Size- & Shape-Independent Tuning of Plasmon Resonance Frequency of Sub 10 nm Gold Nanoparticles

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Abstract

Nanotechnology has unveiled exotic phenomena in materials while concurrently enhancing or annihilating intrinsic ones. The key to controllably extract and exploit these phenomena is through precise control over the architecture (size, composition and pattern formation) of nanomaterials. Nanoparticles (NPs) are ideal features with properties that enable them to function in a vast range of technological domains. Assemblies thereof, create configurations which rely either on their individual or collective response to external stimulus. This fundamental understanding has been implemented with plasmonic NPs (e.g. Au, Ag, Cu), to enable the development of e.g. enhanced molecular sensing, energy harvesting and spectroscopic systems.

The spectral properties of plasmonic NPs have so far been found to be fundamentally dependent on the material of the NP as well as its electronic charge or that of the surrounding medium, the spacing between NPs, their shape as well as size. The presentation will illustrate an enticing means to tune the spectral properties of spherical Au NPs of the same size within a spectral range of ~ 485 - 540 nm, with air as a surrounding medium. The NPs are ligand-free and adequately spaced out (70 ± 10 nm) to minimize proximity effects. It will also be shown how the spectral properties can be further modified or stabilized with an ultra-thin (~ 1nm thick) dielectric shell around each individual NP. To achieve all this, we employ the concept of diblock copolymer micelle nanolithography to synthesize monodisperse, two-dimensional (2D) arrays of sub 10 nm NPs and core-shell systems.¹ 2D arrays of NPs are used here to exploit the advantage of such a configuration: It provides an interesting regime wherein the individual and or collective properties of the plasmonic NPs can be studied and utilized simultaneously. The current platform is as an alternate route to shift the spectral response of sub 10 nm NPs beyond their standard regions of expression.

References

[1] B. N. Mbenkum, A. Diaz-Ortìz, L. Gu, P. A. Van Aken, G. Schuetz, *J. Am. Chem. Soc.*, **132** (2010), 10671-10673.



I. Metal-loaded PS-b-P2VP micelle II. Plasma Treatment

III. 2D Array of Nanoparticles

Figure 1. Schematic representation of NPs prepared via diblock copolymer nanolithography: Crosssection of metal-loaded micelle before (left) and during (middle) plasma treatment, respectively. Representative SEM and high-resolution SEM micrographs (right) illustrate the ordered 2D array of ligand-free Au NPs obtained after plasma treatment.