Coupling effects in tunable layers of metal nanoparticles

S. Mühlig[1], A. Cunningham[2], D. Cialla[3], K. Weber[3], T. Bürgi[2], C. Rockstuhl[1], and F. Lederer[1]

[1] Institute of Condensed Matter Theory and Solid State Optics, Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, D-07743 Jena, Germany
Fax: + 49 (0) 3641 947 177; email: stefan.muehlig@uni-jena.de
[2] Département de Chimie Physique, Université de Genève, Quai Ernest-Ansermet 30, CH-1211 Geneva, Switzerland
[3] Institute of Physical Chemistry, Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, Helmholtzweg 4, D-07743 Jena, Germany

Abstract

In this contribution we study stacked planar arrays of amorphously arranged metallic nanoparticles. These large-scale arrays are fabricated by bottom-up techniques based on electrostatic forces. The system exhibits a high degree of flexibility and allows for a tuning of the separation of consecutive layers at nanometer scale with ultra-high precision. This permits in-depth investigations of coupling effects in such systems. We also study asymmetric stacks where consecutive layers are made from nanoparticles of different materials. This break in symmetry entails the excitation of dark eigenmodes usually inaccessible in symmetric systems made of identical nanoparticles. Properties of these eigenmodes are disclosed experimentally as well as by simulations.

1. Introduction

Metallic nanoparticles (NPs), and in particular their optical properties, have attracted a long-standing interest in the fields of metamaterials (MMs) and plasmonics. The illumination of NPs can drive the free carriers of the metal into resonance at a given frequency. This effect is known as localized plasmon polariton resonance (LPPR). The scattered field at the LPPR can be associated with that of an electric dipole if the NPs are not too large (a rough estimation suggests that their diameters should be smaller than 50 nm). Hence, the coupling of two or more NPs can be understood in a simple dipole-dipole interaction picture. Obviously, two types of eigenmodes can be observed if solely two NPs are coupled [1]. The first type is related to an in-phase oscillation of both electric dipoles and called *bright* eigenmode. The resulting scattering response of the coupled NPs is dominated by an electric dipole contribution and the excited eigenmode can radiate into the far field. The second type is related to a 180° out-of-phase oscillation of both electric dipoles. Since the scattering response of the coupled NPs of such eigenmode can be related to higher-order multipole moments, like magnetic dipoles or electric quadrupoles, this eigenmode radiates only marginally into the far-field and is hence usually termed *dark*.

Both eigenmodes enable different applications. In some cases the excitation of bright eigenmodes in coupled NPs results in strongly enhanced electrical near fields. This field enhancement can be exploited, e.g., for surface-enhanced Raman spectroscopy or to enhance the conversion efficiency of solar cells. On the contrary, in some cases dark eigenmodes in coupled NPs can be associated with an excitation of a magnetic dipole in the structure. A material made of unit-cells offering a magnetic dipole should exhibit a response to an incident magnetic field which can be related under some restrictions to a dispersive effective permeability [2]. These artificial materials, or MMs, are at the heart of many applications in the field of transformation optics which includes most notably cloaking devices.

In this contribution a fabricated MM consisting of two planar arrays of metallic NPs is investigated. The coupling strength between both arrays can be controlled by adjusting their relative distance. By choosing silver and gold as two different NP materials for both layers, the symmetry of the entire sys-

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tem can furthermore be broken due to the different LSPR sustained by spheres from different materials. This allows for the excitation of dark eigenmodes in the MMs.

2. Results

The structure under investigation consists of two planar arrays of spherical metallic NPs. They are separated by a discrete number of polymer layers. The first array consists of gold NPs (radius 10 nm) and the second one of silver NPs (radius 20 nm). The gold NPs are attached at the substrate by electrostatic forces. Therefore, the silica substrate is positively charged contrary to the negatively charged gold NPs. The resulting structure can be seen in Fig. 1 (a). On top of the gold NP array several polyelectrolyte layers (PE-layers) are deposited which are oppositely charged. The optical response of the PE layers is dielectric and it can be characterized by a non-dispersive permittivity of 2.2 in the visible [3]. The top layer consists of a planar array of negatively charged silver NPs, as shown in Fig. 1 (b). Since the thickness of one PE layer is about 1 nm, the distance and therewith the coupling between both metallic NP arrays can be precisely controlled [3]. It can be seen in Fig. 1 (a), (b) that the metal NPs in the respective array are well-separated for gold and sufficiently dispersed for silver. The measured extinction spectra of the individual metal NP arrays are presented in Fig. 1 (c). The simulated extinction of single gold and silver spheres reveals that the optical response of each NP array is dominated by the excitation of the LSPR in individual NPs. Only the silver NP array exhibits a second redshifted resonance in the measured extinction spectrum due to the larger size inhomogeneity of the fabricated NPs [c.f. Fig 1 (b)].

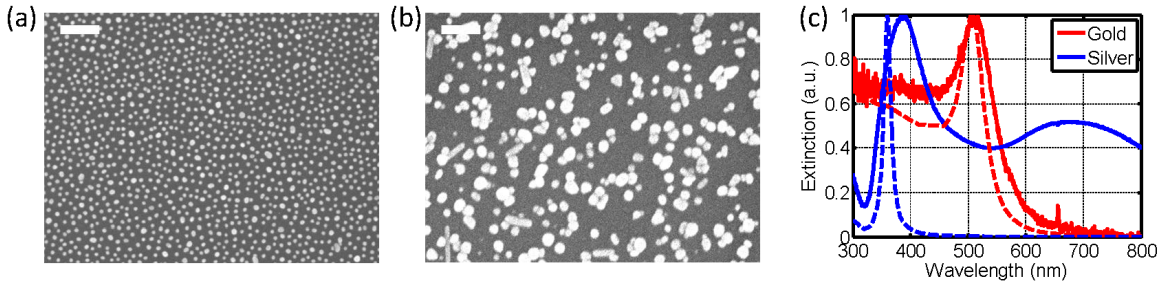

Figure 1 Scanning electron micrograph of an array of gold (a) and silver NPs (b). The scale bar corresponds to 200 nm. (c) Measured (solid curves) and simulated (dashed curves) extinction spectra of the arrays shown in (a) and (b).

A sketch of the experimental situation of two coupled metallic NP arrays is presented in Fig. 2 (a). The measured extinction spectra for various numbers of PE layers separating the gold and silver NP arrays can be seen in Fig. 2 (b). Two dominating resonances are observed. The position of the long-wavelength resonance strongly depends on the separation of the NP arrays whereas the position of the short-wavelength resonance is not affected. By contrast, the strength of the short-wavelength resonance strongly depends on the separation. For an increasing number of PE layers (yielding a decreased coupling of the NP arrays) the amplitude of the extinction at resonance is increased. This is a clear signature for the excitation of a dark eigenmode. This eigenmode does not radiate into the far-field. Therefore, decreasing the coupling (which lowers the radiative losses of the dark eigenmode) should cause stronger and sharper resonances.

To confirm this hypothesis, the optical response from nominally identical structures is simulated. Since it was revealed [Fig. 1 (c)] that the scattering response of the individual metallic NP arrays is dominated by the LSPR of the NPs, we considered only the coupling between one silver and one gold NP in the simulations [Fig. 2 (d)]. The incident electric field is polarized along a diagonal in the *x*-*y* plane as sketched in Fig. 2 (f). The extinction spectra as calculated with an extended Mie theory are shown in Fig. 2 (c). They provide results in excellent agreement with the experiments. The long-wavelength resonance position as well as the amplitude of the short-wavelength resonance depends sensitively on the number of PE layers. Naturally, the full-widths-at-half-maxima in the simulations

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are much smaller since the amorphous arrangement of metallic NPs and their marginal size dispersion are not considered.

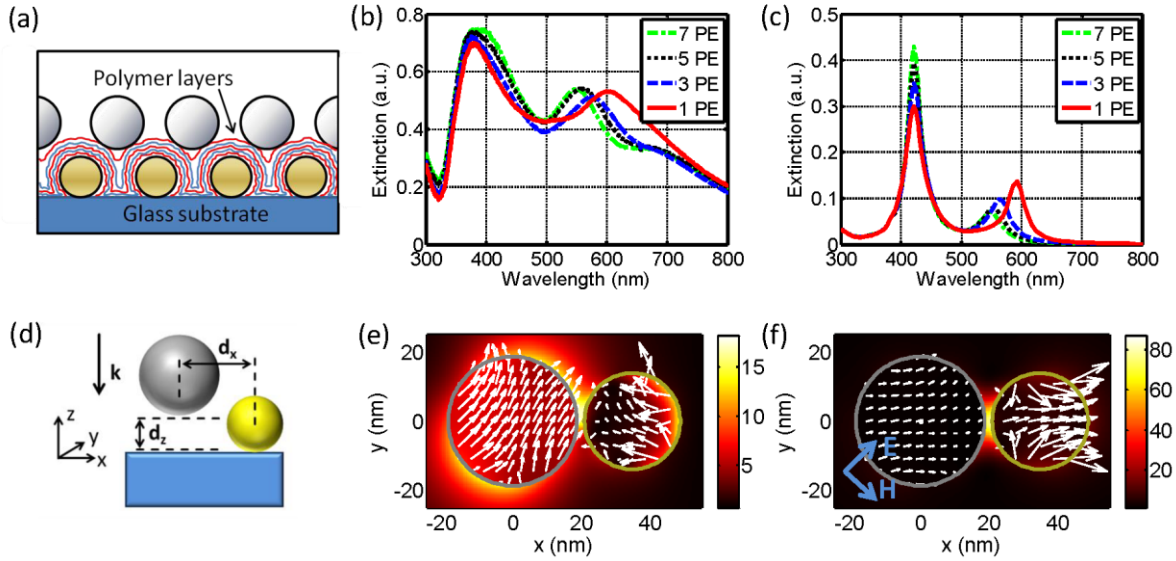

Figure 2 (a) Schematic of the experimental situation. (b) Measured and (c) simulated extinction for a varying number of PE layers separating the gold and the silver NP array. (d) Geometry considered in simulations. Solely the coupling of one gold NP and one silver NP from each NP array is considered. The separation of both NPs is chosen according to the thickness of the PE layers [3]. Field distributions for one separating PE layer for the short- (e) as well as the long-wavelength resonance (f). The ratio of the electric field strength to that of the incident field is shown (colormap) together with the vectorial character of the internal fields (white arrows). The blue arrows in (f) show the polarization of the incident plane wave.

The simulated field distributions of both resonance clearly underline the previously given argumentation. For the long-wavelength resonance the internal fields are oscillating in phase parallel to the connecting line of the NPs. The huge field enhancement of this bright eigenmode can be observed, too. On the contrary, the internal fields for the short-wavelength resonance are out-of-phase. A detailed investigation reveals that they are oscillating out-of-phase along the *x*-axis and in-phase along the *y*-axis. Nevertheless, the excited eigenmode can be clearly identified as a dark one.

4. Conclusions

A fabricated MM consisting of two strongly coupled planar arrays of metallic NPs has been investigated. The bottom-up fabrication technique relying on electrostatic forces allows the fabrication of large-scale arrays with flexible coupling strengths. Considering one silver and one gold NP array, the excitation of bright as well as dark eigenmodes are revealed that strongly depend on the coupling of the NP arrays. In our contribution we will discuss the applications of these large-scale MMs to surface-enhanced Raman (SERS) scattering by presenting experiments and simulations. Especially the contributions of bright and dark eigenmodes to SERS will be discussed.

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