

Ultrafast electron-electron scattering dynamics in an adsorbates/metal nanosystem

Abstract:

The use of 4.2 nm gold nanoparticles embedded in a metal oxide matrix gives the opportunity to investigate ultrafast electron-electron scattering dynamics in combination with electronic surface phenomena via the surface plasmon lifetimes. These gold NPs exhibit a large non-classical broadening of the surface plasmon band, which is attributed to a chemical interface damping. The acceleration of the loss of surface plasmon phase coherence indicates that the energy and the momentum of the collective electrons can be dissipated into electronic affinity levels of adsorbates. As a result of the preparation process, gold NPs are wrapped in a shell of sulfate compounds that gives rise to a large density of interfacial molecules confined between Au and TiO₂, as revealed by FT-IR spectroscopy. A detailed analysis of the transient absorption spectra obtained by broadband femtosecond transient absorption spectroscopy allows separating electron-electron and electron-phonon interaction. Internal thermalization times (electron-electron scattering) are determined by probing the decay of nascent nonthermal electrons (NNEs) and the build-up of the Fermi-Dirac electron distribution, giving time constants of 540 to 760 fs at 0.42 and 0.34 eV above the Fermi level, respectively. Comparison with literature data reveals that lifetimes of NNEs measured for these small gold NPs are more than four times longer than for silver NPs with similar sizes. The surprisingly long internal thermalization time is attributed to an additional decay mechanism (besides the classical e-e scattering) for the energy loss of NNEs, identified as the *ultrafast chemical interface scattering* process. NNEs experience an inelastic resonant scattering process into unoccupied electronic states of adsorbates, that directly act as an efficient heat bath, via the excitation of molecular vibrational modes. The two-temperature model is no longer valid for this system because of (i) the temporal overlap between the internal and external thermalization process is very important (ii) a part of the photonic energy is directly transferred toward the adsorbates (not among "cold" conduction band electrons). These findings have important consequence for femtochemistry on metal surfaces since they show that reactions can be initiated by nascent nonthermal electrons (as photoexcited, out of a Fermi-Dirac distribution) besides of the hot electron gas.