Supplementary Information (SI) for Nanoscale.

Supporting Information

Effect of number ratio and size ratio on the formation of binary superlattices assembled by two sized polymer-tethered spherical nanoparticles

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Materials and methods

Materials

Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, purity: 99.99%) was obtained from Alfa Aesar. Tetraoctylammonium bromide (TOAB, purity 98%) and cetyltrimethylammonium chloride (CTAC, purity: 98%), cetyltrimethylammonium bromide (CTAB, purity: 98%), ascorbic were purchased from Aladdin. Poly (vinyl alcohol) (PVA, average M_w = 13K-23K g/mol, 87-89% hydrolyzed) and hexadecane were obtained from Aldrich. Sodium borohydride ($NaBH_4$) was received from Sinopharm Chemical Reagent. The thiol-terminated functional polymer PS_{2k}-SH ($M_w/M_n = 1.35$, the subscript is M_n of the polymer), PS_{5k}-SH ($M_w/M_n = 1.15$), and PS_{12k}-SH ($M_w/M_n = 1.09$) were obtained from Polymer Source, Inc. The other products were purchased from the Beijing Chemical Factory. All materials used in the experiments were used immediately. The glassware used for synthesis were immersed by concentrated hydrochloric acid and nitric acid with a volume ratio of 3:1 for 20 min and flushed with water for 20 times before experiments.

Preparation of 5.1 nm, 8 nm, 10 nm and 15.4 nm AuNPs

The previous report was used to synthesize AuNPs.[48] For preparing seed solution, a freshly prepared ice-cold $NaBH_4$ solution (0.24 mL, 0.01 M) was injected into 40 mL aqueous solution which contains CTAB (0.1 M) and $HAuCl_4 \cdot 3H_2O$ (2.5×10^{-4} M) with drastic stirring and the stirring is at 300 rpm for 2 min. Subsequently, the above solution was kept at 27°C for 3 h to ensure the seeds grow fully. To prepare the seed growth solution, 1.5 mL ascorbic acid (0.1 M) and 1 mL, 0.5 mL, 50 µL, and 20 µL of seed solution were injected into the CTAC (2.0 mL, 0.2 M) in a 20 mL glass. Then, $HAuCl_4 \cdot 3H_2O$ (2 mL, 5×10^{-4} M) aqueous solution was injected above the solution one time with violent mixing at 27 °C for 15 min. Finally, synthetic AuNPs was obtained and separated directly at 15,000 rpm for 30 min.

Synthesis of 1.7 nm AuNPs tethered with PS_{2k}-SH

The AuNPs with the diameter of 1.7 nm was prepared on the base of the published Brust two-phase strategy.[49] 0.8 mL TOAB in toluene solution (50 mM) were injected into a vial containing 0.3 mL $HAuCl_4 \cdot 3H_2O$ aqueous solution (30 mM) with vigorous stirring and the stirring was until the $HAuCl_4$ was completely dispersed in the toluene phase. Then, the PS_{2k}-SH toluene solution (18 mg, 0.5 mL) was injected into the vial. Subsequently, 0.25 mL freshly prepared ice-cold $NaBH_4$ aqueous solution (0.4 mol/L) and the above solution were mixed with drastic stirring for 3 h. After that, the water was removed and the PS_{2k}-tethered AuNPs were purified by slowly adding selective solvent (methyl alcohol) into toluene phase. The solution after adding the settler was kept at 27°C for 12h without disturbance. Then, the purified PS_{2k}-tethered AuNPs were obtained by repeated centrifugation (14,000 rpm, 20 min), and precipitation using methyl alcohol at least 4-5 times. Finally, the $Au_{1.7}$NPs@PS_{2k} building blocks were collected and redispersed in CF (10 mg/mL).

Surface modification of the spherical AuNPs

PS-SH ligands tethered AuNPs was fabricated according to the previously reported two-step ligand-exchange method.[38] Firstly, the above synthesized AuNPs aqueous solution and PS-SH THF solution (10 mL, mole ratio Au: PS-SH = 1: 0.3) were mixed. The above solution was sonicated for 2 h and incubated for 8 h. Then, the AuNPs were collected by centrifugation (15000 rpm, 30 min) and redispersed in THF. The condensed AuNPs and PS-SH THF solution were mixed for secondary ligand exchange (5 mL, mole ratio Au: PS-SH = 1: 0.15). The AuNPs was subjected to the same sonication, incubation, and centrifugation procedures to prepare the PS-tethered AuNPs. For purifying AuNPs@PS, ethanol was mixed with AuNPs@PS THF solution to precipitate AuNPs@PS. Purification procedures were repeated at least 5 times. In the end, dried AuNPs@PS building blocks were dissolved in CF (10 mg/mL).

Preparation of single-component and binary superlattices

In a standard experiment, AuNPs@PS building blocks and the hexadecane solvent were dissolved in CF (10 mg/mL). For preparing single-component AuNP superlattice, the AuNPs@PS building blocks and hexadecane solvent were mixed with a volume ratio of 3:7. For preparing binary superlattices of AuNPs, the AuNPs and hexadecane were mixed with a volume ratio of AuNPs@PS: hexadecane = 30:70. And two kinds of AuNPs were combined with a specific proportion. Then, mixture solution (0.1 mL) was emulsified by PVA aqueous solution (3 mg/mL, 1.0 mL) and magnetically stirring (3 min, 850 rpm). The CF was then evaporated at room temperature for 3 d without disturbance. Finally, the superstructures were purified by repeated centrifugation three times (11,000 rpm, 10 min) to get rid of the PVA.

Characterization

Transmission electron microscopy (TEM) measurement (JEOL JEM-1400) was executed with the voltage of 120 kV. And TEM samples were obtained by dripping the superstructures aqueous solution onto copper grids and then dried at 25 °C without interference. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray (EDX) elemental mapping of the BNSLs images were recorded by the JEOL JEM-F200 instrument with the voltage of 200 kV. The effective diameters of the large AuNPs and small AuNPs (D_{eff} or d_{eff}) was calculated by center-to-center distance between two adjacent AuNPs of single-component superlattice.

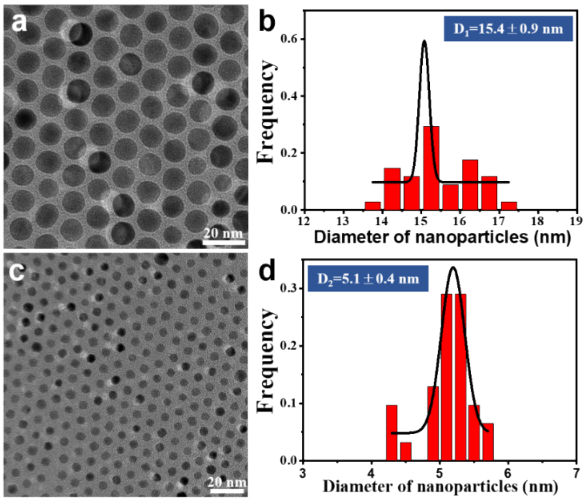

Fig. S1. (a) and (c) are TEM images of the synthesized AuNPs with diameters of 15.4 nm and 5.1 nm. And (b) and (d) are the corresponding size distribution histograms of AuNPs, which are statistics of more than 100 AuNPs by TEM analysis software.

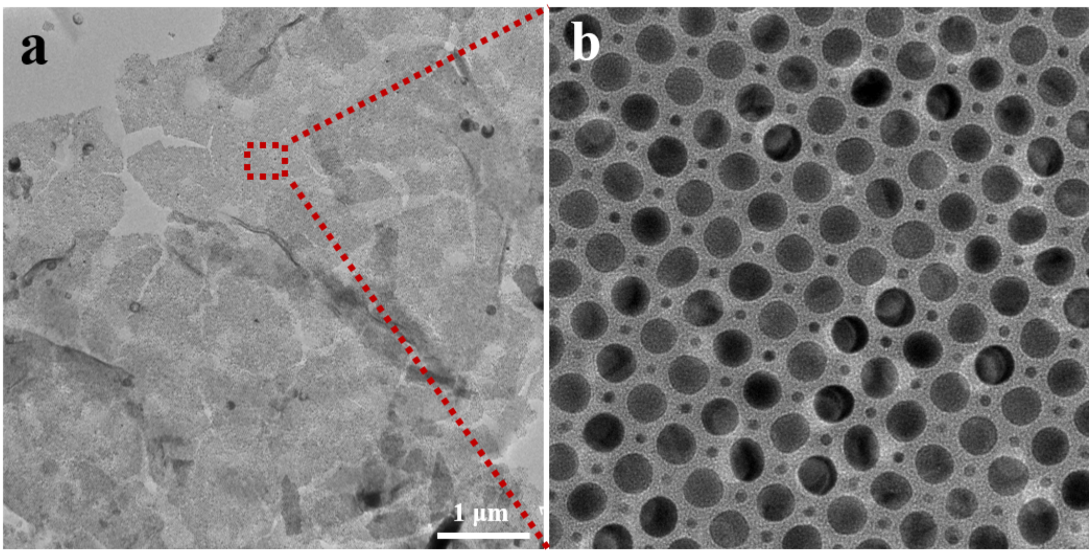

Fig.S2 (a) and (b) Low and magnified TEM images of AB-type BNSLs assembled from $Au_{5.1}NPs@PS_{2k}$ and $Au_{15.4}NPs@PS_{2k}$ building blocks at a number ratio of 1:1, respectively.

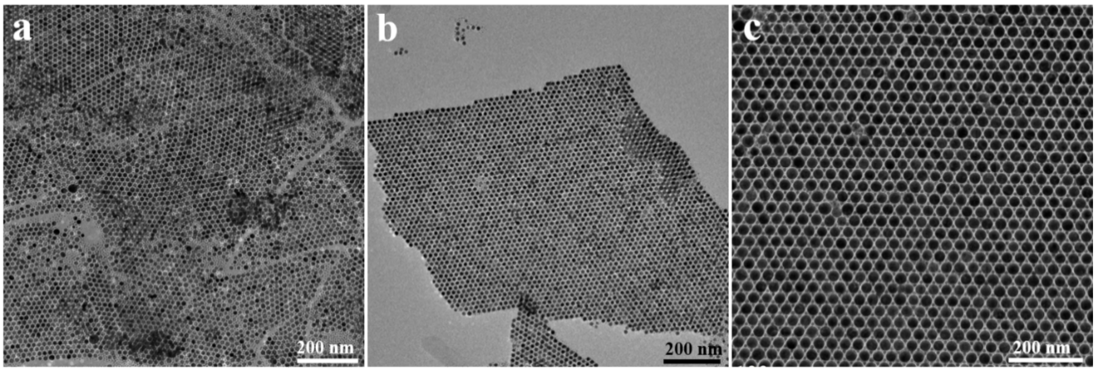

Fig.S3 (a-c) Low TEM images of AB_2-type BNSLs assembled from $Au_{5.1}NPs@PS_{2k}$ and $Au_{15.4}NPs@PS_{2k}$ building blocks at a number ratio of 2:1, respectively.

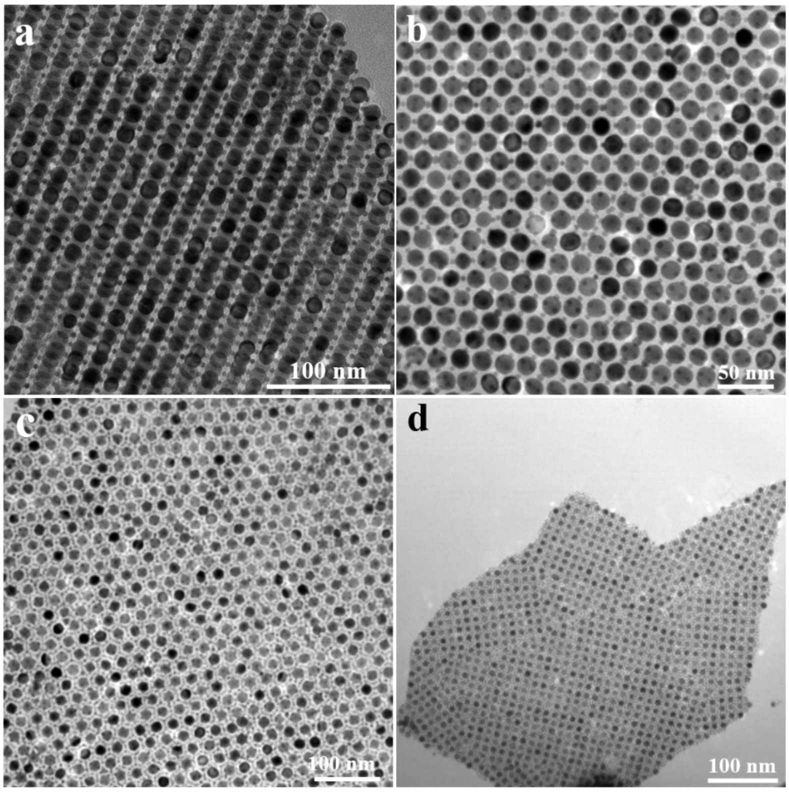

Fig.S4 (a-c) Low TEM images of BNSLs assembled from $Au_{5.1}NPs@PS_{2k}$ and $Au_{15.4}NPs@PS_{2k}$ building blocks with different number ratios. (a) AB_2-type, 3:1; (b) AB_3-type, 3:1; (e) small AuNPs around the larger AuNPs, 7:1; (f) $NaZn_{13}$-type, 13:1.

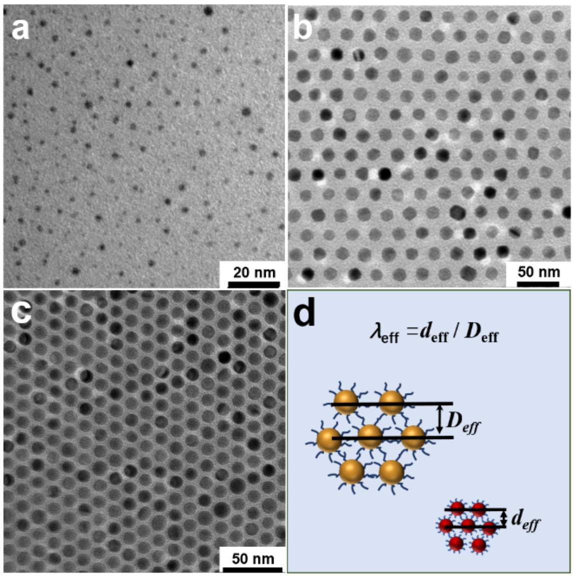

Fig. S5. (a-c) TEM images of single-component superlattices assembled by $Au_{1.7}NPs@PS_{2k}$, $Au_8NPs@PS_{2k}$, and $Au_{10}NPs@PS_{2k}$ building blocks, respectively. (d) Schematic diagrams of the effective diameters of the PS tethered large and small spherical NPs (D_{eff} and d_{eff}).

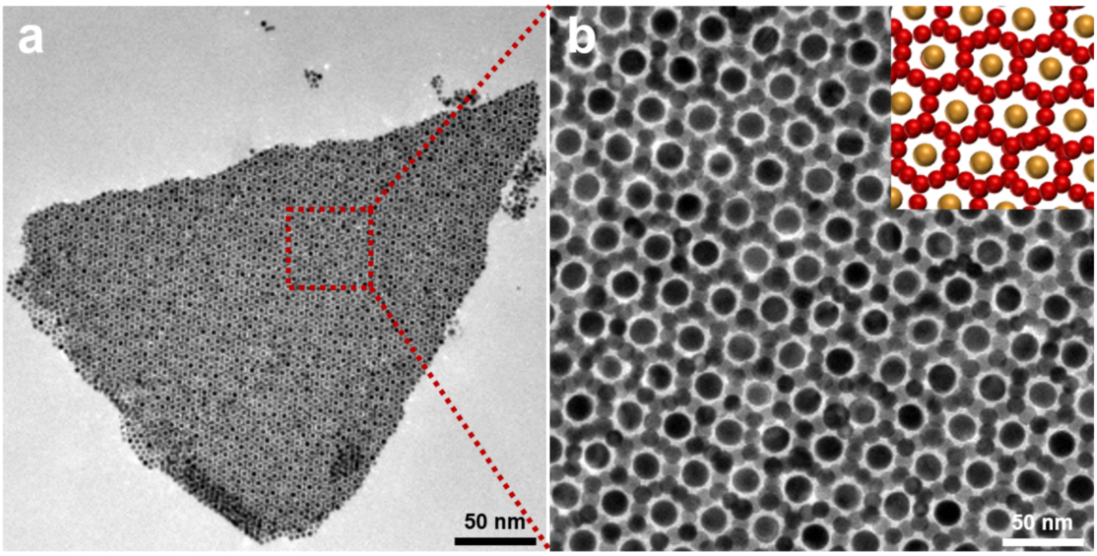

Fig. S6. TEM image BNSLs assembled by $Au_{15.4}NPs@PS_{2k}$ and $Au_{10}NPs@PS_{2k}$ with a number ratio of 1:10.

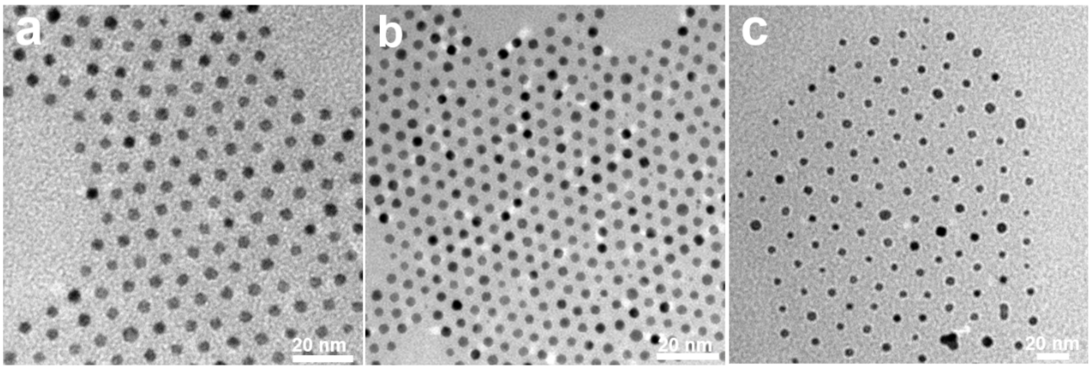

Figure S7. (a-c) TEM images of single-component superlattices assembled from $Au_{5.1}$NPs@PS with different M_n of PS ligands. (a) PS_{2k}; (b) PS_{5k}; (c) PS_{12k}.

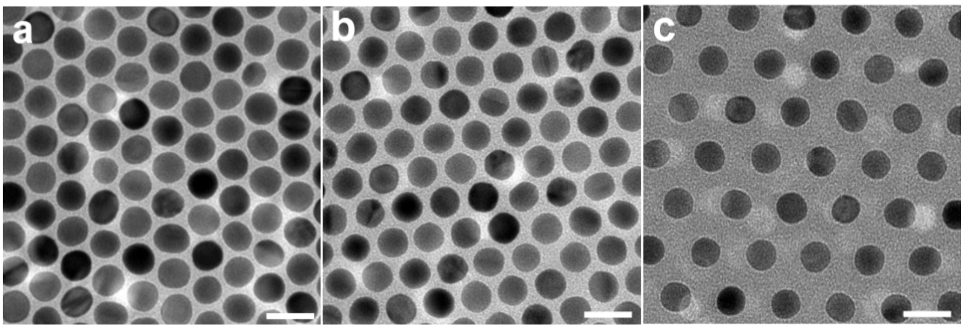

Fig. S8. (a-c) TEM images of the synthesized $Au_{15.4}$NPs with different PS ligands. (a) $PS_{0.8k}$; (b) PS_{5k}; (c) PS_{12k}.

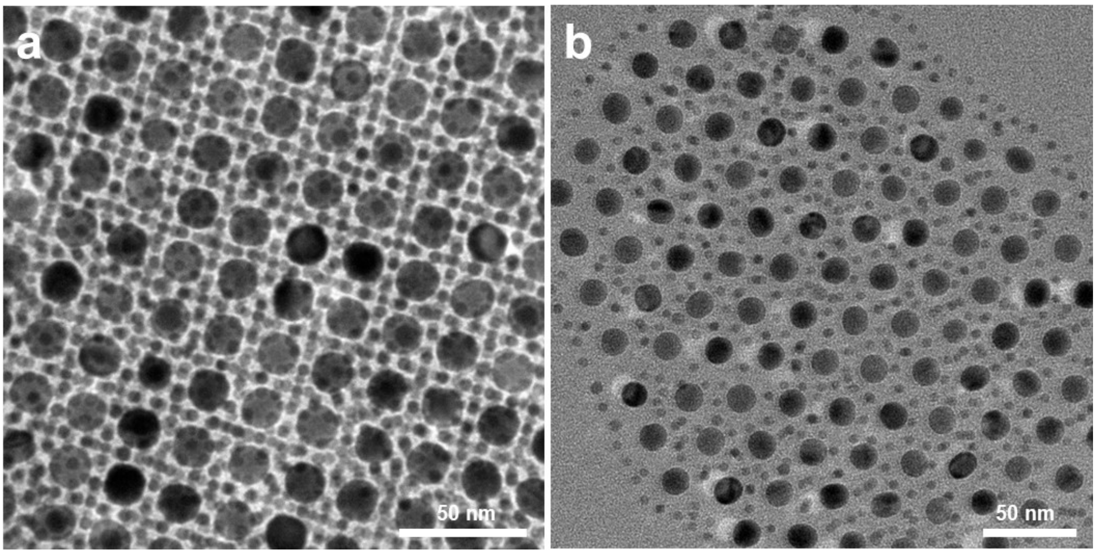

Fig. S9. (a) and (b) TEM images of the BNSLs assembled by $Au_{5.1}$NPs@PS_{2k} and $Au_{15.4}$NPs@PS building blocks with different M_n of PS ligands with a mixing ratio of 13:1 and 7:1, respectively. (a) $PS_{0.8k}$, 13:1; (b) PS_{12k}, 7:1.

Table 1. Influence of the effective size ratio (λ_{eff}) and number ratios of two kinds of AuNPs@PS on the internal structures of BNSLs.

Effective size ratios $[Au]_S/[Au]_L$			**Number ratios $[Au]_S/[Au]_L$**					
Au_SNPs@ PS	**Au_LNPs@ PS**	**λ_{eff}**	**1:1**	**2:1**	**3:1**	**7:1**	**10:1**	**13:1**
$Au_{1.7}$NPs@ PS_{2k}	$Au_{15.4}$NPs@ PS_{2k}	0.2		AB_2				
$Au_{5.1}$NPs@ PS_{2k}		0.4	AB	AB_2	AB_2+ AB_3	Cu_3Au+CaB_6 +$Au_{5.1}$NPs@PS_{2k} around $Au_{15.4}$NPs@PS_{2k}		$NaZn_{13}$
$Au_{5.1}$NPs@ PS_{5k}		0.7		AB_2				
$Au_{5.1}$NPs@ PS_{12k}		0.9		Phase separation				
Au_8NPs@ PS_{2k}		0.5		AB_2				
Au_{10}NPs@ PS_{2k}		0.7		Phase separation			$CaCu_5$	
$Au_{5.1}$NPs@ PS_{2k}	$Au_{15.4}$NPs@ $PS_{0.8k}$	0.4		Phase separation				$NaZn_{13}$
	$Au_{15.4}$NPs@ PS_{5k}	0.4		AB_2				
	$Au_{15.4}$NPs@ PS_{12k}	0.3		AB_2				

Note: Au_SNPs@PS and Au_LNPs@PS refer to the small and large size of AuNPs, respectively.