Femtosecond phase-resolved microscopy of plasmon dynamics in individual gold nanospheres

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Metallic nanoparticles (NPs) exhibit morphology-dependent electromagnetic resonances also called surface plasmon resonances (SPR) which couple to propagating light. These local optical resonances can be exploited to image metallic NPs with high spatial resolution and to probe nanoscale regions in the NP vicinity. Ultrafast optical spectroscopy of metallic NPs is also an intriguing area of research investigating the correlated electronic and vibrational dynamics in nanosized metals. The optical detection of single small metallic NPs with combined high spatial and ultrafast temporal resolution is however a challenging task.

Here, we demonstrate a phase-sensitive four-wave mixing (FWM) microscopy technique in heterodyne detection capable to image single small (< 40nm) gold NPs background-free even in highly scattering and fluorescing environments, and to resolve the ultrafast changes in the real and imaginary part of their dielectric function \cite{1}. The results agree well with a quantitative model (see red dashed lines in figure) of the FWM response which accounts for the transient electron temperature and density in gold via intraband and interband transitions at the SPR. Remarkably, we find that the effect of interband transitions in the excitation is important to explain not only the magnitude of the measured FWM but also its initial dynamics which is dominated by the formation of hot electrons via Auger electron-hole recombination. Beyond fundamental interest, our FWM technique offers background-free detection of the full complex susceptibility change and operates at power levels corresponding to negligible average photothermal heating, hence is compatible with live cell applications \cite{2}. Moreover it can be readily applied to any metal nanostructure. The amplitude and phase-resolved detection demonstrated here provides an intrinsic ratiometric readout which has the potential to bring unprecedented sensitivity in SPR-based applications, for example monitoring nanoscale distance changes with plasmon rulers in cells and tissues.

\cite{1} F. Masia et al Phys. Rev. B. 85, 235403 (2012) \cite{2} ibid Optics Lett. 34, 1816 (2009).