3D in-situ investigation of alloying in individual Au@Ag core-shell nanoparticles

Metal nanoparticles or "nanoplasmonics" have been attracting great attention in material sciences during the past decades due to their specific optical properties based on surface plasmon resonance. Localized surface plasmons (LSP) correspond to resonant oscillations of conduction electrons, which are produced by absorption of visible or UV-light light of certain frequency. Because of these effects, plasmonic nanoparticles are very promising for application in biosensing, photocatalysts, medicine, data storage, solar energy conversion etc. Currently, colloidal synthetic techniques enable scientists to routinely produce nanoparticles of various shapes, sizes, composition and elemental distribution, which in turn strongly affect the LSP properties. However, a thorough understanding of the connection between three dimensional (3D) structure/composition and properties during application (e.g. at high temperatures) is crucial.

Transmission electron microscopy is a powerful technique to investigate individual nanoparticles even with atomic resolution. Moreover, electron tomography enables to study the nanoparticles in 3D with high spatial resolution. However, combining in-situ conditions with electron tomography is far from straightforward. The main challenge is the development of new approaches, which drastically reduce the acquisition time of a tomography tilt series. In the present work, the "incremental tomography approach" is being discussed. In combination with a heating tomography holder, this technique allows us to study 3D alloying in Au@Ag core-shell nanoparticles with different shapes and sizes. Such knowledge is important to understand the stability of the nanoparticles at high reaction temperature or when they absorp heat because of laser illumination.

More specifically, the differences in alloying behavior between core-shell Au@Ag nanorods and nanobipyramids with similar volume and composition will be discussed. Our observations may be related to a different mobility of Au and Ag atoms along various crystallographic directions in the particle. To estimate diffusion constants and understand the peculiarities of the alloying process, 3D diffusion simulations based on Fick's law were carried out. Preliminary models based on elemental distributions prior to heating are sufficient to estimate diffusion constants by visually comparing simulated redistributions with experimental data at different times. However, to obtain more accurate diffusion kinetics values and to understand the alloying mechanism, e.g. reshaping of the particles or missing wedge artifacts should be taken into account. Reshaping of the nanoparticles can be largely minimized by coating with a mesoporous silica shell but its interaction with the Au@Ag particle before and during heating should be investigated. In order to check the uniformity of the silica shell, multimodal electron tomography experiments were carried out, which allow us to visualize both the bimetallic particles and the shell simultaneously.

Further investigations based on the data obtained in this work will enable a better understanding of alloying processes at the nanoscale, required to improve the use of plasmonic nanoparticles for further applications.