Optical excitation of coupled waveguide-particle plasmon modes: A theoretical analysis

V. Yannopapas and N. Stefanou
University of Athens, Section of Solid State Physics, Panepistimioupolis, GR-157 84 Athens, Greece
(Received 18 August 2003; published 29 January 2004)

Using the first-principles layer-multiple-scattering method we developed in previous work, we analyze recent experimental data on the extinction of light by rectangular two-dimensional arrays of gold nanoparticles on a dielectric waveguide. The theoretical results reproduce accurately the measured spectra and provide a transparent physical picture of the underlying processes.

DOI: 10.1103/PhysRevB.69.012408 PACS number(s): 78.66.−w, 42.25.Bs, 73.20.Mf, 78.67.Bf

The extinction spectrum of noble-metal nanoparticles in the visible region is characterized by pronounced resonances due to the excitation of surface particle plasmons.[1] These are collective electron oscillations at the surface of these particles that cause large enhancement of the local field and strong light absorption, effects which are interesting for a variety of applications in the surface-enhanced Raman scattering,[2,3] nonlinear optics,[4,5] optical tweezers,[6] solar energy absorption,[7,8] etc. Using electron-beam lithography and self-assembly techniques, it has become feasible in recent years to prepare well-defined systems of metal nanoparticles with a tailored shape, size, and arrangement, which allow for observing new, interesting, and potentially useful physical phenomena.[9–14]

In previous work we developed an on-shell multiple-scattering formalism for the calculation of the frequency band structure of photonic crystals consisting of nonoverlapping spheres in a host medium.[15–17] The same formalism allows one to calculate the transmission, reflection, and absorption coefficients of an electromagnetic (EM) plane wave incident on a slab of the material and, therefore, it can describe an actual transmission experiment. The slab may consist of a finite number of layers. These can be either planes of spheres with the same two-dimensional (2D) periodicity or homogeneous plates. An advantage of the method is that it does not require periodicity in the direction perpendicular to the layers. For each plane of spheres, the method calculates the full multipole expansion of the total multiply scattered wave field and deduces the corresponding transmission and reflection matrices in the plane-wave basis. For homogeneous plates, the transmission and reflection matrices are directly obtained in the plane-wave basis. The transmission and reflection matrices of a given slab are calculated from those of the constituent layers. The method applies equally well to nonabsorbing systems and to absorbing ones (materials characterized by a complex dielectric function); it can also deal with systems containing strongly dispersive materials such as real metals. In this paper we use the method to study the extinction of light by a periodic monolayer of metallic nanospheres on top of a dielectric waveguide. We compare our results with relevant experimental data and provide a consistent interpretation of the extinction spectra of this system.

The present paper is motivated by recent experimental work of Linden *et al.*[11,12] concerning the extinction of light by 2D arrays of gold nanoparticles on a dielectric waveguide. The particles are arranged on a rectangular lattice, specified by the primitive vectors $\mathbf{a}_1=(a_x,0)$ and $\mathbf{a}_2=(0,a_y)$, on top of a quartz substrate of dielectric constant $\epsilon_{\mathrm{sub}}=2.1$, which is covered with an indium tin oxide (ITO) film of thickness $d=140$ nm and dielectric constant $\epsilon_{\mathrm{ITO}}=3.8$.

An ITO film, sandwiched between air and quartz, can act as a (asymmetric) waveguide for EM waves of frequency above a cutoff value. Following a standard analysis,[18] it can be shown that the ITO film supports transverse electric (TE) guided waves (the electric field oscillates parallel to the interfaces) above a cutoff frequency

$$\omega_{\mathrm{TE}}=\frac{c}{d\sqrt{\epsilon_{\mathrm{ITO}}-\epsilon_{\mathrm{sub}}}}\arctan\sqrt{\frac{\epsilon_{\mathrm{sub}}-\epsilon_{\mathrm{air}}}{\epsilon_{\mathrm{ITO}}-\epsilon_{\mathrm{sub}}}} \tag{1}$$

and transverse magnetic (TM) guided waves (the magnetic field oscillates parallel to the interfaces) above a cutoff frequency

$$\omega_{\mathrm{TM}}=\frac{c}{d\sqrt{\epsilon_{\mathrm{ITO}}-\epsilon_{\mathrm{sub}}}}\arctan\left(\frac{\epsilon_{\mathrm{ITO}}}{\epsilon_{\mathrm{air}}}\sqrt{\frac{\epsilon_{\mathrm{sub}}-\epsilon_{\mathrm{air}}}{\epsilon_{\mathrm{ITO}}-\epsilon_{\mathrm{sub}}}}\right), \tag{2}$$

where c is the velocity of light in vacuum and $\epsilon_{\mathrm{air}}=1$. These waveguide modes are confined within the film. Along any direction parallel to the film they have the form of propagating waves with a wave vector $\mathbf{q}_\parallel$; along the normal direction (z direction specified by the unit vector $\hat{\mathbf{e}}_z$) they decay exponentially to zero away from the film on either side of it. The dispersion curves of these guided modes are shown in Fig. 1. Obviously these modes cannot be excited by an externally incident wave. They cannot match continuously a propagating mode of the EM field outside the film; momentum and energy cannot be conserved simultaneously. When the film is coated with a 2D periodic array of particles, waveguide modes can be transformed from bound to radiative through an umklapp process. This mechanism can be understood as follows. A plane wave of wave number q, incident on the periodic array, generates a number of diffracted beams with wave vectors

$$\mathbf{K}_{\mathbf{g}}^{\pm}=\mathbf{k}_\parallel+\mathbf{g}\pm[q^2-(\mathbf{k}_\parallel+\mathbf{g})^2]^{1/2}\hat{\mathbf{e}}_z, \tag{3}$$

where $\mathbf{g}$ are the 2D reciprocal vectors corresponding to the given lattice and $\mathbf{k}_\parallel$ is the parallel component of the wave vector of the incident wave, reduced within the surface Bril-

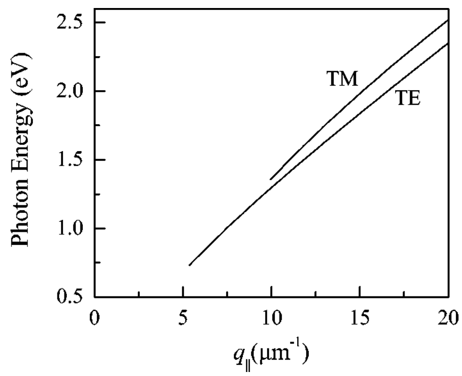

FIG. 1. Dispersion curves of the TE and TM waveguide modes for an ITO film, 140 nm thick, sandwiched between air and quartz.

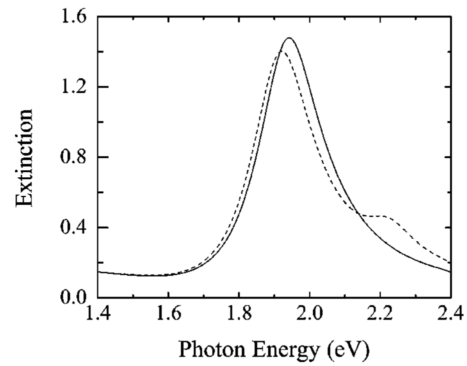

FIG. 2. Extinction spectrum for light incident normally on a square array (lattice constant: 300 nm) of gold spheres (radius: 50 nm) on top of an ITO film (thickness: 140 nm) on a quartz substrate. The solid (dashed) curve is obtained for $l_{\max}=1$ ($l_{\max}=4$).

louin zone (SBZ). If $q<|\mathbf{k}_{\|}+\mathbf{g}|$ we obtain evanescent diffracted beams which can match continuously the corresponding guided waves of the same polarization and of the same $\mathbf{q}_{\|}=\mathbf{k}_{\|}+\mathbf{g}$, provided they have the right frequency. In this way, the waveguide modes are no longer bound within the film, but leak in the outer region, becoming virtual bound states. These quasiguided modes can be excited by an externally incident wave and manifest themselves as peaks in the reflectivity spectrum. Another effect of the periodic coating on the waveguide modes is a folding of the dispersion curves associated with these modes (see Fig. 1) within the SBZ, accompanied with an opening of small gaps at the center and at the boundaries of the SBZ (Bragg gaps) as expected from first-order perturbation theory. This implies that in the reflectivity spectrum of light incident, e.g., normally, on the coated waveguide, we should expect pairs of peaks near the frequencies of the eigenmodes of the bare waveguide corresponding to $\mathbf{q}_{\|}=\mathbf{g}$ and to the proper polarization mode; the separation between the peaks of these pairs reflects the size of the Bragg gaps at the center of the SBZ.

We shall now consider the system studied experimentally by Linden *et al.*,[11,12] i.e., the above waveguide covered with a 2D periodic array of gold nanoparticles. In the experiment, the shape of the individual particles was slightly elongated, with principal axes 120 nm and 100 nm long, and a height of 20 nm. Therefore, in this case, a normally incident light can excite the two dipole particle-plasmon modes associated with the two axes. However, the measurements were performed with light polarized along the shorter axis, so that only the particle plasmons associated with this axis are excited. Consequently, for simplicity, we can assume spherical gold particles with a radius $S=50$ nm which corresponds to the shorter axis of the elongated particles. The phenomena we shall analyze are valid not only for gold particles but for other noble-metal particles as well. Therefore we describe the optical properties of the isolated gold sphere by a dielectric function of the general Drude form

$$\epsilon_{\mathrm{p}}(\omega)=1-\frac{\omega_{\mathrm{p}}^{2}}{\omega(\omega+\mathrm{i}\tau^{-1})}, \tag{4}$$

and treat ω_{p}, the bulk plasma frequency of the metal, and τ, the relaxation time of the conduction-band electrons, as parameters. In the case under consideration we adjust these parameters to reproduce the measured extinction spectrum of a reference system consisting of a square array of gold particles, of lattice constant 300 nm, on top of the waveguide. The extinction is defined, as usual, as $-\ln T$ with T being the transmittance of the system. We know, in fact, that the EM field about a single metallic nanosphere in air exhibits a pronounced dipole surface-plasmon resonance at the frequency $\omega_{\mathrm{p}}/\sqrt{3}$. For a 2D periodic array of such spheres, the EM field (of given $\mathbf{k}_{\|}$) has a virtual bound state (a resonance state of finite lifetime) near the frequency $\omega_{\mathrm{p}}/\sqrt{3}$, as a result of the interacting surface-plasmon resonant states of the individual spheres.[19] The field pattern associated with this virtual bound state peaks about the plane of spheres but drops to a much lower value away from the plane. The virtual bound state manifests itself as a peak in the reflectivity spectrum of the plane of spheres for a given $\mathbf{k}_{\|}$. At the same time resonant absorption by the spheres takes place if dissipation is also present. Therefore a resonance peak in the extinction spectrum is expected due to the virtual bound state. Using $\hbar\omega_{\mathrm{p}}=3.71$ eV and $(\omega_{\mathrm{p}}\tau)^{-1}=0.05$ we calculate an extinction spectrum, for normally incident light ($\mathbf{q}_{\|}=\mathbf{0}$), characterized by a resonance peak centered at $\hbar\omega=1.94$ eV with a full width at half maximum of ≈ 0.19 eV, as reported in the experiment. Our results are shown in Fig. 2. The curve shown by the solid line is obtained using a cutoff value $l_{\max}=1$ in the angular-momentum expansion of the wave field. One can see that this dipole approximation gives essentially the same results with the full multipole treatment (dashed line), except from a minor structure about $\hbar\omega=2.2$ eV. This structure, which is not observed in the experiment, arises from quadrupole contributions and it is smoothed out if we employ the actual dielectric function of gold.[19] In this respect, in what follows we shall use $l_{\max}=1$. We note that the smallest reciprocal vectors of a square lattice of lattice constant 300 nm have a magnitude equal to 20.94 $\mu\mathrm{m}^{-1}$ and the corresponding waveguide modes are out of the considered spectral range (see Fig. 1). Therefore more interesting features in the extinction spectrum are expected if the periodic coating has larger lattice constants, so

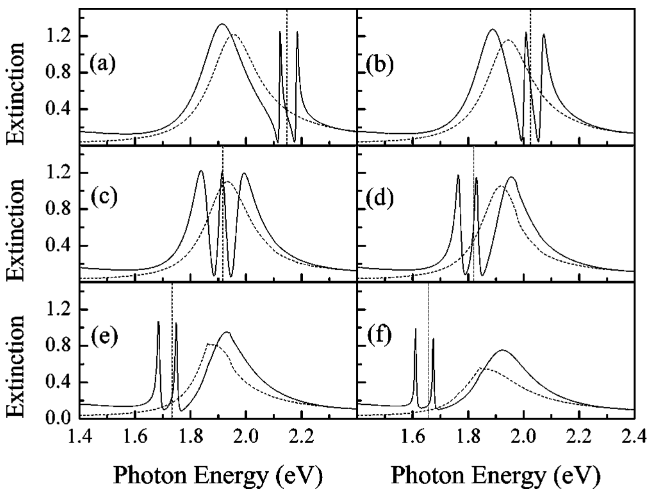

FIG. 3. Extinction spectra for light incident almost normally $[\mathbf{q}_{\parallel}=(0.005\pi\omega_{\mathrm{p}}/c,0)]$ on a rectangular array of gold spheres with lattice constants $a_y=300$ nm and $a_x=350$ nm (a), $a_x=375$ nm (b), $a_x=400$ nm (c), $a_x=425$ nm (d), $a_x=450$ nm (e), $a_x=475$ nm (f), on a 140 nm thick ITO film on a quartz substrate, and polarized along the y axis. The dashed curves show the extinction spectra for the same system without the ITO film. The dashed lines vertical on the abscissa indicate the position of the TE waveguide modes of the bare waveguide (air-ITO film-quartz) for $q_{\parallel}$ equal to the magnitude of the smallest 2D reciprocal vector.

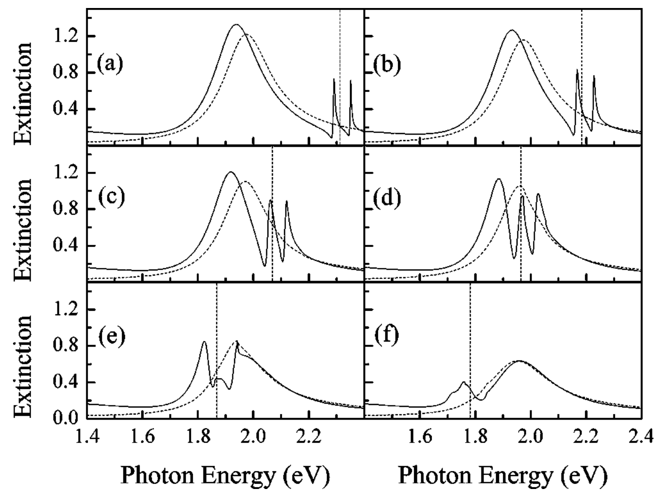

FIG. 4. Extinction spectra for light incident almost normally $[\mathbf{q}_{\parallel}=(0.005\pi\omega_{\mathrm{p}}/c,0)]$ on a rectangular array of gold spheres with lattice constants $a_x=300$ nm and $a_y=350$ nm (a), $a_y=375$ nm (b), $a_y=400$ nm (c), $a_y=425$ nm (d), $a_y=450$ nm (e), $a_y=475$ nm (f), on a 140 nm thick ITO film on a quartz substrate, and polarized along the y axis. The dashed curves show the extinction spectra for the same system without the ITO film. The dashed lines vertical on the abscissa indicate the position of the TM waveguide modes of the bare waveguide (air-ITO film-quartz) for $q_{\parallel}$ equal to the magnitude of the smallest 2D reciprocal vector.

that waveguide modes corresponding to reciprocal vectors of the lattice fall within the spectral region of the particle-plasmon resonance.

Let us consider rectangular lattices with the one lattice constant a_y kept fixed at 300 nm and the other a_x varied from 350 nm to 475 nm in steps of 25 nm, as in the experiment.[11,12] Figure 3 shows the calculated extinction spectra for almost normally incident light, with the electric field oscillating along the y axis. In this case the polarization is perpendicular to the smallest reciprocal vectors $\mathbf{g}_1=(2\pi/a_x,0)$ and $\mathbf{g}_2=(-2\pi/a_x,0)$. Therefore, beams resulting from the diffraction by the plane of spheres and corresponding to $\mathbf{g}_1$ and $\mathbf{g}_2$ are of TE polarization and, consequently, they excite the corresponding TE waveguide modes. We note that the waveguide modes which are excited by diffracted beams corresponding to larger reciprocal vectors fall outside of the spectral range of interest. In this context and according to our previous discussion, we find three distinct peaks in the extinction spectrum: a pair of peaks about the frequency of the TE eigenmode of the bare waveguide corresponding to $q_{\parallel}\simeq g_{\min}$ $(g_{\min}=|\mathbf{g}_1|=|\mathbf{g}_2|)$ and a peak near the plasmonic virtual bound state of the plane of spheres. If the above rectangular arrays of gold spheres are rotated by 90° about the z axis, the polarization of the incident light becomes parallel to the smallest reciprocal vectors $\mathbf{g}_1=(0,2\pi/a_y)$ and $\mathbf{g}_2=(0,-2\pi/a_y)$, and thus the diffracted beams which correspond to $\mathbf{g}_1$ and $\mathbf{g}_2$ excite the corresponding TM waveguide modes. In this case we find a pair of peaks about the frequency of the TM eigenmode of the bare waveguide corresponding to $q_{\parallel}\simeq g_{\min}$ $(g_{\min}=|\mathbf{g}_1|=|\mathbf{g}_2|)$ and the peak of the plasmonic resonance (see Fig. 4). The interaction between plasmonic and waveguide modes, which is stronger the closer in frequency these states are, induces a level repulsion, as can be seen in Figs. 3 and 4. The position of the calculated resonance peaks is in very good agreement with the experiment, although the waveguide resonances, if they are not close to the plasmonic resonance, appear somewhat more pronounced in the calculated than in the experimental spectra. It is worth noting that at strictly normal incidence $(\mathbf{q}_{\parallel}=\mathbf{0})$ the low-frequency TE and the high-frequency TM quasiguided modes cannot be excited for symmetry reasons. However, assuming a slightly off-normal incidence to account for the limited angular resolution of the experimental setup,[20] all quasiguided modes can be excited (see Figs. 3 and 4), and the observed extinction spectra at normal incidence are well reproduced.

In conclusion, using our on-shell layer-multiple-scattering method, we were able to reproduce the observed extinction coefficient of a dielectric waveguide coated with a periodic monolayer of gold nanoparticles, and investigate, starting from first principles, the coupling mechanism between waveguide and particle plasmon modes.

[1] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).
[2] S. Nie and S.R. Emory, Science **275**, 1102 (1997).
[3] N. Félidj, J. Aubard, G. Lévi, J.R. Krenn, A. Hohenau, G. Schider, A. Leitner, and F.R. Aussenegg, Appl. Phys. Lett. **82**, 3095 (2003).
[4] D. Ricard, Ph. Roussignol, and Chr. Flytzanis, Opt. Lett. **10**, 511 (1985).
[5] J.W. Haus, N. Kalyaniwalla, R. Inguva, and C.M. Bowden, J. Appl. Phys. **65**, 1420 (1989).
[6] L. Novotny, R.X. Bian, and X.S. Xie, Phys. Rev. Lett. **79**, 645 (1997).
[7] C.G. Granqvist and V. Wittwer, Sol. Energy Mater. Sol. Cells **54**, 39 (1998).
[8] R. Joerger, R. Gampp, A. Heinzel, W. Graf, M. Köhl, P. Gantenbein, and P. Oelhafen, Sol. Energy Mater. Sol. Cells **54**, 351 (1998).
[9] B. Lamprecht, G. Schider, R.T. Lechner, H. Ditlbacher, J.R. Krenn, A. Leitner, and F.R. Aussenegg, Phys. Rev. Lett. **84**, 4721 (2000).
[10] N. Félidj, J. Aubard, G. Lévi, J.R. Krenn, G. Schider, A. Leitner, and F.R. Aussenegg, Phys. Rev. B **66**, 245407 (2002).
[11] S. Linden, J. Kuhl, and H. Giessen, Phys. Rev. Lett. **86**, 4688 (2001).
[12] S. Linden, A. Christ, J. Kuhl, and H. Giessen, Appl. Phys. B: Lasers Opt. **73**, 311 (2001).
[13] A. Taleb, V. Russier, A. Courty, and M.P. Pileni, Phys. Rev. B **59**, 13 350 (1999).
[14] N. Pinna, M. Maillard, A. Courty, V. Russier, and M.P. Pileni, Phys. Rev. B **66**, 045415 (2002).
[15] N. Stefanou, V. Karathanos, and A. Modinos, J. Phys.: Condens. Matter **4**, 7389 (1992).
[16] N. Stefanou, V. Yannopapas, and A. Modinos, Comput. Phys. Commun. **113**, 49 (1998).
[17] N. Stefanou, V. Yannopapas, and A. Modinos, Comput. Phys. Commun. **132**, 189 (2000).
[18] A. Yariv and P. Yeh, *Optical Waves in Crystals: Propagation and Control of Laser Radiation* (Wiley, New York, 2003).
[19] N. Stefanou and A. Modinos, J. Phys.: Condens. Matter **3**, 8135 (1991).
[20] A. Christ, S.G. Tikhodeev, N.A. Gippius, J. Kuhl, and H. Giessen, Phys. Rev. Lett. **91**, 183901 (2003).