Kristališkumo įtaka cheminiu būdu susintetintų plazmoninių sidabro nanodalelių lokalizuoto paviršiaus plazmonų rezonanso relaksacijos trukmėms

Crystallinity effect on the relaxation times of localized surface plasmon resonance of chemically synthesized silver nanoparticles

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Plasmonic metal nanoparticles (NPs) show great promises in various electro-optical applications such as photocatalysis, sensing, solar cells and medicine [1]. As there are so many plasmonic NPs of different metal, size, shape, crystal structure, etc., it becomes very complicated task to compare their plasmonic properties and choose the best type of plasmonic NPs for applications. We suggest that localized surface plasmon resonance (LSPR) relaxation times can help to compare the plasmonic properties of metal NPs. The LSPR relaxation dynamics consists of several processes such as electron-electron scattering, electron-phonon (e-ph) coupling, and phononphonon scattering. The evaluation of the relaxation time of the long e-ph coupling can be useful for various applications like photocatalysis, while the short one for intense thermal effects can be useful in medicine [1]. To analyze how this e-ph coupling relaxation time can be modified, we analyzed different size monocrystalline silver nanocubes (Ag NCs) and polycrystalline silver spheres (Ag NSs).

In our research, we have demonstrated the transient absorption spectroscopy (TAS) method as a perspective tool for the analysis of plasmonic properties of various crystalline-structure Ag NPs [2]. In addition to the TAS measurements, we have used transmission electron microscopy (TEM) and X-ray diffraction (XRD). We used TEM images to calculate the sizes of Ag NSs and NCs. The sizes of the crystallites were calculated by the Scherrer formula maintained on XRD data. Based on TEM and XRD data we calculated the ration -(Crystallite size/Linear dimension of Ag NPs)². Where crystallite size - parameter calculated with Scherrer formula from silver nanoparticles (Ag NPs) sample XRD data; linear dimension of Ag NPs - linear dimension is the length chosen to evaluate size of Ag NPs. It is the diameter for Ag NSs and the edge length for Ag NCs. We demonstrated that the decay time constant depends linearly on (Crystallite size/linear dimension of Ag NPs)² for polycrystalline Ag nanospheres, while monocrystalline Ag nanocubes do not show any clear dependence on this ratio (Fig. 1).



Fig. 1. Dependence of the *e-ph* coupling time constant on the linear dimension of Ag NPs (a), *e-ph* coupling time constant dependence on (Crystallite size/diameter of Ag NSs)² (b); (Crystallite size/edge length of Ag NCs)² (c). The black and red lines show the guide for eyes. D – diameter of Ag NSs, EL – edge length of Ag NCs. The schematic image of Ag NSs (d) and Ag NCs (e) [2].

The results indicate that the e-ph coupling time could be used to evaluate crystallinity and crystallite size in plasmonic metal NPs.

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Keywords: silver nanospheres, silver nanocubes, electron-phonon coupling, transient absorption spectroscopy, crystallite size, polycrystalline structure

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