Exciting Bright and Dark Eigenmodes in Strongly Coupled Asymmetric Metallic Nanoparticle Arrays

Alastair Cunningham,† Stefan Mühlig,‡ Carsten Rockstuhl,§ and Thomas Bürgi*†

†Département de Chimie Physique, Université de Genève, Quai Ernest-Ansermet 30, CH-1211 Genève 4, Switzerland
‡Institute of Condensed Matter Theory and Solid State Optics, Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany
§Supporting Information

ABSTRACT: The strong coupling between planar arrays of gold and silver nanoparticles mediated by a near-field interaction is investigated both theoretically and experimentally to provide an in-depth study of symmetry breaking in complex nanoparticle structures. The asymmetric composition allows to probe for bright and dark eigenmodes, in accordance with plasmon hybridization theory. The strong coupling could only be observed by separating the layers by a nanometric distance with monolayers of suitably chosen polymers. The bottom-up assembly of the nanoparticles as well as the stratified structures themselves gives rise to an extremely flexible system that, moreover, allows the facile variation of a number of important material parameters as well as the preparation of samples on large scales. This flexibility was used to modify the coupling distance between arrays, showing that both the positions and relative intensities of the resonances observed can be tuned with a high degree of precision. Our work renders research in the field of “plasmonic molecules” mature to the extent that it could be incorporated into functional optical devices.

INTRODUCTION

Metallic nanoparticles, and more specifically the optical properties that they possess, have been used by man for centuries.1 While theoretical explanations for the strong colors exhibited by these particles have existed since the early 1900s, when Gustav Mie solved Maxwell’s equations for the interaction of light with a spherical nanoparticle,2 it is only in recent times that a fuller understanding of the origins of these properties has evolved. Localized surface plasmon polariton resonances (LSPRs) can be excited in metallic nanoparticles when the incident light drives the free electrons of the metal into resonance. In particular, the coupling of LSPRs stemming from different nanoparticles enables the observation of exciting effects at the nanometre scale. A major advancement in this field was made through the introduction of plasmon hybridization theory by Nordlander et al.3 in 2003. This theory is analogous to that used in molecular orbital theory and provides both a quantitative and qualitative means of describing the coupling between the LSPRs of individual metallic nanostructures. In the simplest case it can be applied to two spherical nanoparticles of the same composition,4 however, it can also be used to describe more complicated structures such as compositionally asymmetric dimers,4 thin metallic films,5 systems of metallic nanoshells,6 nanorods,6 and nanostars.7

The excitation of LSPRs in metallic particles with dimensions much smaller than the exciting wavelength yields a scattered electromagnetic field which can be fully described by an electric dipole oscillation. Hybridization theory predicts two distinct classes of eigenmodes for a structure of two strongly coupled metallic spheres, i.e., a dimer. The first is associated with an in-phase oscillation of the electric dipole in both spheres and is therefore termed a “bright” eigenmode since it can radiate into the far field. The second class requires a 180° out-of-phase oscillation of the electric dipoles of both spheres. These eigenmodes are termed “dark” since they cannot radiate into the far field and the optical response is dominated by absorption.

The excitation of bright eigenmodes in coupled metallic nanoparticles can result in huge enhancements of the electric field in narrow spatial domains which can, in turn, be exploited in manifold applications. For example, it can be applied to surface-enhanced Raman spectroscopy8 or to enhance the absorption of light in solar cells.9 Furthermore, due to the highly enhanced fields, the resonance frequency of these bright eigenmodes is very sensitive to the environment, allowing for their use in sensor applications.10 In addition, the large spatial confinement of these enhanced fields can be associated with strongly enhanced local higher order multipole moments which can excite free-space forbidden transitions in molecules.11

One of the more recent applications of plasmonic nanostructures can be found in the field of metamaterials where they are increasingly being used to facilitate the downscaling of structures that exhibit properties such as a dispersive permeability12,13 or permittivity that are exploited for...
cloaking applications or negative refractive index materials in the microwave and infrared regions. Such downscaling is necessary if these properties are going to be routinely observed and utilized at optical frequencies. The dark eigenmodes described above play an important role in this field since the out of phase oscillation of electric dipoles can be related in some cases to a magnetic dipole moment which is the key component in many predicted applications of metamaterials.

One way to excite dark eigenmodes is to use structures that exhibit a considerable amount of asymmetry. Until now, the study of metallic nanoparticles which show asymmetry in either size, shape, or composition has been limited to discussions, both theoretical and experimental, relating to interactions between low numbers of isolated particles. Brown et al. demonstrated Fano resonances and optical nanodiode effects while the observation of both bright and dark eigenmodes along with coupling between plasmonic modes and interband transitions was seen by Sheikholeslami et al. Lithographically produced dimers of Au and Ag nanodisks have also recently been shown to act as nanoantennas for directional color routing, which opens the door to a variety of different applications. Other work concerning heterodimers has shown the possibility of using such structures as nanolenses.

Contrary to the research performed thus far we investigate here a structure composed of large scale arrays of strongly coupled gold and silver nanoparticles (AuNPs and AgNPs). The required asymmetry of the system is induced due to the different LSPR frequencies of AgNPs and AuNPs, and the excitation of dark eigenmodes under plane wave illumination is observed.

In contrast to most of the investigations in the literature considering only a small number of NPs, here large scale arrays of Au and AgNPs separated by integral numbers of dielectric layers, i.e., heterodimers on the cm² scale, are examined. A high degree of control over nanoparticle array separation, which is challenging in itself, is achieved through the use of the already established technique of layer-by-layer buildup of polyelectrolyte (PE) layers, making the structure tunable over a wide parameter range. The lower limit of particle array separation is only governed by the thickness of a single polymer coating, which is on the nanometer scale. This allows precise control over the distance between the adjacent arrays of Au and AgNPs and is the key in observing phenomena that can only be explained by considering the particles in the two layers as strongly coupled. No upper limits exist in terms of the number of either nanoparticle or polymer layers that can be deposited, allowing optical properties to be further tuned as required. Recently, these large scale arrays of metallic NPs have been demonstrated as suitable devices providing lasing action if gain is introduced in the separating polymer layers.

Using novel bottom-up fabrication methods to construct such plasmonic structures affords a number of advantages over more traditional lithographic methods where both time and cost would prove prohibitive for large scale applications. Although no long-range order is observed between the particles deposited within a single layer, this is largely outweighed by the large degree of flexibility that can be achieved and the short-range order governed by the thickness of the PE layers. A high degree of control over a number of material parameters such as particle composition, size, and separation both in and out of the substrate plane exists. In addition, the simplicity and robustness of the approach, coupled with the large-scale of the substrates that can be produced, opens up the possibility of integrating such structures into optical devices and components.

Both experimental and theoretical approaches were used in this work to study in detail the interactions that occur between arrays of compositionally asymmetric metallic nanoparticles. In particular, the excitation of bright and dark eigenmodes in these structures is investigated in detail.

### EXPERIMENTAL METHODS

#### Nanoparticle Growth

All chemicals were purchased from Sigma-Aldrich. All solutions were prepared using Milli-Q water (18.2 MΩ·cm).

AuNPs were prepared according to the well-known Turkevich method. Briefly, 600 mL of a 0.25 mM solution of HAuCl₄ under constant magnetic stirring was heated to 100 °C in an oil bath. The gold ions were then reduced through the addition of 15 mL of a 0.03 M sodium citrate solution. A series of color changes were observed before a deep-red solution was produced and after 15 min the reaction vessel was removed from the oil bath and allowed to cool to room temperature.

AgNPs were synthesized in an analogous way to that used in the preparation of the AuNPs, also known as the Lee–Meisel method, simply replacing the gold salt with a silver one. In brief, 25 mL of an aqueous solution of AgNO₃ (1 mM) was heated to boiling, and 1 mL of an aqueous solution of sodium citrate (0.039 M) was added. The solution was left under continuous magnetic stirring for a period of 1 h before being removed from the heat.

#### Substrate and Film Preparation

Silicon and glass substrates, used for electron microscopy and spectral measurements, respectively, were prepared according to the same method. They were first rinsed with water and ethanol before being dried under a stream of compressed air. The surfaces were then cleaned and hydroxylated through immersion in a piranha solution (3:1 mixture of concentrated sulfuric acid to 30% hydrogen peroxide) for 30 min. Piranha solution is strongly acidic and highly oxidizing and should be handled with caution. The substrates were next rinsed with copious amounts of water and again dried under a stream of compressed air. Subsequently, the surface chemistry was altered through the functionalization with an organosilane. Here, the substrates were immersed in a 5% (v/v) solution of N-[3-(trimethoxysilyl)propyl]ethylenediamine in ethanol for 30 min before being rinsed with water, dried, and set in an oven at 120 °C for a further 30 min.

The positive charge of the terminal amine group on the functionalized substrate allows the deposition of AuNPs or a negatively charged PE layer through purely electrostatic interactions. Similarly, positively charged PE layers can be deposited on either AuNPs or negatively charged PE layers. Single layers of AuNPs were deposited by immersing them in a solution of AuNPs for a period of 4 h. PE layers were deposited from 5 mg/mL solutions of poly(allylamine hydrochloride) or poly(sodium 4-styrenesulfonate) in a 0.1 M solution of sodium chloride in water. PE layers were deposited for 1 min before being rinsed with water and dried under a stream of compressed air. The electrostatic nature of the fabrication process allows for the cyclic buildup of multiple AuNP/AuNP arrays and PE layers.

#### Simulations

The Turkevich and Lee–Meisel methods result in nearly spherical Au and AgNPs, respectively. The measured spectra can therefore be simulated by relying on analytical solutions of Maxwell’s equations for a single sphere.
better known as Mie theory. Here, all the fields, namely the incident, the scattered, and the internal field of the sphere, are expanded into infinite series of eigenfunctions of the Helmholtz equation in spherical coordinates with unknown complex expansion coefficients. These coefficients can be determined by considering boundary conditions at the surface of the sphere. Taking into account transformation rules for these eigenfunctions, the framework of Mie theory can be expanded to handle an arbitrary arrangement of spherical particles. This technique has been used to provide theoretical insights into the properties of dimers and to compare all measured spectra to simulations. In these simulations the material parameters of gold and silver were taken from the literature. Five orders (regarding the series expansions of Mie theory) were taken into account to simulate the optical far-field properties of the dimers, such as the extinction cross sections. This assumption accounts to simulate the optical far-field properties of the dimers, such as the extinction cross sections. This assumption of truncating the series expansion is verified, since we observed no changes in the spectra when increasing the expansion order. All structures were illuminated by a linearly polarized plane wave as described further below. The surrounding was assumed to be a standard dielectric choosing a permittivity corresponding to that of air or the PE layers depending on the experimental situation, as detailed below.

## RESULTS AND DISCUSSION

As outlined in the Introduction, hybridization theory can be applied to identify the possible eigenmodes of two strongly coupled metallic nanoparticles. Figure 1a shows the eigenmodes in a hybridization diagram for two identical metallic spheres that are small enough to be treated as an electrical dipole. Four different eigenmodes are possible. Two of them (namely the $\sigma$ and $\pi^*$) describe an in-phase oscillation of the electric dipoles and are therefore also known as symmetric or bright eigenmodes. The remaining two ($\sigma^*$ and $\pi$) are characterized by an out-of-phase oscillation of the electric dipoles and are therefore referred to as asymmetric or dark eigenmodes. Conversely, heterodimers, such as that shown in Figure 1b, display a net dipole moment in each of the four hybridized eigenmodes. Because of the broken symmetry of the system, all modes can therefore be excited at normal incidence unlike in the previous case. To observe the excitation of dark eigenmodes under plane wave illumination, our structure induces the necessary asymmetry by combining arrays of AuNPs ($\sim$10 nm radius) and AgNPs ($\sim$20 nm radius). In the simulations the structures are considered as individual dimers of the same composition.

Previous work examining the coupling present between two arrays of AuNPs has shown that plasmon hybridization theory can also be applied to such large scale systems. In other words, the entire optical response could be described by a dimer consisting of one NP from each array. The separation between particles within an array was shown to be considerably larger than that between distinct arrays, thus precluding any lateral interactions and meaning that all coupling observed is between arrays that are separated by a distinct number of PE layers. This large separation of NPs in the array was observed in this study only for one array, as can be seen in the SEM images of single arrays of the particles shown in Figure 2. While the AuNPs are well separated and showed no interparticle coupling, the AgNPs tend to coat the substrate in a less homogeneous fashion, with both isolated particles and small aggregates of particles being observed. In addition, as can also be readily observed in Figure 2, AgNPs produced by the Lee–Meisel method exhibit a wider range of particle sizes and shapes when compared to the Turkevich method used for AuNPs, thus making the spectral interpretation of the ensembles more challenging. The AuNPs were calculated to have a mean diameter of 18.3 nm with a sample standard deviation of 2.5 nm compared to a mean diameter of 42.6 nm and a sample standard deviation of 12.6 nm for the AgNPs. While the values for the AgNPs were more difficult to gauge due to the aggregation observed these figures give a good idea of the degree of monodispersity and size control achievable with the two fabrication methods. The variation in particle size, particularly in the case of the AgNPs, causes slight peak broadening in the experimentally measured spectra; however, as will be shown, the dominating resonances of the system can be fully and accurately described by considering a dimer consisting of one AuNP and one AgNP from each array. Therefore, the identification of peaks that correspond uniquely to the interaction between the distinct arrays of Au and Ag NPs and the detection of dark modes is possible for the structure under investigation. The corresponding spectra for the single layers of AuNPs and AgNPs along with the simulated spectra of single nanospheres of each metal can be seen in Figure 3. In the simulations isolated spheres were considered, whereas the measurements were performed on single layers of Au and AgNPs with a filling fraction of 27 and 23%, respectively. The morphological differences between the two arrays have a large effect on their optical properties. A single peak, at the same frequency as an individual particle, is observed for the well...

---

Figure 1. Plasmon hybridization diagrams showing the coupling between, and the dipole moments on, (a) two gold and (b) silver and gold nanosphere dimers.

Figure 2. SEM image showing an array of gold nanoparticles ($\sim$18 nm diameter) and an array of silver nanoparticles ($\sim$43 nm diameter) separated by seven polyelectrolyte layers. Because of the difference in height, the gold nanoparticles, which are underneath, appear slightly out of focus.
The Journal of Physical Chemistry C

separated AuNPs while two peaks, that of the isolated particles and that of the aggregates, are discernible in the case of the AgNPs. The small aggregates, on average comprising 3–4 particles, result in a significantly red-shifted peak that, in addition, is somewhat broadened owing to the variety of both the number of the particles in the aggregates and the size of the particles that form them. Additionally, in the case of the AgNPs, a slight discrepancy exists between the simulated and measured spectra. This is assumed to be as a result of the polydispersity of size and shape present in the sample of AgNPs used to fabricate the samples compared to the perfectly spherical particle of a well-defined size considered in the simulations.

A sketch of the principal structure under study in this work can be seen in Figure 4a. It consists of two strongly coupled Ag NP. This is fully reflected in the simulations. The considered geometry there corresponds exactly to the scenario shown in Figure 4b.

Figure 5a depicts the measured extinction spectra for Au and AgNP arrays separated by a range of different numbers of PE layers. Two resonances with distinct spectral behavior are observed. The resonance at longer wavelengths is shifted to the red for a decreasing number of separating PE layers. Furthermore, the peak amplitude of this resonance stays nearly constant. Conversely, the resonance at shorter wavelengths offers a nearly constant resonance position whereas the peak amplitude depends on the number of PE layers. Increasing the number of PE layers, thus decreasing the coupling between particles, results in an enhancement of the peak amplitude. There is an additional resonance, which can be identified just below 700 nm, present in the experimental spectra which results from the small aggregates in the AgNP array (see Figure 3). This band, however, does not contribute to one of the four hybridized resonances, shown in Figure 1b, that result from the symmetry-breaking coupling between the two well-defined Au and Ag NP arrays and is therefore neglected in the following discussions.

To provide a physical understanding of the observed resonances, simulations are performed considering an arrangement of two spheres, the geometrical configuration of which is shown in Figure 4b. One sphere is made of silver with a radius of 20 nm while the other is made of gold with a radius of 14 nm. The radius of the gold sphere was chosen to be marginally larger when compared with the size of spheres as used in the experiment to obtain a better fit of the experimental spectra. The separations of the spheres in the \( \text{xy} \)-plane, namely \( d_x \) and \( d_y \), are defined as follows: \( d_x = r_{Ag} + r_{Au} + N_{PE}d_{PE} \) and \( d_y = N_{PE}d_{PE} \) where \( N_{PE} \) is the number of PE layers and \( d_{PE} \) their thickness (which was assumed to be 0.9 nm).\(^{22}\) The embedding material was chosen to be a standard dielectric with a permittivity of 2.2 corresponding to that of the PE layers.\(^{22}\) The simulated dimer should mimic the experimental situation in such a way that it considers only the coupling between one gold sphere from the AuNP array and one silver sphere from the AgNP array. Such an approximation seems suitable since, the small aggregates in the AgNP array aside, the lateral separation between the spheres is significantly larger than the separation of the individual NP arrays. The polarization of the incident plane wave in simulations is parallel to a diagonal in the \( \text{xy} \)-plane, so \( \mathbf{E} = E_x\mathbf{e}_x + E_y\mathbf{e}_y \). This accounts for the random arrangement of the dimers in the experiments; for a linearly polarized incident field all dimer orientations appear in the fabricated samples. In a first-order approximation this is identical to a simulation where all possible linear polarizations of the incident field are considered for one specific dimer orientation. The results of the numerical simulations are shown in Figure 5b. The qualitative behavior of the two resonances as observed in the experiments is entirely reproduced in the simulations. Both the red-shift of the longer wavelength resonance and the peak amplitude dependence of the shorter wavelength resonance show excellent agreement with the experimental results. Only a minor discrepancy between the full width at half-maximum of the resonances seen in the simulations and the experiments is observed. However, this is not surprising as the simulations only consider a single heterodimer with a fixed nominal size. This is in contrast to the amorphous arrangement that exists in the actual structures where the size of both NPs possesses a certain dispersion.
Nonetheless, as all major spectral features can be predicted by simulation, it is possible to conclude that the approximation of simulating the complex layered structure by a single dimer is justified.

In the following the observed resonances are studied in detail, and they are correlated to a dark and a bright eigenmode of the structure. Figure 6a shows the resonance position of the long wavelength resonance as a function of the separating PE layers. A nearly perfect agreement between experiments and simulations is observed. In both cases the observed shift in resonance follows the expected exponential trend, converging toward the resonance position of an isolated AuNP for distances that preclude a possible near-field interaction. This shows that the near-field coupling, and therefore the extent of the spectral shifts observed, is strongly dependent on, and can be tuned simply by, controlling the interarray distance or in other words the number of PE layers. The remarkable dependence of the resonance position on the separation of the AuNPs and the AgNPs and the appearance of the resonance at longer wavelengths, when compared to the LSPRs of the single AuNP array, are also clear signatures of the excitation of the bright $\sigma$ eigenmode as was observed for two separated AuNP arrays. Moreover, the impressively huge shift of the resonance wavelength of a dimer structure made from entities with largely disparate resonance wavelengths is a clear indication of the extraordinary strong coupling. This has only been possible by relying on the PE layers that allow for well-defined separation of NPs at the nanometer scale. It should also be noted that no trace of conductive coupling in the dimer, which would have led to largely disparate resonance spectra, has been observed. Figure 6b shows the relative peak amplitude of the shorter wavelength resonance as a function of the separating PE layers. To be precise, from the amplitude of the scattering cross section at 422 nm for 3, 5, and 7 PE layers the amplitude of 1 PE layer is subtracted. Both simulations and experiments show an increasing peak amplitude for an increasing number of PE layers or, in other words, a reduced coupling of the spheres. One explanation of this trend could be the excitation of a dark eigenmode at this wavelength. If the particles are strongly coupled, the eigenmode cannot radiate into the far field, and therefore the amplitude of the extinction is suppressed. If the coupling is reduced, the excitation into the...

Figure 5. (a) Measured and (b) simulated extinction spectra for strongly coupled Au and AgNP layers for different numbers of separating polyelectrolyte layers.

Figure 6. Experimental results (red traces) and simulations (blue traces) are compared for the observed resonances of the extinction (see Figure 5). (a) The resonance wavelengths of the extinction of the symmetric eigenmode (appearing at longer wavelengths in Figure 5 as a function of the separating PE layers. (b) The peak amplitude of the asymmetric eigenmode (appearing at 422 nm in Figure 5) as a function of the separating PE layers relative to the peak amplitude for 1 PE layer. Note that from the amplitude of the scattering cross section at 422 nm for 3, 5, and 7 PE layers the amplitude of 1 PE layer is subtracted.
Illumination is in the shown include the center of the gold sphere. One PE layer has been chosen to separate the particles, as de...

The third arrow (at $x = 20$ nm) shows the polarization of the incident field at the respective time where the snapshot is taken. All $xy$ cross sections shown include the center of the gold sphere. One PE layer has been chosen to separate the particles, as defined in Figure 4b and in the text. Illumination is in the $z$-direction, i.e., normal to the plane shown.

Figure 7. Illustration of the asymmetric (a, c) and symmetric (b, d) eigenmodes for the dimer structure separated by one PE layer. (a) and (b) show the magnitude of the electric field (normalized to the incident field) for both resonances as well as the vectorial character of the internal fields. In other words, the lengths of the white arrows decode the magnitude of the internal field at this position and the direction shows the contribution of the $x$- and $y$-component of the internal field to its magnitude. (c) and (d) depict the excited electric dipoles at both resonances of the gold and the silver sphere as they contribute to the scattered field. These dipoles are sketched as blue arrows coinciding with the origin of the respective sphere. The third arrow (at $x = 20$ nm) shows the polarization of the incident field at the respective time where the snapshot is taken. All $xy$ cross sections shown include the center of the gold sphere. One PE layer has been chosen to separate the particles, as defined in Figure 4b and in the text. Illumination is in the $z$-direction, i.e., normal to the plane shown.

far field is increased and therefore the amplitude of the peak extinction should be enhanced. This is exactly what is observed in experiments and simulations. Additionally, from a material design perspective, the effect also introduces an additional layer of flexibility into the system, allowing for greater control in the fabrication of metallic nanoparticle coated substrates with particular extinction characteristics.

To facilitate a clear identification of the excited eigenmodes of the structure and to reveal their properties in terms of the hybridization scheme, shown in Figure 1, the simulated results of the heterodimer are exploited in the following. In Mie theory, one has direct access to all excited multipole moments of every sphere in a system of spheres that is illuminated by an incident field. The reason is that the scattered fields of all spheres involved are decomposed into the eigenfunctions of the Helmholtz equation, and this expansion is comparable to a multipole expansion in spherical coordinates. Therefore, the excited electric dipole moments (and their phase relation to each other) of the two spheres of the simulated heterodimer can be revealed directly from Mie theory. A detailed discussion can be found in refs 31 and 32. Sketches of these electric dipoles at the two resonance positions for one separating PE layer are shown in Figure 7c,d.

For the long wavelength resonance (Figure 7d) the in-phase oscillation of the electric dipoles is clearly observed which indicates the excitation of the bright $\sigma$ eigenmode. However, as shown in the animation in the Supporting Information, the excited electric dipoles are not strictly oscillating along the connection line of the spheres but are also rotating around the origin of the spheres. This is an effect of the polarization of the incident field which is parallel to a diagonal in the $xy$-plane. This excited eigenmode is dominated by an in-phase oscillation of both electric dipoles and is therefore a bright mode. In addition, as is well-known and studied for $\sigma$ eigenmodes of dimers, the electric field is largely enhanced in-between both spheres as can be seen in Figure 7b which shows the magnitude of the electric field and in addition the vectorial character of the internal electric fields of both spheres. In addition, the in-phase oscillation of the $\sigma$ eigenmode can also be observed. The short wavelength resonance (Figure 7c) offers a completely different picture of the excited dipoles in the silver and the gold sphere. Their oscillation can be understood as an interference of the $\sigma^*$ and $\pi^*$ eigenmodes from Figure 1. Here, the excited dipoles in Figure 7c are oscillating $180^\circ$ out of phase along the connection line of the spheres (the $x$-direction) and in-phase parallel to the connection line (the $y$-direction). This interference is again an effect of the chosen polarization of the incident field which allows both types of eigenmodes to be excited at the same time. As such, in the experiments where the dimers exhibit a random orientation, both eigenmodes ($\sigma^*$ and $\pi^*$) should interfere for every heterodimer at this wavelength. The overall behavior of the eigenmode excited at shorter wavelengths offers an out-of-phase oscillation of the electric dipoles of the involved spheres and is therefore identified as a dark eigenmode. Furthermore, in Figure 7a, which shows the magnitude of the electric field and the vectorial internal fields, the asymmetric character of this eigenmode is obvious, as can be seen in the animation in the Supporting Information. The explanation, given previously, of the increasing peak amplitude in extinction (see Figure 6b) for
an increasing number of PE layers is fully in line with these investigations.

**CONCLUSIONS**

To sum up, we have demonstrated a bottom-up method of fabricating layered arrays of compositionally asymmetric metallic nanoparticles. The symmetry breaking in the structure allowed for the observation of bright as well as dark eigenmodes under plane wave incidence, which, to the best of our knowledge, has never been achieved at such a large scale, with other works concentrating principally on single nanoparticle dimers. The fabrication approach described holds many advantages over other techniques used to produce arrays of plasmonic structures in that large area substrates can be coated in a facile, quick, and comparatively cheap manner. The invariance of important material parameters such as particle composition and size as well as interparticle and interarray separation. This in turn results in an ability to tune the optical properties of the samples, in terms of both spectral positions of the LSPR peaks and their overall intensities. In addition, the layer-by-layer assembly process also gives rise to the possibility of building up samples into the third dimension, one of the key challenges currently facing researchers in the metamaterials community. Furthermore, we have demonstrated that the optical response of such a highly amorphous and complex structure can be described by a reduction of complexity for numerical simulations in such a way that only the strongest coupled elements in the near field are taken into account. In this very precise case the entire optical response could be simulated by a simple heterodimer.

**ASSOCIATED CONTENT**

• Supporting Information
Animations showing time evolution of excited electric dipoles.
This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*Fax +41(0)22 379 61 03; Tel +41(0)22 379 65 52; e-mail thomas.buergi@unige.ch.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Financial support from the European Union FP7 project NANOGOLD and the German Federal Ministry of Education and Research (PhoNa) is acknowledged.

**REFERENCES**