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Exploiting Combinatorics to Investigate Plasmonic Properties in Heterogeneous Ag—Au Nanosphere Chain Assemblies

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Chains of coupled metallic nanoparticles are of special interest for plasmonic applications because they can sustain highly dispersive plasmon bands, allowing strong ballistic plasmon wave transport. Whereas early studies focused on homogeneous particle chains exhibiting only one dominant band, heterogeneous assemblies consisting of different nanoparticle species came into the spotlight recently. Their increased configuration space principally allows engineering multiple bands, bandgaps, or topological states. Simultaneously, the challenge of the precise arrangement of nanoparticles, including their distances and geometric patterns, as well as the precise characterization of the plasmonics in these systems, persists. Here, the surface plasmon resonances in heterogeneous Ag—Au nanoparticle chains are reported. Wrinkled templates are used for directed self-assembly of monodisperse gold and silver nanospheres as chains, which allows assembling statistical combinations of more than 10⁹ particles. To reveal the spatial and spectral distribution of the plasmonic response, state-of-the-art scanning transmission electron microscopy coupled with electron energy loss spectroscopy accompanied by boundary element simulations is used. A variety of modes in the heterogeneous chains are found, ranging from localized surface plasmon modes occurring in single gold or silver spheres, respectively, to modes that result from the hybridization of the single particles. This approach opens a novel avenue toward combinatorial studies of plasmonic properties in heterosystems.

surface plasmons in metal nanoparticles (NPs) owing to the boundary conditions imposed by the spatial confinement in the NPs, therefore these plasmons are called localized surface plasmons (LSPs). The confinement of LSPs and the induced enhancement of the induced electromagnetic fields can be used for applications like plasmonic waveguides,^[1] enhanced optical sensing,^[2] or more efficient solar cells.^[3] Here, the sensitivity of LSPs to the NPs geometry, composition, and arrangement of coupled NPs can be exploited to tune resonance energies and spatial distribution of the LSPs.

Long chains of coupled metallic NPs are of particular interest for the fabrication of optical waveguides with dimensions well below the optical wavelength. By resonant coupling of predominantly dipolar LSPs of the metallic NPs pointing along the chain axis, it is possible to create highly dispersive plasmon bands, giving rise to strong ballistic plasmon wave transport.^[4] Owing to persistent challenges in the selfassembly of geometrically ordered NP chains, practically all experimental studies on this topic deal with homogeneous NP chains or arrangements. Recently, how-

1. Introduction

Surface plasmon polaritons are collective charge density oscillations occurring at interfaces between media of opposite sign of their dielectric function. They give rise to standing waves of

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ever, heterogeneous NP assemblies consisting of different NP species (e.g., sizes, shapes, composition, etc.) and interparticle distances came into focus.^[5] The additional degrees of freedom in these configurations are comparable to the jump from monoatomic to polyatomic molecules or crystals. This principle

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allows generating more complex plasmon modes such as multiple plasmon bands with tunable bandwidths and gaps and with nontrivial topologies and topological edge states.^[6] In one of the first experimental studies based on DNA origami, Roller et al. considered an Au–Ag–Au trimer and found a large low-dissipative coupling of the Au NP mediated by the Ag NP.^[5a] So far, however, complex assembly techniques like DNA origami,^[5a,7] polymeric linkage,^[5b] or sequential capillarityassisted particle assembly^[8] only allow access to a limited set of such assemblies, making statistically relevant investigations tedious. Thus, long heterogeneous NP chains have been theorized^[9] but not synthesized to date.

In this work, we extend the line of research by demonstrating the assembly of well-aligned heterogeneous Ag-Au NP chains of various length and random orderings. This is achieved by template-assisted colloidal assembly of same-size gold and silver spheres with the same polymeric coating, which are mixed stochastically prior to assembly. In this colloidal approach, billions of particles are assembled into millions of chains, eventually obtaining a very large combinatorial parameter space of Ag-Au orderings, virtually accessing all possible combinations up to a line length of 17. To handle the exponential growth of orderings as the chain length increases, we developed an automated classification scheme, which permits a fast selection of particular Ag-Au orderings. Finally, we demonstrate their plasmonic properties and the underlying hybridization principles in the short-chain limit by a systematic study of all possible permutations of four NP chains.

2. Results and Discussion

2.1. Heterogeneous Self-Assemblies

To generate a large number of distinct combinations, a stochastic variant of confinement assembly is used. This method is based on confining a suspension of particles between an elastomeric template and a substrate (silicon wafer or transmission electron microscopy (TEM) grid) during the drying process, enabling evaporation-induced and steric forces to assemble the particles in a dense packing, resulting in particle lines, as visualized in **Figure 1**a–d.

As building blocks, single-crystalline gold spheres were synthesized in a seed-mediated approach to generate spheres with a diameter of (76.7 \pm 4.3) and (22.5 \pm 1.3) nm.^[10] In addition, single-crystalline silver spheres were synthesized by first overgrowing the smaller gold spheres to Au@Ag nanocubes, which were then subsequently etched to generate silver spheres with a diameter of (73.8 ± 3.5) nm.^[11] Owing to the confinement of the plasmonic fields to the interface between the silver surface and the surrounding medium, the small gold core does not change the plasmonic response of the Ag spheres significantly (skin depth of the plasmon mode is much smaller than the thickness of the silver shell) and thus, can be neglected.^[11,12] Consequently, we assume pure gold and silver spheres, respectively (Figure 1a), which were then coated with thiol end-functionalized polyethylene glycol (PEG-SH, Figure S1, Supporting Information) to generate a uniform coating. Overall, this bottom-up synthesis of core-shell structures enables a precise control over size, shape, crystallinity, assembly properties, and the interparticle spacing on the substrate.

For wrinkled template fabrication, polydimethylsiloxane (PDMS) strips are stretched, exposed to oxygen plasma, and subsequently relaxed, resulting in mechanical instabilities, giving rise to periodic wrinkles with an amplitude of 20 nm and a wavelength of 380 nm. By matching the amplitude with the particle size, particle line morphology can be controlled to generate single particle lines later in the process.

Prior to assembly, the assembly substrate is hydrophilized by exposure to an oxygen plasma to adjust the wetting properties to be favorable for confinement assembly. Afterward, the particle suspension, which can be prepared with any gold to silver particle ratio, is cast onto the substrate, confined by the template, and dried under ambient atmosphere. During this process, the Brownian motion of the particles is directed by the flow induced by the evaporating solvent and the steric hindrance applied by the template, which generates the particle lines with an interparticle distance of less than 1 nm on the substrate.

As the Au and Ag particles have the same geometry and polymer coating, they are expected to distribute stochastically



Figure 1. Concept of synthesis and analysis: a) particle suspensions of Ag (upper row) and Au (lower row) nanospheres (left column: bright-field TEM, right column: STEM-EDX) are b) assembled via confinement assembly by first mixing the gold and silver nanoparticle suspensions and confining the droplet between substrate and template. c) After drying, the template is lifted off, revealing the stochastic assembly. d) The composition of the chains can be determined by HAADF-STEM (left), where Au NPs appear brighter than Ag NPs owing to their larger scattering cross section, and SEM-EDX (right).



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Figure 2. Image analysis and statistical evaluation of heterogeneous Ag—Au NP chains: Algorithms applied to a) the SEM image of the assembly allow segmentation of the image into b) single particles, which are part of c) the line ensembles. This enables the assignment of each particle to a particle line. d,e) By comparing the element mappings of silver and gold, particle composition can be assigned. f–h) Variation in gold share (15.5%, 68.2%, and 93.8%, respectively) allows altering the makeup of the complete ensemble. i) The analysis of the gold sphere share in particle lines of length 10 shows the difference between those assemblies and confirms the proclaimed stochastic assembly behavior. j) In combination with the broad distribution of chain lengths, a wide range of compositions is assembled on only one substrate.

within the particle lines. To test this claim, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) was performed on these assemblies as detailed below (Figure 1d).

2.2. Statistical Analysis

To gain a meaningful insight through statistical methods, a sufficiently large sample size is necessary. This is accomplished by analyzing the distribution of about 66 000 particles (depending on the sample) on an area of about 2.8×10^{-9} m² in one SEM-EDX measurement. The acquired images were processed by the following image analysis algorithm to cope with the large sample size. First, the image was binarized by applying a certain threshold to the image. Second, a watershed algorithm was applied to separate the particles from each other. Third, to generate areas that represent the particle lines, the thresholded image was diluted (adding white pixels around each already white pixel). The complete automated process is visualized in **Figure 2**a–e.

This procedure allows assigning each particle to a tuple of pixels and each line to a tuple of particles. The composition can now be resolved by comparing the SEM-EDX intensity sum of silver and gold of each particle (see Figure 2f-h for three different compositions). Subsequently, this assignment is converted to 0 and 1 for silver and gold, respectively, to treat them as a binary sequence for the statistical analysis.

Various statistical tests have been developed for testing random binary sequences owing to their importance in cryptography.^[13] A selection of those tests has been applied to our sequences representing the particle chains; the results are shown in Figure 2i and Figure S3 (Supporting Information). The result of each test on the sample (colored bars) is compared to 1000 Monte Carlo runs of the exact same particle count and gold share, assuming perfect stochastic behavior. The error bars denote the 99th percentile of outcomes around the mean value.

The test depicted in Figure 2i checks the distribution of gold particles within the ensemble of lines of a certain length. For illustrative purposes, all lines including ten particles were considered; similar results could be obtained with lines of different lengths. If the interaction between gold and silver particles is the same as for silver-silver and gold-gold, the assembly should be perfectly random and the graph should follow a binomial distribution. The obtained result clearly lies within the



expected result; therefore, this (among others) concludes that the assembly is truly stochastic by nature.

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Allowing to fully exploit the combinatorial approach, this fabrication approach also features a variance of chain length. The distribution, as shown in Figure 2j, decays at a slow exponential rate. Accordingly, the "line growth" probability is at a much higher rate than previously reported (85–90% in contrast to 70% in the most optimal case, which was achieved by sequential capillarity-assisted particle assembly).^[8] Together with the sheer number of assembled particles, this generates a comprehensive ensemble of all possible line morphologies on one sample, enabling a combinatorial study of their plasmonic properties.

Scaling the examined area to the total substrate area, about 2.36 billion particles on 1 cm² can be expected on average, with about 71% assembled in particle lines of length 2 and higher. The average line comprises 9.25 particles, leading to about 180 million particle lines on one sample. Considering the chain length distribution in Figure 2j, it can be calculated, under the assumption of equal shares of gold and silver spheres, that all particle lines with lengths up to 17 particles (about 1.3 μ m) can be expected on the sample with 99% certainty. Detailed calculations and further examples can be found in the Supporting Information.

To sum up, the combination of millions of chains with a broad chain length distribution in combination with a stochastic distribution of Au and Ag NPs, which is at the same time extensive and tunable, is the core strength of our assembly approach. It eliminates the bottleneck of synthesis and shifts the effort to the detection of the right ordering (an easily automatable task as shown above) and the proper analysis of the features of the desired composition.

2.3. Localized Surface Plasmons on Oligomers (Four NP Chains)

To illustrate the introduced complexity in heterogeneous particle lines, we investigate lines of four particles as a next step in the line of research. As an example, Roller et al.^[5a] showed one specific line of three particles in their study, which is one-sixth of the whole parameter space. Extending this to all possible lines of three particles, five more assemblies would have to be assembled via DNA-origami: an achievable, but time-consuming process. Going further to longer particle lines, this will eventually break down, as the parameter space increases exponentially with line length, unable to be explored with a linear scaling synthesis setup. We choose all lines of four particles now, consisting of ten nonsymmetric permutations, to show that the synthesis method can deliver a comprehensive set of all possible particle lines (about 16 million particle lines of length 4 on one silicon substrate), while keeping the combinatorial complexity manageable to be covered in a single paper. Moreover, it will be shown that the impact of remaining fluctuations in the chain geometry and composition (e.g., with respect to NP distance and shape) are currently rendering a systematic study of longer chains very challenging. Long chains of particular orderings will be therefore considered separately in another study.

To obtain a qualitative understanding of the complex optical properties and underlying hybridization principles^[14] of heterogeneous particle chains, both strategies, bottom-up and top-down, are illustrative. The former begins with degenerate

LSP modes of the single NP constituents of the chain (Au and Ag NPs in our case). After assembly of *n* NPs in a chain, they split into $\approx n$ modes via hybridization. Upon $n \rightarrow \infty$ (i.e., the infinite chain limit), the discrete modes eventually form continuous plasmon bands. For the case of gold chains, the matter has been studied experimentally by, e.g., Mayer et al.^[4] and Barrow et al.^[15] In the top-down approach, the starting points are the already hybridized modes in homogeneous chains of Au or Ag NPs of defined length. The emergent modes in the corresponding heterogeneous chain are then considered as a mixture of the homogeneous ones. We will mainly adopt the latter in the following combined experimental and theoretical study of chains of four NPs.

We focus on the modes as excited by a focused electron beam in a scanning transmission electron microscope (STEM) to facilitate a straightforward comparison to the experimental results obtained from our spatially resolved scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS)^[16] studies. The latter allows studying both optically bright and dark modes owing to the evanescent character of the fields of a focused electron beam.

Following Mie theory,^[17] the LSP mode structure of single spherical NP may be classified by angular momentum quantum numbers (Figure 3a). Usually, the dipolar modes (named p-modes, in analogy to atomic orbitals) of the particle are dominating the excited state if the electron beam is sufficiently separated (impact parameter >10 nm) from the NP. This is mainly owing to the increasing localization, hence decreasing the interaction of the induced electric and magnetic fields of higher multipole modes (i.e., d-modes and higher). At small impact parameters (<10 nm), both p and d modes (and possibly some higher-order modes) contribute significantly (Figure 3b). Owing to the shape of the dielectric function, the Ag modes are higher in energy than their Au counterparts are. Furthermore, the steeper slope of the Ag dielectric function leads to spectrally separated p and d modes, while the Au modes form a smeared out single spectral peak in the corresponding energy range.

These single-sphere LSPs give rise to a simple coupling regime for particle chains, which mainly exhibit two different types of modes:

- Strongly coupling p_x modes (i.e., modes arising from coupled dipoles aligned along *x*), which spread over a large energy band and may be distinguished by the number of field minima. As an example, the (P_{Ag}P_{Ag})₁ mode with one field minimum is shown in Figure 3c.
- 2) Almost degenerate single particle modes of constant energy, involving transversal p_{γ} , $p_{z_{\gamma}}$ and higher-order multipoles, which couple only weakly owing to their short-ranged fields along the chain axis.

This discrimination is an approximation, whose accuracy depends on the coupling strengths and hence particle sizes, distances, etc., for example, there are also hybridized d-modes in Ag dimers (see the $(d_{Ag}d_{Ag})_1^-$ mode in Figure 3c) or p_x d-coupled modes either observable through small energy shifts or characteristic field modulations. A selection of these coupling possibilities for an Ag–Ag dimer is illustrated in Figure S4 (Supporting Information). In the following, we







Figure 3. LSPs on single NP spheres and hybridization via coupling. a) Angular momentum classification of LSP modes according to Mie theory, using a cubic harmonic basis ($I = 0 \triangleq s$, $I = 1 \triangleq p$, $I = 2 \triangleq d$, $I = 3 \triangleq f$, ...). b) Simulated spectrum and modes on Au and Ag spheres as excited by an electron beam focused aloof in front of the spheres. The observable spectral splitting of I = 1 and I > 1 modes in the Ag case is too small in Au and hence not visible. c) Antisymmetric hybridized dimer modes as excited by a focused electron beam including notation used in the text. The underlying hybridization mechanism is similar to the concept of atomic orbital coupling.

distinguish the modes by denoting their dominant character and symmetry (Figure 3c).

As stated previously, important hybridization effects are present in the p_x -coupled modes and, to a lesser extent, p_xd coupled modes. **Figure 4** shows a composition series of four NP chains including their (hybridized) LSP modes. The complete data set of all possible Ag–Au permutations is shown in Figures S5 and S6 (Supporting Information). One sees that the types of observable p_x -coupled modes do not vary throughout the composition series. Indeed, $(pppp)_{1,2}$ and (pddp) modes are present in the homogeneous Au and Ag systems already. It is therefore not surprising that by varying the chain composition they are still present at intermediate spectral positions with a modified mode structure. The observed behavior illustrates the logic behind the previously discussed top-down approach in describing the qualitative evolution of LSP modes in the



Figure 4. a) Simulated and b) experimental LSP spectra and c) corresponding EELS maps of excitation probability for the hybridization in four NP chains of varying Au and Ag content. p_x coupled modes denoted by circles, squares, and triangles are present throughout the differently composed chains. Modes denoted by diamonds (pentagons) correspond to weakly coupling Au (Ag) modes, whereas the Ag bulk mode is labeled by a hexagon. The gray shaded area indicates the spectral regime where plasmonic excitations in Au are suppressed owing to its dielectric function. The notation convention of the coupled modes was introduced in Figure 3.

composition series. Accordingly, the presence of the observed $(pppp)_{1,2}$ modes may be explained by the rather small difference of Au and Ag dielectric functions for energies below 2 eV. However, there are also modes that do not show up in the whole composition series. This mainly pertains to weakly coupling d_{Ag} modes in the spectral range of Au interband transitions. The latter represents another coupling possibility in a wide energy range, yielding broadening (increased damping) and an asymmetry (Fano resonance^[18]) of the spectral peaks. The simulated spectra displayed in Figure 4a reveal a shift of the coupled d and p mode energies depending on the composition of the chain. The blueshift of the excitation energies with increasing Ag percentage is also observable in the experimental data (Figure 4b) and may be used to tune LSP resonance energies in future applications.

The experimental data also demonstrate the sensitivity of LSP resonances to the arrangement of various particles, although there are noticeable discrepancies with the simulations for ideal combinatoric chains. First, the modes of lowest energies are redshifted with respect to the simulated ones in all cases. This suggests a dielectric constant of the surrounding medium larger than the vacuum value ($\varepsilon = 1$), leading to redshifted LSP mode energies. Both the carbon substrate and the organic ligand shell of the particles have dielectric functions larger than one in the optical frequency regime and can potentially cause such redshifts. Additionally, there are specific deviations unique to each chain. Slightly varying distances between the spheres, which influence the coupling strength, as well as shape variations of the single spheres (diameter, deviation from a perfect sphere) are possible causes for this behavior. Moreover, the silver spheres surfaces suffered from degeneration leading to a plasmonic inactive ($\varepsilon > 0$) shell with an uncertain thickness on the Ag spheres, which affected both the distance between the NPs and their dielectric environment. On the one hand, slight shape variations of single NPs do not change their plasmonic properties significantly.^[19] On the other hand, a change of the coupling strength of the arranged NPs, caused by shape anisotropies or varying gaps between the NPs, influences the plasmonic response of the chains considerably. The effect of deviations in the dielectric surrounding depends on the slope of the frequency-dependent dielectric function of the NPs material. The strongest shift of the plasmon mode frequencies can be observed for flat curves. To consider those effects approximately, the dielectric environment was described by an effective medium in previous studies.^[20] Despite discrepancies for the specific chains, the general trend of blueshifted LSP mode energies with increasing Ag content is seen in the experimental data as predicted by the simulations.

Overall, the experimental characterization gives insight into the optical properties and LSP mode coupling behavior of heterogeneous NP assemblies. In the inhomogeneous systems, we found coupled p and d modes already observable in homogeneous Au and Ag chains. Depending on the NP composition the mode structure and the excitation energies of the coupled modes varies, which can be exploited in future applications.

3. Conclusion

We present stochastic confinement assembly as a tool to access a comprehensive ensemble of linear, heterogeneous particle In a closer look at particle lines of length four, we provided a scheme to explain the observed coupling patterns between gold spheres and silver spheres, which were observed in electrodynamic simulations and STEM-EELS measurements. The introduction of silver enables a coupling over a wider energy range. This includes not only the previously observed dipolar longitudinal coupling but also other coupling modes, e.g., coupling of higher-order modes with transversal modes.

Beyond the specific example, our assembly approach allows for the first time the investigation of plasmonic properties in heterosystems in a combinatorial fashion. Especially the combination of such combinatorial procedures with deep learning algorithms has great potential for harnessing plasmonic systems of higher complexity and is subject to further investigations. Here, long heterogeneous arrangements potentially forming complex plasmonic band structures (multiple bands, bandgaps, crossing bands) are of special interest. Thus, the assembly method shown in this work is a key step in terms of plasmonic band engineering.

4. Experimental Section

Materials: Ascorbic acid (AscH₂, $C_6H_8O_6$, >99%), copper(II) hemi(pentahydrate) (Cu(NO₃)₂·2.5H₂O, >99.9%), nitrate hexadecyltrimethylammonium bromide (CTAB, 99%), hydrogen tetrachloroaurate (HAuCl₄, >99.9%), silver nitrate (AgNO₃, 99.9999%), poly(ethylene glycol) methyl ether thiol (PEG-SH, $M_n = 6000 \text{ g mol}^{-1}$), and sodium borohydride (NaBH4, 99%) were received from Merck KGaA, Germany. Sylgard 184 PDMS elastomer kits were purchased from Dow Corning, USA. Acetone (99.98%) and propan-2-ol (99.97%) were purchased from Fisher Scientific, UK. Ethanol was purchased from VWR Chemicals, USA. Hexadecyltrimethylammonium chloride (CTAC, >99%) was obtained from Molekula, UK. All chemicals and solvents were used as received. Silicon wafers were purchased from CrysTec GmbH, Germany. TEM grids (Cu, carbon coated, 200 mesh) were purchased from Electron Microscopy Sciences, USA. Purified water (Milli-Q grade, 18.2 M Ω cm at 25 °C) was used in all preparations. Metal precursor salts were continuously added by a syringe pump system.

Synthesis of Gold Spheres: Spherical gold nanoparticles were synthesized by a protocol from Zheng et al.^[21] and adapted by Steiner et al.^[10] The process follows a seed-mediated approach from Wulff seeds via CTAC-capped seeds to spherical gold nanoparticles.

4.7 mL of a solution containing CTAB (100 \times 10⁻³ M) and 1.25 μ mol HAuCl₄ were tempered for 10 min at 32 °C. Then, 300 μ L of a freshly prepared 10 \times 10⁻³ M solution of NaBH₄ was added at vigorous stirring in a swift one-shot injection into the vortex. Stirring was discontinued after 30 s to allow aging of the particles for 30 min.

Afterward, 40 mL of CTAC (200×10^{-3} m), 5 mL of AA (1 m), and 1 mL of the previously prepared Wulff-seed solution were mixed. Then, 40 mL of a solution of CTAC (200×10^{-3} m) and HAuCl₄ (1.0×10^{-3} m) were added under modest stirring. After 15 min, the solution was centrifuged at 14 500 rcf for 1 h, washed with water, again centrifuged at 14 500 rcf for 1 h, and redispersed in 10 mL of a 10×10^{-3} m CTAC solution.

To further grow these seeds, 200 mL of a solution of CTAC (60×10^{-3} M) and AA (3.9×10^{-3} M) were mixed with 650 µL or 2.6 mL of the above-prepared solution for large (75 nm) or small (22 nm) spherical particles, respectively. Then, 360 mL of a 1.5×10^{-3} M HAuCl₄ in a 60×10^{-3} M CTAC solution was added at 1 mL min⁻¹ with a syringe pump

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added to etch the remaining edges of the particles to generate spheres. Thereafter, the suspension was centrifuged at 350 rcf for 35 min, washed with water, centrifuged again for 35 min at 350 rcf, and redispersed in 10×10^{-3} M CTAC solution. The small spheres were handled in the same way but centrifuged at 3600 rcf for 2 h, respectively.

Synthesis of Silver Spheres: The silver spheres were synthesized in a two-step process. First, small gold nanospheres were overgrown with silver to generate silver cubes^[22] and subsequently catalytically etched to silver nanospheres.^[11]

To synthesize silver cubes, 25 mL of a 10×10^{-3} m CTAC solution were mixed with 0.696 mL of the suspension of the small spheres synthesized above (21.55 $\times 10^{-3}$ m for a final concentration of 0.15 $\times 10^{-3}$ m) and heated to 65 °C. Afterward, 0.300 mL of a 50 $\times 10^{-3}$ m AgNO₃ solution and 0.300 mL of a 200 $\times 10^{-3}$ m AA solution were added simultaneously at a rate of 200 μ L h⁻¹ with a syringe pump setup. Then, 17.7 mL of a 50 $\times 10^{-3}$ m AgNO₃ solution were added simultaneously at a rate of 200 μ L h⁻¹ with a syringe pump setup. Then, 17.7 mL of a 50 $\times 10^{-3}$ m AgNO₃ solution and 17.7 mL of a 50 $\times 10^{-3}$ m AA solution were added simultaneously at a rate of 200 μ L h⁻¹ with a syringe pump. Afterward, the solution was centrifuged at 1000 rcf for 25 min, washed with water, and again centrifuged at 1000 rcf.

To purify the solution from long silver wires, the residue was redispersed in 10 mL of a 30×10^{-3} M CTAC solution and left for 1 h. Then, the supernatant was collected and centrifuged with the same parameters and redispersed in 3×10^{-3} M CTAC solution.

To synthesize silver spheres, the above-obtained suspension was dispersed in 100 mL of a 30×10^{-3} M solution of CTAC and AA (5.625 $\times 10^{-3}$ M). After heating the mixture to 65 °C, 1.5 mL of a 5 $\times 10^{-3}$ M Cu(NO₃)₂ solution were added. The solution was stirred at 65 °C until a diluted solution appeared clearly yellow and when the UV-vis spectra indicated complete removal of the cubic modes, which was roughly after 4 h. The solution was cooled in a cold-water bath. Then, the mixture was centrifuged at 1000 rcf for 25 min, washed with water, and left for 1 h to let AgCl crystals sediment. Afterward, the supernatant was collected and again centrifuged at 1000 rcf for 25 min and redispersed in 3 $\times 10^{-3}$ M CTAC solution.

Functionalization: 0.1 mL of a 20 mg mL⁻¹ solution of PEG-SH (6000 g mol⁻¹) in dichloromethane was added to 2 mL of a 1 mg mL⁻¹ aqueous particle suspension in 0.5 × 10⁻³ M CTAC solution. Then, 1 mL of methanol was added, and the suspension was placed on a shaker for 3 d. Afterward, the mixture was centrifuged at 350 rcf for 50 min, washed with water, again centrifuged at 350 rcf for 50 min, and then redispersed in water to adjust the particle concentration to roughly 50–100 mg mL⁻¹.

Template Fabrication: Adopted from previous work,^[23] wrinkled templates were made in a multistep process. First, 25 g of Sylgard 184 PDMS with a cross-linker-to-prepolymer ratio by mass of 1:5 were prepared by mixing 20.83 g of prepolymer and 4.17 g of cross-linker and pouring it into a leveled polystyrene dish of about 10 cm \times 10 cm. The mixture was allowed to cure for about 24 h at room temperature and then 5 h at 80 °C. Subsequently, the PDMS was cut into 1 cm \times 4.5 cm strips. To generate a template, one of those strips was fixed in a home-built stretching apparatus with a torque of 1.5 cN m. Afterward, the strip was elongated by 40% and O₂-plasma-treated (Flecto 10, Plasma Technology) for 120–150 s at a plasma pressure of about 0.3 mbar and a power output of 100 W. After the procedure, the strip was slowly relaxed. For application, the wrinkled area was cut into 1 cm \times 1 cm pieces.

Preparation of Particle Suspension: Prior to assembly, the particle suspension is prepared by mixing the synthesized and functionalized gold spheres and silver spheres in appropriate amounts, depending on the desired gold/silver ratio in the assembly. The concentration of the stock solution is estimated by ref. ^[24] for gold spheres and ref. ^[25] for silver spheres. For assembly, water and ethanol were added to adjust the ethanol concentration to 20 vol% and the final particle concentration to about 3×10^{15} particles L⁻¹.

Assembly on Silicon Wafers: Silicon wafers were cut into 1.5 cm \times 1.5 cm pieces. These pieces were first submerged in acetone and sonicated for 5 min. This process was repeated with ethanol and isopropanol as a solvent. Afterward, the pieces were dried with pressurized N₂ and stored.

For assembly, the wafer piece was hydrophilized in a plasma etcher for 2 min. Then, 1 μL of prepared particle suspension was carefully placed on the substrate, which was placed on a leveled surface. Afterward, the template was cautiously placed atop the suspension droplet. After drying for at least 3 h, the template was carefully lifted, leaving the assembly on the wafer behind.

Assembly on TEM Grids: For assembly on TEM grids, the TEM grid was hydrophilized in a plasma etcher for 2 min and afterward placed atop a leveled bare silicon wafer. Then, 1 μ L of prepared particle suspension was carefully placed on the TEM grid. The template was mounted on a weight of about 1 kg and slowly lowered onto the substrate. After drying for at least 6 h, the template was carefully lifted, leaving the assembly on the TEM grid behind.

TEM Characterization: TEM measurements were performed with a Libra120 (Zeiss, Germany) with an acceleration voltage of 120 kV. For TEM analysis, 1 mL nanoparticle solution was concentrated to 100 μ L via centrifugation and washed twice to reduce the surfactant concentration below the critical micelle concentration (cmc). Subsequently, 2–5 μ L of these solutions were dried on a 200 mesh copper TEM grid with carbon film. In the statistical evaluation, ± values noted in the text represent the respective standard deviations.

SEM-EDX Characterization: SEM-EDX was conducted on the prepared silicon wafer substrates with an ULTRA PLUS SEM from Carl Zeiss Microscopy GmbH (Jena, Germany) at 20 keV. The dwelling time was set to 2 ms per 14.9 nm pixel, acquiring an image of 4096×3072 pixels. The EDX detector was inserted in between the pole piece and substrate, yielding a higher solid angle than standard detectors. EDX spectra were processed by QUANTAX FlatQUAD software from Bruker Nano GmbH (Berlin, Germany).

STEM-EDX Characterization: STEM-EDX measurements were performed using a JEOL F200 microscope operated at 200 kV using a 100 mm² windowless silicon drift detector.

STEM-EELS Characterization: The plasmonic response of the NP was characterized by STEM-EELS. The measurements were performed at 80 kV in a probe Cs-corrected FEI Titan³ microscope equipped with the Wien monochromator and the Gatan Tridiem energy filter. An electron beam of 1 nm diameter and energy resolution of 75 \pm 5 meV was scanned across the NPs with the dwell time of 30 ms while capturing EEL spectra and high angle annular dark field (HAADF) images at the same time under the convergence angle of 20 mrad and a collection angle of 7 mrad. The obtained spectra showed the characteristic peaks owing to the excitation probabilities in the vicinity of the NPs were extracted. The details of spectra processing can be found in ref. [4].

Image Analysis: For image analysis, the Fiji distribution of ImageJ^[26] and Matlab 2018a were used. First, the grayscale SEM image was thresholded to acquire a binary mask to work with. Second, the watershed algorithm already implemented in the ImageJ software was used to split not completely resolved particles into single particles. This image will be used in the assignment of particles to its tuple of pixels. Third, this image was diluted to add another layer of white pixels to fuse the particles back together to particle lines. This image will be used in the assignment of pixels and subsequently in the assignment of each line to its tuple of particles.

Afterward, the analyze particles feature of the ImageJ software was used to find regions of interest (ROI) consisting of well-separated particles and lines, respectively. Then, each ROI was assigned to its composing pixels, giving a connection between particles/lines and the pixels making up the structure. With a pixel size of about 15 nm, a particle distance of about 30 nm is necessary to distinguish two distinct particle lines. However, the observed distance between particles is either much smaller or much larger than this threshold, leading to no ambiguity in this task.

Subsequently, each particle was assigned its composition by adding up the associated EDX intensities of gold and silver of all pixels belonging to each particle. If the intensity of gold was higher than for silver, the particle was assigned to be gold and vice versa. SCIENCE NEWS _____ www.advancedsciencenews.com

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Electromagnetic Simulations: Electromagnetic simulations of the plasmonic response were obtained using a boundary element approach (MNPBEM code) implemented by Hohenester.^[27] Using that code, the full Maxwell equations were solved for 80 keV primary energy electrons inducing a coupled plasmonic response of four spheres with 70 nm diameter and 0.5 nm gap in between. The dielectric functions of gold and silver are taken from refs. [28] and [29], respectively. The surrounding medium was supposed to be vacuum ($\varepsilon = 1$).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

boundary element method, electron energy loss spectroscopy, plasmonic polymers, stochastic assembly, template-assisted self-assembly

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- M. L. Brongersma, J. W. Hartman, H. A. Atwater, *Phys. Rev. B* 2000, 62, R16356.
- [2] M. Li, S. K. Cushing, N. Wu, Analyst 2015, 140, 386.
- [3] H. A. Atwater, A. Polman, Materials for Sustainable Energy, Macmillan, UK 2010, pp. 1–11.
- [4] M. Mayer, P. L. Potapov, D. Pohl, A. M. Steiner, J. Schultz, B. Rellinghaus, A. Lubk, T. A. F. König, A. Fery, *Nano Lett.* **2019**, *19*, 3854.
- [5] a) E.-M. Roller, L. V. Besteiro, C. Pupp, L. K. Khorashad, A. O. Govorov, T. Liedl, *Nat. Phys.* **2017**, *13*, 761; b) C. Yi, H. Liu,

S. Zhang, Y. Yang, Y. Zhang, Z. Lu, E. Kumacheva, Z. Nie, *Science* **2020**, *369*, 1369.

- [6] a) S. R. Pocock, X. Xiao, P. A. Huidobro, V. Giannini, ACS Photonics
 2018, 5, 2271; b) A. Poddubny, A. Miroshnichenko, A. Slobozhanyuk,
 Y. Kivshar, ACS Photonics 2014, 1, 101; c) C. A. Downing, G. Weick,
 Phys. Rev. B 2017, 95, 125426.
- [7] Y. Zhao, C. Xu, Adv. Mater. 2020, 32, 1907880.
- [8] S. Ni, H. Wolf, L. Isa, Langmuir 2018, 34, 2481.
- [9] M. Yan, J. Phys. Commun. 2019, 3, 115015.
- [10] A. M. Steiner, M. Mayer, M. Seuss, S. Nikolov, K. D. Harris, A. Alexeev, C. Kuttner, T. A. F. König, A. Fery, ACS Nano 2017, 11, 8871.
- [11] A. M. Steiner, M. Mayer, D. Schletz, D. Wolf, P. Formanek, R. Hübner, M. Dulle, S. Förster, T. A. F. König, A. Fery, *Chem. Mater.* 2019, 31, 2822.
- [12] Y. Ma, W. Li, E. C. Cho, Z. Li, T. Yu, J. Zeng, Z. Xie, Y. Xia, ACS Nano 2010, 4, 6725.
- [13] a) L. E. Bassham, A. S. Rukhin, J. Soto, J. Nechvatal, M. Smid, E. Barker, S. Leigh, M. Levenson, M. Vangel, D. Banks, A. Heckert, J. Dray, S. Vo, A Statistical Test Suite for Random and Pseudorandom Number Generators for Cryptographic Applications, National Institute of Standards and Technology, Gaithersburg, MD 2010, https://tsapps.nist.gov/publication/get_pdf.cfm?pub_id=906762; b) D. J. Bernstein, T. Lange, Nature 2017, 549, 188; c) Y. Liu, Q. Zhao, M.-H. Li, J.-Y. Guan, Y. Zhang, B. Bai, W. Zhang, W.-Z. Liu, C. Wu, X. Yuan, H. Li, W. J. Munro, Z. Wang, L. You, J. Zhang, X. Ma, J. Fan, Q. Zhang, J.-W. Pan, Nature 2018, 562, 548.
- [14] E. Prodan, C. Radloff, N. J. Halas, P. Nordlander, Science 2003, 302, 419.
- [15] S. J. Barrow, D. Rossouw, A. M. Funston, G. A. Botton, P. Mulvaney, *Nano Lett.* 2014, 14, 3799.
- [16] J. Nelayah, M. Kociak, O. Stéphan, F. J. García de Abajo, M. Tencé, L. Henrard, D. Taverna, I. Pastoriza-Santos, L. M. Liz-Marzán, C. Colliex, *Nat. Phys.* **2007**, *3*, 348.
- [17] a) C. F. Bohren, D. R. Huffman, Absorption and Scattering of Light by Small Particles, Wiley, New York 1983; b) G. Mie, Ann. Phys. 1908, 330, 377.
- [18] M. R. C. Mahdy, T. Zhang, M. Danesh, W. Ding, Sci. Rep. 2017, 7, 6938.
- [19] F. Kirner, P. Potapov, J. Schultz, J. Geppert, M. Müller, G. González-Rubio, S. Sturm, A. Lubk, E. Sturm, J. Mater. Chem. C 2020, 8, 10844.
- [20] a) K. C. Vernon, A. M. Funston, C. Novo, D. E. Gómez, P. Mulvaney,
 T. J. Davis, *Nano Lett.* 2010, 10, 2080; b) H. Chen, F. Wang, K. Li,
 K. C. Woo, J. Wang, Q. Li, L.-D. Sun, X. Zhang, H.-Q. Lin, C.-H. Yan,
 ACS Nano 2012, 6, 7162.
- [21] Y. Zheng, X. Zhong, Z. Li, Y. Xia, Part. Part. Syst. Charact. 2014, 31, 266.
- [22] M. Mayer, A. M. Steiner, F. Röder, P. Formanek, T. A. F. König, A. Fery, Angew. Chem., Int. Ed. 2017, 56, 15866.
- [23] M. Tebbe, M. Mayer, B. A. Glatz, C. Hanske, P. T. Probst, M. B. Müller, M. Karg, M. Chanana, T. A. F. König, C. Kuttner, A. Fery, *Faraday Discuss.* **2015**, *181*, 243.
- [24] L. Scarabelli, A. Sánchez-Iglesias, J. Pérez-Juste, L. M. Liz-Marzán, J. Phys. Chem. Lett. 2015, 6, 4270.
- [25] D. Paramelle, A. Sadovoy, S. Gorelik, P. Free, J. Hobley, D. G. Fernig, *Analyst* 2014, 139, 4855.
- [26] a) J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.-Y. Tinevez, D. J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, A. Cardona, *Nat. Methods* **2012**, *9*, 676; b) C. A. Schneider, W. S. Rasband, K. W. Eliceiri, *Nat. Methods* **2012**, *9*, 671.
- [27] a) U. Hohenester, A. Trügler, Comput. Phys. Commun. 2012, 183, 370; b) U. Hohenester, Comput. Phys. Commun. 2014, 185, 1177.
- [28] S. Babar, J. H. Weaver, Appl. Opt. 2015, 54, 477.
- [29] H. U. Yang, J. D'Archangel, M. L. Sundheimer, E. Tucker, G. D. Boreman, M. B. Raschke, *Phys. Rev. B* 2015, *91*, 235137.