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# Effect of Gold Coating on Sensitivity of Rhombic Silver Nanostructure Array

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**Abstract** The sensitivity is the most important parameter in the sensing field. Effort was made to study the effect of gold coating on the sensitivity of rhombic silver nanostructure array through numerical simulation using the discrete dipole approximation method. This study shows that thickness of the gold coating can be varied to tune the sensitivity of the rhombic silver nanostructure array. The Au–Ag nanostructure array is found to possess the maximum refractive index sensitivity of 714 nm/RIU when thickness of gold is 20 nm, thickness of silver is 25 nm, and refractive index of the medium is around 1.35. The condition for achieving the maximum refractive index sensitivity can be used for detecting many species of biomolecules and drugs in the future.

**Keywords** Sensitivity · Rhombic · Spectroscopy · Discrete dipole approximation

## Introduction

Nanostructures of gold have attracted considerable attention because of their special physical and chemical properties compared to the bulk counterparts. One of the most fascinating aspects is their optical properties. On the nanoscale, many metals, e.g., silver and gold, exhibit strong absorption in the visible region of the spectrum [1, 2]. The origin of this absorption is attributed to collective conduction band electron oscillation in response to the electrical field of the electromagnetic radiation of light. This optical absorption leads to surface plasmon, partly because net charges are displaced transiently on the particle surface during electron oscillation.

The controllable and tunable optical properties of metal nanostructures are highly desirable for many applications that rely on light absorption of metal, including surface plasmon resonance (SPR) [3, 4], surface-enhanced Raman scattering [5, 6], sensing [7–10], and imaging [11]. The high sensitivity to the surrounding medium and ligand environment has been exploited for biosensing [12]. Adsorbate-induced shift in the SPR band occurs as a result of the local dielectric environment changes caused by the adsorbing molecules. The shift itself is not specific to the chemical or biological species being adsorbed; however, the specificity desired for biosensing applications may be achieved by employing surface ligands with the ability to specifically bind the analyte molecules and eliminating nonspecific surface adsorption [13].

The sensitivity is the most important parameter in the sensing field. The shape, material, and the refractive index around the nanostructure array can change the sensitivity of the nanobiosensor. In the previous work by Zhu et al. [14], it is proposed that rhombic hybrid Au–Ag nanostructure array may be used to avoid oxidation of the silver and to improve the refractive index sensitivity. The effect of gold coating on the sensitivity of the rhombic silver nanostructure array is very important in controlling the optical properties in many applications. In this paper, we focus on the effect of gold coating on the sensitivity of the rhombic silver nanostructure array. The discrete dipole approximation (DDA) method was used to calculate the sensitivity when the thickness of the gold coating on the top of the

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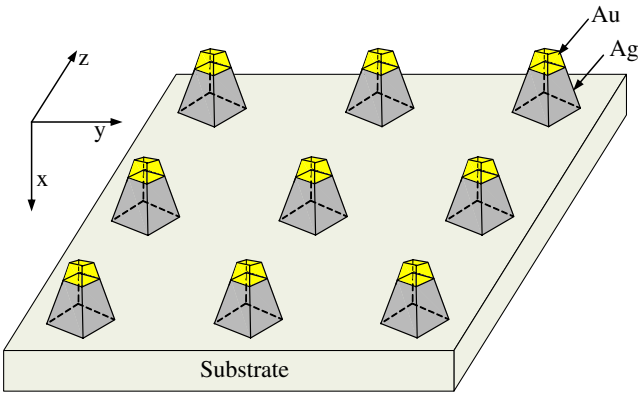


**Fig. 1** The symmetrical two-dimensional infinite gold-coated rhombic silver nanostructure array

rhombic silver nanostructure array changed. The calculated results show that gold coating has significant effect on the sensitivity of the rhombic silver nanostructure array, and the optimal refractive index of the media can be found simultaneously.

## Computational setup

Numerical simulation is performed using the DDA algorithm, which is a powerful numerical method for calculating scattering and absorption for the targets of arbitrary structures. The target is represented as a lattice of polarizable cubic elements ($N$-point dipoles) whose positions and polarizabilities are denoted as $r_i$ and $\alpha_i$. The electrodynamics of this array of dipoles in the presence of an applied plane wave field is then solved exactly. To do this, the polarization induced in each dipole as a result of the incident and retarded fields from the other elements can be expressed as [15, 16]:

$$P_i = \alpha_i E_{\mathrm{loc},i}(r_i) \qquad i = 1, 2, \ldots, N, \tag{1}$$

where the local field $E_{\mathrm{loc}}(r_i)$ is the sum of the incident and retarded fields of the other $N-1$ dipoles. For a given wavelength $\lambda$, the field can be expressed as:

$$E_{\mathrm{loc},i}(r_i) = E_{\mathrm{inc},i} + E_{\mathrm{retard},i} = E_0 \exp(ikr_i) - \sum_{\substack{j=1 \\ j\neq i}}^{N} A_{ij}P_j \qquad i = 1, 2, \ldots, N, \tag{2}$$

where $E_0$ and $k=2\pi/\lambda$ are the amplitude and wave number of the incident wave, respectively. The interaction matrix $A$ is then expressed as:

$$A_{ij}P_j = \frac{\exp(ikr_{ij})}{r_{ij}^3}\left\{k^2 r_{ij} \times (r_{ij} \times P_j) + \frac{1-ikr_{ij}}{r_{ij}^2} \times \left[r_{ij}^2 P_j - 3r_{ij}(r_{ij}P_j)\right]\right\} \qquad (i = 1, 2, \ldots, N, j = 1, 2, \ldots, N, j \neq i) \tag{3}$$

where $r_{ij} = |r_i - r_j|$ is the distance vector from dipole $i$ to dipole $j$. Substituting Eq. 2 and Eq. 3 into Eq. 1 and rearranging Eq. 1, we obtain

$$(\alpha^{-1})P_i + \sum_{\substack{j=1 \\ j\neq i}}^{N} A_{ij}P_j = E_{inc,i} \quad i = 1, 2, \ldots, N, \tag{4}$$

The polarization vectors and electric fields are then obtained by solving $3N$ linear equations of the form

$$A'P = E \tag{5}$$

where the off diagonal elements of the matrix, $A_{ij}'$, is the same as $A_{ij}$, and the diagonal element of the matrix, $A_{ii}'$, is $\alpha^{-1}$. After obtaining the polarization vector **P**, we can calculate cross section of the extinction as

$$C_{\mathrm{ext}} = \frac{4\pi k}{|E_0|^2} \sum_{i=1}^{N} \mathrm{Im}(E_{\mathrm{loc},i}P_i) \tag{6}$$

The computer time used in the DDA method is proportional to the number of the dipoles. Depending on the error tolerance in the calculation, the typical cube size required for convergence (for a noble metal particle) is in the range of 0.5–2 nm, and the method is limited to the calculation of a particle or a cluster of particles whose total size is a few hundred nanometers in each dimension. For a periodic array of particles, the local electric field and polarization is a periodic function in two dimensions. So we need to solve the linear equations for a single unit cell only. But for the sum term in Eq. 2, it is extended to include periodic replicas of as many cells as the numbers, which is needed to converge the expansion.

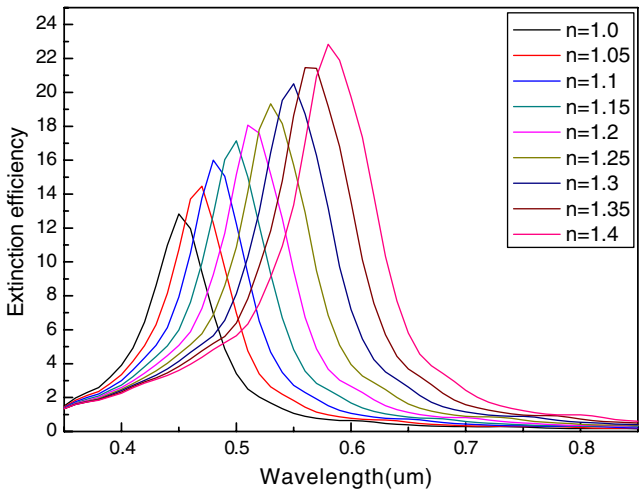


**Fig. 2** Extinction spectra for different effective refractive indexes mediums; the thickness is 25 nm for silver and 0 nm for gold (i.e., no Au coating)

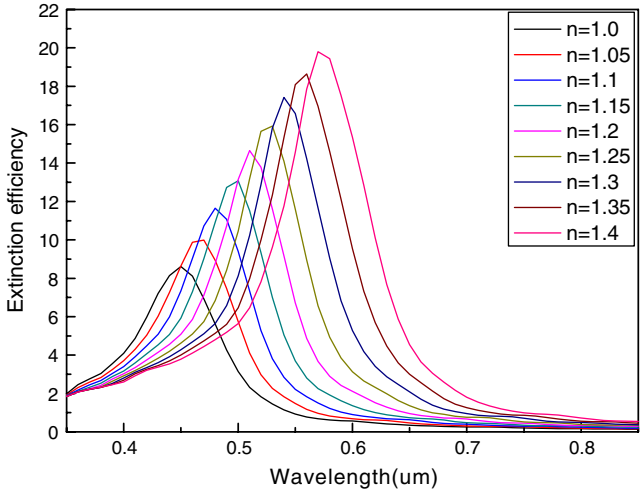


**Fig 3** Extinction spectra for different effective refractive indexes mediums; the thickness is 25 nm for silver and 5 nm for gold

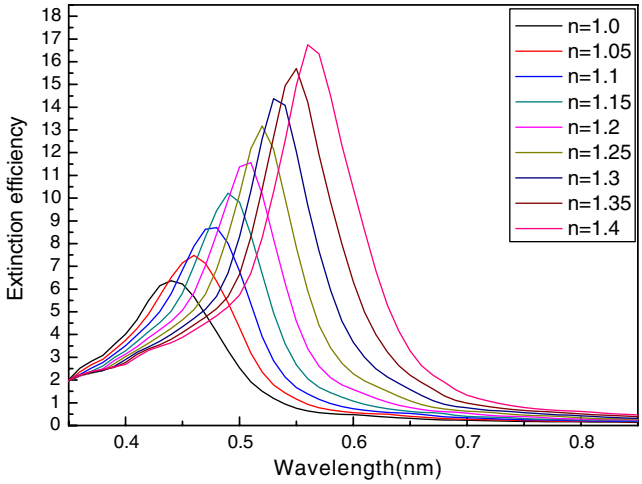


**Fig. 5** Extinction spectra for different effective refractive indexes mediums; the thickness is 25 nm for silver and 15 nm for gold

The extended DDA program of calculating extinction spectra for the two-dimensional infinite arrays is proposed according to the structure character of the rhombic structure while the original DDA program can only calculate extinction spectra of the single particle. The original DDA program DDSCAT 6.1 is from Draine and Flatau; the dielectric constants for gold and silver are taken from Reference [17]. All of our results are calculated by taking the effective index of medium as the external dielectric material and the interdipole spacing is set to be 2 nm in our calculation.

The gold-coated rhombic silver nanostructures are arranged in the symmetrical two-dimensional infinite arrays which lie in the *y*–*z*-plane, and the incident light, which is polarized along the *y*-axis, propagates in the *x*-direction. The incident wavelength is varied from 350 to 850 nm. The infinite rectangular arrays are formed by identical gold-coated rhombic silver nanostructures with in-plane width of about 100 nm. The angle between the arrays and underside is $60^{0,}$ and the period of the gold-coated rhombic silver nanostructure array is 400 nm (Fig. 1).

## Results and discussions

In order to verify the effect of the gold coating on the sensitivity of the rhombic silver nanostructure array, we calculated the extinction spectra of the effective refractive index of the mediums surrounding the Au–Ag nanostructure array. The refractive index sensitivity is defined as $m=\Delta\lambda_{max}/\Delta n$, where $\Delta\lambda_{max}$ and $\Delta n$ denote the peak of

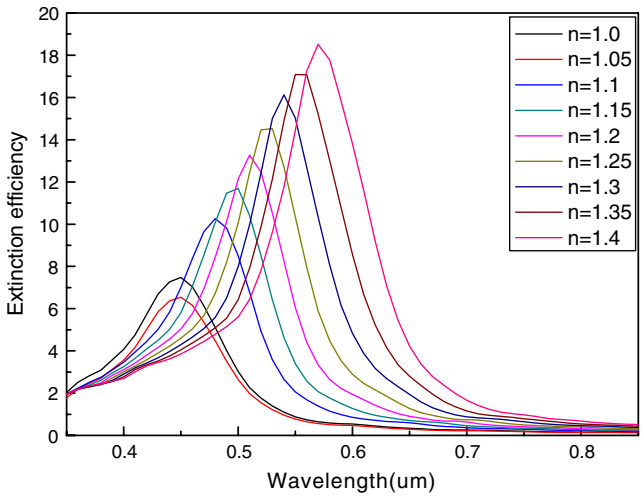


**Fig. 4** Extinction spectra for different effective refractive indexes mediums; the thickness is 25 nm for silver and 10 nm for gold

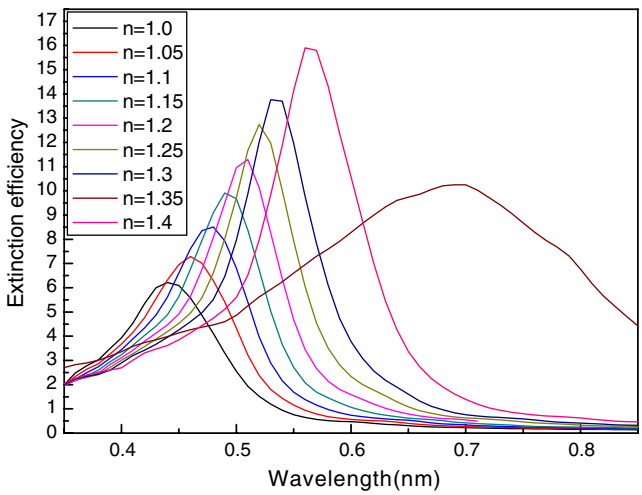


**Fig. 6** Extinction spectra for different effective refractive indexes mediums; the thickness is 25 nm for silver and 20 nm for gold

the wavelength change and the refractive index change, respectively.

The thicknesses of the gold coating were varied from 0 to 20 nm, and the out-of-plane height of silver was fixed at 25 nm for calculating the sensitivity. Figures 2, 3, 4, 5, and 6 show the extinction spectra of different effective refractive indexes mediums surrounding the Au–Ag rhombic nanostructure array. The refractive indexes of the mediums are 1.0, 1.05, 1.1, 1.15, 1.2, 1.25, 1.3, 1.35, and 1.4, respectively. The calculated result shows that the maximum refractive index sensitivities of the Au–Ag rhombic nanostructure array with fixed Ag thickness and different Au thickness are $m=\Delta\lambda_{max}/\Delta n=0.02$ μm/0.05=0.4 μm/RIU= 400 nm/RIU (Figs. 2, 3, and 5), 600 nm/RIU (Fig. 4), and 714 nm/RIU (Fig. 6).

The calculated result shows that the maximum refractive index sensitivity of the Au–Ag rhombic nanostructure array is 400 nm/RIU when the thickness of gold coating is 0, 5, and 15 nm, respectively. The gold coating has no effect on the maximum sensitivity of the silver rhombic nanostructure array. From the calculated results, we can see that the thickness of the gold coating caused the change of the intensity of the extinction efficiency. The intensity of the extinction efficiency decreases when the thickness of the gold coating increases. From Fig. 4, we apparently find that the maximum refractive index sensitivity is 600 nm/RIU when the refractive indexes of the mediums changed from 1.05 to 1.1. This result shows that when the thickness of gold coating is 10 nm, the structure has very high refractive index sensitivity from 1.05 to 1.1.

From Fig. 6, we find that the maximum refractive index sensitivity is 714 nm/RIU when the refractive indexes of the mediums changed from 1.35 to 1.0. This result shows that when the thickness of gold coating is 20 nm, the structure is very sensitivity for the refractive index from 1.35 to 1.0, and the refractive index sensitivity of the gold coating rhombic silver nanostructure array is higher than the traditional triangular silver nanostructure array.

## Conclusion

Gold coating has significant effect on the sensitivity of the rhombic silver nanostructure array. The Au–Ag nanostructure array is found to possess the maximum refractive index sensitivity of 714 nm/RIU when thickness of gold is 20 nm, thickness of silver is 25 nm, and refractive index of the medium is around 1.35. The condition for achieving the maximum refractive index sensitivity can be used for detecting many species of biomolecules and drugs in the future.

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## References

1. Zhang JZ, Wang ZL, Liu J, Chen S, Liu GY (2003) Self-assembled nanostructures. Kluwer Academic/Plenum, New York
2. Heilmann A, Kreibig U (2000) Optical properties of embedded metal nanoparticles at low temperatures. Eur Phys J Appl Phys 10:193–202. doi:10.1051/epjap:2000132
3. Homola J, Yee SS, Myszka D (2008) Surface plasmon biosensors. In: Ligler FS, Taitt CR (eds) Optical biosensors: today and tomorrow, 2nd edn. Elsevier, The Netherlands, pp 185–242
4. Richard BMS, Anna JT (eds) (2008) Handbook of surface plasmon resonance. RSC Publishing, Cambridge. ISBN 978-0-85404-267-8
5. Shanmukh S, Jones L, Driskell J, Zhao YP, Dluhy R, Tripp RA (2006) Rapid and sensitive detection of respiratory virus molecular signatures using a silver nanorod array SERS substrate. Nano Lett 6:2630–2636. doi:10.1021/nl061666f
6. Driskell JD, Shanmukh S, Liu Y, Chaney SB, Tang XJ, Zhao YP et al (2008) The use of aligned silver nanorod arrays prepared by oblique angle deposition as surface enhanced raman scattering substrates. J Phys Chem C 112:895–901. doi:10.1021/jp075288u
7. Aslan K, Geddes CD (2008) A review of an ultrafast and sensitive bioassay platform technology: microwave-accelerated metal-enhanced fluorescence. Plasmonics 3:89–101. doi:10.1007/s11468-008-9059-x
8. Geddes CD, Aslan K (2007) Plasmonic DNA technology. Plasmonics 2:163. doi:10.1007/s11468-007-9046-7
9. Zhu SL, Li F, Du CL, Fu YQ (2008) A novel bio-nanochip based on localized surface plasmon resonance spectroscopy of rhombic nanoparticles. Nanomedicine 3(5):669–677
10. Zhu SL, Du CL, Fu YQ (2009) Biochemistry nanosensor-based hybrid metallic nanostructure array. Sens Actuators B Chem 137:345–349. doi:10.1016/j.snb.2008.11.019
11. Fu YQ, Zhou W (2009) Modulation of main lobe for superfocusing using subwavelength metallic heterostructures. Plasmonics 4:141–146. doi:10.1007/s11468-009-9085-3
12. Haes AJ, Van Duyne RP (2002) A nanoscale optical biosensor: sensitivity and selectivity of an approach based on the localized surface plasmon resonance spectroscopy of triangular silver nanoparticles. J Am Chem Soc 124:10596–10604. doi:10.1021/ja020393x
13. Haes AJ, Van Duyne RP (2003) Nanosensors enable portable detectors for environmental and medical applications. Laser Focus World 39:153–156
14. Zhu SL, Du CL, Fu YQ, Liu AQ (2009) Tuning optical properties of rhombic hybrid Au-Ag nanoparticles: a discrete dipole approximation calculation. J Comput Theor Nanosci 6:1034–1038. doi:10.1166/jctn.2009.1140
15. Jin RC, Cao YW, Mirkin CA, Kelly KL, Schatz GC, Zheng JG (2001) Photoinduced conversion of silver nanospheres to nanoprisms. Science 294:1901–1903. doi:10.1126/science.1066541
16. Schatz GC (2001) Electrodynamics of nonspherical noble metal nanoparticles and nanoparticle aggregates. J Mol Structure Theochem 573:73–80
17. Draine BT, Flatau PJ (2004) User guide for the discrete dipole approximation Code DDSCAT.6.1. Available at http://arxiv.org/abs/astro-ph/0409262.