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Optical Properties of Pure and Alloyed Silver-Copper Nanoparticles Embedded and Coupled in Dielectric Matrixes

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Abstract

In this study by using the boundary element method, influence of various parameters on the response to electromagnetic radiation for pure and alloyed silver-copper was investigated. The results demonstrate decreasing interparticle gap from 20 nm to 1 nm for silver coupled nanoparticles leads to shifting the wavelength of optical extinction peak from 362 nm to 393 nm. Decreasing interparticle gap from 20 nm to 1 nm for Cu coupled nanoparticles leads to shifting the wavelength of optical extinction peak from 323 nm to 336 nm. By an increase in the medium refractive index of 1 to 2 the peak of optical extinction for a coupled Cu nanoparticles with 1 nm gap distance the wavelength of plasmon resonance peak shifted from 336 nm to 366 nm and longitudinal plasmon resonance peak shifted from 498 nm to 559 nm. By changing the composition of an alloy of copper and silver nanoparticles with diameter of 10 nm in dielectric matrix with refractive index 1.3 the wavelength of plasmon resonance peak shifted from 378 nm for pure silver nanoparticles to 530 nm for pure copper nanoparticles. In addition for Cu-Ag alloy coupled nanoparticles with 1 nm interparticle gap, the wavelength of resonance peak shifted from 420 nm for pure silver nanoparticles to 544 nm for pure copper nanoparticles. In the case of embedded nanoparticles for coupled silver nanoparticles with 6 nm gap distance, the wavelength of resonance peak shifted from 396 nm to 409 nm, and for coupled silver nanoparticles with 2 nm gap distance, the wavelength of resonance peak shifted from 414 nm to 430 nm. Furthermore for coupled Cu nanoparticles with 2 nm gap distance, the wavelength of resonance peak shifted from 575 nm to 582 nm. The results could be employed for plasmatic sensor design and fabrication.

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Keywords: Coupled nanoparticles; Surface plasmon; Optical extinction; Boundary element method.

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1. Introduction

A plasmon in metal is the quantized collective oscillation of conduction electrons that excited by electromagnetic radiation. Under an external varying electromagnetic field, electrons will be fluctuate collectively, Liang (2014), Gui et al. (2015). Optical properties of a metal nanoparticle such as silver and copper nanoparticles are determined by its surface plasmon resonance and is closely influenced by properties of composition, size, coupling and inter-particle distance and their surrounding media. Silver and copper nanoparticles have many applications such as high sensitivity bio-molecular detection and diagnostics, refractive index sensors, spectroscopy, and photo-thermal, Budhiraja et al. (2013), Liang (2014). Electromagnetic simulation tools based on theory and various methods make possible to well understanding the plasmonics, Ziegler (2008). There is intensive change in these properties when nanoparticles come into close each other, Jain (2008). This behaviour is due to the coupling of the plasmon oscillations of the interacting particles. The plasmon oscillation generates an enhanced electric field localized on the nanoparticle surface, decaying with distance away from the nanoparticles. The near field of particles can interact with each other strongly. Thus the electric field observed by each particle is the sum of electric fields due to the formation of electric dipole present on the neighbouring particle and incident light field. Electromagnetic simulation tools based on theory and various methods provided well understanding of the plasmonic based on the near and far fields calculation, Ziegler (2008).

In this study influence of various parameters such as the inter particle distance, surrounding medium, composition of particles and the nanoparticles embedded on a substrate, on the scattering and extinction spectra of nanostructures on the response to electromagnetic radiation for silver and copper nanostructures including single, coupled, alloyed and embedded on the surface of dielectric matrix nanoparticles was investigated respectively. Variation in these parameters allows adjusting of both the plasmon resonance frequency as well as the intensity of the optical extinction of a system of plasmonic nanostructures.

2. Simulation Method

In this research, nanostructures response to electromagnetic radiation was modelled by using the silver and copper complex dielectric function, Rakic et al. (1998), and employing a specially designed Matlab toolbox, MNPBEM, using the boundary element method. That calculate the optical properties and electric field enhancement of metallic spherical nanoparticles in different conditions and configurations. The boundary element method is a numerical technique used in to solve Maxwell's equations in frequency space. The particle boundaries are discretized as a two dimensional mesh of vertices and faces. On this mesh the integral equations are solved to obtain surface charges and surface currents. Fields are determined by this charges and currents and consequently it is possible to calculate numerically the electrical field properties, Ziegler (2008).

3. Results and Discussion

To understand the effects that are caused by the interaction of different particles, a dimer of two spherical nanoparticles is the building block of more complex configuration of nanoparticles. Because of the coupling of the plasmon oscillations of a dimer, the frequency of the surface plasmon fluctuation changed. With decreasing inter-particle gap, the plasmon resonance shift toward long wavelengths near exponentially, Jain (2008). Fig. 1a shows for coupled silver nanoparticles with diameters of 10 nm, by decreasing gap from 20 nm to 1 nm, lead to shifting the wavelength of extinction cross-section peak from 362 nm gradually to 393 nm, and optical extinction intensity increase from 315 nm^2 to 389 nm^2. As Fig. 1b shows for coupled Ag-Cu nanoparticles, the wavelength of extinction cross-section peak shift from 362 nm gradually to 371 nm, and at the same time, optical extinction cross section increase from 175 nm^2 to 214 nm^2. As Fig. 1c demonstrates for coupled copper nanoparticles, the wavelength of higher energy extinction cross-section peak, shift from 323 nm slowly to 336 nm, and the optical extinction cross section increases from 42 nm^2 to 61 nm^2. In addition shifting the wavelength of lower energy extinction cross-section peak, from lower wavelengths to 498 nm is appeared and the optical extinction cross section increases from 22 nm^2 to 38 nm^2.

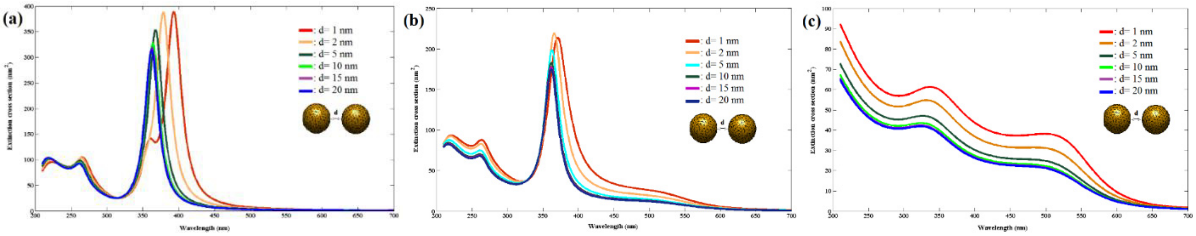

Fig.1. Extinction cross section of 10 nm (a) Ag dimers; (b) Ag-Cu dimers; (c) Cu dimers, affected by changing gap distance between two nanoparticles.

With increasing the dielectric constant of the surrounding medium, the surface charge of the nanoparticle decreases correspondingly. The decrease in the polarization on the particle surface by the polarization of the medium leads to a smaller restoring force, which lead to the red shifts of plasmon resonance wavelength. Depositing stabilizing molecules on the nanoparticle surface influences the plasmon position and width, Haojin (2012). By visible light the dielectric function is affected by the response of the free electrons and by the inter-band transitions which become important at shorter wavelength, Ziegler (2008).

Figure 2a shows increasing the medium refractive index from 1 for air to 2 for typical dilectric medium for coupled silver nanoparticles with diameters of 10 nm with 1nm distance, lead to shifting the wavelength of scattering cross-section peak from 393 nm to 471nm, and thr optical extinction cross section increases from 2.2 nm^2 to 8.9 nm^2. As clearly seen from Fig. 2b for coupled Ag-Cu nanoparticles, the wavelength of higher energy extinction cross-section peak shift, from 371 nm to 425 nm, and extinction cross section increases from 214 nm^2 to 277 nm^2 and the wavelength of lower energy extinction cross-section peak, redshifted to 525 nm. In addition extinction cross section increases from 25 nm^2 to 122 nm^2. For coupled copper nanoparticles as Fig. 2c shows, the wavelength of higher energy extinction cross-section peak, shift from 336 nm redshifted to 366 nm, and extinction cross section increase from 61 nm^2 to 106 nm^2 and the wavelength of lower energy extinction cross-section peak also redshifted to the middle of visible wavelenghts, from 498 to 559nm. In addition fo this configuration of nanoparticles extinction cross section increases from 38 nm^2 to 134 nm^2. The optical properties of noble-noble alloys are studied repeatedly and can be successfully modeled using a linear combination of the dielectric functions of the component metals, Blaber et al. (2010).

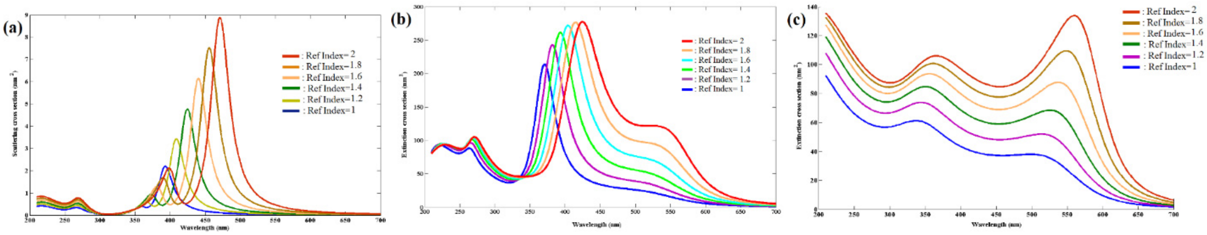

Fig. 2. The plasmon resonance position of a 10 nm (a) Ag dimers; (b) Ag-Cu dimers; (c) Cu dimers with 1nm distance, affected by the medium refraction index.

Figure 3a shows by changing the composition of an alloy of copper and silver nanoparticles with diameter of 10 nm in dielectric matrix with refractive index 1.3 the wavelength of plasmon resonance peak redshifted from UV wavelength at 378 nm for pure silver nanoparticles to the middle of visible wavelengths 530 nm for pure copper nanoparticles. For coupled Cu-Ag alloy nanoparticles with 1 nm inter-particle gap Fig. 3b demonstrates the wavelength of resonance peak shifted linearly from 420 nm for pure silver nanoparticles to 544 nm for pure copper nanoparticles. In addition the calculated results exhibit by increasing copper percentage in Cu-Ag alloy, the wavelength of longitudinal plasmon resonance peak shifted toward shorter wavelengths outer their elements resonance peak interval. This results are in good agreement with the observed results, Bonsak (2010), Murray (2005).

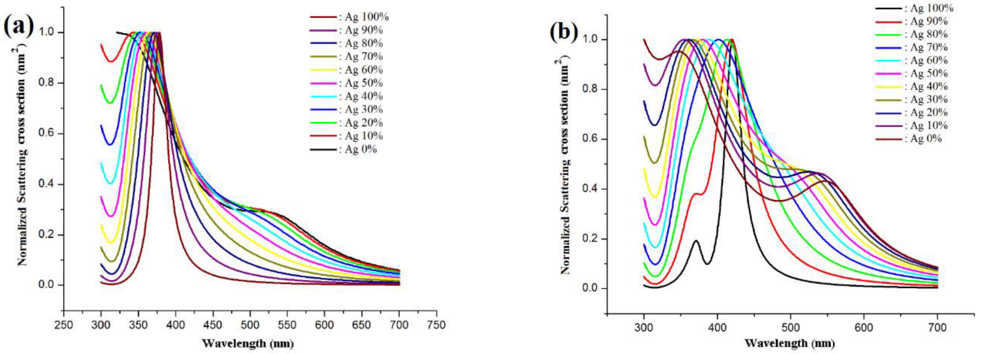

Fig. 3. The normalized scattering cross section of a 10 nm (a) an alloyed copper and silver single nanoparticle; (b) an alloyed copper and silver Coupled nanoparticles with 1nm distance.

Figure 4a shows increasing the medium refractive index of 1.2 to 1.8, for coupled silver nanoparticles with diameters of 10 nm with 6 nm distance on a substrate with refraction index of 2 that could be a typical refractive index of dielectric matrix, lead to redshifting the wavelength of extinction cross-section peak from 396 nm to 409 nm. In addition Fig. 4b shows for coupled Ag nanoparticles with 2 nm distance, the wavelength of extinction cross-section peak, shift from 414 nm to 430 nm. For coupled copper nanoparticles with 2nm distance as can be seen from Fig. 4c, the wavelength of extinction cross-section peak exhibits a redshift from 575 nm to 559 nm. The important results is that all shifts in optical extinction peaks exhibit linear effects which is critical issue for plasmonic sensor design.

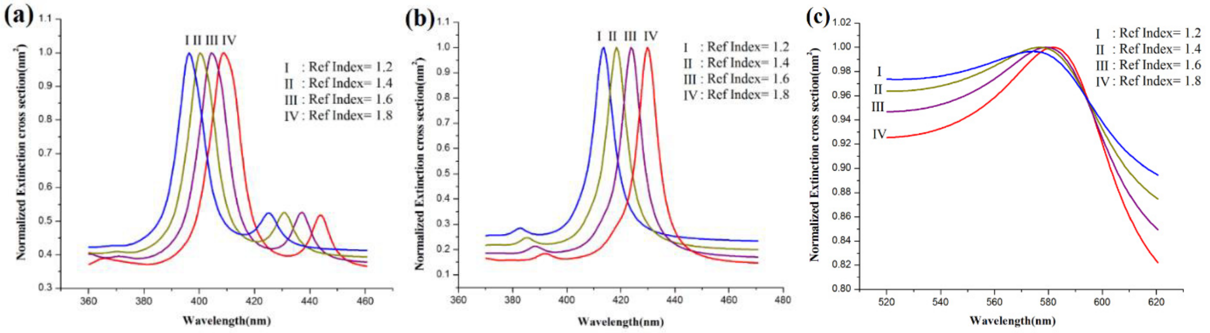

Fig. 4. The normalized extinction cross section for a 10 nm (a) Ag dimer with 6 nm; (b) Ag dimer with 2 nm distance; and (c) Cu dimer with 2 nm distance on a substrate, in mediums with different refractive index.

4. Conclusions

In this research a specially designed Matlab toolbox, MNPBEM, using the boundary element method have been employed for the calculation of optical properties of coupled, alloyed and embedded on the dielectric interface silver-copper nanoparticles in different states. Simulations results show that dependence of the optical response of metal nanoparticles strongly depend on the inherent optical properties of nanoparticles, size and coupling configuration of nanoparticles. In addition by changing the coupling especially inter-particle distance the plasmon resonance peak of a system of coupled nanoparticles could be adjusted in a broad range of wavelength from UV to near infrared wavelengths. In addition the important results is that all shifts in optical extinction peaks exhibit linear effects which is critical issue for plasmonic sensor design.

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