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PLASMONIC LAYERED NANOSTRUCTURES FOR DEEP UV-UV BIOSENSING

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ABSTRACT

The influence of metallic shell on the SPR of metallic nanosphere was investigated using FDTD simulations and Plasmon hybridization method. The metals considered for the analysis are gold, silver and aluminium. The main emphasis is put on refractive index sensitivity (RIS) which is useful parameters for sensing application based on SPR technique. As compared to single metallic nanoparticle or oxide coated nanoparticle, the bimetallic nanoparticle is capable of simultaneously providing large values of sensitivity over a wide spectral range. The order of a RIS factor of 30 nm particle size is Al-Au>Au-Ag>Ag-Au with a value of 245.16 nm/RIU>106.98 nm/RIU>90.32 nm/RIU which shows that Ag-Au core-shell nanostructure shows lowest RIS value whereas, Al-Au shows highest among Au and Ag based nanostructure with the advantage of spectral peak in DUV-NIR region. As compared to core shell nanostructure the multilayered nanostructures support strong and tunableSPR as well as high RIS factorof 510 nm/refractive index unit (RIU) and 470 nm/RIU for Al–Air–Au and Ag-Air-Au, respectively. The MDM structures notonly exhibit higher index sensitivity but also cover a wideUV–NIR wavelengths, making these structuresvery promising for index sensing, biomolecule sensing, andsurface-enhanced Raman spectroscopy.

Keywords: Surface plasmon resonance (SPR), core-shell nanostructure, multi-layered nano structure, Refractive index sensitivity, FDTD, Plasmon hybridization method.

I. INTRODUCTION

In LSPR-based sensors, metallic particles are illuminated by light and localized surface plasmon is excited in the particles [1,2,3]. Their excitation gives rise to a peak known as plasmon resonance wavelength in the extinction spectra. The dependence of the plasmon resonance wavelength on the surrounding medium dielectric constant becomes very useful in the optical sensing of chemical and biomolecular analytes [4]. When the refractive index of the surrounding medium is increased, there is a linear red shift in the plasmon resonance wavelength. By following this shift, it is possible to sense changes in the environment of the nanoparticle. The sensitivity of the plasmon resonance wavelength to the dielectric function of the host medium is defined as refractive index sensitivity (RIS) [4], $RIS = \frac{d\lambda_p}{dn}$, where, $d\lambda_p$ is the variation in plasmon wavelength. To study these factor, a local change in the environment around the nanoparticle is created by depositing a thin layer of material onto the nanoparticle and the surface refractive index sensitivity is calculated as $RIS_S = \frac{d\lambda_p}{dn_l}$, where n_l denotes the refractive index of thin layer. From the point of view of sensing applications, tunability of the resonance wavelength of nanoparticle would allow the optimum selection of nanoparticle depending on wavelength range. Gold nanoparticles are considered as an extremely good candidate for biosensing applications due to their biocompatibility. As compared to gold, silver based nanosensors are known for their narrow spectral width and high detection accuracy. But due to interband activity, both Au and Ag are plasmonically inactive in UV region, where most of the nucleic acids, directed at the four DNA bases adenine (A), cytosine (C), guanine (G) and thymine (T) shows strong absorption band [5]. Therefore, we propose Al as a strong plasmonic active material which supports long-lived LSPRs with high optical cross-sections tunable over a wide energy range, deep into the UV, for sensing applications in the shortest wavelength range which are generally not possible with other metal nanoparticles [6,7]. But the problem with Ag and Al metals, however, is that they easily oxidized in aqueous medium. In contrast to silver, the process is self-limiting in Aluminium giving a stable oxide thickness, which makes it easy to work with even in atmospheres containing oxygen [7,8]. In this paper, the strategies using Au coated bimetallic core-shell and multilayered nanostructure have been proposed to maintain the stability of the Al & Ag nanostructure. We studied the effect of core material and thickness of the shell on Ag and Al coated metallic nanosphere. The three chosen metals Al, Ag and Au constitute an excellent model system where the interband activity varies greatly covering entire UV-NIR region of EM spectrum.

II. THEORETICAL SIMULATION

In this work, we employed FDTD software called Lumerical FDTD solution to carry out FDTD analysis forplasmonic nanostructure [9,10]. We adopt a cubic Yee cell with a side equal to 1nm and a time stepΔt$= 1.31 \times 10^{-18} s$, bounded by Courant condition. For FDTD calculations involving the nanosphere of diameter D, the grid sizes in x, y and z directions are selected in such a way that the value of E-field intensities around nanosphere becomes independent of the grid sizes. This process is carried out by initially selecting grid sizes in x, y and z directions of the order of 1/10th of the size of nanosphere and subsequently reducing the value of grid spacing until a further reduction in grid spacing had no influence on the calculated results around the nanosphere. The FDTD software employed in this work allows selection of different grid sizes for the edges of metallic nanostructures and the bulk media. In our calculations, 0.7 nm grid spacing has been chosen for spacing around the nanosphere. The material data is obtained from Palik and Johnson & Christy which is inbuilt in software [10].

III. RESULT & DISCUSSION

Figure 1(a) and (b) shows the calculated absorption spectra for Au-Ag nanostructure. The particle size is fixed as 20 nm and 30 nm with thickness of shell varied in steps as 1 nm, 2 nm, 3 nm, 4 nm, 5 nm, 7 nm and 10 nm. There are two peaks located at ~504 nm and ~332 nm showing the contribution of Au and Ag as core and shell material, respectively. On increasing the thickness of shell, the longer wavelength peak blue shift to 488 nm whereas shorter wavelength peak red shifted to352 nm. As the thickness of shell increases further, Ag dominates the Au and a single peak starts contributing towards absorption spectra. The fabricated Au-Ag core-shell nanoparticles by laser ablation method shows similar UV-visible absorption spectra with two distant bands appearing at 510 nm and around 400 nm [11]. As Ag ablation time increases, the SPR band in long wavelength gradually blue shifts from 524 nm to 507 nm with gradually increasing SPR intensity. At the same time, the SPR band in the shorter wavelength gradually red shifts from 390 nm to 410 nm with increasing intensity [11].

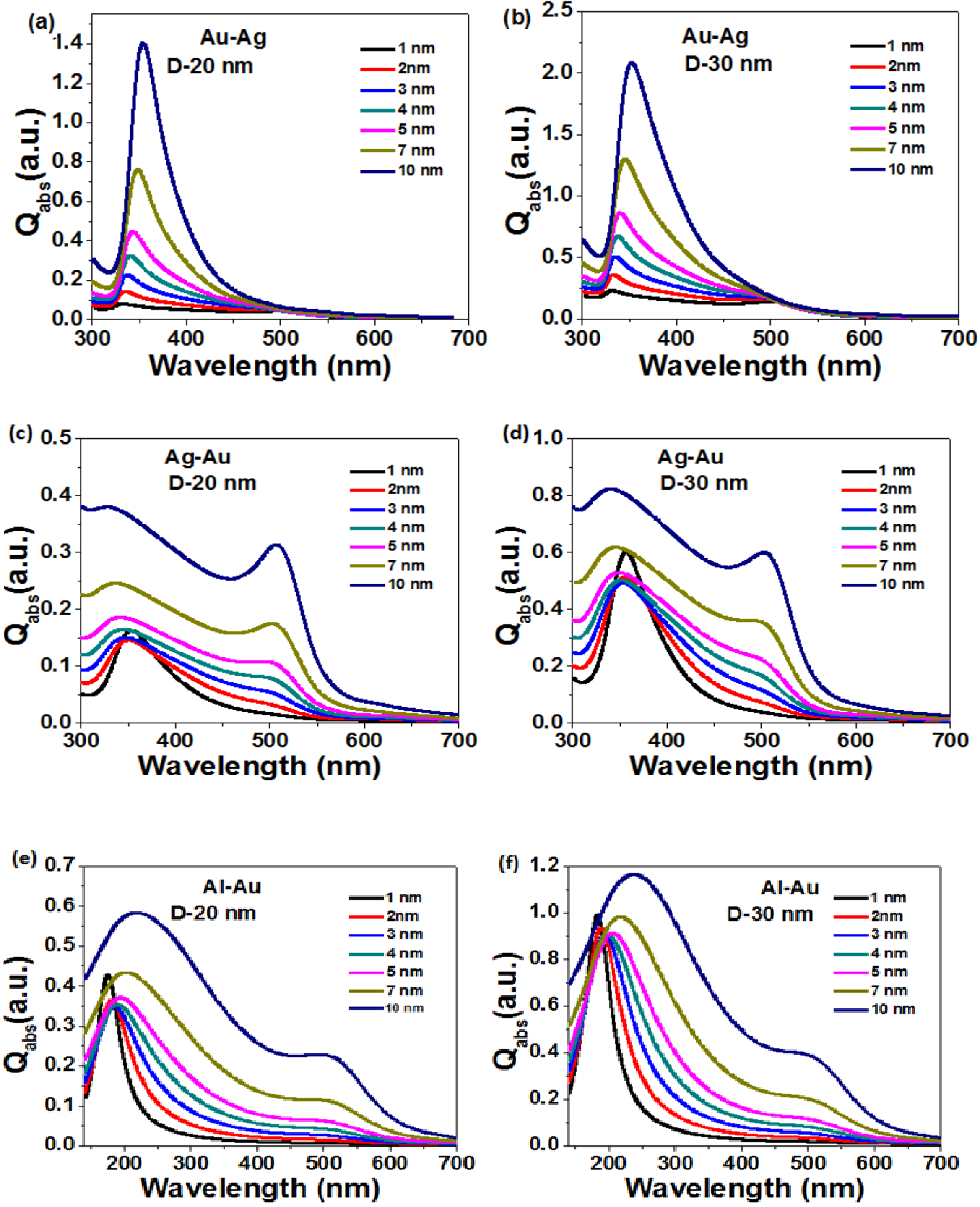

Fig. 1: Shell thickness dependent absorption spectra. The particle size is 20 nm and 30 nm. (a) & (b) Au-Ag, (c) & (d) Ag-Au, (e) & (f) Al-Au

Figure 1 (c) & (d) shows the absorption spectra for Ag nanosphere coated with Au layer i.e. Ag-Au with same size parameter as above mentioned. The SPR absorption band of Ag-Au core-shell is dependent on the thickness of outer Au shell. For thin shell the plasmon peak is present at 355 nm showing the Ag contribution but as the thickness of Au shell increases to 7 nm the absorption spectra shows two peak at 338 nm and 503 nm showing the contribution of core and shell material, respectively. The peak at shorter wavelength is blue shifted whereas peak at longer wavelength is red shifted with increasing thickness of shell. The red and blue shift of absorption spectra can be controlled by thickness of outer layer Au shell. This bimetallic structure has an advantage of giving two peaks of nearly equal intensity in different wavelength region covering the UV-visible range which can be beneficial for sensor application. Apart from Ag-Au core-shell structure if we replace Ag core material with Al material then the same core-shell structure can give benefit of two plasmon peaks in DUV-visible region where most of the biomolecules shows absorption. Figure 1 (e) & (f) shows the absorption spectra of Al-Au core-shell structure. It can be observed that for both the configuration due to larger intensity of Al nanoparticle the plasmon peak towards shorter wavelength dominates over the longer wavelength peak. Only for larger thickness of shell the absorption spectra shows two peak at 237 nm and 500 nm showing the contribution of Al and Au material, respectively.

Apart from two layer nanostructure, the three layered nanoshell as Metal-Dielectric –Metal (MDM) nanostructure is another plasmonic layered structure. Multilayered MDM nanostructure is a new kind of structure which has been synthesized recently and studied theoretically [12-16]. In addition to better SPR tunability, there appears no problem of alloying in such nanostructures as the metallic layers are separated by dielectric ones. Figure 2 shows the schematic picture of multilayered structure. The two metallic layers having radius as R_1 and R_3 are separated by a thin dielectric layer of thickness $t= R_2-R_1$.

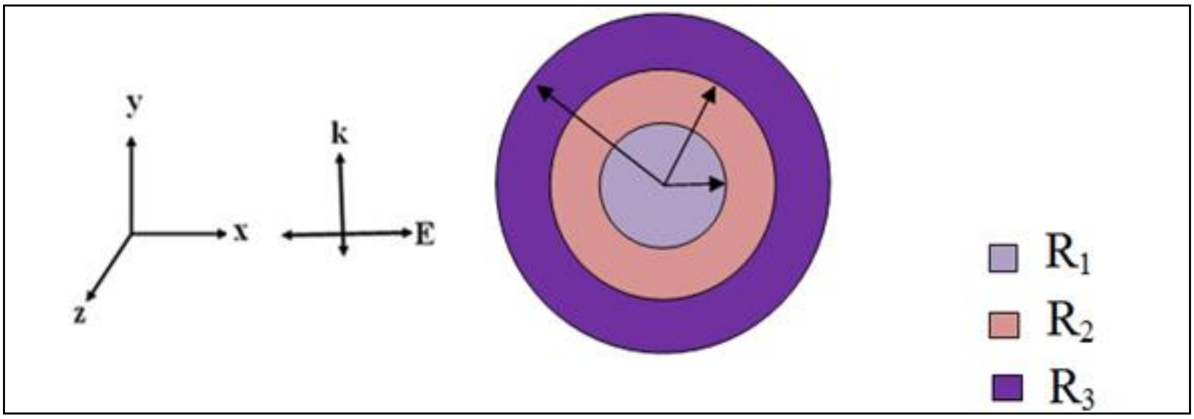

Fig. 2: Schematic of a multilayered metallic nanosphere. The radius of the inner solid sphere is R_1 and outer shell is R_3. The thickness of the dielectric layer is $t= R_2-R_1$. The direction of propagation of EM field incident on the sphere is y-direction and field is polarized along the axis of the sphere (x-axis).

The inner solid sphere and outer shell are composed of different metals with dielectric permittivity ε_{M1} and ε_{M2}, respectively, and ε_l and ε_m are the permittivity of dielectric layers and the surrounding medium. The particle is illuminated with an incident field on xy plane and electric field polarized along x-direction, as indicated in figure 2 by symbol k and E, respectively. Figure 3 shows the absorption spectra for Ag-Air-Au and Al-Air-Au nanostructure. The particle size is kept as 10-15-20 nm and 15-20-25 nm (R_1-R_2-R_3).The calculated shift of plasmon resonance wavelength in MDM structure with thickness of dielectric layer can be explained on the basis of plasmon hybridization theory [12, 13, 17] which says that themodified SPR characteristic of a multi-layered structure isdue to interactions between the plasmon resonance modes ofelementary shape such as sphere and cavity modes of metallicnanostructures. This simple and intuitive model can also be used to understand the plasmon resonance behavior of composite metallic nanostructures of greater geometrical complexity. We now implement the general formalism to the two systems: nanoshell and multilayered nanostructure.

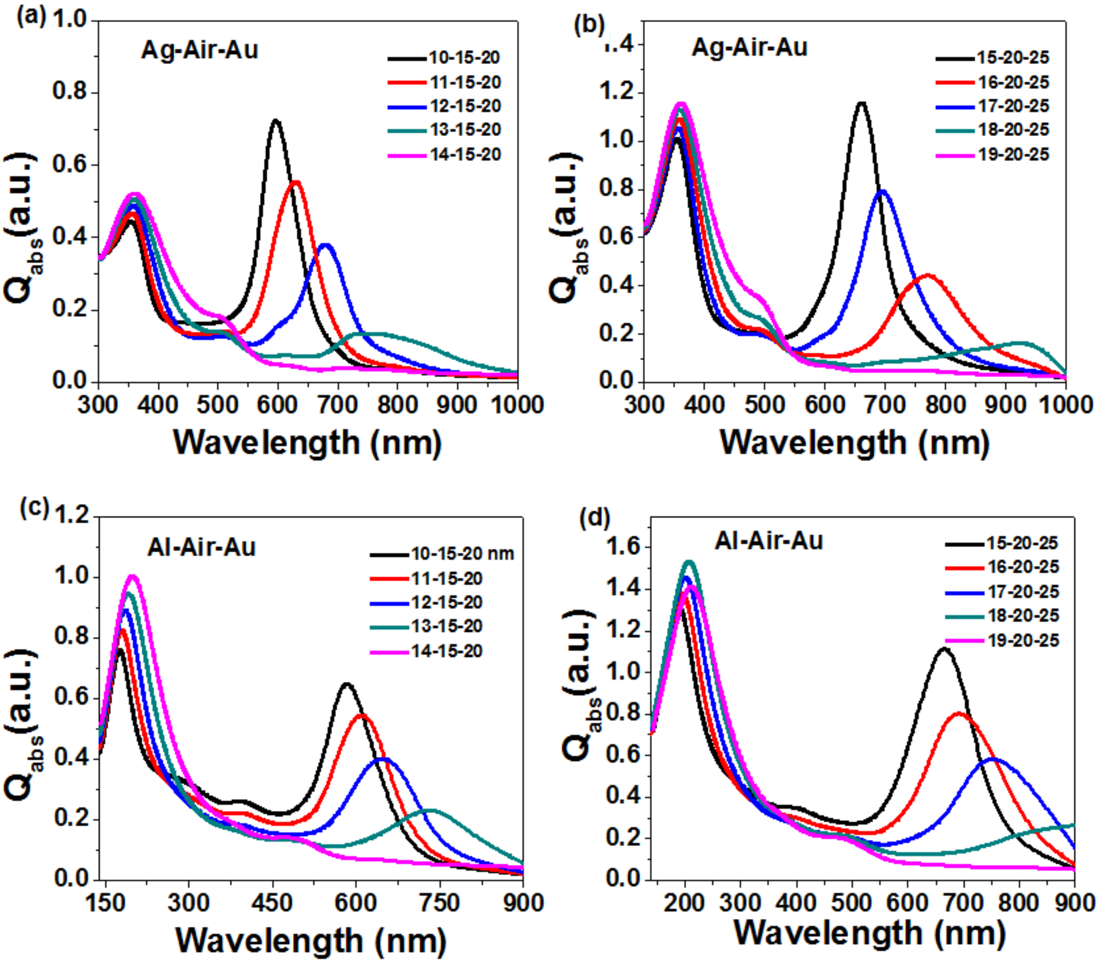

Fig.3: Size dependent absorption spectra of Ag-Air-Au and Al-Air-Au MDM nanostructure. The particle size is 10-15-20 nm and 15-20-25 nm with increasing R_1.

For the nanoshell, the plasmon response can be considered as an interaction between the essentially fixed frequency plasmon response of a nanosphere and that of a nanocavity [12,13]. The sphere and cavity plasmons are electromagnetic excitations that induce surface charges at the inner and outer interfaces of the metal shell. Because of the finite thickness of the shell layer, the sphere and cavity plasmons interact with each other. The strength of interaction between the sphere and cavity plasmons is controlled by the thickness of shell layer. This interaction results in the splitting of the plasmon resonances into two new resonances as the lower energy symmetric or bonding plasmon and the higher energy antisymmetric or antibonding plasmon. The frequencies of these modes are given as [17],

$$\omega_{l\pm}^2 = \frac{\omega_p^2}{2}\left[1 \pm \frac{1}{2l+1}\sqrt{1+4l(l+1)\left(\frac{R_1}{R_2}\right)^{2l+1}}\right] \qquad (1)$$

R_1 and $R_2$are the inner and outer radius of nanoshell. The plasmon resonance in an MDM structure is the interaction between the plasmon response of metallic inner sphere and the outer nanoshell. The energy level diagram for plasmon hybridization in the studied MDM structures is shown in figure 4. Three hybridized modes are obtained for the MDM, the energy mode $\langle\omega_-^-\rangle$ corresponds to the antisymmetric coupling between the symmetric plasmon resonance modes of the outer nanoshell$\langle\omega_-\rangle$ and the sphere plasmon, whereas $\langle\omega_-^+\rangle$corresponds to symmetric coupling between symmetric plasmon resonance mode of outer nanoshell $\langle\omega_-\rangle$ and the sphere plasmon [17]. The coupling between the higher energy antibonding mode of the outer nanoshell$\langle\omega_+\rangle$ and the nanosphere plasmon modes are very weak and only one hybridized mode is produced in this case as$\langle\omega_+^+\rangle$. It can be seen that, with respect to Au only structure bimetallic MDM configuration has more intense $\langle\omega_-^+\rangle$ energy mode with blue shifted $\langle\omega_-^-\rangle$ energy mode. The $\langle\omega_-^-\rangle$ energy mode blue shifted to 352 nm with Ag inner sphere, whereas toward 187 nm with Al inner sphere material irrespective of the particle size. The blue shift in $\langle\omega_-^-\rangle$ energy mode is also observed from Mie theory calculations where with respect to equivalent Au-only structures, the Au-Ag and Ag-Au configurations have more intense $\langle\omega_-^+\rangle$ energy mode with blue shifted $\langle\omega_-^-\rangle$ energy mode [17].

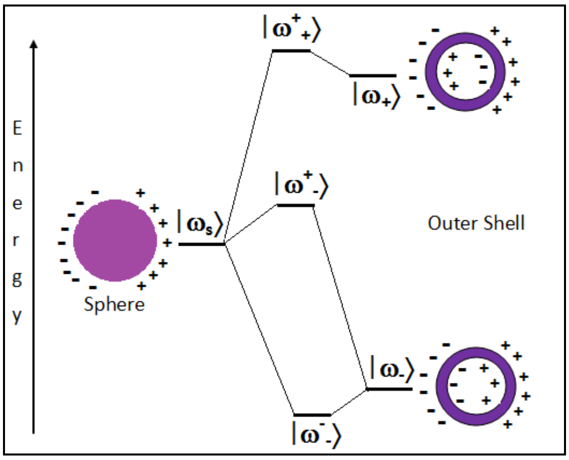

Fig.4: Schematic representation of MDM structure with their corresponding energy level diagram representing plasmon hybridization.

Refractive Index sensitivity

Figure 5 shows the SPR of bimetallic core-shell nanostructure embedded in different dielectric medium (n=1.33,1.36,1.45 and 1.5). The peak wavelength occurring at 507 nm get red shifted to 523 nm on increasing the refractive index of medium for Ag-Au nanostructure. As compared to Au and Ag based core-shell structure, the Al-Au structure shows much sharp peak at longer and shorter wavelength showing the contribution of both Al and Au nanoparticle. The two peaks are at 269 nm and ~507 nm when nanostructure is embedded in water medium. This shows that Al based nanosensor has wider spectral range therefore can be preferred for sensing purpose from UV-NIR region.The regression analysis of plasmon peaks yields the refractive index sensitivity (RIS) of nanostructure in units of nm/RIU. The calculated peak wavelength of the resonance mode with refractive index are fitted with a linear equation $\lambda_p = y \times n + x$. The fitting parameters x and y are given in Table 1.Ag-Au core-shell nanostructure shows lowest RIS value whereas Al-Au shows highest among Au and Ag based nanostructure. The order of RIS factor is Al-Au>Au-Ag>Ag-Au with value of 245.16 nm/RIU>106.98 nm/RIU>90.32 nm/RIU, figure 5. The refractive index sensitivity variation with aspect ratio of core Ag-Au nanorod shows the dependence of RIS factor on thickness of shell [18, 19]. The minimum refractive index sensitivity is shown by Au layer of thickness 4 nm and maximum ~558 nm/RIU is for thickness 1 nm. Since we have chosen thickness of shell as 5 nm therefore the RIS factor is less as compared to Ag-Au nanorod. Figure 5 (b) shows the shift in multiple plasmon peaks of MDM nanostructure embedded in dielectric medium. The effect of the outer Au layer is clearly seen in figure 5(b), the longer wavelength peak shifts to 832 nm in the water and further shifted to 908 nm with an increasing refractive index of the surrounding medium to 1.5. The extinction spectra of Ag-SiO_2-Au calculated using Mie theory shows similar two plasmonic peaks at ~ 1.9 eV and ~ 2.4 eV when embedded in water medium [20]. Apart from this, Al-X-Au shows two plasmon peaks at ~ 239 nm and ~ 781 nm in water. With increasing, surrounding refractive index to 1.5, the peaks red shift to higher wavelength value as ~ 268 nm and ~863 nm. Ag-X-Au nanostructure shows sensitivity of 196 nm/RIU and 470.96 nm/RIU corresponding to the shorter and longer wavelength peak, respectively. Since the plasmonic peak of bare Al and Au nanosphere are far away from each other, therefore, Al-X-Au multilayered nanostructure provides higher index sensitivity. The calculated values show the RIS factor as ~ 168.81 nm/RIU and 510.21 nm/RIU corresponding to the shorter and longer wavelength peak. As the medium refractive index increases the red shift in plasmonic peak due to outer shell material introduce the total red shift in the absorption spectra. Al and Au have larger frequency mode difference compared to Au and Ag nanoparticle due to larger values of bulk plasmon frequency of Al nanoparticle. This causes stronger coupling among Al and Au compared to Ag and Au.

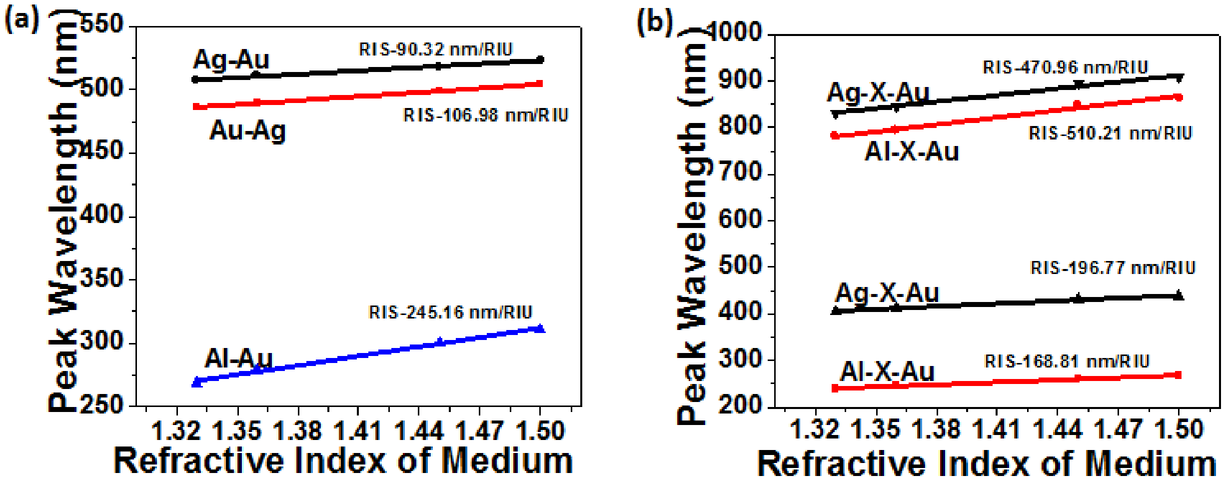

Fig.5: (a) Shift in peak wavelength with refractive index of medium for core-shell nanostructure. The particle size is 30 nm with 5 nm thickness of shell. (b) Variation in peak wavelength with refractive index of medium for bimetallic MDM nanostructure. The particle size is 15-20-25 nm.

Table 1: Fitting parameters x and y of layered metallic nanostructure.

Composition	**x**			**y**	
	Value		**S.E.**	**Value**	**S.E.**
Au-Ag	343.64		2.21	106.99	1.56
Ag-Au	387.39		7.34	90.32	5.20
Al-Au	-55.67		18.02	245.16	12.76
Ag-X-Au	Peak 1	145.04	16.04	196.77	11.36
	Peak 2	205.68	58.12	470.96	41.17
Al-X-Au	Peak 1	15.46	12.49	168.81	8.85
	Peak 2	102.59	68.68	510.21	48.65

IV. CONCLUSION

The plasmon wavelength of a layered nanostructure is studied using FDTD and plasmon hybridization method. The high resolution TEM studies of Al and Ag indicate the presence of the thin oxide layer on their surface which definitely affects the plasmonicbehavior of these materials. Considering this factor, coated metallic nanoparticles are proposed as a bimetallic core shell and MDM multilayered nanostructure. The order of RIS factor for bimetallic core shell nanostructure follows as Al-Au>Au-Ag>Ag-Au with value of 245.16 nm/RIU>106.98 nm/RIU>90.32 nm/RIU which is higher as compared to oxide and bare nanosphere. The sharp dip between two peaks occurring in MDM nanostructure makes them more demanding structure for sensing applications as compared to bimetallic core-shell. The RIS factor is 510 nm/RIU and 470 nm/RIU for Al-Air-Au and Ag-Air-Au nanostructure, which has the highest value among all the different structures with the advantage of plasmonic peak over wider range i.e., UV-NIR, making these structures more demanding in biological sensing, SERS and plasmonic wave guiding.

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