

Fabrication of 2-dimensional disordered assemblies of gold nanoparticles and investigation of localized surface plasmon resonances

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Background incl. aims

Interaction of electromagnetic waves, such as electron beams or light, with conductive material can lead to localized surface plasmon resonances (LSPRs) where the incoming energy can be deposited in a collective excitation of electrons of the conduction band, which in turn can result in coherent localized plasmon oscillations. LSPR in metallic nanostructures, such as nanoparticles (NPs), which are sensitive to geometry, material composition and environment, are currently utilized in a wide range of applications, such as surface-enhanced Raman spectroscopy, plasmonic wave guides, improved solar cells, on-chip particle accelerators and nanoantennas. A host of studies that focus on plasmonic NPs ranging from single NPs with several shapes (cubic, spherical, tetrahedral) over 1D assemblies of NPs such as chains [1], to ordered 2D assemblies of NPs [2] show an increase of the complexity regarding the hybridization behavior of LSPRs eventually lead to delocalized Surface Plasmons.

Furthermore, Anderson predicted in 1977 [3] the absence of diffusion or delocalization of waves in disordered systems, which has been discussed as the underlying mechanism for LSPRs localization in disordered metallic thin films and ultrathin 2D networks [4]. Our aim is to further develop these studies on the surface plasmon localization in disordered structures by (1) developing a novel NPs assembly fabrication method that allows fabricating disordered assemblies of NPs of a wide range of NPs sizes, and (2) probing the LSPR with high-resolution electron energy-loss spectroscopy (EELS). Moreover, the dominant dipolar interaction between the NPs, also facilitates an efficient numerical modeling of these systems, which in comparison with the experiments allows for an in-depth study of the impact of various geometric parameters as well as retardation and life-time damping on the observed localization behavior.

Methods

To synthesize 2D disordered assemblies of gold NPs on a TEM transparent silicon oxide substrate, a new synthesis routine was developed. This procedure is based on sublimation and redeposition of a gold microparticle precursor induced by an electron beam in a scanning electron microscope (SEM) operated at 30 kV. To characterize the assembly of synthesized NPs in terms of size, shape and spreading over the substrate, TEM measurements were conducted subsequently. To study LSPRs experimentally, EELS in scanning transmission electron microscopy (STEM) mode was carried out. The numerical modelling of LSPRs was performed using a self-consistent dipole model.

Results

The synthesized 2D disordered gold NPs assemblies (see Fig. 1a) exhibit a gradient in the NPs mean size, which ranges from 100 nm close to the precursor location down to 2 nm at a distance of more than 20 μm from the precursor location. Additionally, the interparticle distance between the gold NPs increases with increasing distance to the precursor location. The experimental investigation (see Fig. 1b) as well as the numerical simulation (see Fig. 1c) of the LSPRs demonstrate a localization behavior that decreases toward larger energies, which is driven by the disorder of the NPs assembly (mainly the random particle distance). That localization behavior stays in contrast to what was found in ultrathin 2D gold networks

showing increasing of localization towards higher LSPRs energies. By varying the geometric parameters of the NPs assembly in the simulation, we could identify the NPs thickness as the parameter, that determines the energy-dependence of the localization. Specifically, a critical thickness of approx. 10 nm separates the two localization regimes, which correlates to the energy of the dipole mode resonance crucially depending on the thickness of the NPs.

Conclusion

2D disordered assemblies of gold NPs of a wide range of NPs sizes and distances can be synthesized directly on thin substrates facilitating structural characterization and EELS measurements in a TEM. It could be shown that such assemblies exhibit LSPRs with a localization behavior that may be tuned by the NPs sizes (including thickness) and interparticle distances. The proposed synthesis of random NPs assemblies opens new avenues for fundamental studies on Anderson localization in disordered plasmonic structures as well as its applications such as surface-enhanced Raman spectroscopy where localization behavior must be tuned to specific wave lengths.

Graphic:

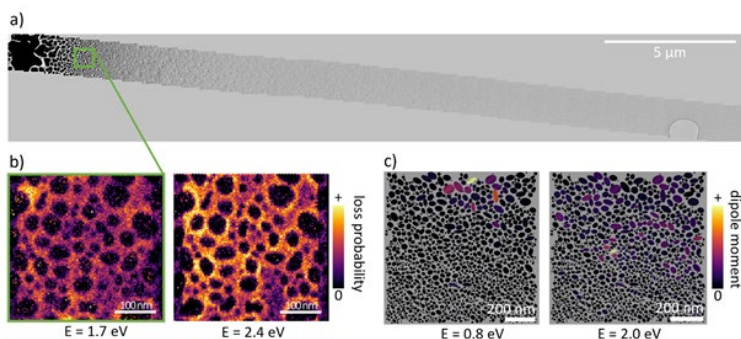


Figure 1 a) Stretched bright-field TEM images showing the disordered assembly of gold NPs over several tens of micrometers. b) LSPR maps obtained by STEM spectrum imaging at energy losses of $E=1.7$ eV and $E=2.4$ eV. c) Simulated LSPR maps derived from a self-consistent dipole model.

Keywords:

SEM, TEM, LSPR, Au-NPs-Synthesis, Disordered-Assemblies

Reference:

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