Strong coupling of light to flat metals via a buried nanovoid lattice: the interplay of localized and free plasmons

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Abstract: We study the optical plasmonic properties of metal surfaces which have a periodic lattice of voids buried immediately beneath their flat upper surface. Light reflection spectra calculated in the framework of a self-consistent electromagnetic multiple-scattering layer-KKR approach exhibit two types of plasmon resonances originating from the excitation of different plasmon modes: surface plasmon-polaritons propagating on the planar surface of metal and Mie plasmons localized in the buried voids. Coupling between these two types of plasma oscillation leads to an enhancement of the surface plasmon-polariton resonances even for close-packed void lattices. Our theoretical model quantitatively agrees with experimental results, demonstrating that planar surfaces can exhibit strong plasmonic field enhancements.

OCIS codes: (240.6680) Surface plasmons; (220.4000) Microstructure fabrication; (290.4020) Mie theory; (290.4210) Multiple scattering; (160.3900) Metals; (050.2770) Gratings.

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1. Introduction

The optical properties of planar metallic photonic crystals have been the subject of extensive research activities in recent years [1-9]. Exploiting plasmonic and photonic resonances supported simultaneously by metallic photonic crystals broadens the capability of comprehensively tuning their optical properties by nano-engineering the structure parameters. Currently much effort is devoted to investigating metals with periodically arranged nanopores, a prominent example of such a crystal. Interest in such structures is based on considerable advances in the template-assisted assembly of microporous and nanoporous metal structures [10-12].

Remarkable effects caused by excitation of plasmons in nanopores have been predicted theoretically for nanoporous metal films, such as extraordinary transmission [13] and absorption [14] of light. Recently, experiments have been performed on the reflection of light from nanoporous metals [10]. In [10] strong resonant dips in the reflectivity spectra are observed from nanoporous metal surfaces formed by periodic arrangements of close-packed spherical voids ('nanocups'). All the effects noted above are caused by excitation of Mie plasmons in voids (void plasmons). However, apart from the Mie plasmons localized in spherical cavities inside the metal, propagating surface plasmon-polaritons can be also excited at the metal planar surface if the period of the void lattice buried beneath the surface is comparable with the surface plasmon-polariton wavelength.

In porous metals, the lattice of voids buried beneath the planar surface of metal plays a two-fold role: (i) the periodic lattice of voids forms a coupling element, which diffracts incoming light into surface plasmon-polaritons (it is well known that surface plasmon-polaritons are non-radiative excitations and, therefore, they can not be excited on a planar surface of metal by incoming light without special coupling elements, e.g., grating or total reflection prism [15]), (ii) localized Mie plasmons are excited in spherical voids. In contrast to

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the surface plasmon-polaritons, void plasmons are *radiative* excitations [16] and therefore they can be coupled to light *directly* without using any special coupling device. Furthermore, it might be expected that localized void plasmons and propagating surface plasmon-polaritons can be brought into resonant interaction by tuning the structure parameters (e.g. void diameter and/or period of the void lattice) or by changing the angle of incidence of the incoming light. Surface plasmon-polaritons on metal surfaces are widely used for spectroscopy of surface epilayers and absorbates in optoelectronics and biophysics. However, in such application it is highly desirable to provide a flat metal surface, while exciting surface plasmon-polaritons in the most effective and practical fashion.

In this paper, we study the optical plasmonic properties of a hexagonal two-dimensional (2D) lattice of spherical nanovoids buried inside the metal below a planar metal surface. Resonant buried spherical voids are shown to be a highly effective coupler for planar metal surfaces. We calculate the reflectivity spectra of such a nanoporous metal surface in the framework of a self-consistent electromagnetic multiple-scattering layer-Korringa-Kohn-Rostoker (KKR) approach [13,14,17]. We investigate both the void (localized) and surface (delocalized) plasmons, focussing on the interactions between these two types of plasma oscillation. Our theoretical results are in a good quantitative agreement with experimental spectra obtained for nanoporous metal surfaces formed by periodically-arranged close-packed open voids buried immediately beneath a flat metal surface.

2. Theoretical model

Let us consider light incident at an angle θ to the surface normal (Fig. 1) of a planar surface of metal that contains a 2D lattice of voids just beneath the surface. The lattice has primitive vectors **a** and **b**, where $|\mathbf{a}| = |\mathbf{b}|$ and $\mathbf{a}\cdot\mathbf{b} = |\mathbf{a}|^2 \cos 60^o$. The plane of incidence of external light is defined by the azimuthal angle ϕ measured with respect to the *x*-axis (Fig. 1). To calculate the light reflected from such a porous surface we use a rigorous solution of Maxwell's equations based upon a multiple-scattering layer-Korringa-Kohn-Rostoker (KKR) approach that makes use of a re-expansion of the plane-wave representation of the electromagnetic field in terms of spherical harmonics [13,14,17]. We describe the dielectric response of the metal (gold) by the metal optical constant experimental data [18].

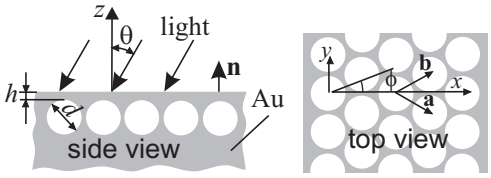

Fig. 1. Nanoporous metal surface with a 2D hexagonal lattice of spherical voids.

3. Results and discussion

In Fig. 2 calculated reflection spectra as a function of photon energy $\hbar\omega$ and angle of incidence θ are shown for a planar gold surface with a single buried 2D hexagonal lattice ($|\mathbf{a}| = 650$ nm) of close-packed voids of diameter $d = 600$ nm. Calculations are performed for *p*-polarized light with the plane of incidence along the Γ–M direction of the first Brillouin zone (see Fig. 3), which corresponds to zero azimuthal angle ($\phi = 0$). The distance from the planar metal surface to the top of the voids, *h*, is chosen to be 5 nm, which is much less than the skin depth (25 nm for gold), in order to ensure a strong coupling between light and plasmons. We also assume that there is a residual dielectric inside the nanopores, which we account for by a non-unity dielectric constant ($\varepsilon_{\text{void}} = 1.3$) inside the nanopores. One can see a series of dips in the reflectivity spectra. The stronger and almost dispersionless resonances are

#10076 - $15.00 USD Received 21 December 2005; received 8 February 2006; accepted 23 February 2006

associated with excitation of Mie plasmons in the voids [14]. The frequencies of these Mie-plasmon resonances are close to the frequencies of the Mie-plasmon modes with orbital quantum numbers l=1, l=2 and l=3 of a single void in bulk gold (marked by horizontal lines in Fig. 2). Higher Mie plasmon resonances in Fig. 2 are slightly red-shifted due to the effect of coupling between Mie plasmons in adjacent voids and disturbance of the Mie-plasmon mode by proximity of the planar surface of metal [14]. The other (dispersive) resonances in the reflectivity spectra originate from the excitation of surface plasmon-polaritons on the planar metal surface. The frequencies of these resonances are close to the frequencies of surface plasmon-polariton modes, which are estimated in the 'empty lattice approximation' (marked by curves in Fig. 2):

$$q_{pq}^2 = \left(\frac{\omega}{c}\right)^2 \frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2},$$

where ω_p is the free electron plasma frequency extracted from the experimental optical dielectric function data [18], $\mathbf{q}_{pq} = \mathbf{k}_{||} + \mathbf{g}_{pq}$ are the surface plasmon-polariton wavevectors, $\mathbf{g}_{pq} = p\mathbf{A} + q\mathbf{B}$ are the in-plane reciprocal lattice vectors, $\mathbf{A} = 2\pi(\mathbf{b}\times\mathbf{n})/|\mathbf{a}\times\mathbf{b}|$ and $\mathbf{B} = 2\pi(\mathbf{n}\times\mathbf{a})/|\mathbf{a}\times\mathbf{b}|$ are the primitive vectors of the reciprocal 2D lattice, p and q are integers, and $k_{||} = \omega \sin\theta/c$ is the in-plane component of the incident light wavevector, which is equal to zero in the case of normal incidence.

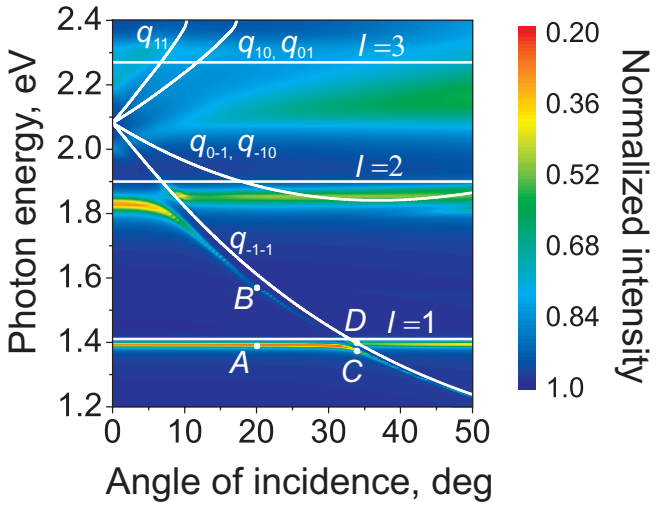

Fig. 2. (color online) Reflectivity spectra for p-polarized light with its plane of incidence along the Γ–M direction (azimuthal angle ϕ= 0) incident onto a planar gold surface with a hexagonal 2D lattice of spherical voids of diameter d = 600 nm as a function of photon energy $\hbar\omega$ and angle of incidence θ. Distance from the planar metal surface to the top of voids, h, is 5 nm and $|\mathbf{a}| = |\mathbf{b}|$ = 650 nm. The curves labeled with q_{pq} indicate the energies of the surface plasmon-polaritons estimated in the 'empty lattice approximation'. The horizontal lines mark the energy of the fundamental (l=1), the second (l=2) and the third (l=3) Mie-plasmon modes of a single void in bulk gold. Reflectivity spectra are normalized to the reflectivity of homogeneous planar surface of bulk gold.

#10076 - $15.00 USD Received 21 December 2005; received 8 February 2006; accepted 23 February 2006

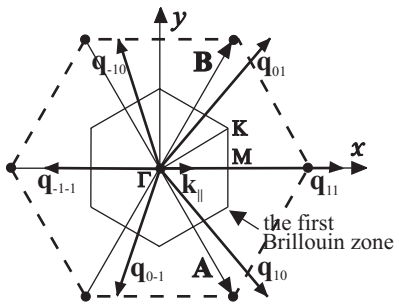

Fig. 3. The first Brillouin zone and the wavevectors $\boldsymbol{q}_{pq}$ of surface plasmon-polaritons in the lowest frequency subband with $\mathbf{k}_{||}$ along the Γ–M direction.

In general, at arbitrary azimuthal angle and oblique incidence onto the hexagonal lattice of voids there are six surface plasmon-polariton resonances observed in reflectivity. This can be understood from the first Brillouin zone diagram and wavevectors of surface plasmon-polaritons belonging to the lowest energy subband ($|q| < 1$, $|p| < 1$) shown schematically in Fig. 3. Note that different surface-plasmon-polariton modes are excited by *p*-polarized or *s*-polarized light with different efficiency: the plasmon-polariton mode with a greater projection of its wavevector onto the external electric field direction is excited more efficiently (for detailed explanation see [19]). Due to symmetry reasons, some of the six surface plasmon-polariton resonances are degenerate along Γ–K and Γ–M directions. Thus only four surface plasmon polariton resonances are seen in the spectra in Fig. 2 with $\mathbf{k}_{||}$ directed along Γ–M.

From Fig. 2 it is clear that Mie plasmons excited in the voids produce much stronger resonance dips compared with those from surface plasmon-polariton resonances. The reason for this is that the Mie plasmons in voids are radiative excitations [16] and hence they couple to light effectively, while surface plasmons are non-radiative excitations and can couple to light only via a coupling element (which is the lattice of voids itself in the structure here). Furthermore, the surface plasmon-polariton resonances on a planar surface of nanoporous metals with close-packed voids are rather weak since the effective grating aspect ratio of such a lattice is too small (i.e. the fractional volume occupied by metal in the porous layer is small) to couple light effectively to non-radiative surface plasmon-polaritons. However, in the anticrossing regime the interaction between Mie plasmons and surface plasmon-polaritons produces two mixed plasmon modes comparable in amplitude (for example, at points *C* and *D* in Fig. 2). This is because in the interaction region these two types of plasmon resonance effectively mix their oscillator strength, so that the stronger Mie-plasmon resonance supplies the weaker surface plasmon-polariton resonance with additional oscillator strength. Thus, in spite of the fact that the periodic lattice of close-packed voids is an inefficient coupler, the surface plasmon-polariton resonances are dramatically enhanced if they couple to the strong Mie-plasmon resonance.

Notice that the surface plasmon-polariton modes in "the empty lattice" are 6-fold degenerate at the Γ point of the first Brillouin zone due to the hexagonal symmetry of the void lattice. We are not able to make a conclusion about the degree of degeneracy of the surface plasmon modes at the Γ point in the real close packed nanovoid structure because the surface-plasmon resonances in such a structure become noticeable only when they are strongly enhanced due to their interaction with Mie plasmons in voids (which is not the case at the Γ point). Apart from this, in actual experiment the problem of probing the Γ point is complicated by the slightly off-axis experimental geometry.

In Fig. 4 the calculated distributions of the normal-to-surface electric-field component induced at the planar surface of nanoporous metal by incoming light, are plotted over several unit cells of the void lattice. We suggest that the normal-to-surface electric-field component is the most representative of the main characteristic features of different plasmon modes in the structure under investigation. In particular, for normal incidence of the incoming light this

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component of the electric field entirely originates from the excitation of plasmons (either Mie plasmons or surface plasmons) in the structure.

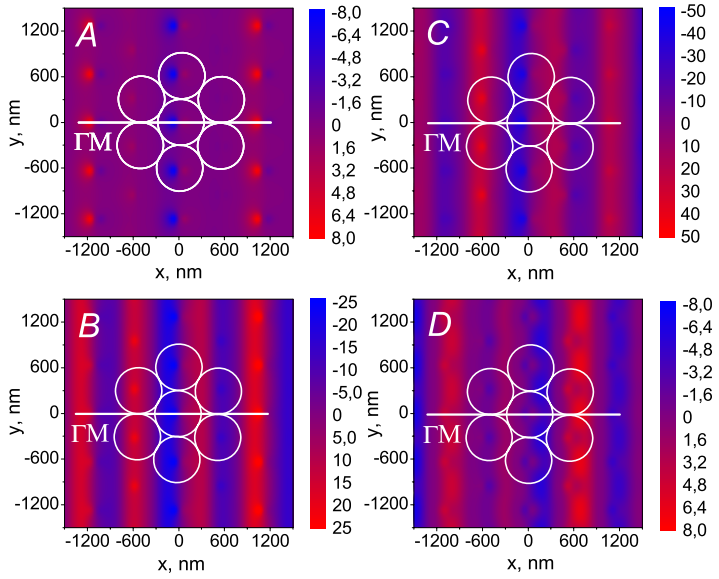

Fig. 4. (color online) Snapshots of the normal-to-surface electric-field component in plasmon modes excited at points *A*, *B*, *C* and *D* of the dispersion plane in Fig. 2 at the same particular time in the optical cycle. Amplitude of the electric field is normalized to the amplitude of electric field in the incident light.

First, let us consider electric-field distributions in the uncoupled fundamental ($l = 1$) Mie-plasmon mode and surface plasmon-polariton mode with $(p,q) = (-1,-1)$ excited at points *A* and *B* of the dispersion plane in Fig. 2, respectively. As expected, the Mie plasmon oscillates with a dumbbell-like field distribution localized in the voids (Fig. 4*A*) which is oriented along the electric field in the incident light (i.e. Γ–M direction). At oblique incidence, the Mie orbitals are slanted with respect to the planar metal surface and the Mie-plasmon oscillations are displaced in phase along the in-plane component of the wavevector of the incident light-wave, $\mathbf{k}_{\|}$, (along Γ–M direction). The uncoupled surface plasmon-polariton mode is a delocalized plane wave with wavevector $\mathbf{q}_{-1-1}$ propagating along Γ–M direction (Fig. 4*B*).

Note that at points *A* and *B* in Fig. 2 the Mie plasmons and surface plasmons do not interact with each other. However, these two types of plasma oscillations become strongly coupled at the angle of incidence corresponding to the anticrossing regime (points *C* and *D* in Fig. 2). In this case two mixed plasmon modes are excited at the surface of the nanoporous metal with equal strength but with opposite phase along the Γ–M direction. This strongly implies that these two modes originate from the bonding and anti-bonding coupling between Mie plasmons localized in voids and collective surface-plasmon oscillations. The field distribution in the mode excited at point *D* clearly demonstrates out-of-phase oscillations of the electric field at the metal surface and in the voids, which suggests that this mode corresponds to the anti-bonding state. The lower amplitude of the normal-to-surface electric field in this mode further supports this conjecture. The surface electric field is enhanced relative to the amplitude of incident field with factors of 25 and 50 at the uncoupled surface plasmon-polariton mode (Fig. 4*B*) and the bonding mixed mode (Fig. 4*C*), respectively. Note that the spatial period of blue/red strips in Fig. 4 *B*, *C* and *D* is determined by the surface plasmon-polariton wavelength $\lambda_{-1-1} = 2\pi/q_{-1-1}$. Therefore, the period of blue/red strips in plots

#10076 - $15.00 USD Received 21 December 2005; received 8 February 2006; accepted 23 February 2006

C and *D* is longer in comparison with that in plot *B* due to the decrease of q_{-1-1} with increasing $k_{\|}$ (see Figs. 2 and 3).

In Fig. 5 measured *p*-polarized reflectivity spectra of a nanoporous gold surface formed by the periodic arrangement of close-packed spherical nanovoids (with $d = 600$ nm) buried just beneath a flat surface of gold are presented. The experimental sample was prepared using a nanoscale casting technique with the electrochemical deposition of metal through a self-assembled latex template [10, 20-22]. A clear anticrossing is seen of the fundamental ($l = 1$) Mie-plasmon mode and surface plasmon-polariton mode with $(p,q) = (-1,-1)$ in the frequency range about 1.4 eV. The second ($l = 2$) Mie-plasmon mode and the surface plasmon-polariton mode with $(p,q) = (-1,-1)$ exhibit an anticrossing in the frequency range around 1.8 eV. These experimental data are in good quantitative agreement with the calculated results shown in Fig. 2. Notice that the resonance of this surface plasmon-polariton mode is practically invisible away from the anticrossing regime in both the experimental and theoretical plots. One can see, however, that the width of plasmon resonances in the experimental plot is broader then predicted by the theory (cf. Figs. 2 and 5). One possible reason for such broadening of the plasmon resonances may be the scattering of electrons from the void boundaries [16] in thin membrane-like metal regions between the close-packed voids. A possible imperfection of the experimental sample may also cause an additional inhomogeneous broadening of the plasmon resonances. Another difference between the experimental data and theoretical results is that the normalized reflectivity reaches unity far from the plasmon resonances in the theoretical plot (Fig. 2), while it does not in Fig. 5 because of a slightly corrugated surface of gold capping above the voids in the experimental sample.

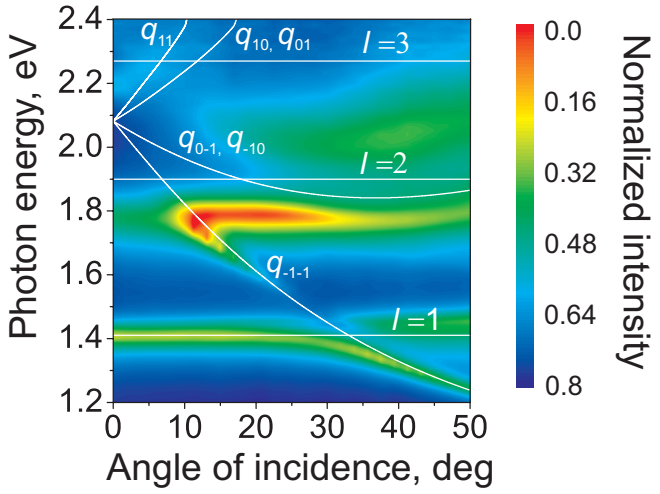

Fig. 5. (color online) Reflectivity spectra measured from the surface of nanoporous gold formed by periodical arrangements of close-packed spherical voids of diameter $d = 600$ nm buried just beneath a flat surface of gold. The measurements were performed for *p*-polarized light with the plane of incidence along the Γ–M direction ($\phi = 0$). Reflectivity spectra are normalized to the reflectivity of homogeneous planar surface of bulk gold.

4. Conclusion

In conclusion, in the strong coupling regime between light and plasmons, extremely intense surface-plasmon-polariton resonances can be excited on the flat surface of nanoporous metals even with buried close-packed voids. This phenomenon paves the way towards developing

#10076 - $15.00 USD Received 21 December 2005; received 8 February 2006; accepted 23 February 2006

various sensors based on surface plasmon-polaritons with high sensitivity operating without contamination of any void openings on the surface.

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