

Supporting Information

Entropy-driven formation of binary superlattices assembled from polymer-tethered nanorods and nanospheres

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EXPERIMENTAL SECTION

Materials. Ascorbic acid (AA, 99% metal basis), cetyltrimethylammonium bromide (CTAB, purity: 99%), poly (vinyl alcohol) (PVA, $M_n = 13\text{k-}23\text{k}$ g/mol, 87-89% hydrolyzed), sodium citrate, sodium borohydride (NaBH_4 , purity: 98%), tetraoctylammonium bromide (TOAB, purity 98%) and cetyltrimethylammonium chloride (CTAC, purity: 97%) were obtained by Aladdin. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, purity: 99.99%) and chloroplatinic and hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, purity: 99.99%) were purchased from Alfa Aesar. The thiol-terminated functional polymers $\text{PS}_{2\text{k}}\text{-SH}$ (the subscript refers to the M_n of the functional polymer, PDI = 1.15), $\text{PS}_{5\text{k}}\text{-SH}$ (PDI = 1.4), and $\text{PS}_{12\text{k}}\text{-SH}$ (PDI = 1.09) were obtained by Polymer Source. Other chemicals were supplied by Beijing Chemical Factory. All the materials were used directly as received. The glassware used to synthesize nanoparticles was cleaned by aqua regia and rinsed with deionized water a dozen times before the experiments.

Synthesis of AuNRs. AuNRs were synthesized through a seed-mediated growth method according to the literature protocols¹. In a standard synthesis of AuNRs, the CTAB-stabilized Au seeds were first prepared. Typically, a 10 mL aqueous solution containing CTAB (0.1 M) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (2.5×10^{-4} M) was prepared in a 20 mL vial. Then, the freshly prepared ice-cold NaBH_4 solution (0.01 M, 0.6 mL) was quickly added into the above vial under vigorous stirring for 2 min. The CTAB-stabilized seeds solution was kept at 25 °C for 1 h to ensure the complete formation of gold seeds. To

prepare the seed growth solution, CTAB (0.1 M, 19 mL) and AgNO₃ (10 mM, 0.2 mL) were mixed at 25 °C. Then, HAuCl₄·3H₂O (1 mL, 10 mM) was added to the above mixture; the solution turned dark yellow. Subsequently, AA (0.1 M, 0.12 mL) aqueous solution was injected into the solution, and the solution turned colorless immediately. To prepare AuNRs, the above CTAB-stabilized seeds solution (0.32 mL) was added into the growth solution at 27 °C. The result solution was left overnight without disturbing to prepare AuNRs. Finally, the AuNRs were purified by centrifugation (13 000 rpm, 30 min) and redispersed in deionized water for further use.

Synthesis of 4.7 nm and 10.0 nm AuNPs. The literature method was used to synthesis AuNPs². For the preparation of CTAB-stabilized Au seeds, the freshly prepared ice-cold NaBH₄ solution (0.01 M, 0.6 mL) was quickly added into a 10 mL aqueous solution containing CTAB (0.1 M) and HAuCl₄·3H₂O (2.5×10⁻⁴ M) with violent stirring for 2 min. Then the above solution was kept at 27 °C for 3 h to ensure the complete growth of CTAB-stabilized seeds. For the preparation of seed growth solution, CTAC (0.2 M, 2 mL), AA (0.1 M, 1.5 mL), and 1.8 mL or 0.05 mL seed solution were mixed in a vial. Subsequently, HAuCl₄·3H₂O (5×10⁻⁴ M, 2 mL) aqueous solution was injected into the above solution with vigorous stirring for 15 min at 27 °C. Finally, 4.7 nm and 10.0 nm AuNPs were purified by centrifugation (15 000 rpm, 30 min) and redispersed in deionized water for ligand exchange.

Synthesis of 1.7 nm AuNPs tethered with PS-SH. The reported Brust two-phase method was used to synthesize the AuNPs with the diameter of 1.7 nm³. HAuCl₄·3H₂O

aqueous solution (30 mM, 0.3 mL) and TOAB toluene solution (50 mM, 0.8 mL) were mixed with vigorous stirring until the HAuCl_4 was transferred into the toluene phase. Afterward, the PS-SH (18 mg, 0.5 mL) toluene solution was added to the above solution. The freshly prepared ice-cold NaBH_4 solution (0.04 M, 0.25 mL) was slowly injected into the above solution with vigorous stirring for 3 h. Then, the toluene was disassociated, and the PS-SH tethered AuNPs were purified by adding ethanol to the toluene solution. The toluene solution was kept at $-20\text{ }^\circ\text{C}$ for 12 h. Subsequently, the PS-SH tethered AuNPs were purified by centrifugation (14 000 rpm, 30 min) and redispersed in tetrahydrofuran (THF). The purification process was repeated 5 times to ensure that the excess PS-SH was removed. The resulting 1.7 nm AuNPs@PS solution was dried and redispersed in chloroform (10 mg/mL).

Synthesis of 3.5 nm PS-SH tethered PtNPs. PtNPs with a diameter of 3.5 nm were synthesized according to the previously reported method, and then the PtNPs were modified by PS-SH through a two-step ligand exchange strategy⁴. Firstly, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (2 mg/mL, 5 mL) and 64 mL deionized water were heated to boil into a vial. Then, a 1.53 mL aqueous solution containing citric acid (0.5 mg/mL) and sodium citrate (10 mg/mL) was injected into the above vial. Finally, 765 μL NaBH_4 aqueous solution (0.8 mg/mL) containing citric acid (0.5 mg/mL) and sodium citrate (10 mg/mL) was added into the above solution with stirring for 15 min. To prepare PS-SH tethered PtNPs, the above solution was added into the same volume THF solution containing PS-SH (mole ratio Au/PS-SH=1:0.3). Then the above solution was sonicated for 2 h and incubated for 12 h. The PS-SH tethered PtNPs were collected by

centrifugation (10000 rpm, 30 min). Subsequently, the concentrated PtNPs@PS solution was injected into PS-SH THF solution (mole ratio Au/PS-SH=1:0.15) for the secondary ligand exchange, followed by the same sonication and incubation. Finally, PtNP@PS building blocks were purified by adding a certain amount of ethanol (5 times) and redispersed in chloroform (10 mg/mL).

Surface modification of AuNPs. To functionalize the surface of the AuNPs and AuNRs with PS-SH ligands, the two-step ligand-exchange approach was used. Typically, the condensed AuNPs or AuNRs aqueous solution (1.0 mL) was added into a THF solution containing PS-SH polymers (10 mL, mole ratio Au: PS-SH = 1:0.3 or 1:0.15 for AuNPs and AuNRs, respectively). Then the solution was sonicated for 2 h and incubated overnight. The above PS-SH tethered AuNPs and AuNRs were directly collected by centrifugation (15000 rpm, 30 min) and redispersed in THF solution (0.5 mL). Then, the redispersed solution was injected into the THF solution of PS-SH (10 mL, mole ratio Au: PS-SH = 1:0.15 or 1:0.075 for AuNPs and AuNRs, respectively) for the secondary ligand exchange, followed by the same sonication, incubation, and centrifugation procedures to obtain the PS-tethered AuNPs or AuNRs. To purify the PS-tethered AuNPs and AuNRs, ethanol was added to the above THF solution to precipitate the PS-tethered AuNPs and AuNRs. Subsequently, the PS-tethered AuNPs and AuNRs were purified by adding some ethanol (5 times). The final products were redispersed in chloroform (10 mg/mL) and stored at -20 °C.

Preparation of single-component and binary superlattices. Typically,

AuNRs@PS, AuNPs@PS building blocks, and the hexadecane solvent were dissolved in chloroform with 30 mg/mL, 10 mg/mL, and 10 mg/mL, respectively. For preparing single-component superlattices of AuNRs or AuNPs, the nanoparticles solution and the hexadecane solution were mixed with a volume ratio of 3:5. For the preparation of binary superlattices of AuNRs or AuNPs, the AuNRs@PS solution, AuNPs@PS solution, and hexadecane solution were mixed by 30:5:50. Then, 0.1 mL of the above mixture was emulsified by PVA aqueous solution (3 mg/mL, 1 mL) with magnetic stirring (850 rpm, 3 min). The chloroform was allowed to evaporate for 3 days to obtain assemblies. The final assemblies were obtained three times centrifugation (10000 rpm, 10 min) to remove the excess surfactant.

Characterization: Transmission electron microscopy (TEM) measurement was performed on JEOL JEM-1400 at an accelerated voltage of 120 kV. The surface morphology of the samples was characterized by Zeiss Merlin Scanning electron microscopy (SEM). Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray (EDX) elemental mapping of the binary superlattices images were recorded by the JEOL JEM-F200 instrument at an acceleration voltage of 200 kV. The effective diameter (d_{eff}) was measured from the center-to-center distance between two adjacent nanoparticles of the single-component superlattice.

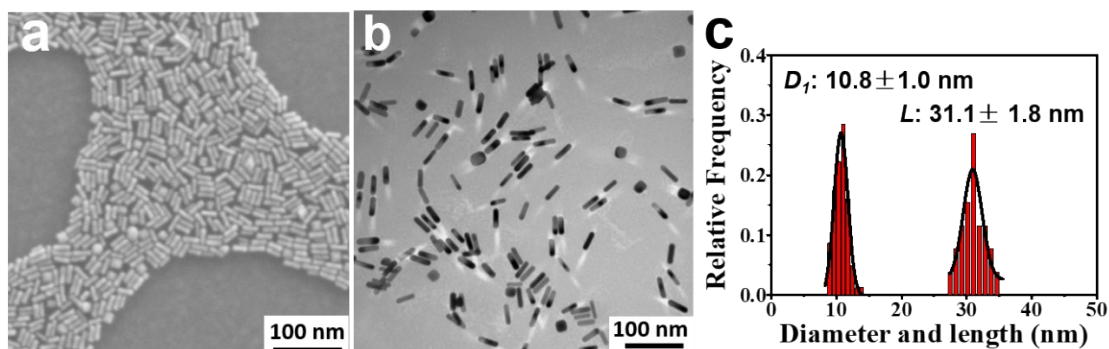


Fig. S1 (a) and (b) are SEM and TEM images of synthesized AuNRs, respectively. (c) The size distribution histogram of AuNRs is obtained from the statistics of more than 100 AuNRs by TEM analysis software.

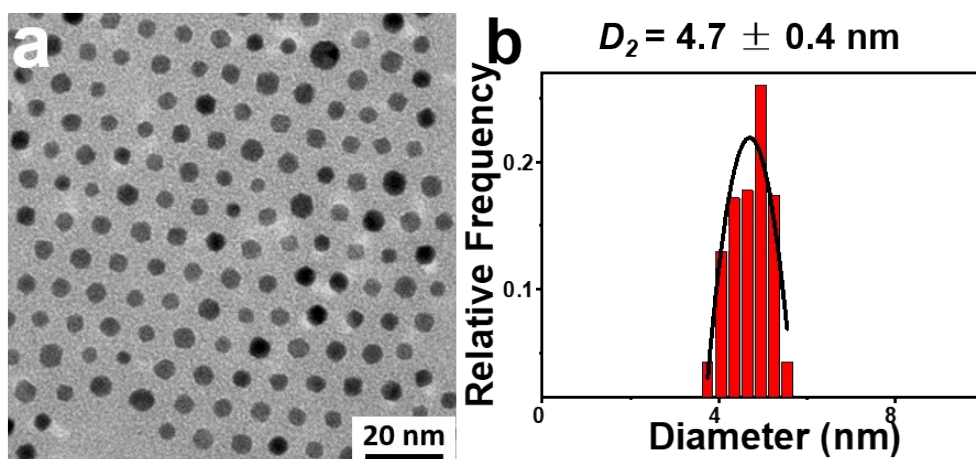


Fig. S2 (a) TEM image of synthesized AuNPs. (b) The size distribution histogram of AuNPs is obtained from the statistics of more than 100 AuNPs by TEM analysis software.

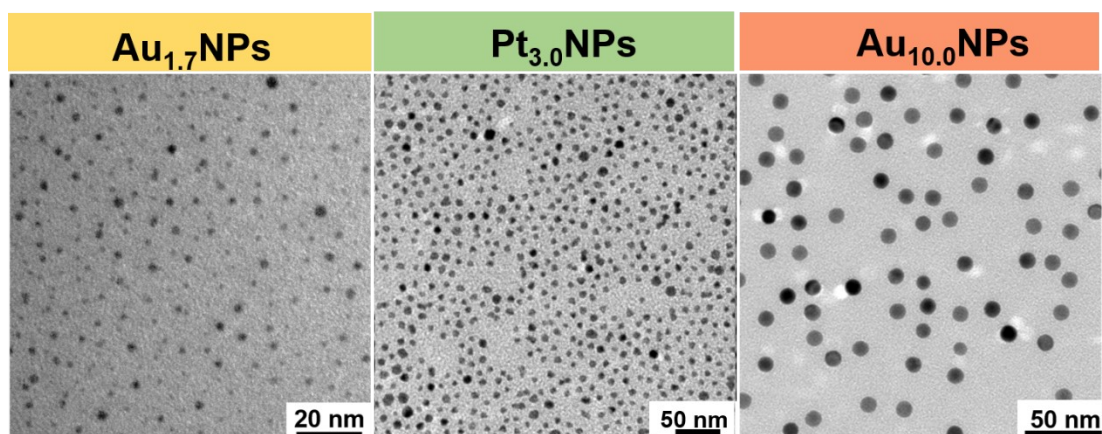


Fig. S3 TEM images of synthesized 1.7 nm AuNPs, 3.0 nm PtNPs, and 10.0 nm AuNPs, respectively.

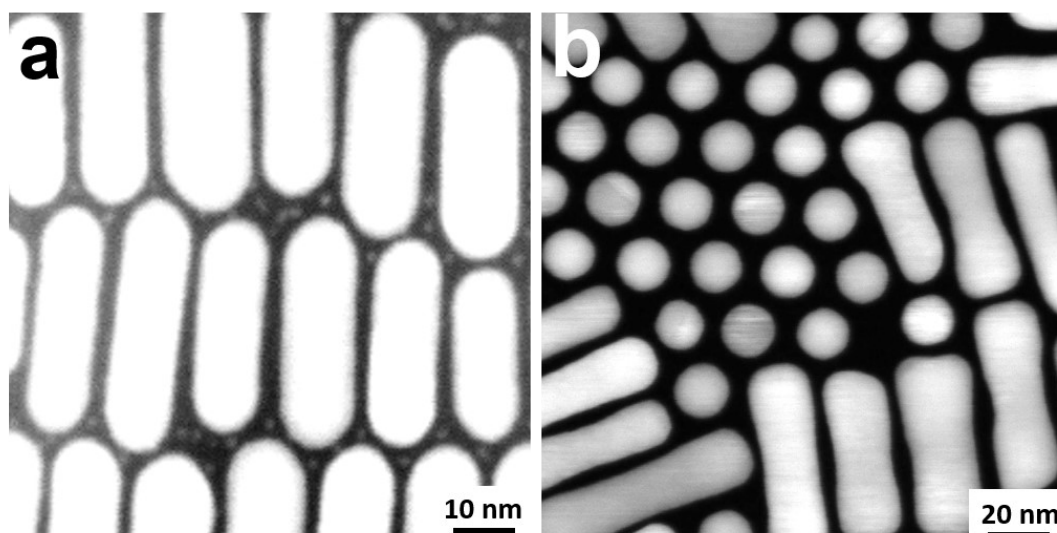


Fig. S4 STEM images of 2D binary superlattices assembled from AuNRs@PS_{2k} and different core diameters of spherical NPs@PS_{2k}. (a) Au_{1.7}NPs@PS_{2k}, and (b) Au_{10.0}NPs@PS_{2k}.

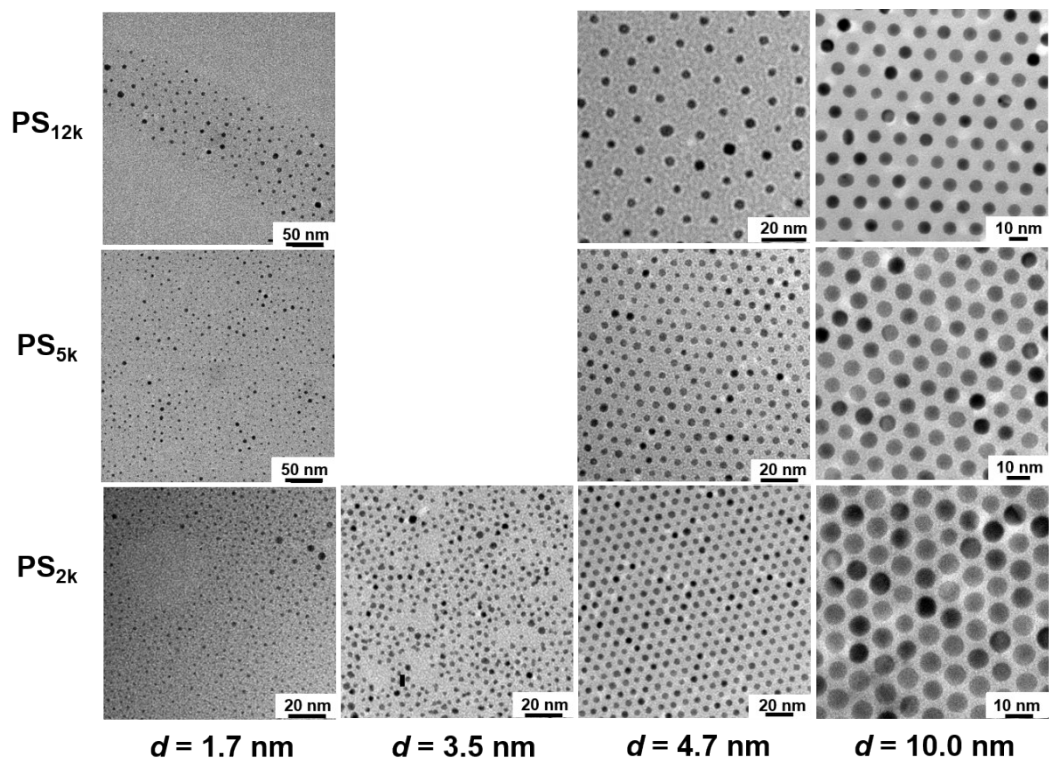


Fig. S5 TEM images of the monolayer superlattices of NPs@PS with different core diameters (d) and M_n of PS ligands.

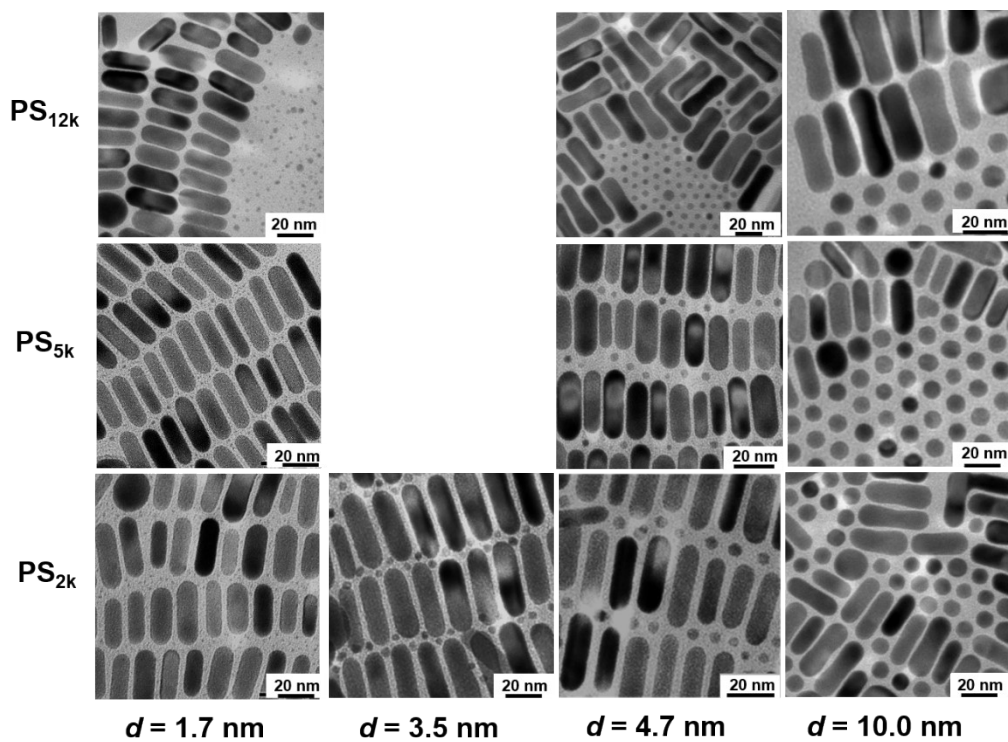


Fig. S6 TEM images of superstructures assembled from AuNRs@PS_{2k} and 1.7 nm, 3.5 nm, 4.7 nm, and 10.0 nm NPs with different M_n of PS ligands.

Reference

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