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

Anna Klinkova,† Héloïse Thérien-Aubin,† Aftab Ahmed‡ Dmytro Nykypanchuk,§ Rachelle M. Choueiri,† Brandon Gagnon,† Anastasiya Muntyanu,† Oleg Gang,§ Gilbert C. Walker,‡ and Eugenia Kumacheva*†

†Department of Chemistry, University of Toronto, 80 Saint George Street, Toronto, Ontario M5S 3H6, Canada
‡Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, United States
§Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

Supporting Information

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 cylindrical 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. In comparison with chains of nanospheres with similar dimensions, composition, and surface chemistry, 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 colinear NCs, and a new coupling mode for NC chains due to the formation of a Fabry–Perot resonator structure formed by face-to-face bonded NCs. The NC chains exhibited stronger surface-enhanced Raman scattering in comparison with linear assemblies of nanospheres. The experimental results were in agreement with finite difference time domain simulations.

KEYWORDS: Nanoparticle, nanocube, nanosphere, self-assembly, nanoparticle chain, SERS, plasmonics

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 chains.3−6 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 ligands.7−14 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 repulsion;7−9 and (ii) alignment of electric dipoles caused by the strong dipole—dipole NP interactions;10−12 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 NPs.16 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 colinearity, although attempts to increase chain rigidity in order to enhance their optical properties have been made.17 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.

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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 nano-spheres (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 colinearity 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.\textsuperscript{18,19}

Recently, Tao et al. reported the self-assembly of polymer-grafted metal NCs embedded in a polymer film.\textsuperscript{20} 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,\textsuperscript{4,21,22} the ability to quench the self-assembly after a particular time interval,\textsuperscript{23,24} and the capability to modify or encapsulate the self-assembled NC chains.\textsuperscript{8,25}

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 colinearity 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, which is in agreement with the results of Tao et al.,\textsuperscript{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,\textsuperscript{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 $M_n = 5000$ g/mol. The electrokinetic potential ($Z$-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 $35 \pm 3$ nm NCs (the TEM images of $25 \pm 2$ and $45 \pm 3$ 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 NC solutions in DMF. The spectra in Figure 2b exhibit three characteristic peaks corresponding to different localized surface plasmon resonance (LSPR) modes\textsuperscript{27} 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 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 with the poor solvent, the PS ligands on the neighboring NCs underwent association, thereby leading to NC self-assembly.\textsuperscript{28} Importantly, the NCs and NSs predominantly assembled in linear chains, which qualitatively agreed with our earlier work conducted for gold NSs with similar surface chemistry and electrokinetic potential ($\zeta \approx 30 \text{ mV}$).\textsuperscript{9} The formation of linear NP assemblies was determined by the minimization of the total energy of the system. Interparticle attraction resulted from the hydrophobic/poor solvency attraction force, while electrostatic repulsion forces between charged NPs in a solvent with a high dielectric constant, led to the end-on attachment of nanoparticles.

The self-assembly of PS-coated NCs was monitored by acquiring the extinction spectra of the self-assembled structures.\textsuperscript{20} 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 $\sim 570$ nm in comparison with extinction spectra of individual NCs. This peak originated from plasmon coupling between NPs assembling in one-dimensional structures in solution\textsuperscript{16} and was used as the first experimental evidence of linear self-assembly of the 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 colinearity in these structures or polydispersity in interparticle distances.

Quantitative analysis of different types of contacts (junctons) between the neighboring NCs in the chain was accomplished by TEM image analysis: we measured an interparticle angle $\alpha$, which was defined as the angle between the two faces of adjacent NCs (Figure 3b, inset). The value of $\alpha$ varied from 0 to $90^\circ$ 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 $\alpha$ 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 toward the formation of nonface-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 $C_w = 20\%$).
Figure 4. Effect of NP size and shape on colinearity 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 $\beta$ (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.

Furthermore, for the chains formed by 35 nm size NCs stabilized with PS of $M_n = 50\,000$ 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 cubelike 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 $2\pi/q_L$, where the position of the first peak $q_L$ 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 $4.6 \pm 2.6, 1.7 \pm 2.5,$ and $3.9 \pm 2.4$ 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 $(7.0 \pm 2, 3.2 \pm 1.5$, and $2.7 \pm 2$ 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 Figure S6 in Supporting Information) 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 $q_L$ peak is significantly broader for 25 nm NC assemblies, which is 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 $\beta$ 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 colinearity of a NP chain corresponded to $\beta = 180^\circ$. Figure 4d shows the histogram of the distribution of angle $\beta$ 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 colinearity 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 colinearity 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 colinearity of the building blocks in the chains.

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 exist.29 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/E₀|²) profiles for the unimers, dimers, trimers and tetrakers 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/E₀|² in the interparticle gaps for trimer chains was 335 in comparison with 63 for the NS assemblies. Because SERS enhancement can be approximated by |E/E₀|², 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). Supporting Information Figures S16 and S17 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 (Supporting Information Figure S12 and S13).

In experiments, however, the self-assembled NP chains show analogy with step-growth polymers and are intrinsically polydisperse. A mixture of unimers, dimers, trimers, and tetrakers is more representative of the experimental situation and can be characterized by the number-average aggregation number Xₐ = (Σnᵢxᵢ)/(Σnᵢ), where xᵢ is the number of NPs in the chain and nᵢ is the number of chains containing xᵢ NPs. In the simulations, the strongest enhancement was achieved for the NC and NS chains with Xₐ = 3 (Supporting Information Figures S15 and S19). Notably, for Xₐ = 3 the calculated enhancement factor was 13 times larger for the NC chains than for the NS chains.

To validate the results of simulations, 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 self-assembly in the water/DMF mixture. 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 Cₐw = 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). We note that based on TEM image analysis, no change in the self-assembled structures was observed, when oxazine was used as a reporter.

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Both NC and NS chains had the average aggregation number SERS enhancement achieved after 2 min-long self-assembly image analysis of self-assembled structures, for the maximum in the interparticle gaps to the total volume of PS (both in the NCs and NSs, respectively (the calculations are presented in Supporting Information). By calculating the ratio between the PS volume of oxazine in DMF.32

The Raman spectrum of the solution of oxazine in DMF was observed at 563 cm⁻¹ in comparison with a solution of oxazine in DMF, indicating that the Raman signal in oxazine was used at 563 cm⁻¹ in the presence of the PS ligands.

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 DMF.32

Importantly, in the control experiment carried out in the solution of NPs and oxazine in DMF (in the absence of water and thus, without self-assembly), a very small increase (10%) in the Raman signal of oxazine was observed at 563 cm⁻¹ in Raman signal of oxazine in DMF, that is, 0.04 nM and 7 μM oxazine. The molecular weight of PS ligands was 5000 g/mol. The concentration of NCs and 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 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.

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 relatively high NP concentration in the system and the acceleration of self-assembly in the presence of oxazine.34 On the basis of 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 Xₐ = 3. When a lower concentration of NPs and oxazine was used, that is, 0.04 nM and 7 μM, respectively (see Supporting Information, Figure S23), the maximum enhancement was achieved after 30 min self-assembly and also corresponded to Xₐ = 3. Both results were in agreement with the results of simulations.

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. On the basis of 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 NC surface) in the chains with Xₐ = 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 Xₐ = 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 colinear 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 intersphere 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 colinear 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 resulted in stronger SERS enhancement factor for the NC chains in comparison with chains of NSs. Notably, plasmonic polymers formed by NCs can be extracted and isolated. 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 subwavelength-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 elsewhere. 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 $\alpha$ between NC facets. The angle $\alpha$ 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 $\beta$ 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 $\sigma_s = P_{scat}/I_0$, where $P_{scat}$ is the scattered power obtained from PM2 and $I_0$ 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. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**

E-mail: ekumache@chem.utoronto.ca.

**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.

**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

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

Synthesis of Au seeded Ag NCs and NSs. Core-shell Au/Ag NCs stabilized with cetylpyridinium chloride (CPC) were prepared using a modified three-step protocol reported elsewhere\(^1\). First, 3 nm-size Au NPs were prepared by quickly injecting 0.60 mL of ice-cold, freshly prepared 10mM NaBH\(_4\) solution into a rapidly stirred mixture of HAuCl\(_4\) (10 mM, 0.25mL) and hexadecyltrimethylammonium bromide (CTAB, 0.1M, 9.75mL). After being stirred for 2 min, the solution was left
undisturbed for 2 h and then diluted to 100 mL with deionized water. Then, 0.6 mL of this solution was added in one portion to a mixture of HAuCl$_4$ (0.2 mL, 10mM), CTAB (4mL, 0.2M), ascorbic acid (3mL, 0.1M) and 43 mL of deionized water. The reaction mixture was quickly shaken and left undisturbed at room temperature for 12 h, yielding a purple solution of octahedral Au NPs. Two washing cycles by centrifugation at 15000 $g$ for 15 min were used to replace the surfactant-rich solution with deionized water. In the final step, 10 mL of the Au octahedral seeds and 1.6 mL of the aqueous 0.1M solution of CPC were mixed in a 20 mL vial placed in an oil bath at 60°C. This step was followed by the sequential addition of AgNO$_3$ (0.2mL, 10mM) and ascorbic acid (0.8mL, 0.1M) under stirring. After 1h reaction, the vial was cooled in an ice-bath. The resulting 25 nm-size NCs were washed twice using centrifugation at 14000 $g$ for 10 min and redispersion in deionized water. To obtain larger NCs, in the last step, the amount of octahedral Au seeds was decreased: to synthesize 35 nm-size NCs, 5 mL of the solution of octahedral Au seeds and 5 mL of water were used, whereas to obtain 45 nm-size NCs, 2.5 mL of the seed solution and 7.5 mL of water were used. The NCs were washed twice by using centrifugation the solution for 10 min at 10000 or 8000 $g$ for 35 and 45 nm-size NCs, respectively, and subsequent redispersion in water. This procedure yields 50 nm-size NCs when 2 mL of the seed solution is used. To synthesize 50 nm-size NSs, we modified the procedure described above in the following way. As synthesized Au octahedral seeds were subjected to etching by a mixture of H$_2$O$_2$ (0.2mL, 1.0M) and HCl (0.2mL, 1.0M) for 5 min, followed by two washing cycles at 15000 $g$ and replacing the supernatant with deionized water.
These Au seeds were used for further Ag growth on their surface, which yielded 50 nm-size NSs. The NPs were purified by centrifugation in the same manner as the 45 nm-size NCs.
**Figure S1.** TEM images of NCs of different edge length: (a) 25 nm, (b) 35 nm, (c) 45 nm. Scale bar is 100 nm. Darker region in the center of each NC is a Au octahedral seed.

**Functionalization of NPs with PS ligands**

A concentrated aqueous solution of NCs (0.5 mL, 0.3 nM) was rapidly injected under sonication into 10 mL of SH-PS solution in dimethylformamide (DMF, 0.1 mg/mL). The mixture was sonicated for 1 min and incubated for 30 min. The NCs were purified from the excess of free, non-attached ligands using six 10 min-long centrifugation cycles at various speed depending on the size of the NCs (12000 g for 25 nm-size NCs, 8000 g for 35 nm-size NCs and 4000 g for 45 nm-size NCs). The final solution was redispersed in DMF to form a stock solution, which was used within 2 weeks after NP preparation. The NSs of 50 nm diameter were functionalized with 5K PS following similar procedure.
Figure S2. Extinction spectra of NCs (red line) and spheres (blue line) of 50 nm stabilized with 5K PS in DMF.

Figure S3. Electokinetic potential of 50 nm-size NCs (a) and 50 nm Ag NSs (b) stabilized with 5K PS. The measurements are taken in DMF.
**Figure S4.** Evolution of extinction spectra in the course of 2 h-long self-assembly of NCs (a) and NSs (b) of 50 nm stabilized with PS with the molecular weight of 50000 mol/g.

**Figure S5.** Self-assembly of 35 nm-size NCs stabilized with PS ligands with different molecular weight. (a) Evolution of extinction spectra of 50-nm-size NCs stabilized with PS molecules with the molecular weight 5000 mol/g over 2 h self-assembly; (b) evolution of extinction spectra of 50 nm-size NCs stabilized with PS with the molecular weight 50000 in the course 24 h self-assembly. (c,d) Representative TEM images of the self-assembled structures formed by NCs stabilized with PS ligands with the molecular weight 5000 mol/g (c) and PS ligands with the molecular weight 50000 mol/g (d). The time of self-assembly is 30 min. Scale bar is 100 nm.
Figure S6. TEM images of linear assemblies of (a) 25 nm-size NCs, (b) 45 nm-size NCs, and (c) 50 nm-diameter NSs. Scale bars are 100 nm.

**Determination of the concentration of NCs and NSs**

The concentration of the NCs and NSs in the stock solutions was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). 50 μL of the stock solution of 50 nm-size NPs was mixed with 0.5 mL of *aqua regia*, equilibrated overnight at room temperature and subjected to a 20-fold dilution with deionized water. The sample was analyzed using ICP-AES to determine the concentration of Au atoms in the core of the NPs. The concentration has been determined by
spectrometric analysis against an independent source, which is traceable to the National Institute of Standards and Technology Standard Reference Material: 3121.

To convert the concentration of Au (determined from ICP-AES analysis) into the concentration of NCs, we calculated the number of Au atoms in an Au octahedron core of the NCs. To determine the concentration of NSs, we calculated the number of Au atoms in the spherical cores of the NSs. The dimensions of the octahedral and spherical cores were determined by the analysis of TEM images. Since Au seeds with the same size were used for the synthesis of NCs with dimensions of 25, 35, 45 and 50 nm, the concentration of all populations of NCs was determined based on the concentration of seeds used in the synthesis of 50 nm-size NCs.

**Determination of the dye uptake upon NPs self-assembly in SERS experiments**

To determine the fraction of the dye uptaken from the solution by PS ligands, we first determined the concentration of oxazine left in the solution after NC or NS self-assembly. The solutions of self-assembled structures were twice centrifuged at 10000 g for 5 min to remove NC or NS assemblies, as well as individual NPs. Then, the concentration of oxazine in the supernatant was determined by UV-Vis spectroscopy. The difference between the concentrations of oxazine remaining in the solution after the self-assembly of NCs or NSs and the control NC- or NS-free solution of the dye was used to calculate the amount of oxazine uptaken by the self-assembled structures.
Calculation of volumes of PS ligands in the interparticle gaps

Based on TEM image analysis, for chains of 50 nm-size NCs and NSs in the water/DMF mixture at $C_w=20\%$, the shortest distance between adjacent NPs was 2.7 nm and the thickness of the PS shell around NPs, except the contact area, was 2 nm. We used these values to calculate the volume of PS in the gap between two NPs surfaces, or hot spot volume between the NPs.

Figure S6 shows the polystyrene bush located in the hot spot. From TEM images we know that between 2 NCs the PS is located between the facets of the cubes, while in the case of the NSs the polystyrene is located in a hyperboloid-shaped bush. The volume fraction of PS bush in hot spot for a chain of $X$ nanoparticles was expressed as follows:

For NCs:

$$V_{\text{eff}} = \frac{(X-1)(DL_1^2)}{X(L_2^2 - L_1^2)}$$

And for NSs:

$$V_{\text{eff}} = \frac{(X-1)\left[\frac{2\pi ha^2}{b^2}\left(b^2 + \frac{h^2}{3}\right)\right] - 2\left[\frac{\pi v}{6}\left(3\mu^2 + v^2\right)\right]}{X\left[\frac{4}{3}\pi r_2^3 - \frac{4}{3}\pi r_1^3\right]}$$

where $D$ is the distance between two adjacent NCs, $L_1$ is the size of a NC edge, $L_2$ is the size of the NC with the PS layer around it, $r_1$ the radius of the core of a NS, $r_2$ the radius of the PS layer around a NS, $d$ the distance between two adjacent NSs, $a$ the distance between the center of the gap and the vertex of the hyperboloid and $b$ the distance between the vertex and the asymptote of the hyperboloid, where
\[ a = \frac{1}{2} \sqrt{-9d^2 + 12dr_i} \quad \text{and} \quad b = -\frac{1}{2} \left( r_i - \frac{d}{2} \right) \frac{\sqrt{-9d^2 + 12dr_i}}{r_i}, \] 

\( h \) is the height of the hyperboloid and \( \mu \) and \( \nu \) the dimensions of the spherical cap of a NS.

**Figure S7.** Determination of the volume of interparticle gap for the chains of NSs (left) and NCs (right). The bottom row shows 3D cartoons of the interparticle gaps.

**Table S1.** Comparison of SERS enhancement factors for the chains of NCs and NSs*

<table>
<thead>
<tr>
<th>Type of NP</th>
<th>Apparent SERS enhancement</th>
<th>% of the dye sequestered by PS</th>
<th>SERS enhancement for sequestered dye</th>
<th>% dye in the interparticle gap (( X_n=3 ))</th>
<th>SERS enhancement for the dye partitioned in the interparticle gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC</td>
<td>26</td>
<td>10</td>
<td>251</td>
<td>1.54</td>
<td>1624</td>
</tr>
<tr>
<td>NS</td>
<td>4</td>
<td>14</td>
<td>31</td>
<td>2.88</td>
<td>105</td>
</tr>
</tbody>
</table>
* as measured, corrected for the amount of dye uptaken by PS ligands, and corrected for the interparticle gaps.

**FDTD simulations for 50 nm size NCs and 50 nm-diameter NSs**

![Graph](image)

**Figure S8.** Calculated extinction cross-section for individual NCs, NC dimers and linear trimers. The plasmon peak of a single NC is in good agreement with the experimental results. The red shift is larger than measured in experiments due to (i) the variation of the gap size and/or (ii) polydispersity and non-co-linearity of NPs in the chains.

![Graph](image)

**Figure S9.** Calculated extinction cross-section for individual NSs, NS dimers and linear trimers. The plasmon peak shifts from 428 to 592 nm from the unimer to trimer configuration.
**Figure S10.** Calculated extinction cross-section for the linear ensembles of NCs with $X_n$ of 2, 3, and 4 with distribution of species characteristic for step-growth polymerization.

**Figure S11.** Calculated extinction cross-section for the chains of NSs with $X_n$ of 2, 3, and 4 with the distribution of species characteristic for step-growth polymerization.

**Figure S12.** Calculated average E-field enhancement for NCs per hot spot volume,
plotted as a function of the wavelength of the incident light. A peak ascribed to Fabry-Perot resonance appears for NC assemblies in the spectral range 700-800 nm.

**Figure S13.** Variation in the calculated Raman enhancement factor, plotted as a function of the aggregation number of the NC chain at the wavelength of incident light of 785 nm.

**Figure S14.** Calculated average E-field enhancement for NCs per hot spot volume for ensembles of NCs with $X_n$ of 2, 3, and 4 with the distribution of species characteristic for step-growth polymerization.
**Figure S15.** Variation in the calculated Raman enhancement factor for NC chains, plotted as a function of the mean aggregation number $X_n$ at incident light wavelength of 785 nm.

**Figure S16.** Calculated average E-field enhancement per hot spot volume for linear NS assemblies as a function of the wavelength of the incident light.
**Figure S17.** Variation in the calculated Raman enhancement factor, plotted as a function of the number of NSs in the chain at incident light of 785 nm.

**Figure S18.** Calculated average E-field enhancement for per hot spot volume for linear ensembles of NSs with $X_n$ of 2, 3, and 4 with distribution of species characteristic for step-growth polymerization.
**Figure S19.** Variation in the calculated Raman enhancement factor for NC chains with different $X_n$ at incident light wavelength of 785 nm.

**Figure S20.** FDTD simulations of extinction spectra of NS trimers with angle $\beta$ equal to 180°, 150°, and 120°.

**Figure S21.** FDTD simulations for non-face-to-face junctions of NCs: E-field profiles calculated at the experimental excitation wavelength 785 nm with incident light polarization parallel to x-coordinate for the dimers of NCs with the angle $\alpha$ of 20° (left) and 45° (right). The map scale is logarithmic.
Structural studies of NC and NS assemblies in solution using in situ small-angle x-ray scattering

Small angle x-ray scattering (SAXS) measurements were carried out on the Bruker-AXS Nanostar U instrument equipped with Cu rotating anode, Vatec 2000 detector and run in the high-resolution configuration. The camera length for the instrument was calibrated using Silver Behenate as a standard. The scattering image was reduced to 1D data intensity $I$ vs. $q$, scattering vector, using Bruker SAXS operating software. For the measurements, the samples were transferred in thin wall borosilicate glass capillaries with a diameter 1 mm (purchased from Charles Supper, MA), and sealed with a hot melt adhesive. The structure factor, $S(q)$, was calculated as a background-corrected ratio of $I(q)/I_0(q)$, where $I(q)$ and $I_0(q)$ are the scattering intensities for assembled and non-assembled nanoparticles, respectively. The peak deconvolution was performed in IgorPro software using MultiPeak fitting package.
Figure S22. Measured structure factors $S(q)$ for the linear assemblies of 25 nm and 50 nm NCs and 50 nm NS.

SERS experiments conducted at reduced concentration of NPs and dye

Figure S23. SERS experiments conducted for the self-assembly of 50 nm-size NCs and 50 nm-diameter NSs in the water/DMF mixture at $C_w = 20\%$ in the presence of 7 μM oxazine. The concentration of NCs and NSs in the solution was 0.04 nM. (a) Raman spectra of the control (red line), solution of self-assembled NCs (green line), and solution of self-assembled NSs (blue line) at maximum measured count. (b) Evolution of Raman signal intensity in the course of self-assembly of 50 nm-size NCs (green symbols) and 50 nm-size NSs (blue symbols) during 2 h-long self-assembly. The dye signal is normalized to DMF signal at 660 cm$^{-1}$. The lines are given for eye guidance. (c) oxazine dye structure.

References