Surface plasmon coupling enhanced dielectric environment sensitivity in a quasi-three-dimensional metallic nanohole array

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Abstract: An enhanced dielectric environment response is observed in a kind of metallic nanohole arrays which are prepared by metal deposition on a sacrificial two dimensional colloidal crystal template. The periodic metallic structures are composed of interlinked metallic half-shells supported on a planar dielectric substrate. When putting in dielectric matrix of different refractive index, the measured sensitivity of the quasi-three-dimensional metallic nanohole array can reach a value of 1192 nm per refractive index unit which shows a five-fold increase as compared with the metallic structures supported on the template. The observed boost in sensitivity is found to originate from a substantially reduced substrate effect, resulting in a pronounced surface plasmon coupling of which its strength is independent of the dielectric environment, a characteristics absent in conventional planar metallic subwavelength hole arrays. These findings are analyzed theoretically and confirmed by numerical simulations.

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OCIS codes: (240.6680) Surface plasmons; (130.6010) Sensors.

References and links


1. Introduction

Surface plasmons (SPs), are coherent electron oscillations that propagate along the interface between any two materials where the real part of the dielectric function changes sign across the interface such as a metal-dielectric interface. The interaction of light with SPs on periodically microstructured metal films can be controlled to yield surprising optical properties [1]. Light transmission through subwavelength holes and slits array in metallic films [1,2] is of particular importance due to its applications in nanoscale SP based sensors, wavelength selective optical filters, and substrates for nonlinear optical process enhancement [3–6]. The optical response of subwavelength hole array in metallic films depends on the SP mode properties, their interactions, as well as their coupling to the incident electromagnetic field. Recent studies have revealed that light transmission resonance of subwavelength hole arrays, a phenomenon generally attributed to delocalized SP modes [7], can be further manipulated by controlling the interference between localized and propagating SP modes [8,9], leading to either an enhancement or suppression of its transmission amplitude [10,11]. On the other hand, SP resonance frequency is sensitive to environmental refractive index (RI) changes, which forms the basis of using the wavelength selective transmission resonances for SP sensing [12–16]. Compared with commercial SP sensing systems which usually operate with a prism coupling in the Kretschmann configuration [17], the advantages of the subwavelength hole array sensors include a simple measurement geometry and great promise for a significant increase in detection array density. Initial demonstrations of a metal nanohole array sensor by Brolo et al. [12] have shown a sensitivity of 400 nm/RIU, which is an order of magnitude lower than achieved using the devices based on the Kretschmann configuration.

To improve the sensitivity of metallic nanohole array to dielectric environmental change, the interactions between delocalized and localized SP modes on subwavelength hole arrays have been explored recently. Lesuffleur et al. have reported a sensitivity of ~600 nm/RIU using a combination of the enhanced transmission effect and localized resonances in a periodic array of subwavelength double-hole structures in a gold film [18]. Stewart and his associates have developed a novel class of quasi-three-dimensional (quasi-3D) plasmonic crystals (PCs) that consist of double-layered, regular arrays of metal nanohole and nanodisk [19]. Such a metallic structure was shown to allow an overlapping of Wood’s anomaly and delocalized SPs as well as a strong coupling between nanoholes and nanodisks. Therefore, the detection sensitivity in the quasi-3D plasmonic crystals can be enhanced to ~800 nm/RIU [19]. Recently introduced mushroomlike composite metallodielectric nanostructures are shown to support an enhancement in the normal electric field compared to the conventional nanohole structure and thus could lead to an improvement of the sensitivity performance [20]. However, to explore these interactions, the resonance location and line shape of the localized SPs within these subwavelength holes need to be controlled in a way which has not been demonstrated as efficient as for the delocalized SP at metal/dielectric interfaces [21]. Another design difficulty in these plasmonic structures is that even if such a strong coupling between localized and delocalized SPs is enabled, it remains an open question as how to further engineer the metallic structures in order to keep minimized the fraction of the enhanced field within the dielectric. The later is of key importance for surface-supported metallic nanostructures when used as SP sensors, which has been studied by Dmitriev et al. for surface-supported individual metallic nanoparticle optical sensors [22].

Normally, the optical response of metallic holes array to bulk dielectric change is dominated by a selective excitation of SP modes at a liquid/metal interface [21], because these modes on the opposite surfaces of the metal film are decoupled due to the inherent asymmetry of a PC supported on a substrate. The SPs on the opposite interfaces could become coupled when the RI of the immediate medium approaches that of the substrate [7]. Nevertheless, Dood et al. have demonstrated experimentally that the hybrid mode in the strong coupling
regime shows a decreased sensitivity as compared with the nonresonant cases [23]. Thus an index matching treatment [24] may have prevented Larson and his associates from observing any substantial improvement in nanohole array dielectric response due to the inherent substrate effect of the plasmonic structures they adopted. For a potentially useful subwavelength hole array, the transmission resonance location is required to show an enhanced response to the dielectric environment in a wide range of RI variation while the transmittance at resonance holds a sufficient intensity.

In this paper, we report the observation of an enhanced optical response in a novel type of quasi-3D metallic nanohole array, which can enable a resonant coupling between the SPs on the opposite surfaces of the metallic film. Our plasmonic structures are composed of monolayer interconnected metal hollow half-shells supported on a planar dielectric substrate and are fabricated by deposition of metal on a monolayer colloidal crystal (CC), followed by a further removal of the CC template. We will show that these plasmonic structures display transmission resonances as the as-prepared metallodielectric structures containing the CC template [25,26]. More importantly, we observed that the sensitivity of the main transmission resonance of the metallic hollow half-shell array sensors can reach a value of 1192 nm/RIU change of the surrounding medium, which shows a fivefold increase compared with that before removal of the CC [27]. The underlying physics is simple. Krishnan et al. [28] have shown that as compared with the asymmetric cases where the environmental RI does not match with the underlying substrate, the electric field on the interfaces could be much enhanced for the symmetric case of an index-matching metal hole array supported on a planar dielectric substrate as a result of resonant coupling of SPs on the opposite surfaces of hole array. The sensitivity in our PCs can be boosted because this index-matching condition is guaranteed in liquids of arbitrary RI, due to a substantially reduced substrate effect associated with the 3D nature of the structure. This high sensitivity and the low-cost fabrication technique developed here substantially increase the attractiveness of using this kind of plasmonic structures for developing nanophotonic elements in applications, including SP enhanced optical sensing and spectroscopy [3–6,12–16].

2. Sample fabrication procedure

The sample fabrication procedure is shown in Fig. 1. In brief, monodisperse silica spheres (1.58 \( \mu \)m diameter) were self-assembled to form two-dimensional (2D) hexagonally-close-packing CCs on a quartz chip using our previously reported method [26]. A thin gold film was sputtered by vacuum deposition on the sphere array, making the microbeads hemispherically covered by gold [29]. The silica template was then etched by using hydrogen fluoride acid to leave the interconnected Au hollow half-shells supported directly on the chip.

![Fig. 1. (Color online) Schematic for fabricating a quasi-3D metallic nanohole array.](image)

Figure 2 shows the scanning electron microscope (SEM) images of the metallic periodic structure before and after dissolution of the silica template. In Fig. 2(a), in addition to the metal-covered silica beads array, Au nanoislands formed on the chip through the pores of the CC during sputtering can be clearly seen. The templated metallic network film has a 2D periodic pore array as well as a strong surface corrugation (Fig. 2(b)). It is noted that to focus on the essence of the underlying physics that dominates the optical response of the hollow Au
half-shell array, any possible effect from the Au nanoislands [30] is excluded at the beginning of our discussions. This is done by transferring the Au network as a whole onto a clean quartz substrate using the method reported in Ref [31].

![Fig. 2. SEM images (tilted view). (a) Au covered silica CC self-assembled on a quartz substrate and (b) the templated quasi-3D Au nanohole array composed of ordered interconnected Au half-shells array on a clean quartz substrate. The silica spheres used have a diameter of 1.58 \( \mu \text{m} \) and the Au film has a nominal thickness \( \approx 50 \) nm. The inset in (b) shows an edge of the quasi-3D structure that had been cut in part, from which the notches at the half-shell rim are evident, indicating that the half-shells are interconnected via short segmented Au nanotubes.]

3. Results and discussions

3.1 Transmission spectra

Figure 3 shows the measured zero-order light transmission spectra of the Au films with and without the CC template supported on a quartz chip surrounded by air, \( \text{CCl}_4 \), and \( \text{CS}_2 \). It is seen that when put in air, both microstructures show a dominant transmission resonance as well as a series of transmission subpeaks. The main resonance for the interlinked hollow Au half-shell array is located at 1251 nm, whereas it is redshifted to a much longer wavelength for the Au film containing the CC. More interestingly, when surrounded by matrix of higher RI such as \( \text{CCl}_4 \) and \( \text{CS}_2 \), these two plasmonic structures show different optical responses. For the Au hollow half-shell array, the main peak shifts substantially to longer wavelength as the RI of the surround is increased, accompanied with a band broadening but with little variation in transmission amplitude (Fig. 3(a)).

In contrast, when the CC template remained, only a small shift was observed for the main transmission resonance upon the increase in RI of the background together with a dramatic decrease in the peak amplitude, as is seen in Fig. 3(b). Figure 3(c) summarizes the wavelength shift of the main peak for both plasmonic structures as a function of the environmental RI. From these measurements, it is evident that the sensitivity becomes much enhanced for the hollow half-shell array after removal of the CC template, although the templated Au microstructured film was still supported on a planar dielectric substrate. The slopes give a sensitivity (defined as \( S = \Delta \lambda / \Delta n \)) of 1192 nm/RIU for the quasi-3D metallic hole array and 223 nm/RIU for the as-prepared structure.
The sensitivity performance of the hollow Au half-shell array could outperform previous individual or random ensembles of metallic nanoparticles which instead rely on the enhanced absorption and scattering as a result of the excitation of localized SPs, including nanoprisms [30], half-coated colloids [32], shells [33], nanorices [34], rings [35], and crescents [36]. Here, in order to enable a comparison of the sensing capability with other metallic nanoparticles, a relative sensitivity defined as the ratio of sensitivity in eV/RIU to the SP energy in unit of eV multiplied by 100% should be calculated because this definition is more appropriate for characterizing the sensitivity for different morphologies of metallic nanoparticles with resonances in the spectrum range from visible to infrared [36]. For our quasi-3D Au nanohole array, the obtained relatively sensitivity is 61%/RIU, which is higher than the highest relative sensitivity of 38%/RIU measured for crescents [36] and the highest value of 40%/RIU for hematite-gold core-shells or rices [34]. Recently, a figure of merit (FOM) defined as the relative sensitivity (eV/RIU) divided by the full width at half-maximum in unit of eV was also introduced to compare peak broadening for different metallic nanostructures [37]. The FOM value was found to be in the range from 0.9 to 5.4 for most metallic nanoparticles [38]. For the interconnected uniform hollow Au half-shell array, the FOM was measured to be 4.1 which is much higher than that obtained for the as-prepared plasmonic structure supported on the silica CC (FOM = 0.7).

3.2 Physical explanations and numerical calculations

To help show that the observed boost in sensitivity is due to a strong resonant SP coupling, it is important first to obtain a plausible understanding of the SP modes that give rise to the transmission resonances of the plasmonic structures before possible numerical model simulations are made which will be given later. For a planar hole array metal film, the transmission resonances due to the excitation of delocalized SP modes can be assigned to reciprocal lattice vectors of the periodic metallic nanostructure [2,7]. It is expected that the strong corrugation in the created subwavelength hole array Au films could lead to a dramatic modification of the properties of the SP eigenmodes from those in flat metal films studied before. Here, as a first approximation, we estimate the transmission resonance wavelength for the present plasmonic structures using the grating coupling condition [17]. For a triangle lattice hole array, the peak positions \( \lambda \) at normal incidence are given by

\[
\lambda = \frac{\sqrt{3}a}{2 \left( i^2 + j^2 + ij \right)^{1/2}} \sqrt{\varepsilon_a \varepsilon_m / \varepsilon_a + \varepsilon_m},
\]

where \( a \) is the lattice constant, \( \varepsilon_a \) and \( \varepsilon_m \) are the dielectric constants of the metal and the matrix, respectively.
where \(a\) is the period of the hole array, \(i\) and \(j\) are integers, \(\varepsilon_d\) and \(\varepsilon_m\) are respectively the dielectric permittivity of the surrounding medium and metal. For \(\varepsilon_m\), we use literature values of gold in Ref [39]. The vertical lines on Fig. 4 indicate the calculated positions of the different resonances, a (1, 0) resonance mode at 1981 nm for an Au/silica interface and a (1, 0) resonance mode at 1367 nm for an Au/air interface, predicted for an Au film with a triangle lattice of nanoholes on a silica substrate with a pitch \(a = 1.58 \mu m\). It is seen that the predicted values can be compared, respectively, with the main transmission resonance observed at 1890 nm for the quasi-3D Au film supported on the silica CC and the one at 1251 nm when the Au film was directly located on the quartz substrate.

![Fig. 4. (Color online) Transmission spectra of the quasi-3D Au nanohole array on a quartz substrate (red line) and the as-prepared plasmonic structure containing the silica template (blue line). Both structures are in air. The vertical lines indicate the spectral positions of the (1, 0) SP resonances predicted for the interfaces of a planar Au film with air (A) and silica (S), using the resonant grating coupling condition.](image)

The above analysis suggests that the primary transmission resonances for the prepared plasmonic structures could be ascribed mainly to propagating SPs. Specifically, for the CC-supported quasi-3D subwavelength hole array, the observed main resonance may be labeled as the (1, 0) Au/silica mode, while for the interlinked hollow Au half-shell array it can be viewed as the (1, 0) Au/air mode even though the metallic structure was supported on a quartz substrate. Thus, it is expected that the Au/silica mode could propagate with a large portion of electric field within the silica template. This explains a linear scaling behavior of the main transmission resonance wavelength as a function of the template sphere RI observed in our previous work [26]. When the template was dissolved, the Au/silica mode should be substantially suppressed due to the 3D nature of the structure, which is in agreement with the experimental observations. Since the metal film is optically thin, minimizing the substrate effect will maximize the coupling between the SP modes on either side of the metal film [23,28]. Such a resonant coupling leads to a boost in the intensity of the Au/air transmission resonance (see Fig. 4). More importantly, since the RI on both sides is always matched in the quasi-3D subwavelength hole array, an enhancement in sensitivity of the transmission resonance wavelength to changes in bulk RI is expected.

Recently, Dmitriev and his associates [22] have successfully achieved a substantial enhancement of the bulk RI sensitivity of surface-supported Au nanoparticle SP sensors by reducing the substrate effect through lifting these metallic particles from a planar substrate to a dielectric nanopillar substrate. It is noted that our strategy to enhance dielectric sensitivity as well as the underlying physics for such an enhancement differs from the work of Dmitriev et al. [22] although the substrate effect in both systems can be reduced.
We now performed 3D numerical calculations to simulate the transmission properties of the plasmonic structures using the finite difference time domain method \[40\]. A grid size of 10 nm is used in the evaluations. The unit cell has periodic boundary conditions and the computational domain is terminated with a perfect matching layer \[41\]. Since no theoretical model is yet capable of modeling such 3D metal nanostructure film, Au distribution is approximated as follows (see Fig. 5(a)). The silica spheres are assumed to be half-coated by Au nanocups with a semi-ellipsoidal outer shape in order to mimic a relatively thick base of the half-shells \[29\]. The Au bridges interlinking adjacent Au bowls are modeled as Au semitubes with a uniform thickness. The silica sphere diameter is 1.58 \(\mu\)m and the RI for silica and the quartz substrate is \(n = 1.46\). The Au shell has a thickness of 50 nm at the base and 10 nm at the rim. To simulate the higher density of Au nanoparticles aggregated in the template sphere contact regions, the Au semitube is assumed to have a 100 nm thickness with an outer radius of 290 nm. The later value could be determined experimentally by measuring the distance between tips of the opposing Au triangles formed on the quartz substrate \[26,30\]. The Au permittivity is described by the Drude model

\[ \varepsilon_{Au} = 1 - \frac{\omega_p^2}{\omega(\omega + i\omega_c)} \]

with the plasma frequency \(\omega_p\) being 8.99 eV and the collision frequency \(\omega_c\) being 0.0269 eV \[39\]. The coordinate is chosen such that the nanoshells lie on the \(xy\) plane. Light is incident along \(z\) axis with its polarization along \(x\) axis.

![Numerical calculation results](image)

Fig. 5. (Color online) Numerical calculation results. (a) The models used in the numerical simulations: Au network (left) before and (right) after removal of the 2D CC. (b) Calculated transmission spectra of the quasi-3D Au film on a 2D silica CC supported on a quartz substrate (blue line) and directly on a quartz substrate (red line). (c) Calculated \(|E/Emax|\) distributions along \(xz\) plane at the main transmission resonance for the two structures. Structural parameters are given in the text.
Figure 5(b) shows the numerical results of the transmission spectra for the quasi-3D subwavelength hole array Au film on a quartz substrate and that containing the CC. The calculations have confirmed the main transmission peak observed in experiments in each case. It is seen that the spectral position of the main transmission resonances are reproduced using the models constructed above. The numerically obtained main transmission resonance is located at 1866 nm and 1238 nm, respectively, for the plasmonic structures with and without the CC. The calculations also confirm the experimental observation that a removal of the CC can lead to a boost in intensity of the Au/air SP mode.

Figure 5(c) shows the calculated distributions of the electric field amplitude in the \(xz\) plane for the mimicked plasmonic structures at their respective main transmission resonance. While a transmission resonance is observed for the plasmonic structure containing the CC, a large portion of the field is seen to be localized inside the dielectric spheres. This explains why small transmission resonance wavelength shift was observed when putting the CC-supported plasmonic structure into solvents of different RI [27]. When the CC is removed so that the quasi-3D subwavelength hole array is supported directly on a planar substrate, the electric fields that experience the maxima are exclusively distributed in regions above the planar substrate which are accessible to detected species. It is also seen that the field enhancement is not exclusively confined to the Au surfaces as is for the index matching planar hole array metal films [28]. A plausible explanation is that the Au half-shells could support partially localized SPs [42,43], which can couple with propagating SPs, leading to a redistribution in electric field enhancement. Hence, two essential features of our quasi-3D subwavelength hole array, the more localized and enhanced SPs field outside the dielectric substrate and the full accessibility to the field enhancement region for detected species, can explain the suppression of the substrate effect and the boost in sensitivity.

### 3.3 Quasi-3D nanohole array with upward halfshell-openings

In the above discussions, the effect from those Au nanoislands formed during sputtering process has been diminished by transferring the quasi-3D subwavelength hole array to a clean substrate. We found that the presence of these particles shows a negligible effect on the dielectric response enhancement even when both nanostructures are located on the same substrate (results not shown). In addition, the orientation of the Au bowl array can be controlled such that the Au bowl bases were in touch with the substrate, as shown in the inset of Fig. 6. We also characterized the sensitivity of such a plasmonic structure and the results are shown in Fig. 6. By comparison with the case in Fig. 3(a), the profiles of transmission spectra are nearly unchanged but the sensitivity shows a small decrease (here \(S = 1021 \text{ nm/RIU}\)). This minute decrease can be explained due to a certain increase in the substrate effect when Au bowl bases touched the substrate.
4. Conclusion

We have demonstrated that by reducing the substrate effect in an interlinked metallic half-shell array prepared via colloidal crystal templating, resonant SP coupling can be enabled, which leads to a dielectric bulk response enhancement. These findings are important for the following reasons. First, they provide a means to achieve resonant SP coupling that is robust to dielectric environmental variations. Second, these are the first experimental results to explore the dielectric bulk response of quasi-3D metal films that support SP-mediated transmission resonance. Third, the quasi-3D metallic nanohole arrays could be exploited for sensing applications and developing low cost plasmonic elements.

Acknowledgements

This work is supported in part by the State Key Program for Basic Research of China and NSFC under grant Nos. 10734010, 50771054 and 10804044. The work was also partially sponsored by NSFC under Excellent Youth Foundation and RFDP.