Abstract

The present thesis focuses on the development of novel self-assembled plasmonic nanoantenna materials and their applications in single molecule surface enhanced optical spectroscopy. Plasmonic nanoantennas concentrate light into small volumes and greatly enhance the local electromagnetic (EM) field near the metal nanostructures leading to a strong enhancement of usually weak single molecule signals. To achieve tremendous signal amplification, the nanoantennas were designed by assembling anisotropic shaped pure Au and Au@Ag nanostars, considering high EM field generated at the sharp edges of nanostars. Further, the programmable nature of DNA origami technique was utilized for self-assembling the nanostructures with tunable interparticle gaps and stoichiometry and precise placement of single fluorophore in the plasmonic hotspot. The designed dimer nanoantennas were used in single molecule surface enhanced Raman spectroscopy (SERS) as substrates. The effect of several parameters such as interparticle gaps, stoichiometry, negative curvature site, and composition of plasmonic nanostructures on Raman enhancement factors (EFs) has been investigated. The SERS EFs of single Texas Red dye molecules located in the conjunction region of Au nanostar dimer structures were found to be in the range of 10 9 -10 10 , which are high enough for single analyte detection. The results indicate that the EF increases on decreasing the interparticle gap sizes from 13 nm to 7 nm but when the gap size becomes ≤ 0.5 nm, no enhancement happens due to quantum tunneling effect. The obtained EFs were higher for dimer structures than monomers due to difference in the generated EM field enhancement. Bimetallic Au@Ag nanoparticles have better plasmonic effects because they combine the best of both metals i.e. enhanced plasmonic properties of Ag and good chemical stability of Au in one structure. The nanoantennas designed using Au@Ag nanostar dimers on DNA origami showed strong broadband field enhancement effects as they significantly enhanced SERS signals of single FAM, Cy3, and TR dye molecules emitting in different visible region. The judicial choice of placing single quantum dot in the plasmonic hotspot instead of organic fluorophores will help in creating functional single QD-based nanosensors with enhanced photo-stability. The thesis highlights a novel green synthetic route for the preparation of blue emitting Si QDs and generation of white light emitting mixture by controlled mixing with orange red emitting Au nanoclusters. Further, the results included in the thesis confirm successful immobilization of single Si QD on DNA origami which is a positive step towards merging a single QD with a single plasmonic nanoantenna. This thesis also demonstrates the applicability of designed Au@Ag nanostar nanoantennas as sensor platform for label-free sensing of single thrombin protein molecule specifically placed in the hotspot and ultrasensitive detection of bacterial biomarker pyocyanin. The work included in the thesis represents a concerted effort to continue the development of novel plasmonic nanoantennas holding great potential to translate into real biomedical applications.