Controlling the Interaction between Light and Gold Nanoparticles: Selective Suppression of Extinction

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The interaction of visible light with the particle-plasmon resonance of metallic nanoparticles can be controlled by geometrical arrangement of nanoparticle arrays. These arrays are placed on a substrate that supports guided modes in the wavelength range of the particle plasmon. Coupling of this particle-plasmon resonance to the directly incident light and to the waveguide modes results in almost complete suppression of light extinction within narrow spectral bands due to destructive interference. Variation of the structure parameters allows continuous tuning of these high-transmission bands across the particle-plasmon resonance.

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Tailoring the light-matter interaction via proper design of periodic nanostructures is one of the most fascinating and active fields of current solid state physics and chemistry. The rapidly growing research activities in this field including the development of photonic crystals [1] attempt to combine quantum confinement of electronic states with simultaneous photon confinement in the same structure. The ultimate goal is to control and optimize the coupling between material excitations and selected modes of the radiation field. In particular, these techniques will allow manipulation of such important parameters as strength and spectral distribution of optical absorption, luminescence, radiative lifetime, etc.

We report on the collective response of metallic nanoparticle arrays to optical excitation. The particle arrays serve as our model system for electronic oscillators, whose coupling to light will be controlled. The optical extinction spectrum of a single metal nanoparticle is governed in the visible by resonantly excited electron plasma oscillations (particle plasmons) [2]. Width and position of the resonance peak are well described by the Mie theory [3].

For regular two-dimensional patterns of gold nanoparticles, Lamprecht *et al.* [4] found significant variations of the position and width of the particle-plasmon resonance with the dot distance, which they attribute to in-phase superposition of scattered light from neighboring particles. Stuart *et al.* [5] have demonstrated qualitative changes of the plasmon resonance structure for statistically distributed metallic nanoparticles which were dipole coupled to a long-living surface-plasmon mode of a metallic film.

In this Letter, we demonstrate the control of the interaction between light and gold nanoparticles which results in a selective and tunable suppression of extinction within the particle-plasmon resonance. This is accomplished by a periodic two-dimensional arrangement of metallic nanoparticles on a dielectric substrate that supports guided optical modes. The potential to tailor the extinction spectrum is due to the collective interaction of metal nanoparticles with light, mediated via the exchange of photons propagating in the waveguide. Continuous tuning of the narrow bands in the resonance is easily attainable by changing the dot separation, or perhaps even more important, by simply varying the angle of incidence of the light beam onto the structure.

For our experiments, we prepared two-dimensional patterns of gold nanoparticles by electron beam lithography [6,7] on 30-nm and 140-nm-thick indium tin oxide (ITO) films on quartz substrates. The shape of the individual particles was slightly elongated, with diameters of 120 nm along the longer axis and 100 nm along the shorter axis, and a height of 20 nm (see inset in Fig. 1). In order to simplify the description, we introduce the following notation: The x axis is parallel to the longer axis of the particles, the y axis points along the shorter axis, and the z axis is defined by the surface normal of the sample. The particles were arranged in rectangular arrays with varying periodicities a_x and a_y for the x axis and the y axis, respectively (see Fig. 1). The lateral extension of the arrays was 100 μm $\times$ 100 μm each.

We performed extinction measurements for normal incidence of a focused white light beam on six different arrays of gold nanoparticles deposited on a 140-nm-thick ITO film. There exist two particle-plasmon resonances for normal incidence associated with the two axes of the particles [8] because of their slightly elliptical shape. These resonances can be selectively excited by linearly polarized light parallel to the corresponding axis. In the following, we concentrate on the particle plasmon associated with the shorter axis. Therefore, all measurements were performed with light polarized parallel to the y axis. The period of the metallic dots along the y axis was kept fixed at $a_y = 300$ nm for all samples, while a_x was changed from $a_x = 350$ nm to $a_x = 475$ nm in steps of 25 nm for the different samples [Figs. 2(a)–2(f), solid line]. For each individual set of samples fabricated within different runs of the lithographic process, we used arrays with a grating constant of 300 nm for both axes for reference purposes to

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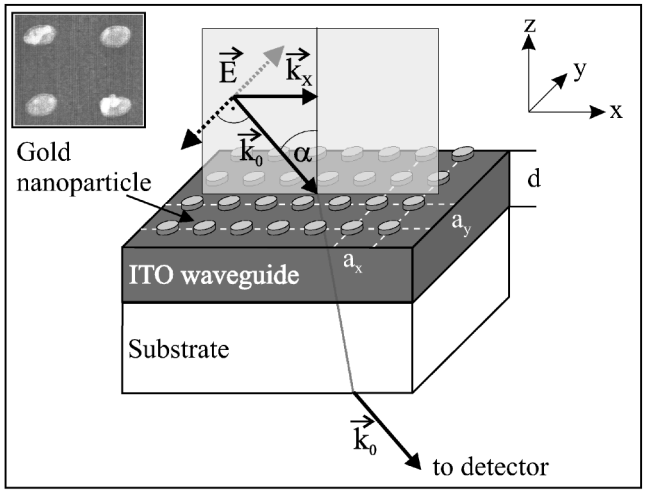

FIG. 1. Sketch of sample geometry. Inset: SEM picture of a gold nanoparticle array on a 140-nm-thick ITO waveguide.

control the influence of varying sample preparation conditions [Figs. 2(a)–2(f), dashed line].

The extinction of this particle plasmon is peaked at 1.94 eV and has a FWHM of approximately 0.19 eV (reference array). When the x-axis periodicity is increased to $a_x = 350$ nm, a new feature is observed: Two dips appear on the high energy side of the extinction spectrum [Fig. 2(a), solid line], separated by 0.04 eV. A further increase of a_x shifts the dips to lower energies, and at the same time they become more pronounced [Figs. 2(b)–2(d)]. For $a_x = 400$ nm, when the spectral position of the dips coincides with the peak of the particle-plasmon resonance, the extinction in the dips is reduced to $\approx 10\%$ of the extinction of the reference field [9]. It should be emphasized that further enlargement of a_x changes the character of this feature from induced transmission to enhanced extinction [Figs. 2(e) and 2(f)].

To explain the experimental results, we propose the following model: Gold nanoparticles are arranged with periods a_x and a_y on top of a substrate (dielectric constant: ϵ_{sub}) that is covered with an ITO film of thickness d and dielectric constant ϵ_{ITO}. The incident light with photon energy $\hbar\omega_0$ has a wave vector $\vec{k}_0$ that lies within the x-z plane and is polarized along the y axis (s polarization). Excitation of the particle plasmon associated with the short axis of the gold nanoparticles leads to absorption and scattering of the incident light and is therefore responsible for the spectrally broad extinction spectrum.

The crucial features of our samples are the regular arrangement of the nanoparticles and the presence of the ITO film below the dots which allow one to control the electromagnetic environment of the nanoparticles. The film can act as a waveguide for photon energies above the cutoff frequency [10]

$$\omega_{\text{cut}} = \frac{c \arctan\left(\sqrt{\frac{\epsilon_{\text{sub}} - \epsilon_{\text{air}}}{\epsilon_{\text{ITO}} - \epsilon_{\text{sub}}}}\right)}{d\sqrt{\epsilon_{\text{ITO}} - \epsilon_{\text{sub}}}}. \quad (1)$$

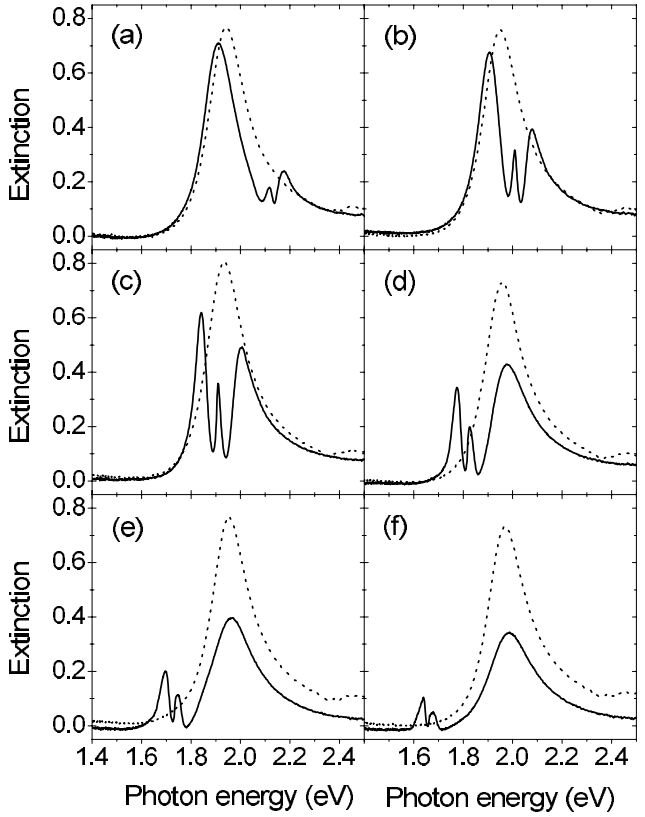

FIG. 2. Extinction [$= -\ln(I_T/I_0), I_T$: transmitted intensity; I_0: incident intensity] of gold nanoparticles on a 140-nm-thick ITO waveguide. Solid lines: arrays with a fixed periodicity of 300 nm along the y axis and increasing periodicity from 350 nm to 475 nm in steps of 25 nm (a)-(f) along the x axis. Dashed lines: reference arrays with a periodicity of 300 nm for both axes.

For our experimental parameters ($d = 140$ nm, $\epsilon_{\text{ITO}} = 3.8$, $\epsilon_{\text{sub}} = 2.1$, $\epsilon_{\text{air}} = 1$, c is the speed of light in vacuum), this cutoff energy is $\hbar\omega_{\text{cut}} = 0.73$ eV. The regular array of metal particles couples part of the incoming polarized light into the waveguide. For our experimental conditions, the first guided transversal electric (TE) mode is excited, which propagates along the x axis. Efficient coupling from free space to the waveguide requires momentum conservation

$$\vec{k}_{wg} = \vec{k}_x \pm i\vec{g}_x, \quad (2)$$

where $\vec{k}_{wg}$ is the wave vector of the waveguide mode, $\vec{k}_x$ is the component of the wave vector of the incident light parallel to the x axis, $\vec{g}_x$ is a reciprocal lattice vector defined by $|\vec{g}_x| = 2\pi/a_x$, and i is an integer. For normal incidence, $\vec{k}_x$ vanishes and therefore $\vec{k}_{wg}$ is solely determined by the period $\vec{a}_x$. In this case, two energetically degenerate waveguide modes propagating in the positive and negative x direction are expected for an unperturbed waveguide. If the excited waveguide mode is resonant to the particle plasmon, the total electric field acting on the nanoparticle is given by the coherent superposition of two components: the electromagnetic field incident from free

space and the field of the waveguide mode. Since the polarizations created by both fields are 180° out of phase [11], we obtain destructive interference between the directly incident radiation and the waveguide mode at the metal dot positions. This interference should result in reduced coupling between the light and the particle plasmon at a spectral position determined by momentum conservation and the dispersion relation of the waveguide modes. Correspondingly, a pronounced dip in the extinction spectrum is expected since the spectral width of waveguide modes is considerably narrower than the particle-plasmon resonance. This scenario resembles the experimental spectra very well with the exception that only one dip is expected for normal incidence while the experiments show two dips. This discrepancy has to be attributed to repulsive interaction of the modes propagating in the $+x$ and $-x$ directions, lifting the degeneracy. This point will be discussed later in more detail in connection with Fig. 4.

Tuning of the increased-transmission bands can be accomplished by varying the periodicity of the metal dot array and the waveguide parameters. Such techniques allow complete control of the light-particle-plasmon interaction.

If the nanoparticle period is increased, the excited waveguide modes are shifted to lower energies and finally out of the particle-plasmon resonance. As a consequence, coupling of light in and out of the waveguide becomes less effective. However, photons coupled into the waveguide will propagate over longer distances and the waveguide will act as an additional loss channel. This mechanism explains the occurrence of extinction peaks found for large periods [see Figs. 2(e) and 2(f)].

Our model makes some intriguing predictions. The reduced extinction should disappear for photon energies smaller than $\hbar\omega_{\mathrm{cut}}$ since it depends on the existence of a waveguide mode. For this purpose, we prepared gold nanoparticle arrays on a 30-nm-thick ITO waveguide ($\hbar\omega_{\mathrm{cut}} = 3.42$ eV), keeping the parameters for size and arrangement of the particles the same as in the first experiment. The extinction spectrum for an array with a period of $a_x = 425$ nm is the solid curve in Fig. 3 and shows no sign of enhanced transmission since the photonic interaction of the particle plasmons mediated

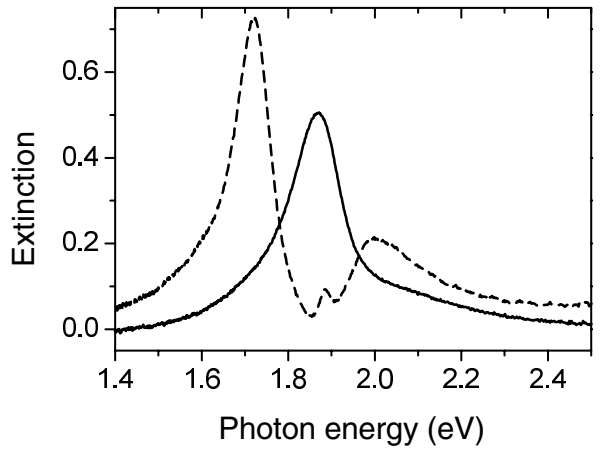

FIG. 3. Extinction spectrum for an array of gold nanoparticles with a period of $a_x = 425$ nm and $a_y = 300$ nm on a 30-nm-thick ITO waveguide. Dashed line: waveguide covered with immersion oil and glass cover slide. Solid line: waveguide without cover.

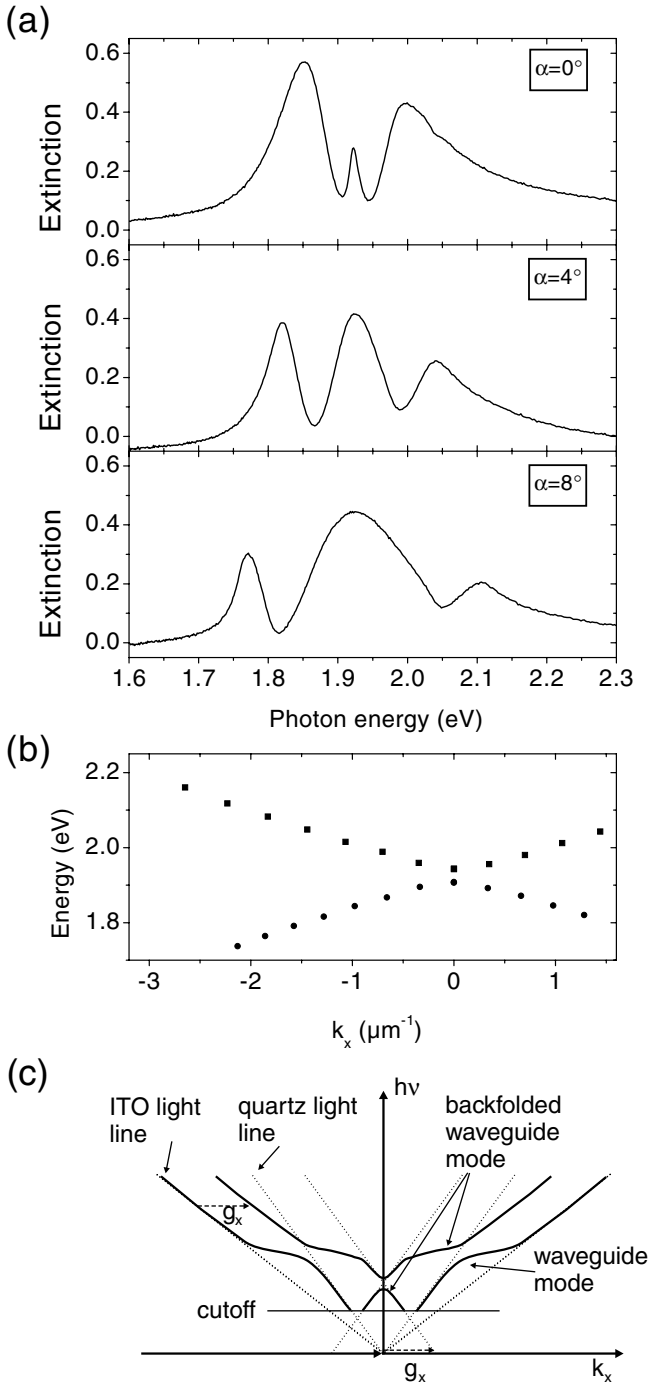

FIG. 4. (a) Extinction spectra for s-polarized light of a gold nanoparticle array with periods $a_x = 400$ nm and $a_y = 300$ nm on a 140-nm-thick ITO waveguide for different rotation angles around the y axis ($\alpha = 0°$, 4°, 8°). (b) Dispersion relation constructed from the measurements. (c) Sketch of the formation of the dispersion diagram around $|\vec{k}_x| = 0$.

by the waveguide is turned off. If immersion oil and a thin glass cover slide are placed on top of the sample the extinction spectrum clearly exhibits two dips (Fig. 3, dashed line). This experimental finding can be explained by the dielectric constant of the cover of the waveguide. Replacing $\epsilon_{\text{air}} = 1$ by $\epsilon_{\text{cover}} = 2.2$ in Eq. (1) shifts $\hbar\omega_{\text{cut}}$ to 1.27 eV and therefore the waveguide supports photonic interaction of the gold nanoparticles again.

According to Eq. (2), the wave vector of the waveguide mode is determined by the grating constant and by the wave vector component of the incident light parallel to the x axis. By rotating the sample around the y axis by an angle α, $|\vec{k}_x|$ can be continuously increased. The influence on the extinction spectrum of a gold nanoparticle array with periods of $a_x = 400$ nm and $a_y = 300$ nm on a 140-nm-thick ITO film for s-polarized light is shown in Fig. 4(a). Two waveguide modes, resulting from adding or subtracting a reciprocal lattice vector to $\vec{k}_x$, can be observed. While the corresponding excitation wavelengths are resonant to the particle plasmon, the two modes manifest themselves as two extinction dips shifting away from each other for increasing α. For larger angles, the modes are tuned out of resonance and therefore appear as extinction peaks. The dispersion relation, i.e., the energy of the waveguide modes as a function of $|\vec{k}_x|$, determined from these measurements, is shown in Fig. 4(b).

For small frequencies, the first TE mode largely extends into the substrate and therefore the dispersion is asymptotically given by the quartz light line. By increasing the frequency, the mode becomes more and more concentrated in the ITO film and dispersion becomes ITO-like. The regular array of gold nanoparticles has two effects on the waveguide dispersion relation. First, the dispersion relation is folded back into the first Brillouin zone by reciprocal lattice vectors [see Fig. 4(c)]. Second, the nanoparticles are responsible for the photonic energy gap in the dispersion at an energy of 1.93 eV with a width of 0.04 eV. To explain the energy gap, we propose a model which contains suitable modifications of the model of Barnes *et al.* [12] for photonic energy gaps in the propagation of surface plasmons on gratings. Bragg scattering of the waveguide modes at the regularly arranged gold nanoparticles leads for $|\vec{k}_x| = 0$ to the formation of two standing waves. One has nodes under the gold nanoparticles, while the other has nodes between the gold nanoparticles. The energy difference between these two standing waves originates from the different overlap of the field patterns with the gold nanoparticles. This interpretation might also explain why the higher energy dip [13] is always slightly more pronounced in Fig. 2.

In conclusion, we have shown that the light particle-plasmon interaction can be tailored in regular gold nanoparticle arrays deposited on top of a dielectric waveguide. Optical transmission measurements on such arrays reveal a drastically modified extinction compared to single particle extinction spectra. In particular, the extinction can be suppressed for narrow spectral bands within the particle-plasmon resonance. It should be mentioned that enhanced extinction is also attainable. These effects are explained as a collective interaction process between light and the gold nanoparticles mediated by the waveguide. In particular, destructive interference between directly incident light and waveguide modes reduces the photonic coupling to the particle plasmon. The spectral position of the reduced extinction bands can be continuously shifted across the particle-plasmon resonance by varying the grating constant of the nanoparticle array or by tilting of the sample surface with respect to the direction of the incident optical beam. Experiments on samples with varying dot array and waveguide parameters emphasize the important role of the waveguide modes for intentional tuning of the photon-plasmon coupling. Our findings can be utilized for the design of two-dimensional photonic devices in the visible and IR and are relevant for optical communication and microlasers. The distinct advantages of our samples are standard planar fabrication techniques and broad tunability of their coupling properties with photons.

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