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Optimizing Gold Nanoparticle Cluster Configurations ($n \leq 7$) for Array Applications

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Abstract

Nanoparticle cluster arrays (NCAs) are novel electromagnetic materials whose properties depend on the size and shape of the constituent nanoparticle clusters. A rational design of NCAs with defined optical properties requires a thorough understanding of the geometry dependent optical response of the building blocks. Herein, we systematically investigate the near- and far-field responses of clusters of closely packed 60 nm gold nanoparticles ($n \leq 7$) as a function of size and cluster geometry through a combination of experimental spectroscopy and generalized Mie Theory calculations. From all of the investigated cluster configurations, nanoparticle trimers with D_{3h} geometry and heptamers in D_{6h} geometry stand out due to their polarization insensitive responses and high electric (E-) field intensity enhancement, making them building blocks of choice in this size range. The near-field intensity maximum of the D_{6h} heptamer is red-shifted with regard to the D_{3h} trimer by 125 nm, which confirms the possibility of a rational tuning of the near-field response in NCAs through the choice of the constituent nanoparticle clusters. For the nanoparticle trimer we investigate the influence of the cluster geometry on the optical response in detail and map near- and far-field spectra associated with the transition of the cluster configuration from D_{3h} into D_{6h} .

Introduction

Electromagnetic radiation incident on noble metal nanoparticles can excite a coherent collective oscillation of the conduction band electrons. The resonance wavelength of this localized surface plasmon (LSP) depends on the shape, size and the material of the particle as well as the refractive index of the surrounding environment.^{1, 2} Tunable electromagnetic coupling of LSPs in close-by nanoparticles makes individual nanoparticles versatile building blocks for engineering higher order structures with entirely new properties. In this regard, plasmonic nanostructures share some similarities with chemical molecules, with the important difference that “plasmonic molecules” are ruled by the laws of electromagnetism (except at very short interparticle separations)³⁻⁷, whereas the properties of chemical molecules are determined by quantum mechanics. As a result of plasmon hybridization³ in nanoparticle clusters, their near- and far-field responses become dependent on the resonance frequency and shape of all constituent nanoparticles, the cluster geometry, and the interparticle separations. Nanoparticle clusters are interesting electromagnetic materials, as they can efficiently localize and enhance incident electromagnetic fields in the junctions and crevices between the particles.⁸⁻¹⁰ This light field concentration in the clusters creates nanoscale volumes with high local E-field intensity, which act as “hot-spots” for surface enhanced spectroscopies, such as surface enhanced Raman spectroscopy (SERS)¹¹ and surface enhanced infrared absorption spectroscopy (SEIRA).¹²

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Supporting Information Available: Figure S1 - S6 are available at <http://pubs.acs.org>.

Nanoparticle clusters can be further integrated and used as building blocks for higher order structures, such as two-dimensional nanoparticle cluster arrays (NCAs).¹³ One appealing characteristic of NCAs is that they can sustain electromagnetic interactions on multiple length scale. The first length scale is defined through plasmon hybridization of the particle plasmons within individual clusters, while the second length scale is defined through interactions between entire clusters. The synergistic interplay of the electromagnetic interactions on different length scales creates a cascade multi-scale E-field intensity enhancement which qualifies NCAs for challenging sensing applications, including bacterial pathogen detection¹⁴ and ultra-trace analytics.¹⁵ A further systematic improvement of NCAs as SERS or SEIRA substrates requires on the one hand a fundamental understanding of the dependence of the near- and far-field responses on array parameters, such as the array geometry and inter-cluster separation, and on the other hand an optimization of the optical responses of the individual building blocks. We focus in this work on the latter and investigate the tunability of the near- and far-field responses of self-assembled clusters as function of cluster size ($n \leq 7$) and configuration by combining single cluster darkfield spectroscopy and multiparticle generalized Mie theory (GMT) algorithms.¹⁶

We used a template assisted self-assembly approach (Figure 1) to generate clusters of 60 nm diameter gold spheres at pre-defined locations. In previous studies, we have found that the self-assembly process yields densely-packed clusters on the pre-defined binding sites if a 180 nm thick photoresist is used, but that the binding efficiency deteriorates with decreasing photoresist layer thickness. This offers the opportunity to generate a broad range of clusters with different configurations on one chip. In this work, we used a photoresist layer of ~120 nm to generate clusters at pre-defined cluster locations to enable a systematic investigation of structure-spectrum relationship of the clusters. To avoid any interactions between the individual clusters, the separation between the individual binding sites was chosen to be $\geq 5 \mu\text{m}$. The regular arrays generated in the template guided self-assemble process represent defined geometric patterns, which enable an unambiguous identification of individual clusters in a scanning electron microscope (SEM). This approach makes it possible to correlate the experimental far-field spectra of individual clusters with their geometry as obtained through SEM.

Experimental Methods

Generating Nanoparticle Clusters

Nanoparticle clusters were formed on indium tin oxide (ITO) coated glass through a combination of e-beam lithography and template-guided self-assembly.^{13, 14} Briefly, poly(methyl methacrylate) (PMMA) resist was spincoated on an ITO-glass chip to form a layer with a final thickness of ~120 nm. Then binding sites with variable diameters between 80 to 200 nm were generated in the PMMA layer with electron beam lithography using a Zeiss Supra 40 VP SEM equipped with an e-beam blanker and through subsequent development with methyl isobutyl ketone/ isopropanol solvent mix (1:3 in volume). The patterned substrates were then incubated with 2 mg/mL polylysine (MW = 15-30 k) solution for 1 hour. After blow-drying, the substrates were incubated overnight with $\text{HSC}_{11}\text{H}_{22}(\text{OC}_2\text{H}_4)_6\text{OCH}_2\text{COOH}$ functionalized 60 nm gold nanoparticles in a 10 mM phosphate buffer (PH = 8.6) containing 20 mM NaCl. The PMMA layer was finally removed through a lift-off in 1-methyl-2 pyrrolidinone (NMP) solvent for 5 min.

Correlation between darkfield scattering spectra and SEM images

All scattering spectra of nanoparticle clusters were acquired with an Olympus BX51WI microscope using a 60X oil immersion objective (N.A 0.65) under darkfield illumination. The substrates were sandwiched between two cover slides and immersed in glycerol with

refractive index of $n_r = 1.474$. The samples were illuminated with a 100W Tungsten lamp which was focused on the sample plane using an oil darkfield condenser (N.A 1.2 to 1.4, corresponding to an incidence angle θ between 54° to 72°). Scattered light from nanoparticle clusters was collected and analyzed with an Andor Shamrock 303 mm focal length spectrometer using a 150 lines/mm grating blazed at 500 nm. The spectra were recorded with an Andor CCD camera (DU401-BR-DD), then background corrected, and finally corrected for the excitation profile of the tungsten lamp by dividing through the spectrum of an ideal white light scatterer. For polarization resolved measurements an analyzer was inserted into the beam path and stepwisely rotated. After spectral characterization the index matching glycerol was removed through immersion into methanol and the samples were transferred into a Zeiss Supra 40 VP scanning electron microscope. The precise location of each cluster in the grid of the array enabled then an unambiguous correlation of the darkfield scattering spectrum with the SEM image of an individual cluster (Figure 1).

Simulation of the far-field and near-field optical characteristics

To interpret the measured scattering spectra of nanoparticle clusters and to estimate the role of the cluster configuration in their near-field enhancement factors, we simulated the far-field scattering and the near-field intensity spectra of 3-7 particle clusters by using the multi-particle generalized Mie theory (GMT). GMT is a classical electromagnetic computational technique that provides a rigorous semi-analytical solution to the problems of wave scattering by arbitrary clusters of L spherical particles.^{16, 17} The total electromagnetic field scattered by the cluster is constructed as a superposition of partial fields scattered by each sphere. The incident, partially scattered and internal fields are expanded in the orthogonal basis of vector spherical harmonics represented in local coordinate systems associated with individual particles: $\mathbf{E}_{sc}^l = \sum_{(n)} \sum_{(m)} (a_{mn}^l \mathbf{N}_{mn} + b_{mn}^l \mathbf{M}_{mn})$, $l=1, \dots, L$. A matrix equation for the Lorenz-Mie multipole scattering coefficients (a_{mn}^l, b_{mn}^l) is obtained by imposing the continuity conditions for the tangential components of the electric and magnetic fields on the particles surfaces, using the translation theorem for vector spherical harmonics, and truncating the infinite series expansions to a maximum multipolar order N . To ensure the accuracy of the GMT simulations, we kept 35 multipolar terms in the sphere-centered expansions of the electromagnetic fields, and set the relative residual error tolerance in the numerical solution to 10^{-8} .

First, the scattering spectra of individual clusters of different geometry were generated under the excitation by a plane wave incident at the 54° degree to the normal to the cluster plane for varying interparticle gaps within the clusters. The spectra were averaged over all possible polarizations of the incident field and cluster in-plane orientations. The incidence angle (θ) and the orientation of the E-field (ϕ) used to characterize the interactions of the incident light with the clusters, as well as the opening angle (α) in a trimer are defined in Figure S1. All the simulations were performed for gold nanoparticles with experimentally obtained gold refractive index values from Johnson and Christy¹⁸ immersed in the ambient medium with the refractive index $n_r = 1.474$. The simulation results were compared to the measured data, and the best fit of the model parameters to the actual cluster configuration was obtained for interparticle gaps of 2 nm, which were subsequently used in the simulations of the near-field intensity spectra. The intensity spectra were obtained under the excitation by a plane wave incident normally to the clusters plane, which corresponds to the experimental conditions of the Raman scattering spectra measurements.

Results and Discussion

Exemplary scattering spectra of a 60 nm nanoparticle and individual clusters comprising 2 to 7 nanoparticles acquired with unpolarized white light can be seen in Figure 2A. The monomer spectrum shows a single peak at 576 nm, while the cluster spectra are red-shifted due to the LSP coupling in the clusters and have resonance wavelengths in the range between 664 - 700 nm. The simulated spectra of the total far-field scattering efficiency in Figure 2B are overall in good agreement with the experimental scattering spectra. The volume-equivalent scattering efficiency is calculated as the ratio of the total scattering (C_{sc}) cross-section of a nanocluster (integrated over all the scattering angles) under plane-wave illumination to the geometric cross section of a volume-equivalent single sphere:

$Q_{sc} = C_{sc} / \pi a_c^2$, where $a_c = (3V_c / 4\pi)^{1/3}$, and V_c is the combined volume of all the nanoparticles in the cluster. The most striking difference between simulated and experimental spectra is the pronounced local minimum in the scattering intensity at 775 nm in the simulated heptamer spectrum.¹⁹⁻²¹ The experimental heptamer spectrum contains a local minimum at 820 nm, but the intensity is less pronounced than in the simulation. The dip in the scattering intensity in the heptamer spectra results from a Fano resonance between a superradiant bright mode and a subradiant dark mode in the cluster.²¹ In the bright mode, LSPs of all the nanoparticles oscillate in phase along the direction of incident polarization, resulting in a strong scattering extinction at 686 nm in the measured spectrum. In the dark mode, the collective dipolar resonance of the nanoparticle hexamer ring oscillates out of phase with the dipolar mode of the central particle. However, if the dipole moment of the outer ring is different from the dipole moment of the central particle, for instance, due to a defect in the geometry of the heptamer, the hybridized antibonding state possesses a net dipole moment. This mode will consequently no longer be subradiant, and as a result, instead of a clear Fano resonance, a less pronounced dip appears in the scattering intensity, as observed in the experimental heptamer spectrum in Figure 2A.

The overall close correspondence between the experimental and simulated spectra confirms that the applied level of theory is appropriate for describing the optical response of the nanofabricated clusters, and we applied it to simulate the near-field characteristics of individual clusters in the next step. The resulting spectra of the near-field intensity enhancement are shown in Figure 2C. It is immediately obvious that the symmetric trimers and heptamers provide the overall highest peak near-field enhancements. The polarization averaged field intensity enhancements of the symmetric trimer and heptamer can reach up to 1600, which is almost 3 times higher than the peak enhancements generated by symmetric clusters with 4-6 nanoparticles (Figure 2C and S2). The trimer and heptamer are therefore exceptional building blocks for optimized NCAs with giant near-field enhancements. Both trimer and heptamer gain significance as building blocks for NCAs not only due to their superb field localization efficiency, but also due to the fact that for both of these highly symmetric clusters the template assisted self-assembly procedure provides a rational fabrication approach. Under assembly conditions that favor dense nanoparticle packing on the exposed binding sites, the ratio of nanoparticle size to binding site diameter determines the average number of bound particles.¹⁴ For 60 nm particles, primarily trimers are obtained with 140 nm diameter binding sites, whereas 200 nm binding sites lead to the preferential formation of heptamers.

Figure 2C clearly shows that the near-field responses of trimers and heptamers peak at different wavelengths. The trimer has a symmetric near-field spectrum that peaks at 680 nm, whereas the heptamer near-field enhancement peaks at 805 nm, which is significantly red-shifted with regard to the trimer and all other investigated clusters. The choice between trimers or heptamers as building blocks for NCAs offers thus an experimental strategy to maximize the E-field enhancement of the NCAs in two different wavelength ranges. A

combination of trimers and heptamers in one NCA could, on the other hand, be a useful strategy to realize a broadband response. A comparison of the trimer and heptamer near-field spectra with the other investigated clusters underlines the strong dependence of the optical response on the cluster geometry in this size range. The D_{3h} trimer and D_{6h} heptamer clusters are clearly outstanding and represent “magic” configurations that enable eximious cluster properties.

In the next step we want to investigate in more detail how the properties of “magic” nanoparticle cluster vary when its geometry is continuously changed. For reason of simplicity, we choose for this purpose the nanoparticle trimer. In addition to the magic D_{3h} (equilateral triangle) configuration, C_{2v} (kinked triangle) and $D_{\infty h}$ (rod) configurations exist for this cluster size. The major difference between these clusters is the value of the angle (α) formed by the three nanoparticles. In Figure 3 we follow the spectral change that is associated with a continuous increase of α in a nanoparticle trimer. The opening of the angle converts the cluster configuration from the D_{3h} point group over the C_{2v} to the $D_{\infty h}$ point group. We show the SEM images and the corresponding far-field scattering spectra for trimers with $\alpha = 60^\circ, 70^\circ, 110^\circ, 180^\circ$.

The experimental spectrum of the D_{3h} trimer shows a narrow resonance, which peaks at 665 nm. This band starts to split when the symmetry of the cluster is reduced to C_{2v} ($\alpha = 70^\circ$). This cluster shows a main peak at 673 nm and a shoulder at 637 nm. As α is further increased to 110° , the resonance splitting becomes more apparent and two separate features are now clearly distinguishable: a blue-shifted resonance at 621 nm and a red-shifted resonance at 698 nm. If α is further increased to 180° to form a $D_{\infty h}$ trimer, the spectrum becomes highly symmetric again containing a prominent resonance at 712 nm. The simulated trimer scattering spectra reproduce the experimental trend (Figure 3B). A symmetric D_{3h} trimer shows a main feature at 676 nm. As α increases to 70° , several resonant features emerge in the cluster spectrum, with resonances at 556 nm, 610 nm, 668 nm and 713 nm respectively. Further mode splitting can be observed as the angle opens to 110° , with three resonant features at 566 nm, 650 nm and 742 nm in the spectrum. When the three particles align in a chain, only two peaks are visible in the cluster spectrum, at 560 nm and 760 nm. There is a systematic red shift of the peak positions between our simulated and experimental data, which could be due to the variations in the gaps between nanoparticles and estimation on the refractive index of surrounding environment. Nevertheless, the performed GMT calculations overall clearly confirm the geometry dependent spectral features in the trimer.

To better understand the peak splitting trend resulted from clusters' symmetry breaking, we trace the evolution of the main spectral feature of the trimer with the change of its configuration in Figure 4A. To get a clearer picture of the hybridized modes symmetry evolution, we set the incidence angle to $\theta = 0^\circ$ and the polarization of the E-field along the x-axis ($\varphi = 90^\circ$). When the opening angle of the trimer (α) changes, the 682 nm feature corresponding to a hybridized LSP state in the $\alpha = 60^\circ$ trimer, which is degenerate in frequency owing to the cluster symmetry, splits into several modes. The low-energy resonant feature continuously red-shifts with increasing α to 715 nm ($\alpha = 70^\circ$) and 737 nm ($\alpha = 110^\circ$) to 755 nm ($\alpha = 180^\circ$). The resonant peaks corresponding to the split modes on the high energy side become progressively less pronounced and eventually disappear when α is increased. To find out the underlying electromagnetic interactions of the hybridized modes in the different cluster configurations, we plot the phase maps of the major field component E_x in the four relevant trimers at the peak wavelengths of their low-energy resonances in Figure 4(B1-B4). The phase of a complex field component $E_x = E'_x + iE''_x = |E_x| \exp \{ \arg(E_x) \}$ is calculated as $\arg(E_x) = \arcsin(E''_x / |E_x|)$ and varies from $-\pi$ to π . These maps reveal the

continuous evolution of the hybridized LSP mode of the trimer from that of a coupled dipole mode of a dimer perturbed by a third monomer in D_{3h} ($\alpha = 60^\circ$) to a longitudinal mode of the $D_{\infty h}$ ($\alpha = 180^\circ$) linear particle chain, which is consistent with the prediction of the plasmon hybridization theory.²² We note that, besides the prominent peaks discussed thus far, all experimental spectra show another high energy resonance at around 525 nm with low intensity. We trace the evolution of the hybridized LSP mode that gives rise to this high-energy resonant feature with contribution from in plane and out of plane transverse modes in Figure S3 & S4.

We also analyzed the effect of the excitation field polarization on the spectral response of different clusters. In Figure 5 we show experimental (**A1-A3**) and simulated scattering spectra (**B1-B3**) of trimers for varying angles of the incident light polarization (ϕ), together with the spatial E-field intensity enhancement distributions calculated for two orthogonal polarization angles (**C1-C3**) and different trimer geometries. The D_{3h} configuration exhibits the weakest polarization dependence in the far- and near-field responses, as well as the highest average E-field intensity enhancement of 1600. This makes the D_{3h} trimer a good building block for NCAs since it enables efficient electromagnetic coupling between nanoparticle clusters along all directions: the cluster do not require a specific alignment. Another cluster configuration that can be reliably obtained with the same fabrication procedure - the $D_{\infty h}$ trimer - provides the intensity enhancement spectrum that is strongly polarization dependent. In this configuration, the E-field intensity enhancement reaches a peak value of 1700 if the excitation polarization is parallel to the ∞ -fold symmetry axis; however, for excitation light with the perpendicular polarization, the enhancement drops to ~ 20 . The lower average enhancement generated under unpolarized (or unaligned) conditions makes the $D_{\infty h}$ trimer a less appealing building block for NCAs.

For some applications it might, however, be desirable to have a SERS substrate that can either sustain multiple modes with distinct resonance peaks²³ or enables switching the E-field maximum between pre-defined wavelengths on one chip.²⁴ The calculated near-field spectrum of the C_{2v} (shown in Figure 5) configuration shows that this cluster is an interesting candidate for these applications since it contains two separate resonances, at 650 nm and 740 nm, which provide peak enhancements factors of 760 and 1550, respectively. The E-field intensity distribution in Figure 5(C3) shows that the two LSP modes are spatially co-localized but are selectively excited at two different wavelengths by the incident light of two orthogonal polarizations. An array of aligned C_{2v} trimers would offer the possibility to switch between the two resonances through rotation of the excitation polarization and thus to modulate the SERS substrate sensitivity for different vibrational bands in the fingerprint region ($500\text{--}2000\text{ cm}^{-1}$) on one chip.^{24, 25} Similar double resonances are seen in the scattering spectra of asymmetric tetramers (Figure S5, S6), which are also potential candidates for generating multi-resonance substrates if their optical responses are systematically studied in the future.

Conclusions

Individual nanoparticle clusters ($n \leq 7$) were constructed from 60 nm gold nanoparticles using a template guided self-assembly procedure. We measured the darkfield scattering spectra of these clusters and correlated the optical spectra with the cluster structures as obtained by SEM. These experimental studies were augmented by generalized Mie theory simulations, which provided information about the E-field intensity spectrum as a function of cluster configuration. The performed studies show that trimers with D_{3h} and heptamers in D_{6h} geometry are good building blocks for NCAs due to their high rotational symmetry and their outstanding E-field intensity enhancement, which is significantly higher than that for all other investigated cluster configurations. The D_{3h} trimer and D_{6h} heptamer represent

“magic” cluster configurations in the investigated size range. The E-field intensity maxima for the D_{3h} trimer and D_{6h} heptamer are of similar magnitude but shifted by approximately 125 nm. The demonstrated strong size and geometry dependence of the near- and far-field responses of nanoparticle clusters provides new opportunities for a rational design of NCAs with defined near- and far-field responses through choice of the geometry of the building blocks.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A-D) Process flow for generating nanoparticle clusters at pre-defined locations on an ITO-glass chip. (E) Darkfield image of a cluster pattern. The individual clusters are spatially well separated and allow recording of single cluster spectra (inset). (F) SEM image of the cluster pattern. Structural details of the individual clusters become apparent at higher magnification (inset). Scale bars in (E) and (F) denote 10 μm .

Figure 2.

(A) Experimental darkfield scattering spectra of nanoparticle clusters with $n = 1-7$ (see SEM images). (B) Simulated scattering spectra for these clusters configurations. (C) Calculated E-field intensity enhancement. The incidence angle θ was set to 54° in (B) and 0° in (C). Scale bars in all SEM images are 50 nm.

Figure 3.

(A) Experimental and (B) simulated scattering spectra of four individual trimers with opening angle $\alpha = 60^\circ, 70^\circ, 110^\circ$ and 180° (see insets). Scale bar denotes 50 nm in all SEM images.

Figure 4.

(A) Simulated scattering spectra of a monomer and of individual trimers with opening angle $\alpha = 60^\circ, 70^\circ, 110^\circ$ and 180° under illumination by a linearly-polarized light incident normally ($\theta = 0^\circ$) to the cluster plane. Inset shows a typical dipole mode of a monomer for the same E-field polarization. (B1-B4) Phase maps of the major field component E_x of the four trimers at 682 nm, 715 nm, 737 nm and 755 nm, which correspond to the feature resonances in (A).

Figure 5. (A1-A3) Scattering spectra, (B1-B3) calculated E-field intensity enhancement spectra (incidence angle $\theta = 0^\circ$) and (C1-C3) spatial distributions of the E-field intensity for typical D_{3h} , $D_{\infty h}$ and C_{2v} trimers for different excitation polarization angles.