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Optical properties of two interacting gold nanoparticles

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Abstract

We study surface plasmon excitation in pairs of identical Au nanoparticles by optical transmission spectroscopy. The samples produced by electron beam lithography consist of 2D particle arrangements with varying interparticle distance. With decreasing interparticle distance the surface plasmon resonance shifts to longer wavelengths for a polarization direction parallel to the long particle pair axis whereas a blueshift is found for the orthogonal polarization. These experimental findings can be explained by a dipolar interaction mechanism.

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Since appropriate technologies are available for fabricating defined metal nanostructures much progress has been made in understanding the optical properties of metal nanosystems [1,2] and we can expect that this field will soon transit from fundamental understanding of its principles to useful applications [3–5].

In principle the collective optical properties of 2D metal nanoparticle (MNP) systems are determined by the properties of the individual particles as resonantly polarizable elements and by the electrodynamic interaction between them. In order

to separate the respective contributions, by an appropriate technology both parameters, particle resonance and particle interaction must be separately controlled experimentally. In previous work the primary interest was focussed on single-particle properties which are due to resonant excitations of the free-electron plasma confined in the particle, usually called particle plasmons [6]. When the particle is small (compared to the wavelength of the interacting light) the resonance properties depend mainly on the particle shape [1,3]. This could be shown by optical extinction spectroscopy of 2D particle arrays produced by electron beam lithography, a technique that provides a high degree of control of the 3D particle shape, the particle orientation and the arrangement pattern. The particle

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shapes could be approximated by three-axial ellipsoids with three principal polarizability axes corresponding to optical resonances which can be tuned in wavelength by varying the axes ratios [1]. In addition, *far-field* interaction effects were reported when the grating constant of the particle arrangement pattern exceeds the wavelength of the interacting light [7].

In this paper, we focus on the *near-field* interaction of two identical gold nanoparticles. When approaching two MNPs to sufficiently short distances an efficient electrodynamic interaction mechanism is expected. Recently Tamaru et al. [8] have investigated a pair of two touching spherical silver particles and found a strong anisotropy in the scattering spectra for different polarization directions. Maier et al. [9] investigated rows of identical gold nanoparticles with interparticle distances short enough to give essential coupling. In the corresponding spectra a strong redshift of the surface plasmon peak was observed for a polarization direction parallel to the row direction which they could explain by comparison of the experimental data to the calculated plasmon dispersion relation.

In order to extend the studies of Tamaru et al. [8] towards a large range of interparticle distances we fabricated and studied a series of 2D gratings of identical gold particles. The distance between two successive nanoparticle rows is varied stepwise, giving particle pairs with defined 1D interparticle distance. The samples are prepared by electron beam lithography, where the sample pattern is transferred by electron beam exposure to a polymethyl metacrylate (PMMA) film spin cast on an indium–tin oxide covered glass substrate. After the evaporation assisted deposition of gold and a lift-off process the final structures on the substrate are obtained. The details of the method are described elsewhere [2]. As by this technique only small sample areas can be covered by nanoparticles the spectroscopic measurements are performed by a spectrometer coupled to an optical microscope.

Fig. 1 shows three exemplary scanning electron microscope (SEM) images of gold particle pair samples (particle diameter 150 nm, particle height 17 nm) with varying 1D interparticle distances of

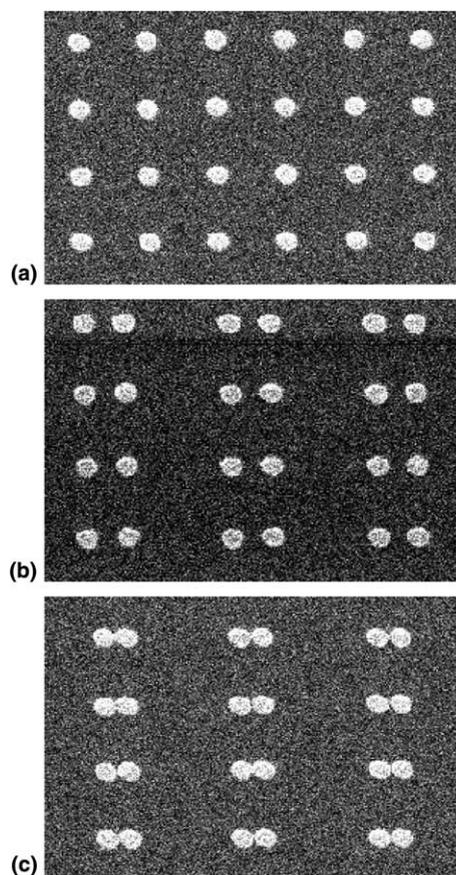


Fig. 1. SEM images of particle pair samples with varying interparticle distance (center-to-center) of (a) 450 nm, (b) 300 nm and (c) 150 nm. The particle diameter is 150 nm, the particle height is 17 nm.

450, 300 and 150 nm. Note that this distance is measured from the center of the particles. The corresponding extinction spectra (including data from a sample with an interparticle distance of 200 nm) are displayed in Fig. 2. In Fig. 2(a) the polarization direction of the incident light is parallel to the long particle pair axis, whereas in Fig. 2(b) it is orthogonal to it. We find a remarkable redshift of the surface plasmon extinction peak with decreasing interparticle distance for the parallel case and a smaller, but nevertheless distinct blueshift for the orthogonal polarization. For the maximum interparticle distance (450 nm) the arrangement pattern is a quadratic grating and thus the corresponding spectra are practically identical. The spectral peak

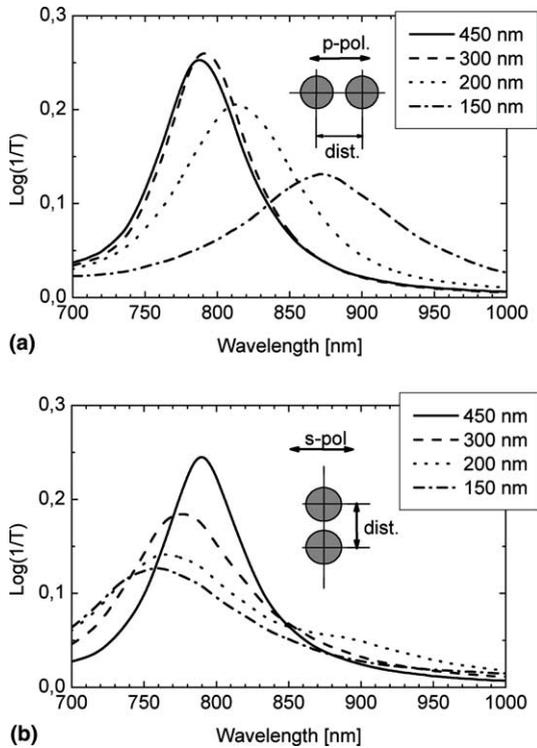


Fig. 2. Extinction ($= \log(1/\text{Transmission})$) spectra of a 2D array of the Au nanoparticle pairs with the interparticle center-to-center distances as the parameter. The orthogonal particle separation is kept constant, as can be seen in Fig. 1. The polarization direction of the exciting light is (a) parallel to the long particle pair axis and (b) orthogonal to it.

position as a function of particle distance is shown in Fig. 3 for both polarization directions for the complete set of seven particle arrays together with the results of a model calculation described below. We note, that we observe no abrupt change in the corresponding spectra, when the two particles touch each other. We rather find a continuous transition from the coupled particle spectrum to the spectrum of an elongated particle.

The observed interparticle-distance dependent behaviour of the resonance peak shift suggests a qualitative interpretation by a simple dipole–dipole interaction model which is well known from, e.g., molecular systems [10]. Due to the confinement of the plasma electrons in the nanoparticle the electric field of the irradiated light creates surface charges which feel repulsive forces. This

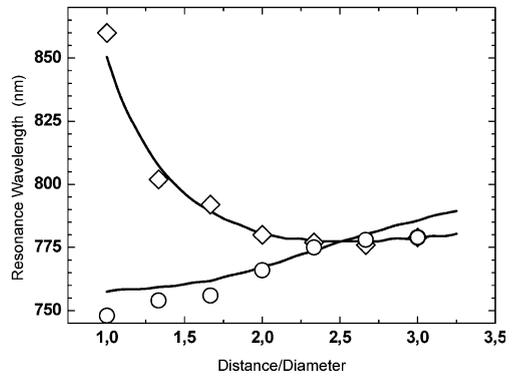


Fig. 3. Spectral position of the extinction maximum vs. interparticle distance for the full set of seven samples (four corresponding spectra shown in Fig. 2) for the polarization directions parallel (circles) and normal (rhombs) to the long particle pair axis. Full lines show the corresponding results of the dipole-pair model calculations.

matches the condition for the system to become resonant. However, when another particle is nearby, upon polarization additional forces act on both particles as sketched in Fig. 4. First, if the driving field is parallel to the long particle pair axis this effect results in a weakening of the repulsive forces for the surface charges. The positive charge of the left particle in Fig. 4(b) faces the corresponding negative charge of the right particle. Due to the attractive forces between these two charge

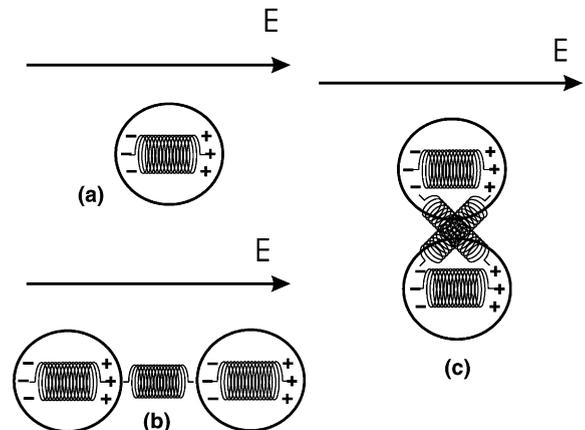


Fig. 4. Sketch to illustrate the electromagnetic interaction between closely spaced nanoparticles, (a) an isolated particle, (b) a pair of close particles with the polarization of the exciting field parallel to the long particle pair axis and (c) orthogonal to the long particle pair axis.

distributions of the different particles the repulsive forces within each particle are weakened, leading to a correspondingly lower resonance frequency. In contrast, when the driving field is normal to the long particle pair axis the charge distributions of both particles act cooperatively to enhance the repulsive action in both particles, thus increasing the resonance frequency.

For quantitative modelling the 2D particle arrangement in our experiment suggests the application of a retarded local field model, which considers the interaction of each dipole with all neighbour dipoles. However, for our specific particle arrangement the dominating interaction mechanism can be considered by a simpler particle-pair model for the following reasons. By reducing the grating constant in the quadratic 2D pattern and looking for the onset of significant spectral changes a minimum distance of about 450 nm is found, where the near-field interaction between particles is still negligible. On the other hand this distance is short enough to prevent far-field effects [7]. Starting with a quadratic 2D particle arrangement (grating constant = 450 nm) a shift of every second particle row reduces only the distance of each particle to its pair partner, whereas the distance to the other neighbours remains constant or increases (see Fig. 1). This ensures that only the interaction with the pair partner is important.

Formally, in the used dipole pair model the electric field at the position of one dipole is given by the sum of the irradiated field and the dipole field of the pair partner. This principle is outlined in several similar cases, e.g., for calculating the dispersion relation in particle chains [9,11]. It is important to mention that in order to correctly describe the dipolar near field, the unabbreviated expressions of the dipolar field had to be used for both polarization directions.

The dipole parameters used in the coupled particle calculations were obtained as follows: the single-particle polarizability was found by fitting modelled transmission spectra to experimental ones which were taken at the maximum particle separation of 450 nm. For this the particle was modelled as an oblate rotational ellipsoid within the electrostatic approximation [6] with the rotation axis normal to the substrate plane. The axes

aspect ratio was determined from the real particle diameter and the particle height. The dielectric function of the particle metal (gold) was taken from the literature [12]. The only fitting parameter to obtain the correct spectral resonance position was the dielectric constant of the medium surrounding the particles which must be a weighted average of the dielectric constant of the substrate glass and the air. The so obtained single-particle polarizability was used as input value for the dipole-pair model.

In Fig. 3 the spectral peak position as a function of particle distance is shown for both polarization directions for a complete set of seven particle arrays together with the theoretical curve resulting from the dipole-pair model. We find good agreement between experiment and theory. The obvious deviations at larger distances can be assigned to the more symmetric case in the experiment. In the calculations only pairs are considered instead of the whole 2D array. Thus a small difference in the resonance positions of the distinct polarizations can be seen for the maximum particle distance, which, due to the 2D symmetry of our samples (see Fig. 1(a)) is not observed in the experiment. This difference in the model results becomes smaller with increasing distance, oscillates in sign due to retardation effects and is damped out at infinite distance. On the other hand, this small difference can be used as an estimate for the error introduced by the simpler dipole-pair model. Within this small error we think, that the theoretical curves strongly suggest the validity of our dipole-pair model especially at the shortest distances.

Direct quantitative comparison of our results with other work in this field is problematic as, to our knowledge, there exist up to now only examples for spherical particles. Nevertheless, concerning the distance dependence of the resonance wavelength our findings agree qualitatively well with the theoretical predictions of Ruppin [13] for in-line and orthogonal polarization, respectively. Experimental results by Tamaru et al. [8] are also obtained with spherical particles but only for the case where the pair partners are touching. In qualitative agreement with us they find a strong redshift for the polarization parallel to the in-line and a moderate blueshift for the orthogonal case.

Due to the different particle shapes and due to the different particle materials the single-particle resonances in Tamaru's and our case are different (approx. 520 and 780 nm, respectively) so we compared the relative shift in the resonance photon energy. Tamaru's results give a factor 0.31 and 0.08, for in-line and orthogonal polarization, respectively, we obtain 0.09 and 0.04. The essentially lower values in our case are suggested to be mainly due to the lower strength of our dipoles due to the lower volume of the oblate particles compared with spheres of the same diameter.

The measured distance dependence in our results also suggest to corroborate the finding by Maier et al. [9] that coupling in particle chains is dominated by nearest-neighbour interaction.

In comparison with theoretical findings of Kottmann and Martin [14] on two interacting cylinders the qualitative spectral evolution of the redshifted plasmon peak fits well. However, a second peak reported in [14] is not found in our case. We assign this result to a quantitatively strong difference in retardation and in differently strong contribution of higher multipoles in both systems.

In summary, we measured the optical properties of gold nanoparticle pairs at short distances, showing a remarkable redshift for a polarization parallel to the long particle pair axis and a blueshift for the orthogonal polarization. This behaviour can be explained by a simple weakening/enhancing of the restoring forces for the plasma electrons due to the presence of the charge distribution of the neighbouring particle.

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