# Photodynamics of silver nanoparticles emdebbed in zeolite thin layers for plasmonic chemistry: A femtosecond transient absorption study

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Nanozeolites[1] are material of choice to stabilize nm-sized metal[2,3] or semiconductor[4] nanoparticles (NPs) with numerous applications in catalysis, photocatalysis or more recently plasmonic chemistry. In most of these applications, the electronic properties of the supported metal govern the reactivity, and notably the electron-rich or electron-deficient character of the NPs that has a complex dependence on the nature of the support and the size of the NPs. In this work, we addressed this issue for zeolite-supported NPs by using transient absorption measurements to characterize the electronic properties of the metal.

Toward this end, nanometer-sized silver (Ag) nanoparticles have been prepared in zeolite LTL and EMT colloidal suspensions[3], from which AgLTL and AgEMT transparent thin layers have been deposited on $CaF_2$ plates. From the HRTEM images, both samples contain Ag NPs supported on the zeolithe nanocrystals but their dispersion and size differ. To perform the pump-probe measurements under controlled atmosphere, the as-prepared films were placed in a vacuum cell coupled to a broadband UV-Vis femtosecond transient absorption set-up

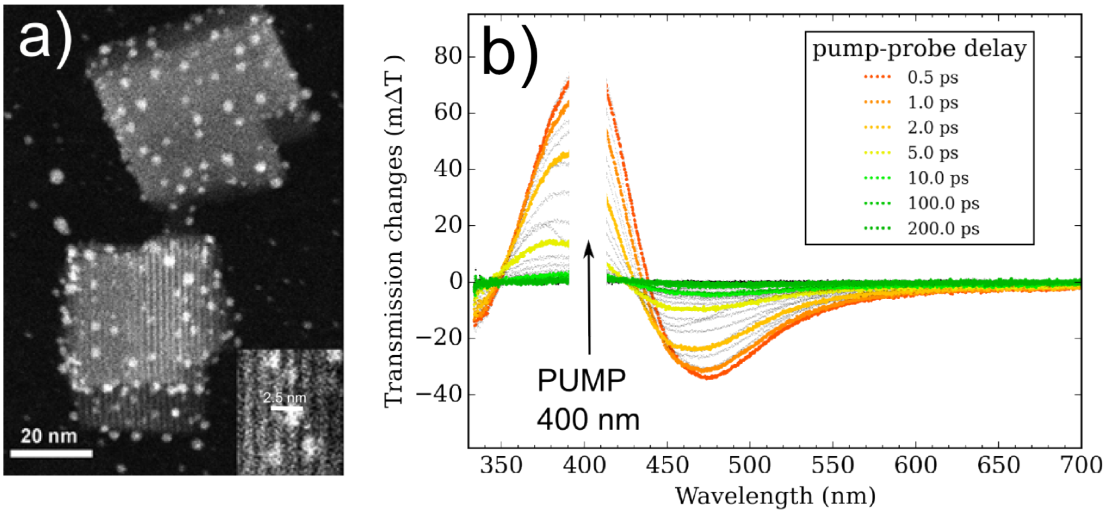

Figure 1: a) HRTEM image of Ag-LTL zeolite nanocrystals, b) transient spectra recorded in Ag-LTL films, under vacuum ($\lambda_{pump}$ = 400 nm, E = 0.1 $mJ/cm^2$)

The photodynamics of the hot-electrons formed upon optical excitation at 400 nm and 350 nm was investigated. From the analysis of the electron-phonon relaxation dynamics, the results shows that in Ag-LTL samples, the absorption of 1 photon / NPs is sufficient to generate a hot-electrons distribution with an initial equivalent temperature above 4000 K, and the subsequent increase of the metal lattice of several hundreds of degrees. It is concluded that in Ag-LTL, the NPs behave essentially as ‘free’ silver nanoparticles. The situation is found different for Ag-EMT samples, for which the ultrafast dynamics of the hot-electrons revealed a strong coupling with the zeolite framework. This conclusion is supported by theoretical calculations of the DOS of silver-containing zeolite that show that the vacant orbitals of the oxygen atoms of the zeolite framework are lying close to the Fermi level of the Ag NPs.

In addition, the influence of water and methanol molecules on the photodynamics of the Ag-NPs was also characterized. The adsorption of water in the zeolite pores has nearly no effect at low vapour pressure and is only detected when the micropores are filled. In contrast, methanol shows a specific interaction with the metal already in the low-pressure part of the adsorption isotherm.

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