Structural and Optical Properties of Self-Assembled Chains of Plasmonic Nanocubes

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ABSTRACT

Solution-based linear self-assembly of metal nanoparticles offers a powerful strategy for creating plasmonic polymers, which, so far, have been formed from spherical nanoparticles and nanorods. Here, we report linear solution-based self-assembly of metal nanocubes (NCs), examine the structural characteristics of the NC chains and demonstrate their advanced optical characteristics. Predominant face-to-face assembly of large NCs coated with short polymer ligands led to a larger volume of hot spots in the chains, a nearly uniform E-field enhancement in the gaps between co-linear NCs and a new coupling mode for NC chains, in comparison with chains of nanospheres with similar dimensions, composition and surface chemistry. The NC chains exhibited a stronger surface enhanced Raman scattering (SERS) signal, in comparison with linear assemblies of nanospheres. The experimental results were in agreement with finite difference time domain (FDTD) simulations.

One-dimensional nanoparticle (NP) arrays exhibit directional coupling of electronic, magnetic and optical properties as a result of interactions between the excitons, magnetic moments and surface plasmons, respectively, of individual NPs. New collective properties of linear chains of NPs offer potential applications of these nanostructures in functional nanomaterials and nanodevices^{1,2}. Self-assembly of NPs is a powerful, scalable and cost-efficient strategy for the fabrication of chains with small and controllable interparticle spacing. To utilize directional nanoscale forces acting between NPs, their surface is generally, site-specifically functionalized with low- or high-molecular weight molecules to induce "bifunctionality", which results in NP polymerization in linear chains³⁻⁶. Recently, it has been shown that bifunctionality is not necessary to break the symmetry in NP self-assembly: linear chains have been formed from shape-isotropic NPs uniformly coated with low- or high-molecular weight ligands⁷⁻¹⁴. Several proposed mechanisms of solution-based linear NP assembly included (i) preferred end-on attachment of charged NPs, due to the contribution of electrostatic interparticle repulsion⁷⁻⁹; (ii) alignment of electric dipoles caused by the strong dipole-dipole NP interactions¹⁰⁻¹²; and (iii) reorganization of polymer ligands into a dense cylindrical brush between the neighboring NPs, which favored the formation of linear chains^{13,14}.

In particular, one-dimensional arrays of metal NPs (also called "plasmonic polymers"¹⁵) exhibit interesting optical properties, such as multiple surface plasmon resonance peaks, red-shift of the surface plasmon resonance with increasing number of NPs in the chain, and the formation of hot spots in the gaps between adjacent NPs¹⁶. Currently, solution-based self-assembly of plasmonic polymers has been achieved for metal nanospheres and nanorods. Linear assembly of other types of NPs can bring new interesting and potentially useful properties, but this is yet to be explored. Furthermore, plasmonic polymers formed by nanospheres or nanorods have two limitations

originating from the NP structure. First, NP chains were intrinsically flexible, that is, they lack NP co-linearity, although attempts to increase chain rigidity, in order to enhance their optical properties, have been made¹⁷. Second, due to the shape of nanospheres or curved tips of cylindrical nanorods, hot spots between the neighboring NPs in the chains have an intrinsically small volume and can accommodate a limited number of reporter molecules, if surface enhanced Raman scattering (SERS) is their targeted application.

We hypothesized that solution-based assembly of nanocubes (NCs) can render new optical properties to plasmonic polymers and can address the limitations listed above. Figure 1 illustrates the linear assemblies of NCs (top) and nanospheres (NSs) (bottom). Both types of NP building blocks have the same composition, dimensions and surface chemistry. It can be expected that NCs assembled in a chain in the face-to-face manner would exhibit a higher co-linearity and a larger volume of hot spots than chains of NSs, and can, potentially, accumulate a larger amount of SERS reporter molecules. For example, it has been established that NC dimers prepared by drying a colloidal solution on a substrate exhibit a maximum SERS enhancement for the face-to-face NC configuration^{18,19}.

Recently, Tao *et al.* reported the self-assembly of polymer-grafted metal NCs embedded in a polymer film²⁰. The polymer matrix acted as a poor solvent and the self-assembly was diffusion-limited, due to the low NC mobility in the viscous medium. Simulations were performed for NCs interacting via van der Waals attraction, however accounting for the role of the polymer "solvent" was challenging. In addition, in comparison with solution-based NC self-assembly, this method provides a limited control over the self-assembly kinetics^{4,21,22}, the ability to quench the self-assembly after a particular time interval^{23,24}, and the capability to modify or encapsulate the self-assembled NC chains^{8,25}.

Figure 1. Schematics of self-assembled linear structures formed by NCs (a) and NSs (b). The grey shell around the NCs and NSs represents the ligands capping the surface of NCs and NSs. Zoomed in schematics (left) show with green color hot spots formed between adjacent NCs (top) and NSs (bottom).

In the present work, we conducted solution-based self-assembly of Ag NCs. We report the following new and potentially, useful features of the NC chains. First, we show qualitatively and quantitatively that NCs assembled in a face-to-face configuration form linear chains with a significantly higher rigidity (or higher co-linearity of NCs) than chains of NSs with a comparable size, composition and surface chemistry. Second, we show the predominant face-to-face assembly of large NCs coated with a thin layer of polymer ligands, in agreement with the results of Tao *et al.*²⁰, but for solution-based reaction-controlled NC self-assembly. Finally, using FDTD simulations we establish that chains of face-to-face assembled NCs exhibit a new coupling mode originating from the Fabry-Perot resonator structure of “bonds” formed by adjacent NCs in the chains. We show that NC assemblies have a stronger electric field (E-field) enhancement than the chains of NSs and support the results of FDTD simulations experimentally in SERS experiments.

Starting from the same 16 nm-size Au octahedral seeds, we conducted seed mediated synthesis

of Ag NCs,²⁶ which yielded NCs with the edge length in the range from 25 to 50 nm. In a different series of experiments, we etched Au octahedral seeds to generate spherical seeds, which were used for the synthesis of 50 nm-diameter NSs. The NCs and NSs were functionalized with thiol-terminated polystyrene (PS) with the number average molecular weight $M_n=5,000$ g/mol. In order to explore the effect of the molecular weight of the polymer ligand on the morphology of NC chains, we also we capped 35 nm-size NCs with PS molecules of $M_n=50,000$ g/mol. The electrokinetic potential (ζ -potential) of both the NCs and NSs in dimethylformamide (DMF) was -36 mV.

Figure 2a shows a typical transmission electron microscopy (TEM) image of as synthesized 35 ± 3 nm NCs (the TEM images of 25 ± 2 and 45 ± 3 nm NCs are given in Supporting Information). An image analysis of 250 NCs revealed that they had narrow size distribution (polydispersity 5%) and were slightly truncated at the corners. The octahedral Au core was apparent in the center of each cube, due to the higher electron density of Au than Ag component of the NCs

Following ligand exchange and surface functionalization of the NCs with PS molecules, we acquired the extinction spectra of the NCs with different dimensions in DMF solution. The spectra in Figure 2b exhibit three characteristic peaks corresponding to different localized surface plasmon resonance (LSPR) modes²⁷ of the NCs: the major peak with the spectral position at 425, 440 and 475 nm for the 25, 35, and 45 nm-size NCs, respectively, and two shoulder features at 349 and 378 nm (the latter shoulder is hardly discernible for 25 nm-size NCs, due to its proximity to the major peak at 425 nm).

Figure 2. Properties of individual Ag NCs. (a) Representative TEM image of 35 nm-size NCs. The scale bar is 20 nm. (b) Extinction spectra of PS-coated NCs with dimensions 25 (green), 35 (red), and 45 (blue) nm. The spectra are acquired from NC solutions in DMF.

The self-assembly of the NCs and NSs was triggered by reducing the quality of solvent for the PS ligands. We added water to the solution of NCs in DMF to reach the total water concentration in the DMF-water mixture of $C_w=20\%$. To minimize unfavorable interactions between the poor solvent and PS molecules, the PS ligands on the neighboring NCs associated, thereby leading to NC self-assembly²⁸. Importantly, the lowest surface energy of the system corresponded to the linear NC self-assembly (Figure 3a and b), similar to our earlier work conducted for NSs with similar surface chemistry and electrokinetic potential⁹.

The self-assembly of PS-coated NCs was monitored by acquiring the extinction spectra of the self-assembled structures²⁰. In the course of self-assembly, the extinction spectra of the NCs (Figure 3c) exhibited the appearance and increase in intensity of the secondary plasmon peak at ~ 570 nm, in comparison with extinction spectra of individual NCs. This peak originated from plasmon coupling between NPs assembling in one-dimensional structures in solution¹⁶ and was used as the first experimental evidence of linear self-assembly of the NCs.

Figure 3. Effect of NC dimensions on junctions formed by NCs in the chains. (a, b) Representative TEM images of the chains formed by 25 nm (a) and 45 nm-size NCs (b). Scale bar is 50 nm. (c) Evolution of extinction spectra for self-assembly of 35 nm NCs stabilized with 5K PS over 2 h. (d) Population distribution histogram of the junction angle α between two adjacent NCs in the self-assembled chains formed by NCs with dimensions 25 nm (green), 35 nm (red), 45 nm (blue). Bins of 10° were used. The histogram is based on an analysis of 350 measured angles for each NP population. The inset defines the angle α between the two neighboring NCs.

In addition to extinction experiments, the solution-based linear self-assembly of NCs and NSs was confirmed by *in situ* small-angle X-ray scattering (SAXS). The structure factor, $S(q)$, measured as a background corrected ratio of $I(q)/I_0(q)$, where $I(q)$ and $I_0(q)$ are the scattering intensities of assembled and unassembled NPs, respectively (see Supporting Information, Figure S22) showed first-order peaks q_1 for assemblies of 50 nm-diameter NSs and 25 nm-size NCs and higher order peaks for 50 nm-size NCs. The positions in higher-order diffraction peaks in the structure factor $S(q)$ of NS chains scaled approximately as multiples of the first peak position, suggesting the formation of a periodic one-dimensional structure. The absence of higher order

peaks for 25 nm-size NC and NS assemblies suggested a shorter correlation length in the chains, which could originate from deviations from the co-linearity in these structures or polydispersity in interparticle distances.

Quantitative analysis of different types of contacts (junctions) between the neighboring NCs in the chain was accomplished by TEM image analysis: we measured an interparticle angle α , which was defined as the angle between the two faces of adjacent NCs (Figure 3b, inset). The value of α varied from 0 to 90°, with $\alpha = 0^\circ$ for an ideal, parallel face-to-face NC arrangement. Figure 3c shows the histogram of the fraction of populations of angles α in NC chains. The fraction of NCs assembled in a face-to-face orientation (taken at $\alpha < 10^\circ$) was significant for all NCs, however for 45 nm-size NCs it was 2.4- and 1.8-fold higher than for 25 and 35 nm-size NCs, respectively, as shown in Figure 3d.

We note that the formation of face-to-face contacts between NCs is expected due to the screening of a greater PS-capped surface area from the poor solvent, in comparison with the edge-to-edge, edge-to-face, or vertex-to-vertex NC assembly. Yet, this preferred self-assembly mode was predominantly realized for the large, 45 nm-size NCs stabilized with short (relative to the NC size) PS ligands. The cubic shape of smaller NCs, was screened by the polymer layer, thereby making their self-assembly more forgiving towards the formation of non-face-to-face contacts. The transition from the random NC attachment to the preferential face-to-face NC bonding mode occurred for the ratio of NP size/polymer layer thickness in the range from 10 to 18 (the thickness of the polymer layer was determined from the analysis of TEM images of the NCs assembled in the water/DMF mixture at $C_w=20\%$).

Furthermore, for the chains formed by 35 nm-size NCs stabilized with PS of $M_n=50000$ g/mol (the ratio of NP size/polymer layer thickness of 8), we observed no preference of face-to-face NC orientation over other attachment modes (see Supporting Information, Figure S5). In this case, the cube-like shape of the building blocks was screened by the high-molecular weight polymer.

Image-based analysis of angles between the faces of adjacent NCs in the chains provided important information on the general trend of NC-NC bonds in the chains, however this method relied on the analysis of 2D projections of the chains dried on a TEM grid, which could change the fraction of NC-NC contacts with a particular NC configuration, in comparison with that in the solution. To corroborate our image analysis-based findings, for the chains of small and large NCs, as well as large NSs we used *in situ* SAXS measurements to determine interparticle (center-to-center) distances as $2\pi/q_1$, where the position of the first peak q_1 in the SAXS pattern was the deconvolution from scattering peak using Lorentzian function. This center-to-center distance is the most probable distance (and not an average distance) between the NCs or NSs in the chain. Using the interparticle distances determined in SAXS experiments and NP dimensions determined by the TEM image analysis, we determined the gap between adjacent metal surfaces in the chains to be 4.6 ± 2.6 , 1.7 ± 2.5 , and 3.9 ± 2.4 nm for the 25 and 50 nm-size NCs and 50 nm-size NSs, respectively. These interparticle distances agreed with those measured in TEM images of the NP chains (7.0 ± 2 , 3.2 ± 1.5 , and 2.7 ± 2 nm for the 25 and 50 nm-size NCs and 50 nm-size NSs, respectively), which implied that the imaged structures well-represent the species self-assembled in solution. The TEM images in Figure 4 (and SI) also suggested that the distribution of interparticle distances was broader for smaller NCs, due to their less regular face-to-face orientation in the chains, in comparison with larger NCs. This feature was qualitatively reflected

in *in situ* SAXS measurements as the q_1 peak is significantly broader for 25 nm NC assemblies, in contrast with 50 nm NC assemblies (Figure S22, Supporting Information).

Next, we characterized the rigidity of the chains formed by the NCs with different dimensions and 50 nm-diameter NSs. Figure 4a-c shows representative TEM images of the chains of 25 and 45 nm-size NCs, as well as the chains formed by the NSs, all capped with PS ligands with the molecular weight 5000 g/mol. To characterize the rigidity of the chains quantitatively, we used the angle β between the lines connecting the centers of three consecutive NPs (NCs or NSs) in the chain (see inset to Figure 4e). In this configuration, the maximum co-linearity of a NP chain corresponded to $\beta=180^\circ$. Figure 4d shows the histogram of the distribution of angle β in the chains formed by the NCs with different dimensions, as well as the 50 nm-diameter NSs. For smaller-size NCs and for the NSs, the co-linearity between adjacent particles was noticeably lower with a large fraction of angles in the range $120^\circ \leq \beta \leq 180^\circ$. In this configuration, the competition of electrostatic repulsion between the first and the third NPs (Figure 4e, inset) and NP attraction (the surface tension forces leading to the screening of PS-poor solvent interactions)⁹, led to “forgiveness” in the NP attachment to the chain end and the formation of kinks along the chain.

Co-linearity assembly with $160^\circ \leq \beta \leq 180^\circ$ was observed for ~75% of chains of 45 nm-size NCs. A stronger NC co-linearity in these chains originated from two factors: predominant face-to-face contacts between adjacent NCs (providing the maximum screening of interactions of PS ligands with a poor solvent) and the electrostatic repulsion acting between the first and the third NPs (favoring the formation of straight chains with $\beta \approx 180^\circ$). Thus we conclude that plasmonic

polymers formed by 45-50 nm-size NCs had the highest fraction of face-to-face contacts and the largest co-linearity of the building blocks in the chains.

Figure 4. Effect of NP size and shape on co-linearity of NPs in the chains. (a-c) Transmission electron microscopy images of chains of (a-c) NCs with dimensions 25 (a), 35 (b) and 45 (c) nm; (d) 50 nm-size NSs, scale bars are 100 nm. (e) Histogram of the distribution of populations of angle β (defined in the inset) for the chains of 50 nm-diameter spheres (pink) and NCs with dimensions 25 (green), 35 (red), and 45 (blue) nm. Bins of 20° were used. The average aggregation number of the chains is 3. The histogram is based on an analysis of 250 triplets of NCs and NSs.

Next, for the unimers, dimers, trimers and tetramers of such NCs, that is, the most abundant species in the system, we carried out finite difference time domain (FDTD) simulations (similar chains of 50 nm-diameter NSs were simulated for comparison). The "bond" between two faces of adjacent NCs in a face-to-face configuration is represented by a thin dielectric PS layer confined between the two metal (silver) surfaces. Such a metal-insulator-metal structure can support even and odd plasmonic modes, however for a vanishingly thin dielectric layer, only odd modes exist²⁹. The pair of face-to-face assembled NCs forms a Fabry-Perot resonator with a resonant wavelength determined by the NC dimensions and the thickness of the PS-filled gap between the neighboring NCs^{29,30}. If the Fabry-Perot resonance corresponds to the excitation wavelength, strong enhancement in optical properties is expected (e.g., in Raman scattering). For a chain of

50 nm-size NCs, we determined that the Fabry-Perot resonance occurred at the wavelength of 750 nm (Figure S12 and S13, Supporting Information), which provided high local field enhancement for the excitation wavelength of 785 nm (later used in SERS experiments).

Figure 5 shows normalized E-field intensity ($|E/E_0|^2$) profiles for the unimers, dimers, trimers and tetramers of NCs and NSs and the corresponding average E-field enhancement factors for the interparticle gaps. A 1000-fold increase in E-field intensity occurred both for adjacent NCs or NSs. Yet, due to the dominant face-to-face assembly of the NCs, the average value of $|E/E_0|^2$ in the interparticle gaps for trimer chains was 335, in comparison with 63 for the NS assemblies. Since SERS enhancement can be approximated by $|E/E_0|^4$, the theoretical enhancement for the NC trimer chains was 28 times stronger than the enhancement factor for the NS trimers.

We note that linear assemblies of NCs and NSs can exhibit a different dependence of the Raman enhancement factor on the chain length. The Raman enhancement factor depends on the location of LSPR, on the generation of hot-spots in the gaps between NPs, and on optical absorption, that is, on loss in the metal, which increases with increasing number of NPs in the chain. We conducted simulations to evaluate the dependence of the Raman enhancement factor on the number of NPs in the chain (varied from 1 to 4). Figures S16 and 17 show that for NS chains, the LSPR red-shifts as the number of NSs in the chain becomes larger. Although the system becomes more lossy, the resonance effect dominates, leading to the higher E-field enhancement in longer chains. On the other hand, chains of NCs exhibit a Fabry-Perot resonance with the spectral position determined by NC dimensions and only weakly dependent on the chain length. Thus, the Raman enhancement factor is governed by the hot-spot strength and optical absorption. The trade-off between optical absorption and local field enhancement results in the highest Raman enhancement for trimer NC chains (Figure S12 and S13).

In experiments, however, the self-assembled NP chains show analogy with step-growth polymers and are intrinsically polydisperse.⁴ A *mixture* of unimers, dimers, trimers and tetramers is more representative of the experimental situation, and can be characterized by the number average aggregation number $X_n = \frac{\sum n_i x_i}{\sum n_i}$, where x_i is the number of NPs in the chain and n_i is the number of chains containing x_i NPs. In the simulations, the strongest enhancement was achieved for the NC and NS chains with $X_n = 3$ (Figures S15 and S19). Notably, for $X_n=3$ the calculated enhancement factor was 13 times larger for the NC chains than for the NS chains.

Figure 5. FDTD simulations of 50 nm-size NPs and their linear assemblies. Examples of TEM images of NP dimers formed after 2 min-long assembly of NCs (a) and NSs (b). Scale bars are 20 nm. (c,d) Electric field profiles calculated at the excitation wavelength 785 nm, as used in experiments, with incident light polarization parallel to x-coordinate for (c) an individual NC (top left) and face-to-face assembled NCs dimer and trimer (top right and bottom, respectively), and (d) for the individual NS (top left) and for the NSs dimer and trimer (top right and bottom, respectively). Map scale is logarithmic. Numbers above the subfigures in (c) and (d) show the average E-field enhancement factors per hot spot volume.

To support the simulation results, we examined SERS properties at the excitation wavelength of 785 nm (close to the Fabry-Perot resonance) for the chains of 50-nm-size NCs and 50 nm-diameter NSs. The self-assembly of these NPs was conducted in the DMF-water mixture in the presence of the Raman reporter oxazine. It has been earlier established by our group that oxazine molecules partition in the associating PS ligands upon in the water/DMF mixture³¹. In the present work, after mixing solutions of NCs or NSs with oxazine (both in DMF) and triggering linear self-assembly of the NPs by adding water to $C_w = 20\%$, we monitored the evolution of ensemble-averaged SERS spectra of oxazine as a function of self-assembly time. The experiments were conducted using 30 μM oxazine in 0.2 nM solution of NCs or NSs in the DMF/water solution. (The results of experiments conducted at dye and NP concentrations of 7 μM and 0.04 nM, respectively, are shown in Supporting Information, Figure S5).

Figure 6a shows the Raman spectra of oxazine corresponding to the maximum SERS enhancement in assemblies of NCs and NSs, as well as for the solution of oxazine in the water/DMF mixture (used as a control system). The enhanced bands at 563 and 604 cm^{-1} corresponded to the vibrational modes of the phenoxazine ring of oxazine and were consistent with the Raman spectrum of the solution of oxazine in DMF³². Importantly, in the control experiment carried out in the solution of NPs and oxazine in DMF, that is, without self-assembly, a very small increase (10%) in Raman signal of oxazine was observed at 563 cm^{-1} , in comparison with a solution of oxazine in DMF, indicating that the Raman signal enhancement in the mixed solvent stemmed from the partition of the dye in the PS ligands.

Figure 6b shows that the maximum SERS enhancement was achieved already after 2 min of NC or NS self-assembly. Fast NP self-assembly was attributed to the high NP concentration in the system and the acceleration of self-assembly in the presence of oxazine³¹. Based on the TEM

image analysis of self-assembled structures, for the maximum SERS enhancement achieved after 2 min-long self-assembly both NC and NS chains had the average aggregation number $X_n = 3$. When a lower concentration of NPs and oxazine was used, that is, 0.04 nM and 7 μ M, respectively (see Supporting Information, Figure S23), the maximum enhancement was achieved after 30 min self-assembly, and also corresponded to $X_n = 3$. Both results were in agreement with the results of simulations.

Figure 5. Evolution of SERS spectra acquired at 785 nm excitation wavelength in the course of self-assembly of 50 nm-size of NCs and NSs in the water/DMF mixture at $C_W=20\%$ in the presence of 30 μ M oxazine. The molecular weight of PS ligands was 50000 g/mol. The concentration of NCs or NSs in the system was 0.2 nM. (a) Raman spectra of the control with no NPs (red line), NS chains (blue line) and NC chains (green line) at maximum measured count. The self-assembly time is 2 min. (b) Evolution of Raman signal intensity at 563 cm^{-1} , following the self-assembly of NCs (green symbols) and NSs (blue symbols). The dye signal is normalized by the DMF signal at 660 cm^{-1} . In (b) the lines are given for eye guidance.

Following SERS experiments, we determined the amount of the dye partitioned in the PS ligands in the NCs and NSs in the course of self-assembly (Supporting Information). The uptakes of oxazine by the PS layer were 10 and 14%, respectively, of the total amount of oxazine introduced in the system (we assumed a similar uniform distribution of oxazine across the PS

layer capping the NC and NS surface). Although the area of NCs was 1.9-fold larger than that of NSs, a lower uptake of oxazine by the NCs than by the NSs was presumably caused by the denser packing of the PS molecules on the planar NC surface, than on the curved surface of NSs. Based on the intensities of SERS signals at 563 cm^{-1} and the concentration of oxazine in PS shells (both in the interparticle gaps and on the free NP surface), we calculated the SERS enhancement factors for the chains of NCs and NSs to be 251 and 31, respectively (the calculations are presented in Supporting Information). By calculating the ratio between the PS volume in the interparticle gaps to the total volume of PS (both in the interparticle gaps and on the free NC surface) in the chains with $X_n=3$, we found the fraction of the dye in the interparticle gaps for the NC and NS assemblies (see Supporting Information, Figure S7 and Table S1) and found that the SERS enhancement factor in the interparticle gaps was 16 times greater for the chains of NCs than for the NS chains. This experimental result was in quantitative agreement with the results of FDTD simulations, which for the distribution of species with $X_n=3$ showed a 13 times greater enhancement for the NC chains than for NS chains.

The optical properties of the chains of 45-50 nm NCs originated from several factors, all of which stemmed from the large fraction of face-to-face NC contacts. First, there was a nearly uniform E-field enhancement in the gaps between NCs in the chains. For the face-to-face co-linear NCs, the hot spots were characterized by a constant distance between adjacent metal surfaces (except for the NC corners), whereas for the neighboring NSs, the E-field had a maximum enhancement in the line of the shortest distance between the NSs (decaying as the inter-sphere distance increased). Second, the PS-filled gaps between the neighboring NCs had a 1.5-fold larger volume than the gaps between adjacent NSs, leading to the larger amount of

oxazine in hot spots in NC chains (see Supporting Information, Figure S7). Finally, the Fabry-Perot resonator structure

contributed to the stronger enhancement in the chains of NCs, in comparison with NS chains.

In summary, we explored solution-based linear assembly of NCs and determined new structure-property relationships for plasmonic polymers made from these nanoscopic building blocks. The self-assembly of large NCs coated with a relatively thin layer of polymer ligands led to their preferential face-to-face attachment in linear chains and resulted in more rigid chains, compared to assemblies of NSs or chains of smaller NCs. The preferential face-to-face NC assembly resulted in a larger volume of hot spots, a nearly uniform E-field enhancement in the gaps between co-linear NCs and new coupling modes for plasmonic polymers formed by the NCs, in comparison with linear assemblies of spherical NPs with similar composition dimensions, composition and surface chemistry. These features led to stronger SERS enhancement factor for the NC chains, in comparison with chains of NSs. Our results suggest that optical properties of self-assembled plasmonic polymers can be programmed by using NP building blocks with particular shapes and dimensions, with potential applications in sub-wavelength-scale sensing and imaging enhancement.

Methods

Synthesis of Au seeded Ag NCs and NSs. Core-shell Au/Ag NCs stabilized with cetylpyridinium chloride were prepared using a modified three-step protocol reported elsewhere²⁶. In the next step, using ligand exchange, we functionalized the NPs with PS molecules. See Supporting Information for the detailed procedure.

Self-assembly experiments. A stock solution of NCs in DMF (0.5 mL) was placed in a 20 mL vial. The self-assembly of the NCs was triggered by the dropwise addition of 0.5 mL of the DMF/water mixture at a concentration of water of 40 vol %, in order to reach the final concentration of water $C_W = 20$ vol %. A similar approach was used for the self-assembly of NSs. The self-assembly process was monitored by acquiring absorption spectra of the solution of NSs or NCs as a function of the self-assembly time. The TEM images of the resulting nanostructures were obtained using Hitachi H-7000 transmission electron microscope. The samples were prepared by depositing a droplet of the NPs or NC solution onto the carbon-coated copper TEM grids, exposing the droplet to the air for 20 s, and quickly removing the solvent with a KimWipe to prevent drying of the solution onto the grid.

Statistical analysis of self-assembled structures. Transmission electron microscopy images were analyzed using MATLAB. The positions of the edges and of the center of mass of each NP were obtained by image analysis. The mutual orientation of the neighboring NCs in the chain was characterized by measuring the angle α between NC facets. The angle α was calculated using the scalar product of the vectors defined by two adjacent edges (of 2D projection of two adjacent facets). The rigidity of the chain was characterized by the angle β defined as the angle between the centers of mass of two consecutive pairs in the NP trimer.

SERS experiments. A Raman reporter, oxazine 720, was introduced into the solution of 50 nm-size NPs or NCs in DMF (0.5 mL). The resulting solution was incubated for 12 h. After that, 0.5 mL of the DMF/water mixture with water content of 40 vol % was added dropwise under stirring into the NP or NC solution to reach $C_w = 20\%$. Immediately after the addition of the DMF/water mixture, that is, the beginning of self-assembly of NPs or NCs, the Raman spectra of the solution were acquired using a compact Raman spectrometer (Advantage Raman Series, DeltaNu, 785 nm laser line, the laser beam diameter of 35 μm at the focal point).

Electromagnetic simulations. Optical properties of NCs and NSs were investigated using FDTD simulations. The simulation domain was terminated by a perfectly matched layer to ensure minimum reflections from the boundaries. To calculate the absorption and scattering cross sections, we employed the formalism of the total field scattered field (TFSF). We introduced a set of two-dimensional power monitors, which formed two surfaces enclosing the NPs, one inside the TF region (power monitor 1, or PM1) and the other in the SF region (power monitor 2, or PM2). We calculated the absorption cross-section of the nanostructures by evaluating the net power flow into PM1, which represented the power loss in the NPs. The total power exiting PM2 was used for the calculation of the scattering cross section as $\sigma_{\text{scat}} = P_{\text{scat}} / I_s$, where P_{scat} is the scattered power obtained from PM2 and I_s is the intensity of the light source. The extinction cross-section was determined by the summation of scattering and absorption cross sections. A mesh override region was also introduced with a mesh size of 0.4 nm for accurate modeling of the structure. The calculated cross-sections are shown in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information. Detailed procedure for the synthesis and surface functionalization of NCs and NSs, zeta potential measurements of PS-functionalized NPs, extinction measurements and TEM images of individual NPs and their assemblies, results of additional SERS experiments, calculation of SERS enhancement factors for NC and NS assemblies, FDTD simulations for individual NP and their various assemblies, results of *in situ* SAXS measurements of various NC and NS assemblies.

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Author Contributions

A.K., H.T.-A. and E.K. designed the study, analyzed the results, and wrote the manuscript. A.K. contributed to all experimental work. R.M.C. and A.M. assisted with NCs synthesis, dynamic light scattering measurements and electron microscopy. H.T.-A. performed Matlab analysis. A.A. performed the FDTD simulations and analyzed the results. G.W. contributed in the design of SERS experiments and analysis of experimental results. B.G. assisted with Raman measurements. O.G. and D.N. contributed to the design and analysis of SAXS experiments. D.N. assisted with SAXS measurements. The manuscript was written through contributions of all authors.

ABBREVIATIONS

NP, nanoparticle; NC, nanocube; NS, nanoshpere; TEM, transmission electron microscopy; SERS, surface enhanced Raman scattering; LSPR, localized surface plasmon resonance, FDTD, finite difference time domain, DMF, dimethylformamide; CPC, cetylpyridinium chloride.

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