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Thesis Title:	*MODELING AND ANALYSIS OF POST PLASMONIC EFFECTS IN OPTICALLY EXCITED METAL NANOSYSTEMS*

Abstract

Plasmonic nanoparticles such as gold (Au) and silver (Ag) with their heterogeneous nanocomposite structures have aggrandized in multitude of applications including biomedical imaging (optical, dark field, photoacoustic, etc.), sensing techniques including wavelength shift LSPR bands and Surface Enhanced Raman Spectroscopy (SERS), photothermal therapy, and drug delivery. Their usage is made plausible by optical excitation of suitable wavelength and subsequently triggering local surface plasmon resonance (LSPR). To manipulate LSPR, this field of nanotechnology requires appropriate modification and design of nanostructures in terms of size, shape, surface functionalization, coating, interparticle coupling, etc. These modifications are inevitable to achieve better performance and sensitivity via one or more of these objectives: 1) higher absorption, 2) field enhancement and 3) thermodynamic stability.

Though the unique capabilities of coatings/shell on nanomaterials are quite promising, post effects of optical excitation intuitively can be claimed to disturb the core-shell nanostructures. This thesis investigates the cause of perturbations in plasmonic as well as core-shell hetero-structures and their bulk and surface morphologies via few possible intermediate phenomena like electric field enhancement, thermal expansion, heat generation, gas evolution, boiling, ablation, breakdown, and plasma formation. These mechanisms occur under specific conditions of temperature, irradiation timing, laser intensity, nanoparticle shape, environment matrix, pulse duration, beam diameter, etc. On the other hand, in addition to investigation on structural damage, the thesis also analyzes and study a plasmonic system formed *via* optical excitation as stimulus or trigger to induce formation of clusters, how plasmons couples in an elongated self-assembly with a conductive interface.

In this thesis, we have explored few mechanisms which induce morphological or structural change, on composite hetero-nanostructures with a dielectric coating on gold nanoparticles. We used finite element method (FEM), MATLAB and theoretical analysis to numerically compute and predict the intensity range where we can expect such breakdown. First we explored structural damage on smaller nanoparticles like silica coated spherical Au nanoparticles (AuNP@SiO_2). Using nanosecond pulsed laser (10ns) we have showed the possibility of structural breakdown which was characterized using transmission electron microscopy (TEM) images and scanning electron microscopy images (SEM). An intensive literature and theoretical model backup the fact that, structural failure in these core-shell nanospherical structures happens due to differential thermal expansion of core-shell pair and that rupture or deformation happens throughout the silica coating.

Following this we extended our study towards silica coated Ag nanoprism (AgNPr@SiO_2) which exhibits a different breakdown mechanism. Due to the triangular geometry and high

scattering of Ag than that of Au, a low input intensity could create a field enhancement near the corners causing damage to initiate near the corners. Numerical models were used to analyze the localization of intensity near corners and estimate the numerical value range of breakdown. Thus, a more controlled breakdown is achieved and with a low laser fluence. These nanosystems are anticipated to have significant impact on biomedical applications, providing futuristic possibilities for non-invasive methods as suitable agent carriers. These agents can be injected non-invasively and remotely activate to respond to external stimuli in convenient sites inside a real-life sample.

Finally, we have investigated the effect of optical excitation on plasmonic clusters connected covalently by a conductive inter-particle interface. For this we have selected gold nanoprisms (AuNPrs) and modified triangular edges with a synthetically modified diacetylene monomer. Upon exposure to ultra-violet light (254 nm) the diacetylene undergoes photo-polymerization to poly-diacetylene resulting in formation of interparticle assembly and initiate clustering. We anticipate that the interface comprising of conductive polymers allows interparticle plasmonic exchange upon suitable light excitation.

Theoretical simulation and experimental findings suggested that upon suitable optical excitation, post-excitation on plasmonic nanosystems, core-shell analogues as well as interparticle clusters undergoes various changes. The resultant transformation in these nanosystems varies for different structures depending on factors such as size, shape, coating and nature of laser used for excitation. The study presented in this thesis will provide insight in to plasmon interactions based structural instabilities and changes in plasmonic nanomaterials during interaction with electromagnetic (EM) waves.