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Patchy Metal Nanoparticles with Polymers: Controllable Growth and Two-Way Self-Assembly

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We report a new design of polymer-patched gold nanoparticles (AuNPs) with controllable interparticle interactions in terms of their direction and strength. Patchy AuNPs (*p*AuNPs) are prepared through hydrophobicity-driven surface dewetting under deficient ligand exchange conditions. Using the exposed surface on pAuNPs as seeds, a highly controllable growth of AuNPs is carried out via seed-mediated growth while retaining the size of polymer domains. As guided by ligands, those pAuNPs can self-assemble directionally in two ways along the exposed surface (head-to-head) or the polymer-patched surface of *p*AuNPs (tail-to-tail). Control of surface asymmetry/coverage on pAuNPs provides an important tool in balancing interparticle interaction (attraction vs. repulsion) that further tunes assembled nanostructures as clusters and nanochains. The self-assembly pathway plays a key role in determining the interparticle distance and therefore plasmon coupling of pAuNPs. Our results demonstrate a new paradigm in directional self-assembly of anisotropic building blocks for hierarchical nanomaterials with interesting optical properties.

1. Introduction

There has been remarkable progress in controlled synthesis of metal nanoparticles (NPs) with a variety of shapes, sizes, and chemical composition.¹⁻³ Those metal NPs as building blocks provide tremendous opportunities in design of functional materials using bottom-up self-assembly.⁴⁻¹⁴ Synthesis favors symmetry to lower the surface energy under given synthetic conditions;¹⁵ however, selfassembly benefits from asymmetry.¹⁶⁻¹⁸ Adding asymmetry on NP building blocks has a significant impact on interparticle interaction that guides and potentially programs self-assembly in a specific pathway. Using truncated tetrahedral quantum dots as an example, asymmetric surface ligand modification on their (1011) and (0002)facets led to the formation of quasicrystalline superlattices with a 10fold rotational symmetry.¹⁹ Reducing or breaking the symmetry on the surface of NPs, therefore, provides directional interparticle interaction to guide the self-assembly of NPs in an unprecedented way. To this end, one area that has drawn increasing interest is the selective ligand modification of metal NPs to form so-called patchy NPs.^{20, 21} Ligands can pattern the surface of NPs through a number of methods, including templated surface modification,^{22, 23} site-specific grafting,²⁴⁻²⁶ phase separation of mixed ligands,²⁷⁻³¹ and hydrophobicity-driven phase segregation.^{32, 33} As a post-synthetic method, surface ligands pattern the surface of metal NPs having predesigned nanostructures without re-designing and re-synthesizing of NPs. When grafting hydrophobic polymers on plasmonic metal NPs, hydrophobicity-driven surface dewetting has proved to anisotropically pattern the NP surface as demonstrated by

Kumacheva,³² Nie³⁴ and us.^{35, 36} When transferred from a good to a selective solvent, hydrophobic polymer ligands show a transition from isotropic (core-shell) to anisotropic (patched) coating on metal NPs, namely surface dewetting.³⁷ As a result, distinct properties between the covered and exposed NP surface can potentially provide directional interparticle interaction to assemble patchy NPs.²⁵ While asymmetric patches with various chemical compositions can guide the self-assembly as reported recently,³⁸⁻⁴⁰ there is very limited controllability over the balance of attractive and repulsive interparticle interactions that play a key role in determining the self-assembly outcomes.





In the current contribution, we report a versatile synthetic strategy to precisely pattern gold NPs (AuNPs) with well-defined

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ligand coverage and/or topologically asymmetric patches. We further demonstrate to use the asymmetric ligand distribution to guide the self-assembly of patched AuNPs (pAuNPs) in two opposite directions, namely head-to-head (H-H) and tail-to-tail (T-T). The key findings are three-fold. First of all, we resolve the synthetic challenges in controlling surface asymmetry/coverage to balance interparticle interaction. Through the combination of hydrophobicity-driven surface dewetting and seed-mediated growth, the exposed Au surface can further grow with a great size precision to tune ligand coverage on pAuNPs stoichiometrically (Scheme 1). Second, those pAuNPs can self-assemble directionally in two ways: along the exposed surface (or H-H) or the polymer-patched surface of pAuNPs (or T-T). By selectively removing the capping ligands or chemically grafting hydrophilic poly(ethylene oxide) (PEO) on the

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newly grown Au surface, we can switch the two self-assembly pathways (Scheme 1). The two-way self-assembly shows a distinct impact on the interparticle localized surface plasmon resonance (LSPR) coupling. Third, the balance of attractive and repulsive interparticle interactions provides a powerful tool to vary the selfassembly outcomes in both H-H and T-T pathways. With dedicated re-balance of thermodynamic driving forces, the self-assembly kinetics and nanostructures of *p*AuNPs in each pathway can be controlled. Our results therefore open up enormous new possibilities to design not only symmetry-breaking metal NP building blocks but also their assembly with predictable nanostructures with new ensemble properties.

2. Results and Discussions



Figure 1. (a) Scheme illustrating the preparation of *p*AuNPs and seed-mediated growth to control surface coverages and topologies. (b, c) Low-resolution TEM images of *p*AuNP-14 (b) and *p*AuNP-38 (c). The inset in c shows the polycrystalline Au core with an arrow indicating the direction of the polymer patch. (d, e) TEM of *p*AuNP-14 seeds (d) and *p*AuNP-38 (e) at different tilted angles: -55° , -20° , 20° and 55° (left to right). (f, g) Histogram of *d*_{Au} before (f) and after growth (g). (h) *in situ* UV-vis monitoring the growth of *p*AuNP-38 nm with a time interval of 30 s.

The preparation of initial Janus-type pAuNPs was carried out using a previously reported procedure.³⁶ In brief, PS₂₀₀-SH (M_n=20.7 kg/mol, D=1.1) and PS₄₀-*b*-PEO₁₁₄ (M_n = 9.2 kg/mol, D=1.1, Figure S1) were dissolved in N, N-dimethylformamide (DMF). Pre-concentrated citrate-capped AuNP solution (14.6±1.3 nm, Figure S2) was then added dropwise into the above DMF solution. After gentle shaking, the solution was incubated at room temperature overnight, followed by the addition of deionized water (15 vol% relative to DMF) as a non-solvent to trigger the coil-globule transition of PS. The glass vial was then sealed and annealed at 100 °C for 1 h. After cooling, the formed

Janus-type *p*AuNPs were quenched by injecting the solution into excess water. *p*AuNPs were centrifuged three times to remove free polymers. The LSPR peak of *p*AuNPs is 527 nm in water (Figure S3), about 8 nm redshift as compared to original AuNPs. Those *p*AuNPs are very stable in water and no change was seen after one-year storage.

The nanostructure of pAuNPs was first revealed by transmission electron microscopy (TEM, Figure 1b-c). pAuNPs show typical snowman shapes where the polymer domain forms a micelle-like patch on the surface of AuNPs. AuNPs appear darker than the polymer domains, due to their difference in electron density. The diameter of AuNPs (d_{Au}) and the size of polymer micelles (d_{poly} , cross with AuNPs) was measured to be 14.8±1.1 nm and 20.3±2.2 nm (Figure S3), respectively. Low-resolution TEM confirms the high uniformity of pAuNPs with a yield of >95% for Janus-type patched pAuNP-14 (Figures S3-S4). pAuNP-14 was examined by TEM at different tilted angles (Figure 1d). The projected polymer domains at high tilted angles (55° and -55°) become crescent and obviously smaller as compared to the projected images at low tilted angles, while the size and shape of AuNPs had a minimum change. This is due to the overlap of AuNPs and polymer domains at high tilted angles which shields the lighter polymer domains. Those results confirm the formation of asymmetric polymer coverage on AuNPs. All pAuNPs likely have polymer domains directly dried on the TEM grids because the high-angle images show the flat interface of polymer domains with the grid. The formation of Janus-type pAuNPs is driven by the surface dewetting under deficient ligand exchange (DLE) as reported previously.^{32, 34, 36} When transferring from a good solvent to a poor solvent for PS-SH, the collapsed PS ligands de-wetted the surface of AuNPs, leading to the formation of polymer patches in the presence

of PS_{40} -*b*-PEO₁₁₄. The surface coverage of AuNPs by the polymer domain, denoted as A_{c} , is ~62% as estimated from TEM (Figure S5).

Those Janus-type pAuNPs have two distinct surfaces, *i.e.*, the exposed surface (likely capped by citrate, see below) and the covered surface by polymer micelles. Using the seed-mediated growth, metals (or a second metal) can further grow from the exposed surface to tune the A_c while polymer domains retain frozen below the glass transition temperature (Tg, ~110 °C). The typical growth solution was prepared by mixing cetrimonium bromide (CTAB), HAuCl₄ and ascorbic acid (see details in SI).⁴¹ After adding pAuNP-14 as seeds, the growth was evidenced by the solution color change (Figure 2g). At an Au equivalence (Au_{eq}) of 24 (Au in the growth solution relative to pAuNP-14 nm) to grow pAuNP-38 (Figures 1c and S6 and Table S1), upon the mixing of the seed solution and the growth solution, the color turned from light pink to purplish red gradually. As monitored by UV-vis (Figure 1h), the LSRP for pAuNP-14 seeds peaked at 527 nm and an immediate increase of the peak intensity was seen along with the red shift to 534 nm after 30 s. The LSPR absorbance of pAuNPs kept increasing in the first 5 min, due to the larger molar absorption coefficient (ɛ) for larger AuNPs given their constant molar concentration.42 A new shoulder peak was found at 638 nm after 3 min. This is somewhat different from the size increase of Au due to the layer-by-layer growth, known as the Frankvan der Merwe mechanism, where no shoulder peak is expected for spherical AuNPs with a larger size.⁴¹ The shoulder peak is presumably due to the asymmetric growth of AuNPs along the exposed surface of *p*AuNPs, leading to the appearance of the dipole resonance mode. Similar LSPR peaks were reported in the formation of Au@Au dimers.⁴³ The d_{Au} increases to 38.9±2.2 nm (Figure 1g), while the size of polymer domain (d_{poly}) is 19.3±2.4 nm (Figure 2f), comparable to that of pAuNPs-14 seeds.



Figure 2. (a-d) TME images of *p*AuNPs with different Au sizes: 19.9 ± 1.9 nm (a); 24.6 ± 1.3 nm (b); 28.4 ± 2.1 nm (c); and 30.8 ± 1.6 nm (d). (e) Plotting the diameter of *p*AuNPs against Au_{eq}. Red square: the ideal size with 100% conversion and black circle: the measured size from TEM. (f) Plotting *d_{poly}* of Janus-type *p*AuNPs against the diameter of Au core. (g) Images of *p*AuNP aqueous solutions with different Au sizes. (h) UV-vis of *p*AuNPs with different Au sizes.

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The seed-mediated growth also provides great precision on the size of freshly grown Au domains by varying Au_{eq}. Figures 2a-d show the TEM images of *p*AuNPs at various Au_{eq}. When increasing Au_{eq}, a continuous growth of Au domains was observed in the range of 14-38 nm. All these *p*AuNPs show uniform distribution with a high yield of >90% to Janus-type *p*AuNPs (Figures S7-S9). For example, at Au_{eq} = 6, *d*_{Au} increased to 24.6 nm as *p*AuNP-24, while the *d*_{*poly*} remained as 19.4 nm. The yield of Janus-type *p*AuNP-24 nm is close to 95% where only one polymer domain attaches on AuNPs. More quantitatively, the size of Au domains fits well against the Au_{eq} through a scaling law, *d*_{Au} \propto Au_{eq}^{0.37}. It is very close to the power law of Au_{eq}^{0.33} assuming the conversion of HAuCl₄ to be 100%. Those results suggest that the growth of Au domains was mediated and initiated on the exposed surface of *p*AuNP-14 seeds.

The growth of *p*AuNPs also has a strong impact on the LSPR absorption of AuNPs. Figure 2g shows the typical image of *p*AuNP solutions at different Au_{eq}. With a larger Au domain, the solution became deeply red. With $d_{Au} > 30$ nm, the solutions were slightly purplish. The UV-vis spectra of *p*AuNPs are given in Figure 2h. As the concentration of *p*AuNP-14 remained as 0.288 nM, the peak intensity had an obvious increase with the size of AuNPs. For $d_{Au} > 30$ nm, *p*AuNPs show a similar shoulder peak at 634 nm, close to that of *p*AuNP-38 at a long growth time (Figure 1h). Those results are consistent with the asymmetric growth on *p*AuNP-14 seeds.

Interestingly, no significant change of polymer domains was seen during the seed-mediated growth (Figure 2f). The d_{poly} is approximately 20 nm regardless of the size of Au domains. Polymer domains were likely frozen in water; therefore, the size of freshly grown Au domains that are only covered by CTAB can be independently tuned. Since the d_{poly} as well as the polymer-Au interface did not vary, the surface coverage of *p*AuNPs with polymer ligands (A_c) would continuously decrease (Table S2 and Figure S5). Qualitatively, the A_c will be propositional to d_{Au} ⁻² (see details in SI). For *p*AuNP-19, the A_c is 33%; the A_c further decreases to 8.7% for *p*AuNP-38. It is therefore expected that those *p*AuNPs would have controllable surface ligand composition and coverage.

We further confirm the critical role of the second capping ligand, *e.g.*, CTAB, in the controlled growth of new Au domains during the seed-mediated growth. With a strong capping ligand, like CTAB, cetyltrimethylammonium chloride (CTAC), polyvinylpyrrolidone (PVP), and poly(acrylic acid) (PAA), we observed a similar growth trend of *p*AuNPs where spherical Au domains were seen after growth (Figure S10). In the presence of a weak ligand like citrate, multi elongated Au islands were grown on *p*AuNP-14 seeds. Those Au islands were easily distinguished, and they had smaller interfaces with the original seeds, similar to those obtained without the second capping ligands (Figure S11). This presumably is attributed to the fast deposition rate where the weak ligands allow the fast binding and diffusion of adatoms.⁴⁴ We measured the UV-vis spectra of *p*AuNPs grown with different second capping ligands at $Au_{eq} = 6$. The LSPR peaks of *p*AuNPs for CTAC, PVP and PAA capped *p*AuNPs is around 540 nm (Figure S10), close to *p*AuNP-24 nm with CTAB. Those LSPR peaks are sharp, indicating the uniformity of newly grown Au domains. However, *p*AuNPs grown with citrate have two distinct LSPR peaks located at 536 nm and 613 nm, arising from those elongated Au islands.



Figure 3. (a-c) Low-resolution TEM image (a), EDX mapping and HADDF (b), high resolution TEM (c) of Ag@pAuNP-14. (d-f) Low resolution TEM image(d), EDX mapping and HADDF (e), high resolution TEM image (f) of Pt@pAuNP-14.

Our synthetic strategy can be further extended to design other more sophisticated patchy structures on AuNPs, like A-B-C topological heterotrimers with two different patches.^{45, 46} Noble metals, like Ag (Figures 3a-c and S12), Pd (Figures S13-S14) and Pt (Figures 3d-f and S15), can be grown on *p*AuNP-14 seeds.⁴⁴ The examples of Ag and Pt domains selectively grown from the exposed Au surface have a yield of >95% and reasonable uniformity. The energy-dispersive X-ray spectroscopy (EDX) mapping and high-angle annular dark-field (HAADF) images confirm the formation of asymmetric coating (Figure 3). The high-resolution TEM images suggest that, i) Ag and Au have a close interface given the close match of their lattice structures (Figure 3c); and ii) Pt domains form as a corona with a porous structure on *p*AuNP-14 seeds (Figure 3f) under this specific condition.^{45, 47}

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Scheme 2. Two-way self-assembly strategy of *p*AuNPs: H-H and T-T modes.

Surface anisotropy was further used to guide the self-assembly of those NP building blocks. Using *p*AuNPs as an example, the unique two-way self-assembly in H-H and T-T modes as directionally guided by polymer patches is illustrated in Scheme 2. In the H-H mode, we use the van der Waals interactions of the exposed Au surface capped with CTAB. After selective removal of CTAB, *p*AuNPs form aggregates along the exposed Au surface while the polymer patches stabilize such assemblies.⁴⁸ Strong interparticle plasmon coupling is expected since no ligands are in between *p*AuNPs. In the T-T mode, the exposed Au surface of *p*AuNPs was further grafted by hydrophilic polymer ligands like PEO₄₅-SH. After removal of polymer domains, *p*AuNPs become amphiphilic where PEO₄₅-SH and PS₂₀₀-SH pattern the surface of AuNPs as Janus-type amphiphiles (PEO-*p*AuNP-PS). In the poor solvent of PS, PEO-*p*AuNP-PS can assemble in the T-T mode with a weak plasmon coupling due to the large interparticle distance. More importantly, the delicate balance of the A_c enables to control the interaction strength, in addition to simply providing directional forces among *p*AuNPs. It is, therefore, possible to access hierarchical assemblies with directional and controllable interparticle forces.



Figure 4. UV-vis absorption spectra (a-c) and TEM images (d-f) of *p*AuNP-14 nm (a,d), 28 nm (b,e) and 38 nm (c,f). All experiments were carried out in ethanol/water mixture (9/1, vol) at room temperature.

To trigger the H-H self-assembly, the aqueous solution of *p*AuNPs was first centrifuged twice to remove excess CTAB. The final *p*AuNPs were re-dispersed in 0.1 mL of water, followed by adding 0.9 mL of ethanol.⁴⁸ The self-assembly was monitored by *in situ* UV-vis spectroscopy. Using *p*AuNP-28 nm as an example, a large hump appeared as a shoulder peak in the range of 600-700 nm after incubation for 1 h (Figure 4b). This shoulder peak grew gradually, and the solution color turned from red to purplish. The peak at 604 nm became much more pronounced at a longer incubation time and no further decrease at 533 nm was seen after 1 h incubation. The self-assembly was quenched by adding excess PVP. We assigned this new UV peak to the strong plasmon coupling of assembled *p*AuNP-28. A similar trend was found for *p*AuNP with different Au sizes (Figures S18-S20); however, the plasmon shift is highly determined by the size

of AuNPs.⁴⁹ For *p*AuNP-38 nm, the new peak at 676 nm rose as fast as compared to that of *p*AuNP-28 nm (Figure 4c). It took around 3 h to have the comparable peak intensity with the main LSPR peak at 534 nm. As the A_c decreased, larger *p*AuNPs had more surfaces capped by CTAB. The removal of CTAB, essentially driven the selfassembly, would theoretically provide stronger interparticle attraction, although larger AuNPs have a slower diffusion in solution. As a control, *p*AuNP-14 seeds did not show any color change even after 24 h (Figure 4a), indicating that *p*AuNP-14 seeds with a high A_c were stable in ethanol/water mixture. Note that, the H-H selfassembly of *p*AuNPs is irreversible and cannot be reversed by changing the ratio of ethanol/water.



Figure 5. (a, b) UV-vis spectra of PEO-SH grafted 14 nm-*p*AuNPs (a) and PEO-SH grafted 28.4 nm-*p*AuNPs (b) assembly. (c-f) TEM images at two different magnifications of PEO-SH grafted 14 nm-*p*AuNPs (c and e) and PEO-SH grafted 28.4 nm-*p*AuNPs assembly (d and f).

Assembled nanostructures of pAuNPs were further examined by TEM. Figure 4d shows pAuNP-14 seeds incubated in ethanol/water after 24 h. Well-dispersed individual pAuNPs were observed, consistent with the UV-vis result (Figure 4a). When increasing the Au domains of pAuNPs, there is a clear morphological transition from individual NPs to clusters and eventually to chains (more TEM results in Figures S16-S22). The typical TEM image of assembled pAuNP-28 nm is given in Figure 4e. With the A_c of 16.3%, clusters of pAuNP-28 were seen under TEM. Dimers and trimers are the major products with a total yield of 81% (Figure S19). All those clusters have polymer domains facing out to the solvent in order to stabilize these nanoclusters. Noticeably, there is nearly no interparticle spacing seen from TEM. Adjacent AuNPs were in close contact where the near field coupling of AuNPs is strong, as seen by UV-vis. Further increasing the size of Au domains leads to the formation of larger aggregates that better shields the interface of uncovered Au with the solvent. For pAuNP-38, the dominant assemblies were short nanochains. Among those nanochains, the Au domains of pAuNP-38 formed different packing, including linear chains, zig-zag chains and bundled double chains (see schemes and more images in Figure S21), while polymer patches were around the surface of those aggregates.

In case of the T-T self-assembly, the exposed surface of *p*AuNPs was first modified through ligand exchange with hydrophilic PEO₄₄-SH in water.⁵⁰ After PEO₄₄-SH replaced CTAB, we used DMF to dissolve and further remove free CTAB and PS₄₀-*b*-PEO₁₁₄ through centrifugation (see experimental details in SI). The final *p*AuNPs were thus patterned asymmetrically with PEO₄₄-SH and PS₂₀₀-SH as Janus-

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type PEO-pAuNP-PS (Scheme 2). As amphiphiles, ⁵¹ they can assemble in a selective solvent like water. Figures 5c and e show TEM images of PEO-pAuNP-PS assemblies obtained from pAuNP-14 in water. Since pAuNP-14 has an A_c of 62%, the AuNP surface is largely covered with PS₂₀₀-SH. There is a strong hydrophobicity to drive the selfassembly to form nanochains (~97% of AuNPs in chains). Some chains are very long, up to a few micrometers. These nanochains are very different from the H-H nanochains as given in Figure 4f. There are clear gaps in between adjacent AuNPs which were filled with PS_{200} -SH (see more zoomed-in images in Figure S23). The UV-vis results of the T-T nanochains are exhibited in Figure 5a. A large and broad LSPR band with a peak at 539 nm was seen. It is similar to that of nanochains formed by PS-grafted AuNPs in literature.52-54 It is noteworthy that the T-T self-assembly is reversible. When redispersing those nanostructures in DMF, a good solvent to both PEO and PS, the LSPR peak of pAuNPs can be fully restored. Subsequent dialysis against water would trigger re-self-assembly reversibly, resulting the formation of T-T assemblies.

The assembled nanostructures of PEO-pAuNP-PS obtained from pAuNP-28 are compared using TEM (Figures 5d and f). As the Ac of pAuNP-28 nm reduced to 16.3%, the hydrophobicity of those PEOpAuNP-PS became weaker. Those amphiphilic AuNPs only formed clusters in water. The yield of dimers and trimers is ~65%; while ~29% of AuNPs did not assemble as measured from TEM (Figure S24). Under TEM, lighter polymer domains formed by hydrophobic PS₂₀₀-SH are also visualizable (Figure 5b). Among those clusters, the gap between AuNPs is around 4.2 nm. Those results confirm, again, the T-T assemblies were formed along the AuNP surface grafted with PS200-SH. The LSPR peak of these clusters appeared at 542 nm (Figure 5b), in good agreement with our TEM observation. The larger LSPR shift as compared to that of nanochains (Figure 5a) is presumably due to the size increase of AuNPs. In addition, for A-B-C heterotrimers, similar T-T assemblies could be designed using the hydrophobicity of PS. Pt@pAuNP-14 as an example formed more complicated clusters along the surface covered by PS where Pt domains covered by PVP were at the ends to stabilize those clusters (Figure S25).

Conclusions

To summarize, we demonstrated the combined use of hydrophobicity-driven surface dewetting and seed-mediated growth to precisely pattern AuNPs with different surface coverage and topologically tune the asymmetric patches on AuNPs. The formation of Janus-type polymer patches was carried out under DLE conditions to produce high-quantity and water-soluble *p*AuNPs. Using the exposed surface on *p*AuNP-14 nm as seeds, we showed a highly controllable growth of AuNPs while retaining the size of polymer domains. The growth on *p*AuNPs could be extended to different metal precursors, like Ag, Pd and Pt, to yield the A-B-C heterotrimers. As the freshly grown surface of AuNPs was covered by capping ligands, like CTAB, such surface anisotropy could further trigger the two-way self-assembly. By selective removal of CTAB, *p*AuNPs assembled along the exposed Au surfaces as the H-H assembly,

driven by van de Waals interactions of uncovered Au surfaces. Reducing the A_c that increases the attractive interaction among pAuNPs resulted in clear morphological transitions from individual NPs to clusters and nanochains. The further modification of the exposed Au surface with PEO₄₅-SH could drive the T-T self-assembly where the hydrophobic PS collapsed in its non-solvent. We showed that the assembly modes played a key role in controlling the interparticle distance and therefore plasmon coupling of AuNPs.

Self-assembly of pAuNPs selectively grafted by amphiphile polymers, including linear block copolymers,⁵⁴⁻⁵⁶ random copolymers,^{57, 58} and mixed homopolymer brushes^{51, 59-61} has been demonstrated previously. The formation of Janus-type amphiphilic pAuNPs was usually carried out through selective surface modification templated by liquid-liquid^{62, 63} or solid-liquid^{45, 64} interfaces. A well-known example from Li et al. demonstrated the use of PEO-SH single crystals that physically adsorbed AuNPs to allow the selective modification on the exposed surface with poly(methyl methacrylate). In spite of the directional interaction to guide the selfassembly, the balance of interparticle driving forces, i.e., the attractive interaction to drive self-assembly and the repulsive interaction to stabilize assembled nanostructures, has not been possible in previous designs. Combining the surface dewetting and seed-mediated growth, our strategy provides a clear solution to precisely design and essentially program the interparticle interaction. The current design allows us to not only control over the directional self-assembly of pAuNPs in those two-way approaches, but also to precisely tune the interparticle interaction to vary the self-assembly nanostructures. Our results illustrate an alternative way for the directional self-assembly of anisotropic building blocks with a great potential in programmable hierarchical assemblies. As an outcome, the two-way self-assembly of pAuNPs can tune plasmon coupling strength. In case of H-H self-assembly, the strongly coupled pAuNPs can be further used in sensing through surface enhanced Raman scattering (SERS) spectroscopy^{65, 66} and/or plasmonenhanced photocatalysis⁶⁷.

Author Contributions

H.D., Y.L. and J.H. conceived and designed the experiments. H.D., T.M., J.W., C-H.L., and H.T. performed the experiments, H.D., M-P.N, Y.L. and J.H. participated in discussions. The manuscript was drafted by H.D. and J.H. and all co-authors have contributed to revise and finalize the manuscript.

Conflicts of interest

There are no conflicts to declare

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