominant on the ps timescale. Final cooling through coupling to the environment returns the system to the initial state over tens of ps. The plasmon dephasing time gives direct information about the quality of the nanostructure, its homogeneous broadening and the intrinsic loss (radiative or non-radiative) mechanisms [3]. Electron-electron and electron-phonon scattering mechanisms are instead crucial in defining the electrical and thermal conductivities of the sample and they offer a direct comparison between the bulk material and the nm-size properties, thus highlighting the non-trivial changes in the optical response induced by the presence of the LSP. While currently available ultrafast spectroscopy systems can easily study the electron-phonon scattering, the detection of the transition from an out-of-equilibrium to a thermalized electron distribution demands an extreme temporal resolution.

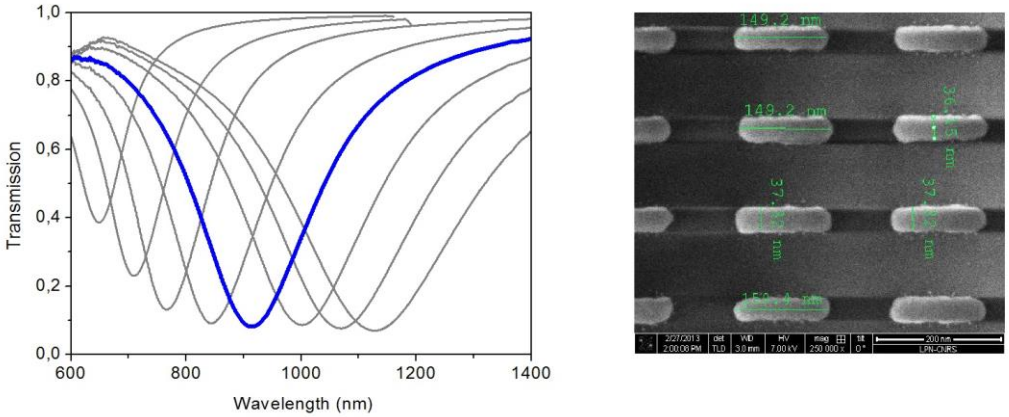

Fig. 1. Left panel: Transmission spectra at the plasmonic resonance for the different gold nanoantennas. Right panel: SEM image of the antenna used in the experiments.

The aim of this study is to understand the effects of the early electron-electron thermalization process on plasmonic resonances. We perform ultrafast pump-probe measurements on an array of non-interacting gold nanoantennas obtained by electron beam lithography. A precise control of the nanoantenna size and shape allows a fine tuning of the plasmon resonance in the visible and near IR energy range (Fig. 1). Gold is a noble metal particularly suited to study the thermalization dynamics that takes place when an out-of equilibrium electron distribution is created in the conduction band by an impulsive optical excitation [4].

Here we focus on the ultrafast response of 40x150 nm gold nanoantennas. We excite the samples with a 13-fs near-IR pump centered at 900 nm and follow in real time, with a time-delayed probe, the evolution of the plasmonic resonance. Fig. 2a reports the experimental differential transmission map spanning a broad spectral range around the extinction peak of the nanoantenna (cf. left panel in Fig.1). Interestingly, the dynamics below 920 nm wavelength (Fig.2c) show a peculiar ultrafast (less than 100 fs) change in sign that can be observed also in the shift of the isosbestic point to higher energies in the transient spectra (Fig. 2d). The shape and temporal evolution of these transient spectra suggest that the overall electron dynamics in the nanoantenna is coupled to a strong modulation (broadening and shift) of the plasmonic resonance.

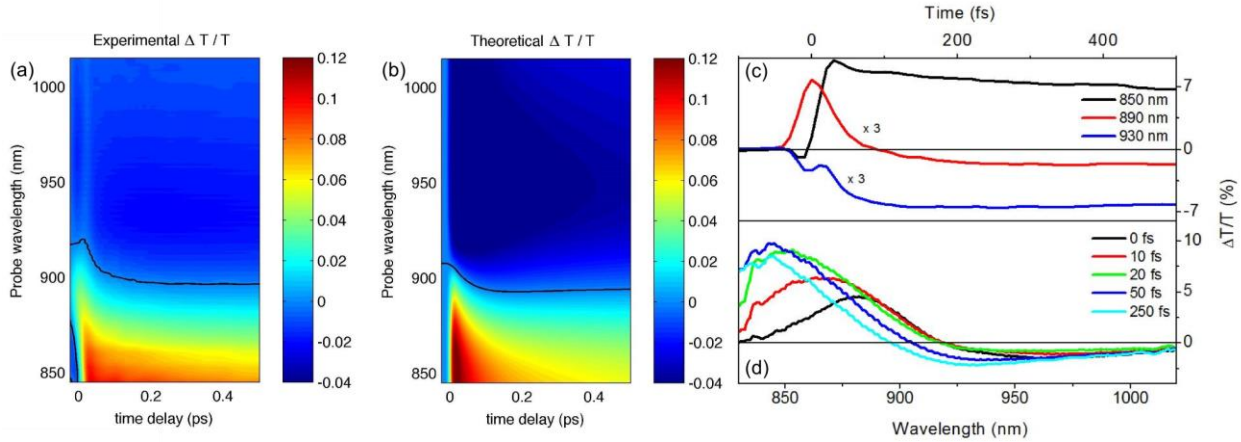

Fig. 2. (a) Pump-probe experimental map for the nanoantenna presented in Fig. 1 as a function of time and probe wavelength and (b) theoretical modeling based on a three temperature model. (c) Dynamics at 850 nm and 890 nm and (d) transient spectra at different pump-probe delays.

A theoretical modeling of the pump-probe map (Fig. 2b) shows very good agreement with the experimental results (Fig. 2a). The experimental data are simulated using a semiclassical model based on an extended version of the two-temperatures model (TTM), which has been recently demonstrated to quantitatively reproduce the ultrafast transient optical response of a thin gold film in the visible range [4]. In the present study the same model is applied to single out all the thermalization processes which contribute to the complex transient optical response exhibited by the nanoantenna in the near infrared. According to these simulations, the peculiar dynamics detailed above is ascribable to the interplay between the two contributions arising from thermalized and non-thermalized carriers, giving rise to a modulation of the interband optical transitions of gold. The near infrared resonance of the antennas enhances the dynamics of non-thermal charges far from Fermi level. For this reason, the study of the plasmonic resonance allows investigations on fundamental electron-electron interactions.

Our experiments clarify the very early processes of electron thermalization in gold nanostructures and open a route to the possibility of controlling a plasmonic resonance by exploiting the transient evolution of a photoexcited electron distribution and its non-linear optical response.

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