Influence of the Solvent on the Dynamics of Excited Electrons in Plasmonic Nanoparticles of Silver

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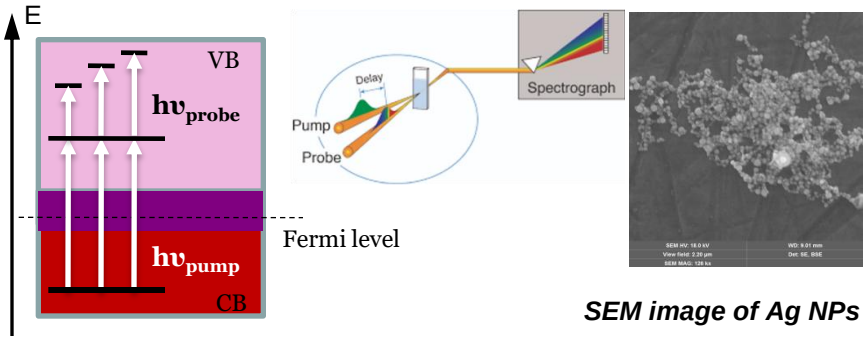
The phenomenon of localized plasmon resonance is an attractive topic of research in the last few decades due to the possibilities of its practical application. Flash photolysis methods are used to study the dynamics of electronic excitation in plasmon nanoparticles (NP) of metals. This is due to the fact that this method is very highly sensitive, allows detecting single NPs and investigating the dynamics of fast-flowing processes.
Hear, the effect of the solvent on the dynamics of excited electrons in the Ag NP was investigated.

Flash photolysis method and transient absorption of Ag NPs



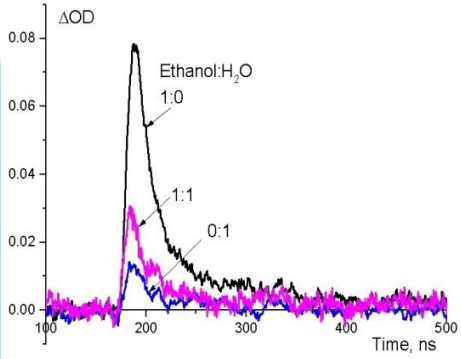
SEM image of Ag NPs

Silver NPs were synthesized by laser ablation of a silver target in ethanol using an Nd:YAG laser with λ_{gen} = 532 nm, pulse duration of 8 ns and energy of 73 mJ. The average diameter of the NPs (ZetasizerS90, Malvern) was equal to 19.3±4.1 nm. Next, solutions were prepared with a constant concentration of NP Ag, but with a different ratio of ethanol and water, which was equal to 1:0, 1:1 and 0:1.
The absorption spectra of the samples were measured using a Cary-300 spectrophotometer (Agilent). The spectra and kinetics of the transient absorption were studied by pulsed photolysis using an LP-980K spectrometer (Edinburgh Instr.) when excited by Nd:YAG laser radiation (LQ215, SolarLS) with λ_{exc} = 355 nm with pulse energy E =15.6 mJ and pulse duration t_{pulse} = 7 ns.

Data on the optical density parameters of stationary (D) and transient (ΔOD) absorption of Ag NPs in solutions with different ethanol:water ratios, λ_{exc}= 355 nm, λ_{reg}= 380 nm

Ethanol:H_2O ratio	λ_{max}, nm	D	ΔOD	τ_1, ns	τ_2, μs
1:0	396	0.064	0.077	26.6	107
1:1	400	0.073	0.030	24.5	–
0:1	400	0.090	0.014	20.2	–

Measurements have shown that the spectrum of stationary absorption of plasmonic NP Ag in ethanol, water and water-ethanol solutions practically does not change. The maximum of the steady–state absorption spectrum of NP Ag shifts to the red region with an increase in the proportion of water in the solution - from 396 to 402 nm. At the same time, there is also an increase in optical density from 0.064 to 0.09.



Transient absorption kinetics of Ag NPs in solutions with different ethanol:water ratios

In contrast to transient absorption, the solvent composition has a strong influence on the kinetics of transient absorption of plasmonic NPs (Fig. 1, Table). The maximum optical density of the transient absorption ΔOD is observed for a solution of NP silver in ethanol. When water is added, it drops 2.5 – 5 times. The duration of the transient absorption of NP Ag is also reduced – the long-term component almost completely disappears already at the ethanol ratio:water is 1:1.
The long-lived transient absorption of NP Ag can be explained on the basis of the concept of interfacial micro-convective heat exchange between the surface of the NP metal and the molecules of the medium.