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Plasmonic Copolymers | Very Important Paper

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Copolymerization of Metal Nanoparticles: A Route to Colloidal Plasmonic Copolymers**

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Abstract: *The resemblance between colloidal and molecular polymerization reactions is very useful in fundamental studies of polymerization reactions, as well as in the development of new nanoscale systems with desired properties. Future applications of colloidal polymers will require nanoparticle ensembles with a high degree of complexity that can be realized by hetero-assembly of NPs with different dimensions, shapes, and compositions. A method has been developed to apply strategies from molecular copolymerization to the co-assembly of gold nanorods with different dimensions into random and block copolymer structures (plasmonic copolymers). The approach was extended to the co-assembly of random copolymers of gold and palladium nanorods. A kinetic model validated and further expanded the kinetic theories developed for molecular copolymerization reactions.*

Self-assembled one-dimensional nanostructures are rapidly gaining attention because of their fundamental importance as model systems for molecular polymerization reactions[1] and potential technological applications.[2] In particular, linear polymer-like structures assembled from metal nanoparticles (NPs), termed plasmonic polymers,[3] exhibit strong interactions between the surface plasmon resonances of NP repeat units, which lead to promising applications of plasmonic polymers in nanocircuits,[4] nanoscale light transport,[5] nanoantennae,[6] and sensing.[2b,7] The optical properties of plasmonic polymers can be controlled and tuned by changing their degree of polymerization, NP orientation, and interparticle spacing.[8]

The next step in developing new plasmonic nanostructures is to move from a homopolymer to a copolymer structure by assembling NPs with different sizes[9] and compositions,[10] and by varying the order in which distinct NPs are incorporated in the chain. Similar to the self-assembly of colloidal homopolymers,[11] the self-assembly of plasmonic copolymers can greatly benefit from synthetic strategies developed for molecular copolymerization,[12] if a proper use of analogies and differences between these two processes is made.

Currently, linear co-assembly of distinct types of NPs is limited to few examples of alternating or block copolymers formed by spherical NPs.[13] No quantitative analysis of the co-assembly process and its comparison to copolymerization reactions has been reported. Linear co-assembly of anisotropic NPs, for example nanorods (NRs) with different dimensions and compositions, has not been studied, although such structures may have new optical properties, owing to higher-order plasmonic modes.[9,14]

In the present work, we report a molecular copolymerization approach to the co-assembly of gold NRs with different dimensions into random and block copolymer structures. For each structure we analyzed the change in composition, degree of polymerization, and heterogeneity. The approach is further extended to the copolymerization of NRs with different compositions. The proposed methodology offers a polymer synthesis-based strategy for producing one-dimensional nanomaterials with varying compositions and structures. This work is also important for fundamental studies of optical properties of linear plasmonic heterostructures. In particular, the theoretical prediction of new Fano plasmon modes in chains composed of gold NRs with different dimensions can be experimentally examined by single particle spectroscopy.[15]

To examine copolymerization of NRs with different lengths, we synthesized gold NRs with the mean diameter and length of 12 and 99 nm, respectively,[16] and fine-tuned the NR length in an end-etching process using HCl and H_2O_2.[17] With increasing etching time, the longitudinal surface plas-

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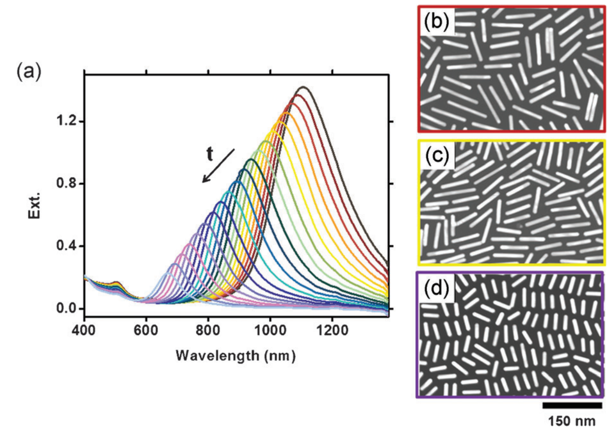

Figure 1. Tuning the length of gold NRs. a) Temporal variation in extinction spectra of the NRs during the course of the etching process. Starting from the 99 nm-long NRs at beginning of etching process at $t=0$ (black curve), the spectra were acquired every 5 min. b)–d) STEM images of the NRs with average lengths of b) 95 nm, c) 80 nm, and d) 50 nm. The mean diameter of the NRs was constant at 12 nm. The frame color around the STEM images matches the color of the corresponding extinction spectrum.

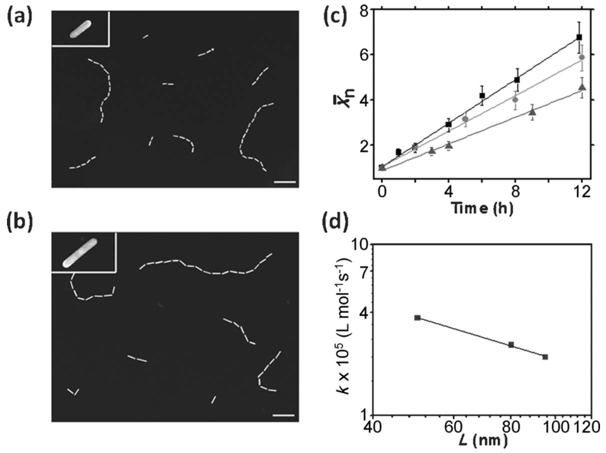

Figure 2. Homopolymerization of NRs with different lengths. a), b) STEM images of the NR chains formed after 4 h-long self-assembly time from a) 50 nm-long and b) 80 nm-long NRs. Insets: high-magnification STEM images of the corresponding individual NRs. $C_w=15$ wt%. Scale bars: 200 nm. c) Variation in the average degree of polymerization, $\bar{X}_n$, of the NR chains with self-assembly time, for 50 nm-long (■), 80 nm-long (●), and 95 nm-long (▲) NRs at $[M]_0=0.1$ nM.[21] The lines are linear fits. d) Variation in the rate constant of self-assembly of the NRs with different mean lengths. The slope is −0.81.

mon resonance (LSPR) band[18] of the NRs was gradually blue-shifted, while the transverse surface plasmon band was invariant (Figure 1 a), indicating a reduction NR length and a close-to-constant diameter of NRs. After a particular time, the etching process was terminated, yielding NRs with a desired length. Figure 1 b–d show scanning transmission electron microscopy (STEM) images of the NRs with different lengths used in the present work. The resultant NRs were end-functionalized with thiol-terminated polystyrene (PS) molecules with a molecular weight of $M_n = 12\,000$ g mol^{-1}.[11f]

The end-to-end association of NRs in chains was initiated by adding water to the solution of PS-functionalized NRs in dimethylformamide (DMF), to a final water concentration $C_w = 15$ wt%. To minimize the surface energy of the system in a poor solvent, the PS ligands formed physical bonds between the NR ends, thereby leading to the formation of a polymer-like structure.

To examine the effect of NR reactivity in copolymerization process, we studied the kinetics of the self-assembly of NRs with different lengths, L, in homopolymer structures. Figure 2 a,b show STEM images of the NR chains formed by 50 nm- and 80 nm-long NRs, respectively. Each population of NRs underwent an end-to-end assembly in linear structures with a limited degree of branching. Similar to molecular polymerization, the growth of NR chains was characterized by the temporal change in their number-average degree of polymerization, $\bar{X}_n$, as:

$$\bar{X}_n = \frac{\sum n_x x}{\sum n_x} \qquad (1)$$

where x is the number of NRs in the chain and n_x is the number of chains containing x NRs. For the NRs with lengths of 50, 80, and 95 nm, the value of $\bar{X}_n$ increased linearly with the self-assembly time (Figure 2 c), in a process analogous to reaction-controlled step-growth polymerization.[1,19] With increasing NR length, the self-assembly rate decreased, that is, a longer time was needed to achieve a particular value of $\bar{X}_n$. The rate constant k, calculated from the slope of the linear dependence of $\bar{X}_n$ versus time ($k = (\mathrm{d}\bar{X}_n/\mathrm{d}t)/4[\mathrm{NR}]_0$) was 3.72×10^5, 2.58×10^5, and 2.19×10^5 L mol^{-1} s^{-1} for the NRs with the length of 50, 80, and 95 nm, respectively.

The reduction in reactivity of longer NRs presumably originated from their reduced mobility (scaling as $1/L$), which led to a lower reaction frequency between NR ends. Moreover, longer NRs had a larger excluded volume v_e (scaling as $v_e \approx L^2$),[20] which was not accessible to other NRs, as a result of steric repulsion (Figure 2 d).

Copolymerization of NRs with different reactivities was studied for the 50 nm-long and 80 nm-long NRs undergoing self-assembly with the difference in rate constants of about 30%. Later in the text, we refer to these NRs as to SNRs and LNRs, respectively. The individual solutions of SNRs and LNRs in DMF were mixed to achieve the ratio of number densities of SNRs-to-LNRs of 0.8:1.0, with a total NR concentration of 0.18 nM. Following the addition of water to $C_w = 15$ wt%, the NRs with different lengths co-assembled in linear copolymer structures with a limited extent of branching. The STEM images of the copolymers were processed and analyzed using a Matlab program (Supporting Information). Figure 3 a shows a representative STEM image after Matlab processing, in which the SNRs and the LNRs are labeled blue and red, respectively.

We analyzed the kinetics of the co-assembly of SNRs and LNRs by examining the variation of $\bar{X}_n$ with the self-assembly time. The value of $\bar{X}_n$ increased linearly with time (Figure 3 b) in the range of the study, consistent with numerical simulations of the reaction-controlled step-growth copolymerization (Supporting Information). The effective rate constant of

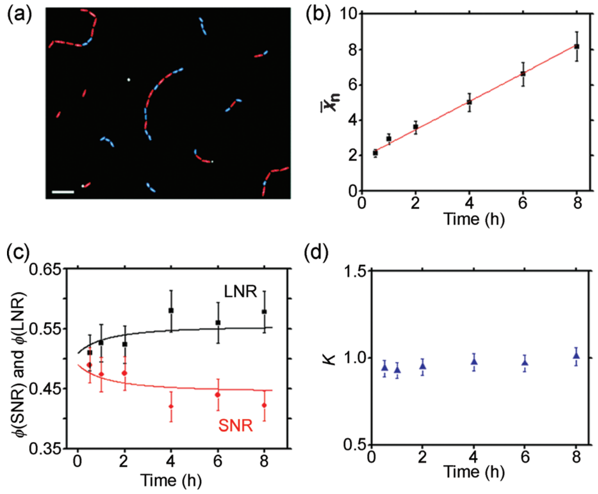

Figure 3. Co-assembly of gold NRs with different lengths. a) Matlab program-processed STEM image of chains formed by SNRs (blue) and LNRs (red). The scale bar is 200 nm. b) Variation in the average degree of polymerization of the chains formed from SNRs and LNRs, plotted as a function of self-assembly time. c) Temporal variation of the fractions of SNRs and LNRs in the chains. d) Variation in the microheterogeneity coefficient with self-assembly time. The mean length of the SNRs and LNRs was 50 and 80 nm, respectively. Each experimental point was calculated based on the analysis of 250–550 chains (a total of 600–2200 NRs).

copolymerization was determined as $k_{\text{copol}} = (\mathrm{d}\bar{X}_n/\mathrm{d}t)/2([S]_0 + [L]_0)$ and found to be $2.97 \times 10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, where $[S]_0$ and $[L]_0$ are the initial concentrations of SNR and LNR ends, respectively. In the early stage of copolymerization, k_{copol} can be expanded as:

$$k_{\text{copol}} = k_{\text{SS}} f^2 + k_{\text{LL}}(1-f)^2 + 2k_{\text{SL}} f(1-f) \tag{2}$$

where $f = [S]_0/([S]_0 + [L]_0)$ is the fraction of SNRs at time $t = 0$, and k_{SS}, k_{LL}, and k_{SL} are rate constants of the reactions between a SNR chain-end and another SNR chain-end, a LNR chain-end and another LNR chain-end, and a SNR chain-end and a LNR chain-end, respectively. Importantly, the value of k_{SL} of $2.89 \times 10^5\,\mathrm{L\,mol^{-1}\,s^{-1}}$ calculated from Eq. (2) was intermediate between the rate constants of homopolymerization of SNRs and LNRs, that is, $k_{\text{SS}} > k_{\text{SL}} > k_{\text{LL}}$.

Next, we studied the temporal variation in the composition of copolymer chains, characterized as the fractions of SNRs (ϕ_{SNR}) and LNRs (ϕ_{LNR}) in the chains as:

$$\phi_{\text{SNR}} = \frac{N_{\text{SNR}}}{N_{\text{SNR}} + N_{\text{LNR}}} \text{ and } \phi_{\text{LNR}} = 1 - \phi_{\text{SNR}} \tag{3}$$

where N_{SNR} and N_{LNR} are the numbers of SNRs and LNRs in the chains, respectively. Figure 3c shows the temporal variations in ϕ_{SNR} and ϕ_{LNR}. After 1 h, both NR types were co-assembled in the copolymer chains in close-to-equal amounts, although the initial ratio of number densities of SNRs-to-LNRs was 0.8:1.0. This effect resulted from the partial compensation of the higher reactivity of SNRs by the higher concentration LNRs in the reaction system. With increasing self-assembly time, the fraction of SNRs in the chains decreased, owing to their faster consumption, leading to the reduction of concentration of unreacted SNRs. For the opposite reason, the fraction of LNRs in the chains increased. After 8 h, at conversion $p = 0.875$ (calculated as $p = 1 - 1/\bar{X}_n$), the fractions of SNRs and LNRs in the chains were 0.42 and 0.58, respectively, and deviated by only 0.02 (or 3.5%) from the values expected for complete conversion. The experimental results correlated with theoretical variation in copolymer composition, plotted on the same graph. The results shown in Figure 3c implied that at high conversion, the composition of copolymers will be represented, or will only slightly deviate from the initial composition of the co-monomer mixture,[22] similar to molecular copolymerization.

The change in composition of the reaction mixture has important consequences: while we observed a linear growth of $\bar{X}_n$ vs. time (Figure 3b), after a sufficiently long time this dependence is expected to become non-linear. The time interval required for the deviation from linearity to appear reduces with a larger difference between k_{LL} and k_{SS} (Supporting Information, Figure S2a), that is, with increasing "asymmetry" of the system. However, even for $k_{\text{LL}}/k_{\text{ss}} \ll 1$, the non-linear effects are predicted to be weak, if the concentration of LNRs is considerably lower than that of SNRs. In this case, the reaction is dominated by the SNRs, as they have a higher concentration and react faster (Supporting Information, Figure S3).

Finally, the microstructure of the copolymer was characterized by using a microheterogeneity coefficient, K, as:[23]

$$K = \frac{P_{\text{SNR-LNR}}}{P_{\text{SNR-LNR}} + 2P_{\text{SNR-SNR}}} + \frac{P_{\text{SNR-LNR}}}{P_{\text{SNR-LNR}} + 2P_{\text{LNR-LNR}}} \tag{4}$$

where $P_{\text{SNR-LNR}}$, $P_{\text{SNR-SNR}}$, and $P_{\text{LNR-LNR}}$ are the fractions of dyads of elementary monomer units SNR-LNR, SNR-SNR, and LNR-LNR, respectively. In molecular copolymerization, K values of 0, 1, and 2 correspond to block, random, and alternating copolymers, respectively. In our work, the values of $K = 0.94$ and $K = 1.01$ after the self-assembly times of 0.5 and 8 h, respectively, showed a weak increase with time (Figure 3d), yet, the value of K remained close to unity. We stress that in contrast to molecular copolymerization, in which an insignificant difference in co-monomer reactivities is generally assumed, in our experiments the SNR and LNR co-monomers had a circa 30% difference in the self-assembly rate constants. Nonetheless, after 8 h assembly, the difference in comonomer reactivity and the difference in their initial concentration, was not sufficient to induce block formation.

We extended the copolymerization approach to the co-assembly of co-monomers with different compositions, namely palladium NRs with the mean length and diameter of 270 and 20 nm, respectively, and gold NRs with the mean length and diameter of 183 and 19 nm, respectively. The NRs were synthesized as described elsewhere.[24,25] Following the synthesis, CTAB at the ends of the NRs was replaced with thiol-terminated PS molecules with a molecular weight $M_n = 50\,000\,\mathrm{g\,mol^{-1}}$. We first tested the homopolymerization of palladium NRs by adding water to the NR solution in DMF to $C_w = 15$ wt%. Figure 4a shows a representative STEM image of the palladium NRs assembled in the end-to-end manner,

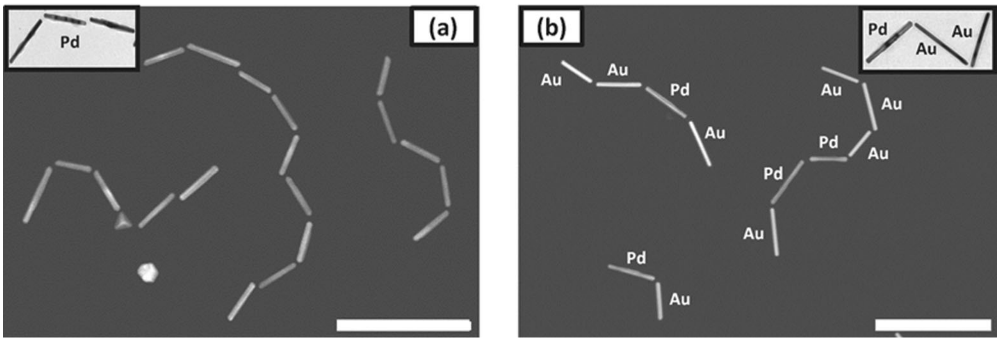

Figure 4. Copolymerization of palladium and gold NRs. a)–b) STEM images of a) homopolymers of palladium NRs, and b) copolymers of palladium and gold NRs with initial concentrations of 8.6 and 43 nm, respectively. Insets: high-magnification transmission electron microscopy (TEM) image of fragments of a) a Pd NR chain and b) a Pd-Au chain. $C_w = 15$ wt%. The self-assembly time was 48 h. Scale bars: 500 nm.

which confirmed the dominant regiospecific attachment of PS ligands to the NR ends. For the self-assembly time of 48 h, a linear increase of $\bar{X}_n$ with self-assembly time occurred with a rate constant $k = 3.2 \times 10^2$ L mol^{-1} s^{-1}. Owing to the low rate of self-assembly, the chains reached a $\bar{X}_n$ of only 2.2. Furthermore, because of the large mass of palladium NRs, the chains with $x > 10$ precipitated.

For the co-assembly of gold and palladium NRs, we mixed their individual solutions in DMF to achieve the ratio of number densities of gold-to-palladium NRs of 1:0.2. Following the addition of water to $C_w = 15$ wt%, the NRs co-assembled into copolymer structures. Figure 4b shows an STEM image of copolymers formed after 30 h self-assembly. Palladium NRs were distinguished from gold NRs owing to their rougher surface and a lower electron density. After 48 h, the copolymer chains had a fraction of gold NRs of 0.72 and microheterogeneity coefficient $K = 1.13$, which reflected a stronger asymmetry of the system than in the case of LNRs and SNRs. Yet, for the selected self-assembly time, the value of K did not strongly deviate from unity, indicating the formation of a random copolymer.

For the co-assembly of block copolymer structures from gold SNRs and LNRs, we used two synthetic strategies that are commonly utilized in the synthesis of molecular block copolymers.[19,26] Figure 5a (left) shows the two-prepolymer approach to NR block copolymers. We separately prepared homopolymer structures from SNRs and LNRs in the DMF/water mixture at $C_w = 15$ wt%, each at $\bar{X}_n \approx 2$, by assembling them for 2 and 3 h, respectively. Upon mixing the solutions of homopolymers, the chains of SNRs and of LNRs underwent copolymerization. In the one-prepolymer method (Figure 5a, right), after the assembly of LNR homopolymer with $\bar{X}_n = 5.5$ in a water/DMF mixture, we introduced individual SNRs. In a separate experiment, we assembled SNR chains and added individual LNRs.

The copolymerization of the LNRs and SNRs was monitored by imaging the self-assembled structures and by measuring their extinction spectra in the course of copolymerization. For the two-prepolymer method, a representative MATLAB-processed STEM image (Figure 5b; Supporting Information, Figure S5) shows diblock and triblock copolymers, as well as individual NRs, homopolymers, and chains with short SNR-LNR fragments. Figure 5c shows the distribution of all the species in the system. A large (ca. 80%) population was represented by diblock and triblock copolymer structures. The value of microheterogeneity coefficient, $K = 0.5$ indicated the formation of a large fraction of block copolymers.

For block copolymers prepared by the one-prepolymer method, we analyzed the STEM images of the chains to examine the temporal change in $\bar{X}_n$ of the LNR and SNR blocks (Figure 5d). While the value of $\bar{X}_n = 5.5$ for the LNR blocks changed by less than 2%, the value of $\bar{X}_n$ of the SNR blocks showed the expected linear increase, because of the dominant effect of the attachment of SNR monomers or oligomers to the ends of LNR blocks or to each other. This effect was expected for the ratio of concentrations of LNR chains and individual SNRs of 0.18:1.0, respectively (resulting from equal initial concentrations of individual SNRs and LNRs and from $\bar{X}_n = 5.5$ for the LNR prepolymer).

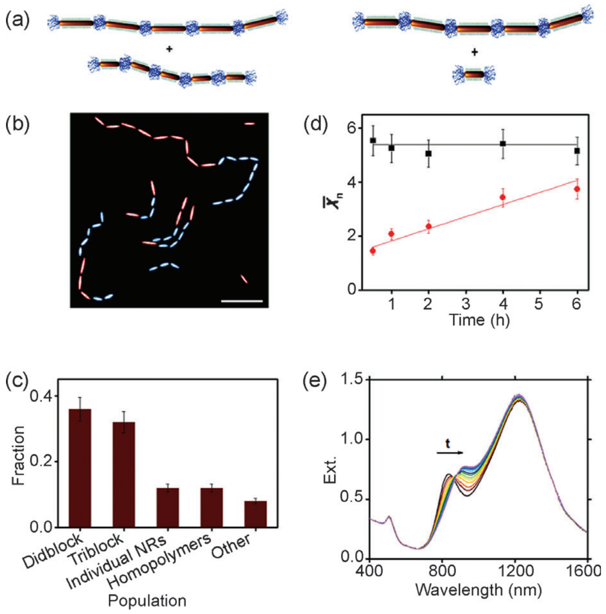

Figure 5. Formation of block copolymer from SNRs and LNRs. a) Illustration of two-prepolymer (left) and one-prepolymer (right) methods for step-growth copolymerization of block copolymers. b) MATLAB-processed STEM image of the chains formed by the two-prepolymer method. Scale bar: 200 nm. c) Distribution of species following NR co-assembly by a two-prepolymer method. "Other" refers to multiblock and branched chains. d) Temporal variation in $\bar{X}_n$ of blocks formed by SNRs (red circles) and LNRs (black squares) in copolymers assembled by a one-prepolymer method. e) Extinction spectra of the SNRs and LNRs undergoing copolymerization by a one-prepolymer approach.

The dominant growth of SNR blocks was also supported by the variation in extinction spectra of plasmonic chains (Figure 5e), which exhibited a red-shift of the λ_{LSPR} corresponding to SNRs.[8,14] With progressing co-assembly time, the λ_{LSPR} corresponding to the chains of LNRs remained invariant at 1221 nm, indicating that the formation of new LNR-LNR contacts was negligible. Concurrently, the λ_{LSPR} of the SNRs red-shifted from 835 to 916 nm, suggesting that individual SNRs co-assembled in an end-to-end manner either by forming chains of SNRs, or by forming SNRs blocks attached to the LNR blocks. While the association of LNR chains with SNRs or with chains of SNRs did not lead to a shift of λ_{LSPR} of the LNR chains, a slight increase of the peak intensity was observed, presumably because the LSPR of the LNR chains was close to saturation.[8c,14] A similar change in extinction was observed for block copolymers produced by adding LNR monomers to a SNR prepolymer: the λ_{LSPR} of SNR chains remained constant, while the value of λ_{LSPR} of the LNRs red-shifted (Supporting Information, Figure S6).

In summary, our work provides molecular guidance for the generation of one-dimensional plasmonic heterostructures (plasmonic copolymers) that are formed by nanoparticles with distinct dimensions and compositions. These structures uniquely match the needs of single particle spectroscopy and are challenging to achieve by top-bottom approach. They provide an excellent model system for the fundamental studies of plasmonic properties (such as Fano plasmon modes) that are caused by the asymmetry of nanostructures with unequally sized building blocks. Furthermore, the ability to visualize self-assembled nanostructures allows for the analysis of different stages of copolymerization process, and in contrast to molecular polymerization, reveals the mechanism of copolymerization of “asymmetric” monomers.

Experimental Section

The self-assembled NR structures were imaged by STEM (Hitachi HD-2000) at 200 kV and TEM (H-7000) at 100 kV. A dilute solution of the NRs or a dispersion of self-assembled NRs was cast onto a carbon-coated copper grid and the solvent was quickly removed with a Kimwipe towel.

Analysis of STEM images was performed using a MATLAB program. Each NR was approximated as an ellipsoid and the length of the NR was approximated as the major axis of the ellipsoid. The threshold between populations of SNRs and LNRs was set at 62.5 nm, allowing the analysis of the fraction of LNR-LNR, SNR-SNR, SNR-LNR connectivity.

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