Optical sensing based on plasmon coupling in nanoparticle arrays

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Abstract: The performance of bi-periodic arrays of gold nano-particles for molecular sensing applications is studied using the Fourier Modal Method (FMM). We show that the electromagnetic coupling between the particles can be optimized to increase their sensitivity to a weak change of the shallow dielectric environment. Especially, arrays whose elementary cell consists of a dimer of two closely packed particles are found to be at least three times more sensitive than single particle arrays.

OCIS codes: (240.5420) Polaritons,(260.3910) Metals optics of, (130.2290) Sensing

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In the context of optical sensing, the interest of plasmonic structures relies on their high sensitivity to very small variations of the dielectric function at the metal surface. A light absorption change can be detected when e.g. a molecular recognition occurs between a bio-receptor molecule attached to the metal sensor and one biomolecular counterpart. As the active area of plasmonic sensors is defined by the localization of the surface plasmon field, their sensitivity can be enlarged by increasing the plasmon mode confinement. Resonant noble metal nanoparticles with dimensions of a few tens of nanometers and sustaining Localized Surface Plasmon (LSP) modes have been proposed as good candidates for increasing both integration and sensitivity compared to conventional extended thin metal films [1]. Recently, several groups have overcome the challenge of sensing with a single metallic particle [2, 3, 4], reaching a zeptomole sensitivity.

While an isolated metal nanoparticle constitutes the smallest plasmonic system, interactions within an ensemble of nanostructures can give rise to a much higher field confinement. From SERS (Surface Enhanced Raman Scattering) spectroscopy, it is now well known that "hot spots" appearing at the surface of a film of random metallic clusters are mainly responsible for the dramatic enhancement of the Raman signal from the analyzed agent [5]. Recent advances in fabrication techniques using electron-beam lithography have allowed for finer control of the fabricated structures and thus are opening up new possibilities in the field of plasmon optics [6, 7]. Especially, several works have been dedicated to investigate LSP field interactions within bi-periodic arrays of resonant nanoparticles [8, 9, 10]. Depending on the inter-particle distance d, two coupling regimes can be distinguished: For very short d, coupling between adjacent particles involves the sharply evanescent fields bounded to the metal surface (near-field coupling); on the other hand, when the particle spacing becomes larger than the incident wavelength, far-field (dipolar) interactions with a $1/d$ dependence dominate. On this basis, surfaces patterned with 2D metallic gratings have been proposed as efficient SERS substrates [11, 12]. In this paper, the Fourier Modal Method (FMM) is used to investigate the performance of bi-periodic gold particle arrays for sensing purposes. Our main result is the combination of near-field and far-field dipolar coupling as a possible way to optimize the sensitivity of metal particle-based sensors.

To investigate the potential for sensing of metal nanoparticle matrices, both their far-field and near-field response are of interest. On one hand, by mapping the electric near-field intensity at the vicinity of the particles, we assess the spatial distribution of the plasmon modes and thus evaluate the sensor's active area. On the other hand, extinction spectroscopy provides the

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collective resonances of the system and its sensitivity to a slight modification of the surrounding dielectric environment. Both near- and far-field responses are calculated using the Fourier Modal Method (FMM) also known as Coupled Wave Method. This method has shown to be well suitable for dealing with light wave-plasmon interactions [13]. We suggest to the reader interested in the details of the method and its improvements to read references [14, 15, 16, 17].

The first structure we study, sketched in Fig. 1, consists of a periodic array of gold particles lying onto a glass substrate. The particles have a cylindrical shape with 100 nm diameter base and 20 nm height and are arranged into a square lattice with period D. The optical index of the substrate is assumed to be constant ($n = 1.449$) over the visible spectral range, while the wavelength-dependent optical index of gold follows experimental values from reference [18].

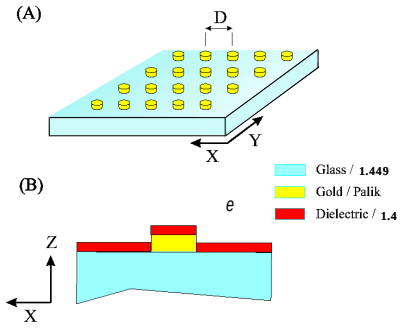

Fig. 1. (A) Schematic description of the studied structure formed by a bi-periodic arrangement of gold nanoparticles lying onto a glass substrate. The particles have a cylindrical shape with 100 nm diameter base and 20 nm height. (B) Cross-section through one period of the arrangement when covered with a thin layer (thickness e) of optical index 1.4.

Figure 2 (A) shows the calculated extinction $-\log(T(\omega))$ of the particle array (T being the energy transmission factor) as a function of the incident wavelength and for different period values. The illumination is performed under normal incidence by a plane wave linearly polarized along the X axis. Also, in order to allow for a quantitative comparison between the different curves, they were normalized according to the filling factor f of each particular structure. In the considered spectral range, each spectrum displays a single extinction peak associated to the lowest-order (dipolar) LSP mode sustained by the individual particles. By changing the separation distance, the coupling strength evolves through the coherent summation of the dipolar fields. Despite the rather large inter-particle distance, a strong dependence of the central wavelength and bandwidth is observed. Such a dependence, reported experimentally by Lamprecht *et al* [9], can be interpreted as a consequence of the modification of the electromagnetic density of states around each particle induced by the neighbors. For the sensing purposes we are interested in here, $D = 300$ nm appears to be an optimum value as it corresponds both to the highest extinction and the sharpest resonance bandwidth.

For this period, the distribution of the near-field intensity, computed 5 nm above one of the particles from the array, at resonance ($\lambda = 580$ nm), is given in Fig. 2 (B). At this height, the local field is not homogeneous over the whole particle surface but exhibits dipolar lobs along the incident field direction. This distribution is very similar to what is observed for isolated uncoupled particles.

In order to evaluate the sensing ability of the system, the calculation of the extinction spectrum is repeated when the system is covered by a thin dielectric layer of thickness e (see Fig. 1 (B)). A refractive index of 1.4 was chosen as an average value for modeling a layer

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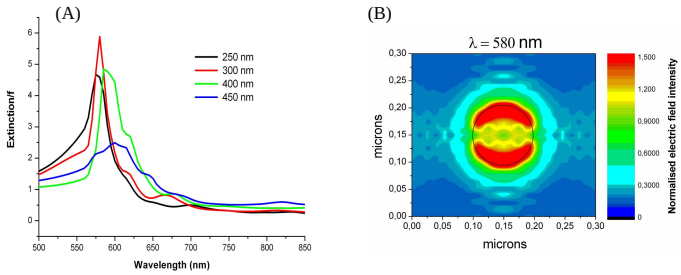

Fig. 2. (A) Extinction spectra of an infinite gold particle matrix for different values of the period D. Each curve has been normalized by the corresponding structure filling factor f (B) Map of the electric near-field intensity calculated 5 nm above one of the particles for the case where $D = 300$ nm. Note that all the field maps are normalized with respect to the incident field amplitude

of biological molecules. Due to the specifications of the numerical code, this layer is defined in such a way that it covers all surfaces parallel to the XY plane, including the glass surface between the particles. These areas do not actually contribute to modify the extinction spectra of the whole structure as only the gold/dielectric interfaces play a role. However, as a result of the approach followed, the vertical sidewalls of the particles are partially covered. Despite these limitations, the results obtained give a good qualitative approximation of the shallow refractive index change induced by the presence of an organic material. While a first 5 nm-thick dielectric layer models the presence of a bio-receptor at the metal surface, we simulate the frequency shift resulting from the chemical binding with a molecular counterpart by the presence of an additional 5 nm thin layer of the same refractive index. The curves obtained for the case where only one layer is present (only the functionalization layer 5 nm) are compared to the case where two layers are present (functionalization plus binding layer, $e = 10$ nm). The results (cf. Fig. 3) show that as the layer thickness increases, a weak red-shift $\Delta\lambda = 4$ nm of the central resonance occurs.

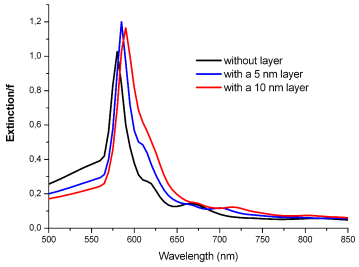

Fig. 3. Evolution of the extinction spectrum of a gold particle matrix as a function of the thickness e of a thin dielectric covering layer ($n = 1.4$)

In the previous configuration, where the particles are mainly coupled by far-field dipolar interaction, the sensitivity of the array is defined by the distribution of the plasmon fields around each gold dot, as shown in Fig. 2 (B). Because near-field coupling involves the sharp evanescent plasmons fields bounded at the metal surface, one can expect to obtain tiny light spots much more confined than the particle volumes in the case of closely arranged particles. In particular,

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the configuration where two resonators are closely packed to form a dimer is of particular interest [19, 20].

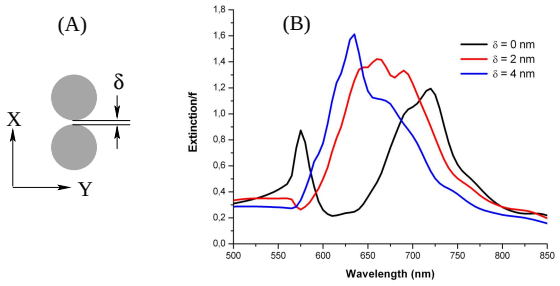

Fig. 4. Evolution of the extinction spectrum of a dimer matrix with the gap distance δ. The incident field is polarized along X

In the discussion that follows we consider a new configuration where the elementary cell of the grating is formed by a dimer of two identical particles aligned along the X axis (Fig. 4 (A)) and where the pitch D is fixed to 300 nm. For this kind of configuration we first study the behavior of the system when the inter-particle distance δ is changed (Fig. 4 (B)). We observe a very strong dependence on δ when the incident field is polarized along the dimer axis. A change of only 4 nm (from $\delta = 4$ nm to $\delta = 0$ nm) is sufficient to completely modify the spectral response, resulting in both a red-shift of the central resonance frequency and a broadening of the plasmon bandwidth as observed experimentally in reference [21]. This can be interpreted in terms of the interaction between the surface charges formed at the particle surface [19]. In the extreme case of touching particles ($\delta = 0$), the spectrum displays an additional resonance at lower wavelengths attributed to a quadrupolar-type mode. Indeed, when getting in contact, the two particles behave as an equivalent bigger particle sustaining higher order resonances [22, 23]. Note that the spectral response of the system under the orthogonal incident polarization state (along the Y axis, not shown) stays basically unaffected by the same variation in inter-particle distance δ.

As expected, the electric near-field intensity maps around the dimers show completely different field distributions compared to the case of a single particle array (Fig. 5 (A)). In the case where $\delta = 4$ nm the field is mainly confined inside the air gap within a round spot with 30 nm average diameter (FWHM). For touching particles ($\delta = 0$ nm), similar *hot spots* appear with a distribution depending on the considered resonance peak.

From a practical point of view, current fabrication techniques do not allow for a precise control of inter-particle distance with nanometer precision. Nevertheless, the fabrication of touching or slightly fused particles is feasible with a good control on lithography dose and lift-off [21]. Taking that into account, we have opted to focus our study on the sensitivity of arrays of *touching* dimers to local variations of the dielectric function. Note that the array pitch has been kept fixed at $D = 300$ nm, as it was found to offer the best compromise between a high extinction and a high field confinement.

Compared to the single-particle matrix, the dimer-matrix shows a significantly different response and a much increased sensitivity to variations on the dielectric layer thickness. If one just considers the central peak shown in Fig. 5 (B), which in the absence of a layer is centered around 720 nm, a strong blue shift of approximately 50 nm is observed when the first 5 nm layer is added. An additional peak shift of 8 nm occurs when the layer thickness is increased to a total of 10 nm. The decreasing magnitude of the shift arises from the very sharp transversal confine-

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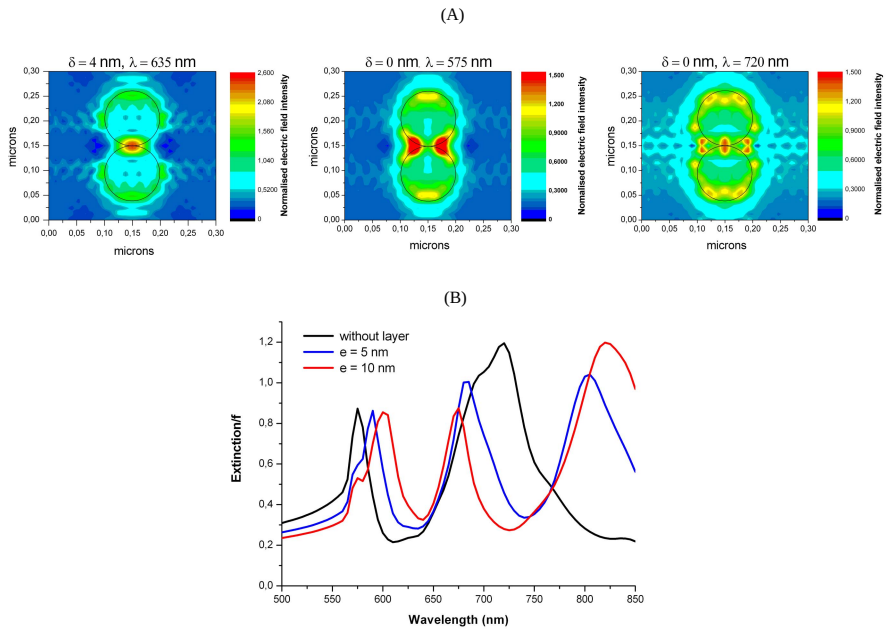

Fig. 5. (A) Map of the electric near-field intensity calculated 5 nm above one of the dimers. Left: $\delta = 4$ nm, $D = 300$ nm and $\lambda = 635$ nm. Middle: idem for $\delta = 0$ nm at $\lambda = 575$ nm. Right: idem for $\delta = 0$ nm at $\lambda = 720$ nm. (B) Extinction spectra of a dimer matrix ($D = 300$ nm, $\delta = 0$ nm) as a function of the thickness e of the dielectric layer on top of the dimers.

ment (along the Z axis) of the LSP fields. In the case of the peak centered around 580 nm, the transversal field confinement is weaker, and the behavior is quite linear over the range of film thicknesses considered. The sensitivity to the increase of e results three times larger than in the case of an array of isolated particles ($\Delta\lambda = 12$ nm). In order to achieve the maximum sensitivity one should consider, whenever possible, the full extinction spectra. In that case, and especially taking into account that small variations in local refractive index result in shifts in the individual peak locations *and* in the distance between peaks, a high enhancement in sensitivity is achieved.

In conclusion, we have presented a numerical study of the performance of periodic metallic arrays for sensing purposes. Our results show that their extinction spectra are highly sensitive to small variations in the thickness of a covering dielectric layer. Despite their broad resonance bandwith, arrays with unit elements formed by two touching particles display a much higher sensitivity than single-particle arrays. This gain in sensitivity is attributed to confined light spots *(hot spots)* created near the contact point of the two particles by near-field coupling. We believe that such an array of metallic dimers may open up the way toward the detection and study of molecular binding at very low concentrations.

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