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Macroscopic Strain-Induced Transition from Quasi-infinite Gold Nanoparticle Chains to Defined Plasmonic Oligomers

Anja Maria Steiner,[†] Martin Mayer,^{†,‡} Maximilian Seuss,[†] Svetoslav Nikolov,[§] Kenneth D. Harris,^{†,||} Alexander Alexeev,[§] Christian Kuttner,^{*,†,‡} Tobias A.F. König,^{*,†,‡,||} and Andreas Fery^{*,†,‡,⊥}

[†]Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Physical Chemistry and Polymer Physics, Hohe Str. 6, 01069 Dresden, Germany

[‡]Cluster of Excellence Centre for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, 01062 Dresden, Germany

[§]George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 771 Ferst Drive NW, Atlanta, Georgia 30332, United States

^{||}National Institute for Nanotechnology, 11421 Saskatchewan Drive, Edmonton, AB T6G 2M9, Canada

[⊥]Department of Physical Chemistry of Polymeric Materials, Technische Universität Dresden, Hohe Str. 6, 01069 Dresden, Germany

S Supporting Information

ABSTRACT: We investigate the formation of chains of few plasmonic nanoparticles—so-called plasmonic oligomers—by strain-induced fragmentation of linear particle assemblies. Detailed investigations of the fragmentation process are conducted by *in situ* atomic force microscopy and UV–vis–NIR spectroscopy. Based on these experimental results and mechanical simulations computed by the lattice spring model, we propose a formation mechanism that explains the observed decrease of chain polydispersity upon increasing strain and provides experimental guidelines for tailoring chain length distribution. By evaluation of the strain-dependent optical properties, we find a reversible, nonlinear shift of the dominant plasmonic resonance. We could quantitatively explain this feature based on simulations using generalized multiparticle Mie theory (GMMT). Both optical and morphological characterization show that the unstrained sample is dominated by chains with a length above the so-called infinite chain limit—above which optical properties show no dependency on chain length—while during deformation, the average chain length decrease below this limit and chain length distribution becomes more narrow. Since the formation mechanism results in a well-defined, parallel orientation of the oligomers on macroscopic areas, the effect of finite chain length can be studied even using conventional UV–vis–NIR spectroscopy. The scalable fabrication of oriented, linear plasmonic oligomers opens up additional opportunities for strain-dependent optical devices and mechanoplasmonic sensing.

KEYWORDS: plasmonic nanoparticles, supra-colloidal assemblies, plasmonic coupling, template-assisted colloidal self-assembly, generalized multiparticle Mie theory, atomic force microscopy

Assemblies of plasmonic nanoparticles are at the center of attention in nanophotonics because they can be utilized for absorbing, directing, and distributing the energy of light as well as for tailoring near-fields.^{1–4} The underlying physical mechanism is an optically excited collective surface plasmon resonance of localized surface plasmons.^{5,6} Among the different plasmonically active assemblies, linear chains of nanoparticles, referred to as plasmonic polymers or colloidal polymers, are of special interest. These plasmonic polymers can provide directional, plasmonic waveguiding

properties, as well as polarization-dependent field enhancement. Even two adjacent particles give rise to optical effects such as (I) hot spot excitation (*i.e.*, coherent field enhancement),^{7,8} (II) anisotropic resonant modes (*i.e.*, distinct longitudinal and transversal modes that are excited by light polarized parallel or perpendicular to the geometric particle

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axis, respectively),⁹ and (III) plasmonic hybridization due to net dipole enhancement (*i.e.*, bright mode) or net dipole moment extinction (*i.e.*, a dark mode).^{10,11} For longer particle chains, the energetically lowest mode is referred to as the super-radiant mode.^{12–14}

An essential parameter governing many of these optical effects is the number of particles (n) forming a chain.¹ Above the infinite chain limit, n_{inf} ¹⁵ (reached at $n_{\text{inf}} = 10$; see Supporting Information Figure S1), the n dependence of plasmonic properties is limited; however, shorter chains below n_{inf} (*i.e.*, plasmonic oligomers) are highly responsive to variations in n . This high-sensitivity regime opens up additional possibilities in sensing and energy propagation, based on stimulus-responsive switching among different plasmonic resonances.^{12,16,17} Therefore, controlling n below the infinite chain limit is an active topic in nanophotonics, which has been tackled using several approaches.

An intuitive rationale was achieved by Link *et al.* as well as Mulvaney *et al.*, who established the concept of plasmonic oligomers underlining the high sensitivity of the collective optical properties to the number of repeat units and their spatial order.^{12,17} Another self-assembly strategy was established by Kumacheva and co-workers to control the “degree of polymerization”, bond length, and bond angle of plasmonic particle chains in solution for stronger surface-enhanced Raman scattering.^{18,19} Guerrero-Martínez and co-workers reported a solution-based synthetic procedure to fabricate selected plasmonic oligomers in high yield controlled by light, which are important for optical metamaterial applications.²⁰

Major challenges in the field include achieving large-area assembly of oligomers with a narrow distribution of chain length n , as well as the oriented assembly of such structures on surfaces. Both are key steps toward exploiting the particular optical properties of plasmonic oligomers in nanophotonics and enable the study of their optical characteristics in detail.

In this work, we demonstrate a scalable approach for the assembly of plasmonic oligomers, which addresses these issues. The plasmonic oligomers are formed by first assembling chains above the quasi-infinite chain limit, then fragmenting them using mechanical deformation of an elastomeric substrate. Detailed studies of morphological and optical responses indicate that oriented, well-defined plasmonic oligomers could be achieved, and the average length of linear particle ensembles could be controlled experimentally by exploiting physicochemical interactions.

RESULTS AND DISCUSSION

Concept of Macroscopic Strain-Induced Fragmentation of Linear Particle Assemblies. We synthesized gold nanoparticles using a three-step, seed-mediated growth procedure,²¹ achieving single-crystalline gold spheres with narrowly distributed diameters of 70.5 ± 1.2 nm (see Supporting Information Figure S2). The surfactant hexadecyltrimethylammonium chloride (CtaC), used during synthesis, was removed by ligand exchange with bovine serum albumin.²² These nanoparticles were arranged by template-assisted self-assembly in wrinkled templates,²³ yielding highly regular assemblies of close-packed nanoparticle lines over a centimeter-squared area.¹⁵ Using wet-contact printing, the linear particle assemblies were transferred onto elastomeric polydimethylsiloxane (PDMS) substrates (Figure 1a). To accomplish a quantitative transfer, the substrate was coated with a polyethylenimine (PEI) adhesion-promoting layer²⁴ which

Figure 1. Macroscopic strain-induced fragmentation of quasi-infinite nanoparticle chains into defined oligomers. (a) Photograph of a 1 cm² PDMS sample with linearly arranged NPs fabricated via template-assisted colloidal self-assembly (inset: reflection).¹⁵ (b) Schematic depiction of the fragmentation of close-packed nanoparticle chains into oligomers upon external strain along the particle lines. (c) Detailed illustration of a chain subunit, which consists of an inelastic, protein-coated gold nanoparticle on an elastic polydimethylsiloxane support (PDMS) with polyethylenimine (PEI) adhesion layer. The protein-coated gold nanoparticles are robustly immobilized by partial embedding in the PEI layer.

provides robust immobilization of the particles based on partial embedding within the PEI layer (Figure 1c). By atomic force microscopy (AFM), we determined the embedding depth to be approximately 20 nm (see Supporting Information Figure S3). With the application of macroscopic uniaxial strain (Figure 1b), mechanical stress is directly transferred to the quasi-infinite particle chains (Supporting Information Figure S1), yielding fragmentation of the close-packed assemblies into particle oligomers (as will become evident in the following).

The strain-induced breakup of quasi-infinite chains was investigated by two completely independent and noninvasive characterization methods: (I) *in situ* AFM and image analysis and (II) UV–vis–NIR spectroscopy to measure the ensemble-averaged optical properties.

Characterization of Morphological Changes Applying External Strain. AFM imaging allows strain-dependent variations in surface morphology to be tracked with nanometer-scale resolution. AFM measurements (Figure 2) were performed both without external strain and at values of 10%, 20%, and 30% (for more details, see Supporting Information S3). Without external strain (Figure 2a), the substrate is predominantly covered by close-packed, quasi-infinite particle chains (Figure 2a, inset). The small population of oligomers (<25%) present before mechanical deformation can be attributed to preexisting defects in the self-assembled chains which arise during either the templating or the transfer processes. These prefragmented chains do not affect the strain-induced fragmentation process, as will be shown later (mechanical modeling, Figure 3). At higher magnification (Figure 2c), individual particles can be clearly identified, as highlighted by the line profile (Figure 2d, top) for the chain of particles boxed in Figure 2c. With stretching of the elastic substrate, a regular breakup of the particle chains into smaller fragments was observed (Figure 2b and Supporting Information Figure S4). The particles do not separate from one another uniformly; instead, the chains tend to split into several-particle

Figure 2. Morphological characterization *via in situ* AFM imaging with applied external strain. Height images reveal (a) predominantly closed-packed, quasi-infinite particle chains at 0% strain and (b) defined particle oligomers (subchains) at 30% strain. The false color insets illustrate the length of individual chains (red, long chains; blue, short chains). (c,e) Higher-magnification images show that individual particles in a fragmented chain can be resolved and tracked. (d) AFM line profiles show the progression of the fragmentation process upon increasing external strain. The data for 0% and 30% strain were extracted from the images shown in panels (c) and (e), respectively, and the data for 10% and 20% strain were extracted from AFM images included in the [Supporting Information Figure S4](#).

segments (Figure 2e). The distance between segments continuously increases with strain, whereas the interparticle distances within segments remain fixed. This evolution can be clearly tracked in the line profiles of Figure 2d. The splitting of particle lines is accompanied by the formation of cracks within the embedding support. Due to the Poisson effect, uniaxial stretching is accompanied by lateral contraction. From the AFM images, we measured a 16% contraction of the interline spacing at 30% applied strain, which is roughly consistent with the value expected ($\epsilon_{\text{perp}} = 17\%$) based on the tabulated Poisson's ratio for PDMS ($\nu = 0.5$).²⁵

The observed fragmentation patterns can be explained based on the critical stress for overcoming interparticle cohesion. Three primary forces contribute to the mechanical environment of particles within the chain: particle–substrate adhesion, interparticle cohesion, and elastic stress within the substrate. Assuming a fully elastic substrate, applied mechanical strain generates a proportional stress within the substrate that is also transferred to the particle chain. The elastic modulus, E ,

describes the stress/strain relationship, and therefore, this experimentally adjustable parameter influences the fragmentation mechanics. Assuming perfectly stiff particles, the response to applied stress is determined exclusively by the ratio of particle–substrate adhesion to interparticle cohesion, as depicted schematically in Figure 3.

Adjusting the adhesion/cohesion ratio, three different scenarios are possible (Figure 3a):

In scenario 1, the interparticle cohesion is significantly greater than the particle–substrate adhesion (Figure 3a, left). In this case, elastic stress can never overcome interparticle cohesion, and the particle assembly slips on the substrate in response to applied strain.

In scenario 2, cohesive and adhesive forces are roughly equivalent, leading to a sequence of fragmentation events under applied strain (Figure 3a, middle). Once the external stress is sufficient to overcome the cohesion of a single particle–particle bond, the chain ruptures at the weakest position, resulting in local relaxation of the stress field. With additional strain, stress

Figure 3. Schematic mechanism of the breakup of quasi-infinite particle chains and mechanical simulations. (a) Based on the ratio of interparticle cohesion to particle–substrate adhesion, mechanical strain may result in three possible scenarios: (1) for dominant cohesion, the particle slip on the substrate; (2) if cohesion and adhesion are on the same order, fragmentation takes place; (3) for dominant adhesion, multiparticle chains immediately separate into individual particles with strain. (b) Changes of the average oligomer length with strain as predicted by lattice spring modeling of quasi-infinite chains (53 particles with periodic boundary conditions) for the three adhesion/cohesion ratios noted.

once again begins to accumulate until the next rupture event is triggered. Because the distance between stress relaxation points is larger for longer chains, these long chains are more likely to rupture than shorter chains. Consequently, the system favors fragmentation into oligomers with a narrower distribution of chain lengths, and adjusting the cohesion/adhesion can tune the oligomer length at a given strain.

In scenario 3, interparticle cohesion is negligible in comparison to the adhesion on the substrate (Figure 3a, right). In this case, the particle chain does not locally stiffen the substrate, and any appreciable external stress transmitted to the particle chain leads to widespread cohesive failure. As a consequence, the chains separate into isolated particles at low strain.

In a previous publication,¹⁵ we estimated an interparticle distance of 2 nm based on the optical response of unstrained, quasi-infinite particle lines prepared in the same way. At this distance, an energy of $90 k_B T$ is required to separate a single dimer of 70 nm gold particles.²⁶ This makes scenario 3 rather improbable. To distinguish between scenarios 1 and 2, analysis of the chain length distribution is necessary. In the case of scenario 1, only chain translation would be observed. As can be seen in the false color images in Figure 2a,b (insets), fragmentation and a narrowing of the chain length distribution take place with strain, indicating that scenario 2 is at work. Thus, we conclude that adequate adhesion and robust

immobilization are provided by partial embedding (~ 20 nm, Supporting Information Figure S3) of the particles into the substrate.

To further validate this conclusion, we conducted mechanical simulations computed by the lattice spring model for different adhesion/cohesion ratios spanning several orders of magnitude (Figure 3b). For low $E_{\text{adhesion}}/E_{\text{cohesion}}$ ratios (0.33), when the cohesive forces dominate, the chain remains fully intact $\sim 9\%$ strain. Above 9%, the chain fragments, but the oligomer length remains above the infinite chain limit to the maximum simulated strain (27%). For high $E_{\text{adhesion}}/E_{\text{cohesion}}$ ratio (166.56), when the adhesive forces dominate, the initial chain quickly fragments into single particles (as is already evident at a strain of $\sim 7\%$). Between these cases (for $E_{\text{adhesion}}/E_{\text{cohesion}} = 3.33$), when the adhesive and cohesive forces are roughly equivalent, the initial chain breaks up into smaller fragments, whose sizes progressively decrease with increasing strain (Supporting Information Figure S6).

Based on the simulation results, surface interaction should be a control parameter for changing the preferred number of particles per oligomer. To test this hypothesis, we conducted experiments using different polymers as the adhesion layer, for which different interaction ratios can be expected (see Figure 4).

For high-molecular-weight, branched PEI, the fragmentation process takes places as reported above (compare Figure 2). By

Figure 4. Control of the fragmentation process by adjusting the adhesion between particles and substrate. For a branched and high-molecular-weight PEI, fragmentation takes places indicating balanced interaction forces (a, top 0%, bottom 30%), as discussed above (compare Figure 2). For a linear and low-molecular-weight PEI, almost no fragmentation into oligomers can be observed (b, top 0%, bottom 30%). The different susceptibility for breakup is clearly visible in the normalized chain length distributions (for details, see Supporting Information Figure S13).

using low-molecular-weight, linear PEI, reduced adhesive interactions can be expected. Thus, almost no fragmentation can be observed up to a strain of 30% (see Figure 4). Consequently, we showed that by means of adjusting the physicochemical interactions, the susceptibility for breakup can be controlled. In the following, we will focus on the first case of pronounced fragmentation and conduct detailed investigations on the oligomer length distribution.

Polarization-Dependent Optical Characterization of Reversible Fragmentation. As the AFM analysis clearly indicates a transition from predominantly long chains to oligomers below the infinite chain limit, one can expect a distinct impact on the optical properties.

To determine the influence of the mechanical deformation on the plasmonic properties, polarization-selective, trans-

mission-mode UV-vis-NIR spectroscopy was used. The extinction spectra of the ensembles were recorded stepwise at strains from 0% up to 50%. The strain-induced spectral variations strongly depend on polarization (optical anisotropy). For polarization perpendicular to the particle chains (transversal excitation), a minor resonance shift was observed (see Supporting Information Figure S7). Figure 5a shows the extinction spectra with longitudinal polarization, averaged over a macroscopic area of $3 \times 4 \text{ mm}^2$. Without external strain, two longitudinal modes occur.¹⁵ The dominant resonance corresponds to the so-called super-radiant mode, which appears at the highest wavelength (i.e., lowest energy).¹⁷ This mode is known to be most sensitive to structural changes.¹⁵ Applying a mechanical strain results in a nonlinear shift of the super-radiant mode toward lower wavelengths (Figure 5b). For 50% strain, a blue shift of 59 nm was measured. The optical changes for increasing strain can be described by an exponential decay: $\lambda_{\text{LSPR}} = \lambda_0 + A \exp(-\varepsilon/\varepsilon_0)$, with λ_{LSPR} as the peak position, $\lambda_0 = 705 \pm 3 \text{ nm}$ as the lower bound offset, $A = 52.3 \pm 4.5 \text{ nm}$ as the amplitude, and $\varepsilon_0 = 10.3 \pm 2.2\%$ as a scaling parameter for the strain ε .

Independent from the morphological AFM analysis (*vide supra*), the optical data allow conclusions about the mechanism of chain breakup. The existence of an observed optical shift suggests structural evolution and excludes scenario 1. The lower wavelength limit λ_0 of 705 nm excludes scenario 3 as the long lines are not completely broken down to monomers (compare Supporting Information Figure S7).^{27,28} Instead, λ_0 suggests that fragmentation took place following scenario 2.

The reversible nature of the chain fragmentation was evidenced over several stretch-and-release cycles (Figure 5c). The deviation of the LSPR peak position between the cycles can be attributed to two main sources. First, slight variations of the peak position might occur owing to the macroscopic stretching by hand. Second, the diffuse scattering contribution of the PDMS significantly affects the background correction. Apart from aging effects of the PDMS substrate, no hysteresis was found for the plasmonic switching from long to short assemblies (see Supporting Information Figure S5), giving rise to possible mechanoplasmonic applications.

Statistical Correlation between Morphological and Optical Analyses. We statistically analyzed the chain fragmentation to track the evolution of chain lengths (degree of polymerization, X) during strain. For this purpose, both morphological and optical data were statistically evaluated and compared, and the distribution of chain lengths was evaluated. As a first step, the AFM images were analyzed to locate the position of every particle. Based on these coordinates, the

Figure 5. Polarization-dependent optical characterization via UV-vis-NIR spectroscopy upon external strain. (a) Normalized and offset extinction spectra for longitudinal excitation from 0% up to 50% strain. (b) Corresponding plasmonic mode shift (LSPR) as a function of the applied strain. (c) Longitudinal plasmonic response with cyclic stretching (to $\varepsilon = 50\%$) and relaxation (standard deviation, gray).

Figure 6. Statistical correlation of the morphological and optical analyses. Direct comparison of the oligomer length distribution as obtained from AFM image analysis (red bars) and deconvolution of UV–vis–NIR spectra (gray bars). For the deconvolution, the experimental extinction spectra (inset, blue curves) were matched with modeled distributions of oligomers (inset, black curve). The ensemble-averaged spectra of oligomer distributions were calculated based on the optical properties of individual oligomers obtained by electromagnetic simulations (Supporting Information S2, Figure S8).

length of all chain assemblies was identified using the diameter of one particle as the break-off criterion (see Supporting Information Figure S9 for a graphical illustration of the AFM analysis). At this separation distance, the electromagnetic interaction ceases and strong plasmonic coupling can no longer occur.^{27,28} The AFM statistics in Figure 6 (red histograms) illustrate the oligomer distributions weighted by the number of particles ($X_{w,AFM}$, weight-average). The corresponding oligomer distribution weighted by the number of oligomers ($X_{n,AFM}$, number-average) can be found in the Supporting Information Figure S10.

As a second step, the optical data were statistically analyzed through spectral deconvolution. The overall extinction spectra represent the ensemble-averaged responses of individual chain fragments. Based on previous findings we assume that (I) by applying external strain, particle chains are ruptured without

influencing the interparticle distances (*i.e.*, the particle-to-particle separation within a fragment is unaffected); (II) there is negligible plasmonic coupling between adjacent oligomers; (III) the chain length distribution can be described by an exponentially modified Gaussian distribution (see Supporting Information eq S2). Based on these assumptions, GMMT was applied to calculate the extinction cross sections of idealized assemblies (1 to 20 particles) with a uniform interparticle spacing of 2 nm. Based on these reference spectra, the oligomer distributions (gray histograms) were evaluated from the experimental spectra (Figure 6, blue curve) by matching against the modeled spectra (Figure 6, black curve) of the ensembles of oligomers. The calculated spectra closely match the experimental data, especially concerning the position and width of the super-radiant mode. The underestimation of the lower wavelength could be attributed to the partial embedding in the support, which was accounted for by an effective medium (no symmetry breaking, no substrate effects). For the individual GMMT simulations of different chain lengths and their weighted quota in the ensemble, see Supporting Information S2 (Figure S8).

The distributions derived from the optical analyses (X_{optics}) in Figure 6 (black histograms) are depicted in relation to the relative extinction cross sections of the oligomers and normalized against their Au^0 content. In this way, the number of particles per chain as well as the nonlinearity of the extinction cross sections is taken into account. Consequently, the distributions are weighted against the normalized number of particles. From the accordance of the two independently calculated histograms (*i.e.*, the microscopy and optical analyses), it can be concluded that the assumptions noted above are reasonable (see Figure 3).

By comparing the histograms evaluated for different strains, distinct trends become apparent. A significant fraction of long particle chains is present at 0% strain, but the distribution rapidly shifts in favor of shorter chains as the applied strain increases (Figure 6). Likewise, a narrowing of the distribution can be recognized as the strain is increased most notably in the range from 0 to 10% strain but also at higher strains. Figure 7a shows the evolution of the mean oligomer length with applied strain as obtained from the different analysis methods. The

Figure 7. Quantitative analysis of the mean oligomer length and dispersity. (a) Statistical comparison of the number-averaged ($X_{n,AFM}$, orange squares) and weight-averaged means ($X_{w,AFM}$, red diamonds) of the plasmonic oligomer length obtained by AFM image analysis as well as the mean oligomer length determined from optical analysis (X_{optics} , black triangles). (b) Degree of polymerization dispersity (eq 1) calculated as a function of the applied strain. Insets show representative AFM images of the plasmonic fragmentation.

analysis of the AFM data yields both a weight-averaged mean ($\bar{X}_{w,AFM}$, weighted by number of particles; see Figure 6) and number-averaged mean ($\bar{X}_{n,AFM}$, weighted by number of oligomers; see Supporting Information Figure S10). The plots of $\bar{X}_{n,AFM}$, $\bar{X}_{w,AFM}$, and $\bar{X}_{optic}$ all reveal the decay of the mean oligomer length with increasing strain. For the optical analysis, however, the nonlinear increase in extinction with increasing chain length needs to be considered (see Supporting Information Figure S8e). In contrast to the AFM analysis, not every oligomer has the same influence on the statistics. Consequently, the optical results $\bar{X}_{optics}$ correspond to the particle-weighted mean of the plasmonic oligomer length distribution. This can be explained by the normalization of the optical data for the Au⁰ content, as discussed above. Comparing the results obtained by optical and AFM analysis (see Figure 7a), however, the mean oligomer length determined from optics matches better with the number-averaged mean of the AFM analysis. This can be traced back to the nonlinear increase in extinction with increasing chain length, as mentioned before. As expected, the number-averaged $\bar{X}_{n,AFM}$ is smaller than the weight-averaged $\bar{X}_{w,AFM}$. Their ratio can be interpreted as the dispersity of the chain length distribution (eq 1):

$$\bar{D} = \frac{\bar{X}_w}{\bar{X}_n} \quad (1)$$

This degree of polymerization dispersity ($\bar{D}$), formerly referred to as polydispersity index,²⁹ is well-known from the description of polymers.³⁰ Figure 7b shows the pronounced and continuous strain-dependent reduction of the chain length dispersity ($\bar{D}$, AFM). Thus, it can be concluded that strain-mediated fragmentation can be employed for the controlled fabrication of low-dispersity, oriented linear particle assemblies below the infinite chain limit. Tweaking the ratio of cohesive and adhesive interactions might enable tailoring of the desired chain length, as will be addressed in future work.

CONCLUSION

In this work, we fabricated oriented plasmonic oligomers below the infinite chain limit, solving a fundamental problem in plasmonic self-assembly. This was achieved by the controlled fragmentation of quasi-infinite particle chains into oligomeric subchains under the influence of external strain. The key factors mechanically influencing this fragmentation process are the interparticle cohesion and particle–substrate adhesion, which were in the focus of this study, but as well substrate modulus, as discussed below. Each is representing a design parameter that may be independently controlled to tailor the materials' system. We expect this adaptability to be especially advantageous in real-world applications with practical design constraints. A particular application could, for example, require a specific functional coating surrounding the plasmonic nanoparticle, and this may limit the designer's ability to adjust the interparticle cohesion. Despite this limitation, the relationship between oligomer length and mechanical strain could still be controlled through adjustment of either the substrate modulus or particle–substrate adhesion.

To demonstrate the fragmentation concept, we focused on controlling the oligomer length distribution by varying the particle–substrate adhesion, and we were able to reliably split linear colloidal assemblies into oligomeric subchains with narrow length distributions. We limited our experimental studies to homogeneous elastomeric substrates, and therefore,

we observed uniform, reversible fragmentation. We expect, however, that the particle chains could be irreversibly fragmented into smaller assemblies by substituting the elastomeric substrates with stiffer and permanently deforming substrates. Also, by spatially patterning any of the three key design parameters (adhesion, cohesion or substrate modulus), it should also be possible to controllably modulate the oligomer length across the substrate.

The fragmentation scenario was validated by AFM and UV–vis–NIR spectroscopy, two complementary, independent, and noninvasive characterization methods. Applying external strain, a nonlinear shift of the longitudinal plasmonic mode was observed, suggesting a strain-induced transition from long to short particle chains. The close correlation between the structural and optical findings establishes (I) that for chain gaps beyond one particle diameter, the plasmonic coupling between two subchains can be neglected and (II) that the uniform interparticle distances of 2 nm within assemblies is not affected by external strain. The robust immobilization of the colloidal particles on the elastomeric substrate by partial embedding in a PEI adhesive layer is important in creating these conditions.

The use of mechanical strain to tune plasmonic properties (mechanoplasmonics), as employed herein, is becoming increasingly widespread in the literature. Previous works describe mechanical perturbation of randomly absorbed particles,³¹ closely packed particle monolayers,^{32–34} and lithographically fabricated array-type structures.^{35–37} Whereas we focused our investigations on deformations along the assemblies, additional optical properties, such as collective plasmonic resonances, could arise from off-axis or multiaxial deformation. Additional, changes in shape and/or material of the used nanoparticles as well as assemblies with 2D/3D hierarchy would lead to more complex optical effects like higher-order plasmonic modes and collective interactions.

In this context, the use of colloidal assembly is particularly promising for the integration of oriented oligomers onto elastomeric substrates, which can be achieved by simple contact printing.

Mechanical stimuli are powerful tools for the scalable fabrication of oriented linear plasmonic oligomers, tunable below the infinite chain limit. This might find application in functional optical devices below the diffraction limit, such as optoelectronic elements tunable by external stimuli or strain-dependent mechanoplasmonic applications. For surface-enhanced sensing, the reversible switching of the nanostructure may be utilized to trap/infiltrate target molecules into uniform hot spots.

EXPERIMENTAL SECTION

Materials. Ascorbic acid (AA, C₆H₈O₆, >99%), bovine serum albumin (BSA, 98%), hexadecyltrimethylammonium chloride (CtaC, 25 wt % in water), hydrogen tetrachloroaurate (HAuCl₄, >99.9%), polyethylenimine (PEI, M_w 25 kg/mol, highly branched), PEI solution (M_w 2 kg/mol, linear, 50 wt % in water), and sodium borohydride (NaBH₄, 99%) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 1 M) solutions and trisodium citrate (Na₃C₆H₅O₇, >99%) were supplied by Grüssing. Hexadecyltrimethylammonium bromide (CtaB, 99%) was received from Merck KGaA. Sylgard 184 PDMS elastomer kits were purchased from Dow Corning. All chemicals were used as received. Milli-Q-grade water (18.2 MΩcm, pH 8) was used as solvent in all preparations.

Synthesis and Functionalization. *Seed-Mediated Growth of Gold Nanospheres.* The seed-mediated growth protocol for the

synthesis of spherical Au nanoparticles was adapted from Zheng *et al.*²¹ The clusters used in that work were, however, substituted with Wulff seeds,^{38,39} and thus, seed concentration, injection rate during growth, and other such parameters were adjusted (*vide infra*).

Preparation of 2 nm CtaB-Capped Au Seeds. Briefly, 4.7 mL of a solution consisting of CtaB (100 mM) and H₂AuCl₄ (2.5 mM) was prepared and stored at 32 °C for 10 min. Next, 300 μ L of a freshly prepared NaBH₄ (10 mM) solution was added quickly under vigorous stirring. Stirring was stopped after 1 min, and the seeds were then stored for 25 min at 32 °C, followed by aging for 15 min at 40 °C to ensure complete removal of excess NaBH₄.

Preparation of 8 nm CtaC-Capped Au Seeds. Aqueous solutions of CtaC (200 mM, 20 mL), AA (100 mM, 15 mL), and the initial CtaB-capped Au clusters (250 μ L) were mixed in a 100 mL beaker. An aqueous H₂AuCl₄ solution (0.5 mM, 20 mL) was then quickly injected under stirring. The reaction was allowed to continue at room temperature (RT) for 15 min. The seeds were collected by centrifugation at 15 000 rcf for 1 h, washed with Milli-Q water, and then redispersed in 10 mL of aqueous CtaC solution (20 mM).

Preparation of 70 nm CtaC-Capped Au Nanoparticles. First, aqueous solutions of CtaC (50 mM, 200 mL), AA (1 M, 780 μ L), and 8 nm CtaC-capped seeds (500 μ L) were mixed. In a separate vessel, 400 mL of a growth solution including H₂AuCl₄ (1.5 mM) and CtaC (55 mM) was prepared and equilibrated at 45 °C. This growth solution was added dropwise using a syringe pump system at an injection rate of 0.5 mL/min, and the reaction was allowed to continue for 12 h at RT after the injection was finished. The final product was collected by centrifugation at 320 rcf for 40 min and washed twice using a 2 mM CtaC solution. For further use, the nanoparticles were redispersed in 15 mL of aqueous CtaC solution (2 mM).

Protein Functionalization. Three milliliters of CtaC-capped Au nanoparticle solution was concentrated by repeated centrifugation steps of 40 min at 320 rcf to adjust the CtaC concentration to 1.0 mM (*i.e.*, the critical micelle concentration of CtaC). Immediately prior to functionalization, the surfactant concentration was reduced below the critical micelle concentration to 0.23 mM by dilution with 10 mL of water. The 0.23 mM solution was then quickly added to a 30 mL BSA solution (pH 8, 10 mg/mL) containing 0.02 wt % trisodium citrate under bath sonication. After 20 min sonication, the solution was centrifuged at 340 rcf for 1 h, and the concentrated nanospheres were redispersed in one drop of pH 11 NaOH solution and diluted with 30 mL of a 1 mg/mL BSA solution (pH 10) containing 0.02 wt % trisodium citrate. Finally, after incubation overnight at 4 °C, the functionalized gold nanospheres were washed three times at 340 rcf for 1 h with a pH 11.5 NaOH solution.

Template-Assisted Self-Assembly and Transfer. *Template Fabrication.* To yield crack-reduced wrinkled templates with a wavelength and amplitude of approximately 370 nm and 35 nm, respectively, the previously published procedure²⁴ was adopted. PDMS was prepared by casting 25 g of the mixed cross-linker/prepolymer mixture (1:5, 4.17 g: 20.83 g) in a leveled polystyrene dish (10 $\times$ 10 cm²) and degassing in vacuum. The PDMS mixture was cross-linked in two steps: 24 h at room temperature and then 5 h at 80 °C for. The cured PDMS was cut into 1 $\times$ 4.5 cm² strips. These strips were fixed with a torque of 10 cNm in a home-built stretching apparatus and elongated by 40%. The strips were then O₂-plasma-treated (Flecto 10, Plasma Technology) for 120 s at a power of 100 W and at an oxygen pressure of 0.3 mbar. The plasma-treated PDMS was then cooled to RT and slowly and mechanically relaxed. The wrinkled PDMS substrates were cut into 1 $\times$ 1 cm² sections to be used as templates.

Nanoparticle Assembly. The corrugated PDMS stamps were used as templates to guide the arrangement of nanoparticles into close-packed linear assemblies *via* spin-coating as previously reported.¹⁵ Immediately before spin-coating, the wrinkled PDMS templates were hydrophilized in the plasma etcher for 45 s (100 W, 0.3 mbar O₂). Four microliters of concentrated nanoparticle suspension ([Au⁰] = 12 mg/mL, adjusted to pH 11) was then manually spread onto the PDMS template, and the samples were spun in a two-stage process (30 s at 1500 rpm, followed by 30 s at 4000 rpm, photoresist spinner, Headway Research Inc.). The red color of the initial suspension became slightly

rose/gray after 30 s at 1500 rpm due to contact between the Au nanoparticles, and the increased rotational speed (4000 rpm) was used to minimize the formation of drying fringes.

Wet-Printing Transfer. The nanoparticle assemblies immobilized inside the grooves of the PDMS templates were transferred onto flat PDMS substrates by wet-transfer printing.¹⁵ For this purpose, PDMS with a cross-linker/prepolymer mixing ratio of 1:15 (1.56 g/23.44 g) was prepared and cured as above. To achieve complete transfer of the protein-coated particles, an adhesion-promoting layer on the target substrate was necessary: the PDMS strips were incubated with a PEI solution (10 mg/mL) for at least 3 h, washed with Milli-Q water, and dried under a nitrogen stream. For the transfer, a 15 μ L droplet of water (pH 9) was placed on the PEI-coated PDMS strip, and the particle-filled PDMS stamps were pressed onto the target substrates with a constant pressure of 100 kPa. After approximately 2 h, the liquid had evaporated and the stamp was removed, leaving the nanoparticles chains on the target PDMS substrate.

Simulation Methods. *Generalized Multiparticle Mie Theory Simulations.* The optical properties of ideal spherical particles were analytically solved using Mie theory.⁴⁰ As recently published by Hanske *et al.*,¹⁵ exact solutions of the optical properties of systems containing a finite number of coupling spheres were obtained through GMMT.⁴¹ In this work, an algorithm developed by Xu⁴² and Gustafson⁴³ was employed, using optical data by Johnson and Christy from 400 to 1300 nm.⁴⁴ The original code by Xu was modified and extended to allow more efficient, parallelized calculations.

Mechanical Simulation. In our mechanical simulations, we use the lattice spring method⁴⁵ to model the elastic PDMS surface. The gold nanoparticles located on the PDMS substrate are represented by rigid spherical shells that interact with one another *via* a Morse potential. The strength of the Morse potential characterizes the cohesive interactions. The gold nanoparticles and PDMS surface interactions are governed by harmonic bonds which set the adhesive forces. The model is implemented using large-scale atomic/molecular massively parallel simulator (LAMMPS).⁴⁶ For details, see [Supporting Information S1](#).

Characterization. *Strain-Dependent AFM Imaging.* AFM images were recorded on a MFP-3D Bio with the NanoRack stretching stage (Asylum Research, An Oxford Instrument Company, Santa Barbara, CA) in tapping mode with a cantilever of a nominal spring constant of 26 N/m (OTESPA-R3, $f_R \approx 300$ kHz, Bruker). The recorded AFM images were statistically evaluated by a homemade IgorPro 7 (Wavemetrics, USA) algorithm. For details, see [Supporting Information S3](#) (Figure S12).

Optical Characterization. Optical spectroscopy was performed on a Cary 5000 spectrometer (Agilent, USA) using the Cary universal measurement accessory in the range from 400 nm to 800 nm for liquid and from 500 nm to 1000 nm for solid samples. Stretching of the sample was performed on a homemade stretching apparatus. The spot size was fixed to 3 $\times$ 4 mm² for UV-vis and NIR detectors.

Deconvolution of Experimental Spectra. Experimental extinction spectra were deconvolved into simulated ideal spectra using an IgorPro 6 (Wavemetrics, USA) curve-fitting function. For details, see [Supporting Information S2](#) (Figure S8).

Microscopy. TEM measurements of the gold nanoparticles at all relevant stages of the synthesis were performed using a Zeiss 922 OMEGA EFTEM at an accelerating voltage of 120 kV. Samples were prepared by drying 5 μ L droplets on Quantifoil 300 mesh copper grids with carbon films placed on a hydrophobic film to trap the droplet during drying. Mean particle diameters were statistically evaluated based on measurements of 350 gold nanoparticles, and the reported error represents the standard deviation of these measurements.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsnano.7b03087](https://doi.org/10.1021/acsnano.7b03087).

Animation of the mechanical simulations by lattice spring modeling (AVI)

Additional data for the infinite chain limit; experimental data for the synthesis; embedding depth of the nanoparticles in the support; mechanical simulations; simulated extinction cross sections; and in-detail explanations for the performed AFM image analyses and spectral deconvolution (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: kuttner@ipfdd.de.

*E-mail: koenig@ipfdd.de.

*E-mail: fery@ipfdd.de.

ORCID

Tobias A.F. König: 0000-0002-8852-8752

Notes

The authors declare no competing financial interest.

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