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Enhanced Optical Response of Al, Rh, Ag, and Au Nanosphere Dimer in Uniform Electric Field

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ABSTRACT

Localized Surface Plasmon Resonance (LSPR) mediated electromagnetic field enhancement play a vital role in enhancing the performance of bio-molecular sensors, photovoltaic cells and Raman spectroscopy (e.g., in SERS) etc., to name only a few. It is now well established that the field amplification factor (mode squared field) ~10^6 for spherical shaped plasmonic nanoparticle dimers is significantly higher than the amplification factor of a monomer which is ~10^3. In this work, a theoretical and semi-analytical approach based on multipole spectral expansion is used to investigate the electric field enhancement in the gap region of spherical nanoparticle dimers of Al, Rh, Ag, and Au. The dimer exhibit rich spectra compared to its isolated counterpart. For example, in contrast to a monomer, the dimer spectra consists of multiple resonant peaks which can be fine tuned by varying particle size and/or inter-particle separation. Moreover, the enhancement in dimer is several orders higher than that in monomers. Rich spectral features in dimer spectra arise from the interaction between particle plasmons of constituent NPs and their hybridization, which results in the splitting of plasmonic energy levels. We carry out, systematic investigation of these systems to quantify the effect of particle size, interparticle separation and metal type (Al, Ag, Au, Rh) on electric field enhancement.

***Keywords*:** Enhancement, nanoparticle, dimer, plasmonics, hybridization

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1. INTRODUCTION

The recent explosive progress in Plasmonic Nanostructures has been based on the optical properties of metallic nanoparticles. The appeal of surface plasmon excitations at metal dielectric interface due to huge and various applications typically arise due to large electromagnetic field enhancement near metallic nanoparticles.

Recently the near field enhancement in the vicinity of metallic nanostructures upon excitations of their surface plasmon resonances have attracted substantial attention and are used to amplify linear optical effects, such as surface enhanced Raman spectroscopy [1], surface plasmon enhanced photoluminescence, fluorescence [2] and also support many non-linear optical process like second/ third harmonic generation [3], two photon absorption induced luminescence [4].

The optical response or electric field enhancement of Plasmonic nanostructures is strongly dependent on geometry as well as combination of plasmonic nanostructures. For example isolated spherical nanoparticle shows electric field enhancement of the order of 103 which is quite insensitive for SERS measurements. Moreover in case of spherical nanoparticle the spectrum can be tuned by varying the radius of nanoparticle and dielectric constant of embedded medium. A class of new plasmonic nanoparticle called core@shell or nanoshell (NSH) which is widely used in medical and spectroscopic measurement due to more tunable properties. NSH consist of core material coated by concentric thin shell layer [5, 6].

This feature of NSH makes more tunable and adjustable for different applications. Nanoshell also supports the plasmon resonances and gives a relatively large electric field enhancement (10^4) as compared to isolated spherical nanoparticle (10^3). But for SERS measurement (detection of single molecule technique), this electric field enhancement is not sufficient. To amplify this field enhancement, dimer geometry is an appropriate choice for SERS enhancement. Monomer and dimer geometry shows drastically different optical response.

This different behavior can be easily understood by hybridization theory [7]. Nanoparticle dimers are useful for researchers because they have large electromagnetic field enhancements in the gap region due to particle-particle interaction. The plasmonic properties of nanoparticle dimers have been studied by various methods [8, 9], but still there is a wide scope to harness the unexplored potentials in the field of plasmonics.. A quantam mechanical approach is used to study the plasmon resonances of dimer system as a function of interparticle separation.

It is analyzed that for above 1 nm interparticle separation, classical electromagnetic theory is obeyed to study the dimer plasmons [10]. Finite element method (FEM) is used to study the optical response of core shell silver nanoparticle dimer in the visible region as a function of inter surface gap [11]. Here we consider coupled nanosphere (dimer) placed in uniform electric field. For proposed geometry, specific multipoles can be choosing according to system parameters. Inspite of direct solution, we consider Multipole spectral expansion method MSE) based approach for the present study.

The manuscript is organized as follows. Section II describes the theoretical formulation of the problem and its implementation to NSP Dimer. Sec. III includes the results discussion. Finally, Sec. 4 presents summary with significant remarks and future scope of the work.

2. THEORY

Schematics of the system which consist nanosphere dimer placed in uniform electric field is shown in Fig. 1. To extend MSE based approach to the nanosphere dimer, an interaction matrix approach based on using the eigenstates of the single inclusion has been used. In this picture, we consider a plasmonic system consisting of two nanospheres having interparticle separation S. The centre of one nanosphere can always be considered at the origin (here Left) and hence the centre of other nanosphere (here Right) will always be shifted relative to the origin.

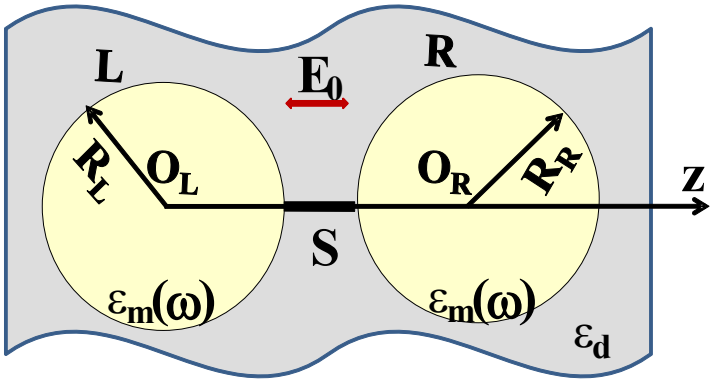

Figure 1. The schematic of dimer system of coupled spherical nanoparticles (SNPs) under consideration. Here, left and right NPs are labeled as L and R, their centre as O_L and O_R and their radii as RL and RR, respectively. Both NPs are considered embedded in a homogeneous dielectric medium (ε_d). The dimer system is exposed to homogenous external electric field Eo along z-direction which excites localized surface plasmons (LSPs) of NPs.

To analyze such a plasmonic system relative to a common origin, the eigenstates of this nanosphere will have to be expressed relative to defined common origin. In order to deal with a nanosphere which is not centered at the origin, we need to make transformation of eigenstates. In such a case, the function consisting of multipoles has to be expanded about the shifted origin. Both metallic nanospheres may be described through frequency dependent dielectric function, $\varepsilon_m(\omega\omega$ and assumed to be embedded in a host medium characterized by its dielectric permittivity, εd. This system is placed in a uniform external electric field ($\vec{E} = E_0\hat{z}$) of magnitude E0 and directed along +z-direction (or, external potential $\Phi_{ext} = -E_0 z = -E_0 r\cos\theta$). The presence of the nanosphere dimer modifies the potential or electric field. By using proposed numerical approach which is valid within quasi-static approximation, the general expression for the potential at point P, outside the inclusion is given by

$$\Phi_{induced}(r) = \sum_{\lambda}\sum_{l}\sum_{l'} \frac{s_{l'}}{s(\omega) - s_{\lambda}} \left(I_{L,l} B_{Ll}^{\lambda} + I_{R,l} B_{Rl}^{\lambda}\right)\left[(B_{Ll'}^{\lambda})\psi_{L,l'}(r) + (B_{Rl'}^{\lambda})\psi_{R,l'}(r)\right]$$

By solving overlap integrals, calculating dimer matrix element and eigenfunctions of left & right sphere in above Eq., we get the induced potential, $\Phi_{induced}(r)$ at a given position r. The overall electrostatic potential in the gap region is obtained by adding external potential and induced potential. The evaluation of electric potential is done at two neighboring positions and electric field is then calculated using basic relation, $\mathbf{E} = -\nabla\Phi$.

3. RESULTS AND DISCUSSION

This section provides the results of our investigations based on theoretical approach described in Sec. II. Present study considers plasmonic nanoparticles (PNPs) made of aluminum ($_{13}$**Al**), silver ($_{47}$**Ag**), gold ($_{79}$**Au**) and rhodium ($_{45}$**Rh**) in spherical, core@shell (NSH) and dimer configuration. Radius of each constituent nanoparticle is denoted by R, aspect ratio (a/R) of core @shell (NSH) is denoted by x and the interparticle separation (surface to surface) in dimer configuration is denoted by S. Unless mentioned otherwise, both plasmonic nanoparticles (PNPs) in the dimer system will be considered spherical in shape and identical in size (R) and composition ($\varepsilon_m(\omega)$).

The optical response of PNPs is described through photon energy ($\hbar\omega$) dependent optical constants of Johnson and Christy for Au and Ag [12], A. D. Rakic for Al [13], and Palik for Rh [14].

The field amplification factor $A(\omega) = \left|\frac{\mathbf{E(r)}}{\mathbf{E_0}}\right|^2$. as a function of $\hbar\omega$ of isolated spherical nanoparticles of Ag, Al and Au is presented in Fig. 2.

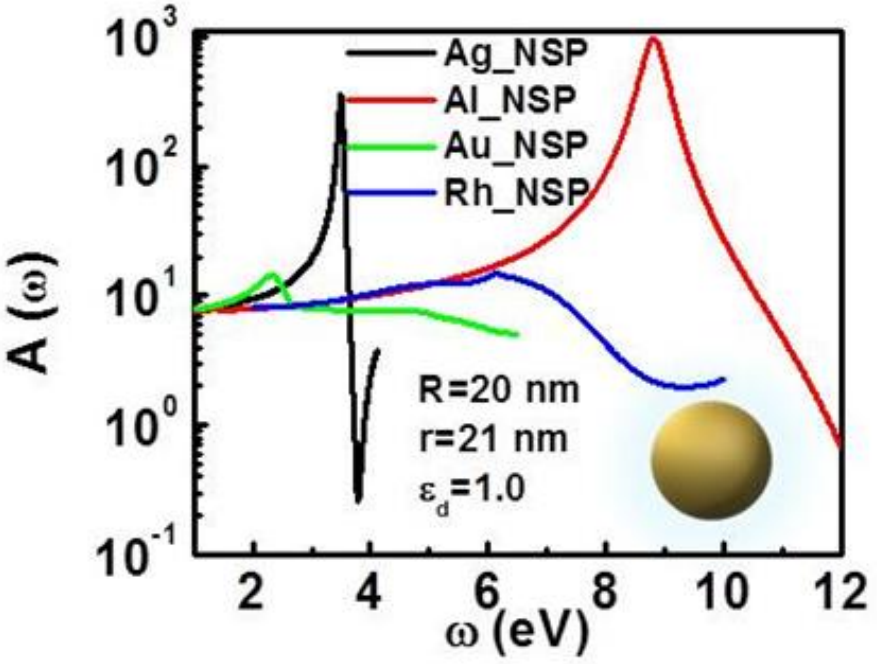

Figure 2. Amplification factor A(ω) as a function of ħω for isolated spherical nanoparticles of Ag, Al, Au and Rh of nanoparticle radii, R = 20 nm embedded in a medium of dielectric constant εd = 1.0

In Fig. 2, shows the field amplification spectrum as a function of energy (eV) of isolated spherical nanoparticle (NSP) at observation point, r = 1.0 nm away from the particle surface. it is observed that in case of isolated spherical nanoparticle, the electric field amplification factor is the order of 10^3. In case of isolated spherical nanoparticle, silver shows field amplification is 3.27×10^2 at 3.43 eV, aluminium shows field amplification 1.07×10^3 at 8.79 eV, gold shows field amplification 1.3×10^1 at 2.32 eV and rhodium shows field amplification 1.54×10^2 at 5.98 eV. It is noticed that the field amplification spectrum in case of isolated spherical nanoparticles is not sufficient for many applications like SERS measurements. Only single peak is observed and tuning parameters is very less for isolated nanoparticle.

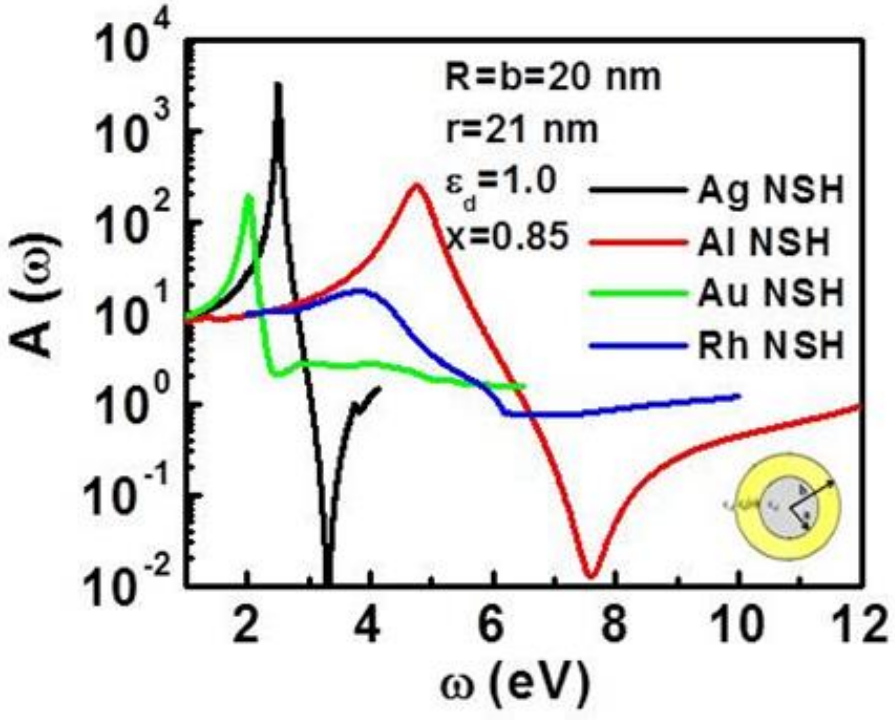

Figure 3. Amplification factor A(ω) as a function of ħω for core@shell (NSH) nanoparticles of Ag, Al, Au and Rh of nanoparticle radii, R = 20 nm embedded in a medium of dielectric constant $\varepsilon_d = 1.0$.

It is observed that in this case the field amplification is the order of ~10^3 to 10^4. Silver shows field amplification is 3.8×10^3 at 2.48 eV, aluminum shows field amplification 2.60×10^2 at 4.80 eV, gold shows field amplification 1.85×10^2 at 1.99 eV and rhodium shows field amplification 1.7×10^1 at 3.88 eV. NSH geometry has superior to NSP geometry due to more spectral tuning options. By changing aspect ratio, the spectrum can be tuned in desired spectrum region. But still, the field amplification in case of NSH geometry is also quite insensitive for SERS measurements. To overcome this bottle neck, dimer geometry is used to calculate the field amplification factor which can be used for SERS measurements. Fig. 3. shows the spectral variation of electric field enhancement with photon energy (eV) of Ag, Al, Au and Rh in dimer configuration.

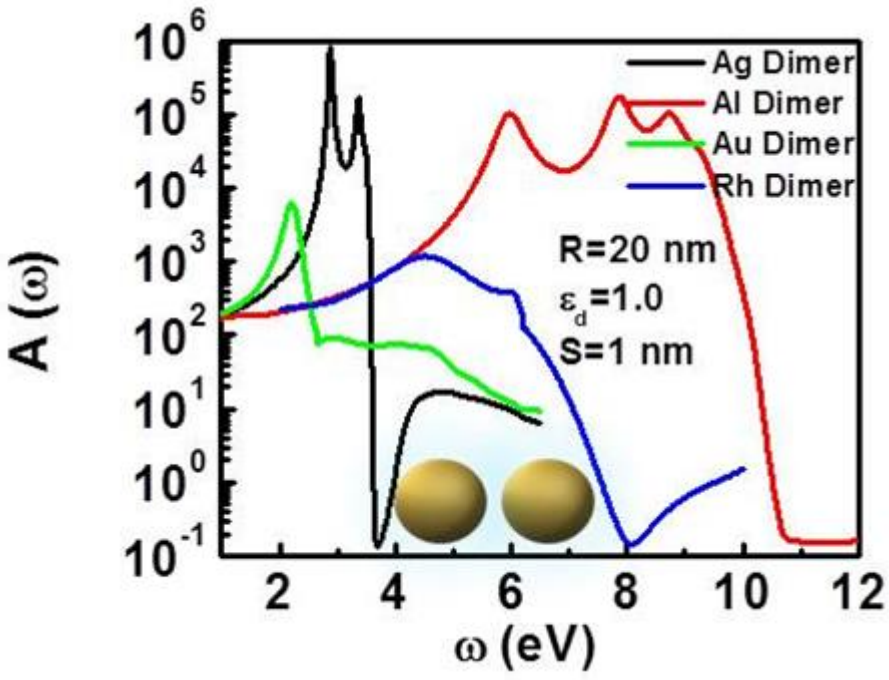

Figure 4. Amplification factor A(ω) as a function of ħω for nanosphere dimer nanoparticles of Ag, Al, Au and Rh of nanoparticle radii, R = 20 nm embedded in a medium of dielectric constant εd = 1.0. Surface to surface separation (S) is 1 nm.

The important observations of Fig. 4 are summarized as follows: (I) the multiple peaks are observed in dimer configuration (II) multiple resonant peaks showing field amplification of order of ~10^6. (III) It is also found that resonant position for silver is 2.86 eV/ 7.1×10^5, aluminum is 5.93/1.0×10^5, gold is 2.21 eV/ 7.1×10^3 and rhodium is 4.42 eV/ 1.34×10^3 in dimer.

Silver and gold shows resonant peaks in visible or near infrared region, while resonant peaks of aluminium and rhodium lies in Deep-UV region of spectrum. The electric field enhancement is due to the interaction between surface plasmon modes of two nanosphere in the presence of electric field.

4. CONCULSION

A theoretical model for Electric Field Enhancement or field amplification of Nanosphere (NSP) dimer is used using Multipole Spectral Expansion method. The proposed model is efficient to deal with other complex geometry. For the system means NSP dimer ~10^6 order field enhancement is predicted. Role of higher order multipoles are explored.

We have investigated the field enhancement behavior of Al, Rh, Ag, and Au nanoparticle dimers, covering UV-Vis spectral rang which enables to deal with SERS spectroscopic measurements due to extensive exhibit tunable optical properties.

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