Electromagnetic coupling between a metal nanoparticle grating and a metallic surface

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The electromagnetic coupling between a two-dimensional grating of resonant gold nanoparticles and a gold metallic film is investigated. We report on the observation of multipeaks in the extinction spectra attributed to resonant modes of the hybrid system, resulting from the coupling between the localized plasmon of the nanoparticles with the underlying surface plasmon mode. Simulations based on the Fourier modal method give good agreement with the experimental measurements and allow for the identification of the respective contributions. © 2005 Optical Society of America

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The universal theory of dipole–surface interaction describes the modification of the radiative properties of a dipole near a surface by interaction with its image dipole.[1] The influence of the surface becomes even stronger when it sustains electromagnetic surface modes that dramatically modify the electromagnetic local density of states at the dipole vicinity. For instance, a strong dependence in the fluorescence lifetime of a molecule close to a metal–dielectric interface is observed when its surface plasmon polariton (SPP) provides an additional deexcitation channel.[2]

Similarly to molecules, the population decay of particle plasmons or localized surface plasmon (LSP) occurs mainly through transformation into photons (radiation damping). Consequently, a nearby metallic surface introduces some changes in the LSP of randomly arranged metallic particles. In particular, their resonance frequency becomes dependent on the particle–surface distance.[3,4] Furthermore, due to energy exchanges between LSP and SPP, the underlying surface plasmon wave tends to enhance the interparticle electromagnetic coupling.[5] In the case where, instead of being randomly distributed, the particles are arranged in a periodic array, the coupling with the SPP is expected to be double, combining a LSP–SPP interaction with some grating coupler effects.[6] The system thus exhibits a complex optical response,[7] which is a signature of hybrid resonances.

In this Letter the intricate coupling processes between an array of particle (localized) plasmons and a surface (delocalized) plasmon are investigated by extinction spectroscopy. The measurements, corroborated by simulations based on the Fourier modal method, bring us to a further understanding of the different dominating contributions.

The configuration we study (see Fig. 1) consists of a square grating of gold nanoparticles separated from a thin, transparent gold layer (10 nm thickness) by an indium tin oxide (ITO) spacer (50 nm thickness). A thin 2 nm Ti layer was used to increase adherence of gold to ITO. The lithographically fabricated particles have roughly a cylindrical shape with a 120 nm diameter and 20 nm height. The grating period D has been varied between 230 and 300 nm in steps of $\sim$20 nm. The extinction spectra of the system have been measured with a transmission optical microscope coupled to a microspectrometer by a multimode optical fiber. A 100× objective lens (NA=0.8) combined with an adjustable diaphragm allows for a detection area of $\sim$100 μm, matching the dimensions of each of the gratings.

Figure 2 shows the extinction spectra under unpolarized illumination and normal incidence of the reference system, in the absence of the gold layer, for different pitch values. Each of the curves is charac-

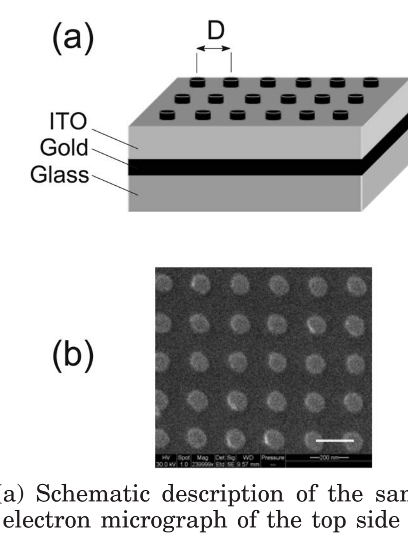

Fig. 1. (a) Schematic description of the sample and (b) scanning electron micrograph of the top side (scale bar of 200 nm).

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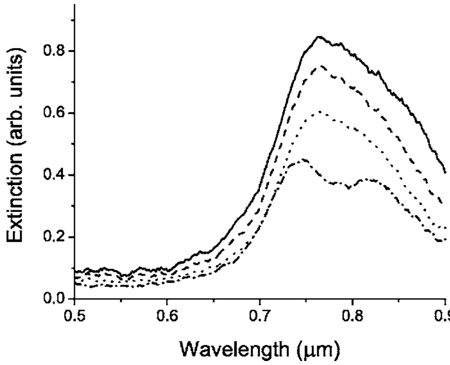

Fig. 2. Experimental evolution of the extinction spectrum with pitch D for the reference system, in the absence of the gold layer. D varies from 230 nm (solid curve) to 300 nm (dashed–dotted curve).

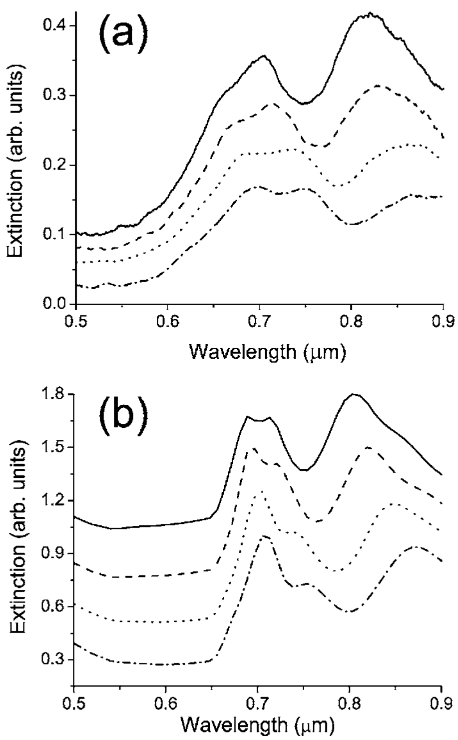

Fig. 3. Evolution of the extinction with pitch D for the full system (gold particle grating/ITO/gold layer). (a) Experimental, (b) theoretical. In both cases the curves have been translated vertically for further clarity. The D values are the same as for Fig. 2.

terized by a single resonance peak associated with the first-order (dipolar) LSP mode of the single particles. No significant shift of the central peak wavelength is observed when the interparticle distance is varied. Such an effect is indeed expected to be resolved over a wider range of separation distances D.[8]

The measurements have been repeated for the complete system including the gold layer [Fig. 3(a)]. Two specific effects can be attributed to the presence of the metallic film: (i) Instead of the single LSP band, the extinction displays in this case two clear resonances. (ii) Unlike what occurs in the reference system, a significant dependence of the curve on the grating period is now observed. Both of the effects (i) and (ii) are well restituted by simulations based on the Fourier modal method[9] (FMM) [Fig. 3(b)]. Discrepancies on the peak bandwidths and positions are attributed to the differences on the actual gold dielectric function with the tabulated values from the literature,[10] the use of Ti, and the distribution on the particles' sizes.

These observations are in agreement with previous results reported by Félidj *et al.*[7] although in their configuration the particles lay directly on the metal film. To get further insight into the physical origin of the extinction peaks, the dispersion diagram of the system has been computed for $D=300$ nm. The dispersion is extracted from the scattering matrix of the structure by looking for the complex poles of its determinant.[11] In Fig. 4(b) the modulus of the determinant of the scattering matrix is plotted when both the wave vector and the frequency are real. The modes are obtained from the loci of the minima. The direct comparison of the cross cut along $k_{\parallel}=0$ with the corresponding extinction curve shows unquestionably that the observed peaks are due to resonant excitations of electromagnetic modes of the coupled system and do not result from destructive interferences as suggested in Ref. 12. Note, however, that unlike what shows the experimental and theoretical extinction, the different modes would be expected to have significantly different amplitudes. The fact that the dispersion calculation does not account for the modes coupling by the incidence may explain this difference.

To identify the respective contributions of the localized and extended plasmon modes, the dispersion of the two uncoupled subsystems, namely, the array of

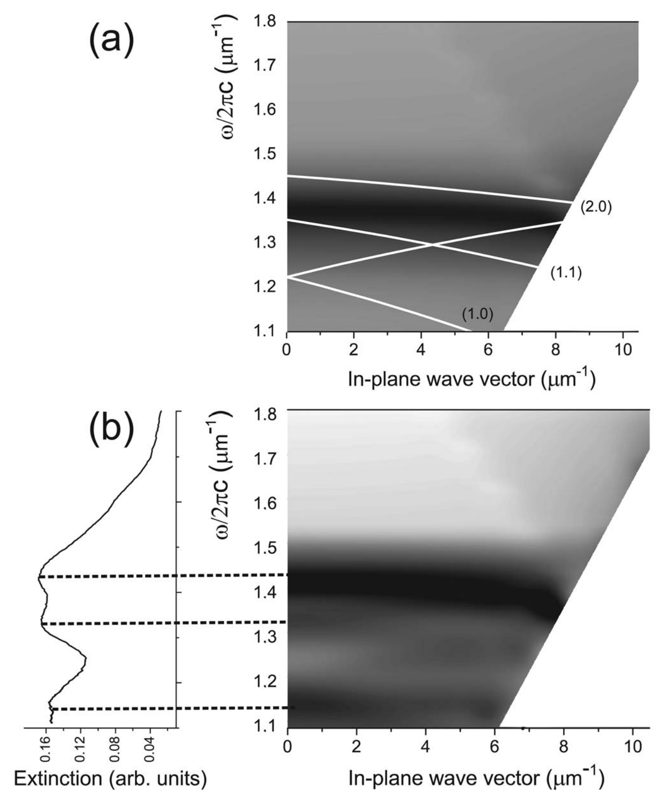

Fig. 4. Dispersion diagram of the two uncoupled subsystems (a) and of the full system (b) for $D=300$ nm. The right-hand cut corresponds to the air light line.

particles (particles–ITO–glass) and the metal film (ITO–gold–glass), are plotted in Fig. 4(a). The SPP lines are given by folding the actual gold–glass SPP dispersion curve. Note that in this configuration the gold–ITO SPP is negligible. A comparison with the full system dispersion diagram shows how the coupling occurs. On the one hand, the lower SPP line gives rise to a first mode with a bandwidth similar to the one of the LSP resonance. On the other hand, the presence of the gold layer induces a significant blueshift of the LSP band. Its modulation for low $k_{\parallel}$ values is attributed to its overlapping with the two closest SPP branches (1,1) and (2,0).

At this stage, a full understanding of the experimental extinction measurements can be given. Although we are under a global strong coupling regime, the higher wavelength peak mainly results from the excitation of the lower SPP branch (1,0) by grating coupling. Its shift with the periodicity is a consequence of the change in the folding when modifying the first Brillouin zone size. On the contrary, the resonance at a lower wavelength is mainly attributed to the LSP resonance of the array of nanoparticles. However, the presence of a weak dip, which is strongly dependent on the period value, evokes an additional contribution from the SPP. The matching of the separation between the two subpeaks with the frequency gap between the two overlapped SPP branches for all the D values confirms this hypothesis. We understand that at the frequencies where the SPP curves cross the LSP band, the extinction of the particles is increased by enhanced dipole–dipole coupling between the particles as described in Ref. 5.

To summarize, the full coupling mechanism can be roughly sketched as follows. On the one hand, the incident propagative light from the illumination is coupled to the LSP mode of the single particles that interact with their closer neighbors both in the upper air space and through the SPP surface wave. This process gives rise to a first single extinction peak. On the other hand, due to the periodicity of the particle arrangement, a remaining part of the LSP energy is transferred to the SPP by grating coupling and is trapped at the gold–glass interface leading to a second peak. This study provides a further understanding of systems based on arrays of resonant metallic nanoparticles coupled to metallic film. From a practical point of view, it may open the way to the engineering in a controllable and predictable way of the spectral properties of metallic nanoparticle-based systems to reinforce their applicability especially in sensing and surface enhancement Raman scattering.

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