Supporting Information

Self-Assembly of Gold Nanocubes into Three-Dimensional Hollow Colloidosomes and Two-Dimensional Superlattices

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Experimental Section

Materials. Cetyltrimethylammonium bromide (CTAB, purity: 98%) and ascorbic acid were obtained from Aladdin. Nile Red and Poly (vinyl alcohol) (PVA, average M_w = 13K-23K g/mol, 87-89% hydrolyzed) were purchased from Aldrich. Sodium borohydride ($NaBH_4$) and hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, purity: 99.99%) were purchased from Sinopharm Chemical Reagent. The thiol terminated functional polymer PS_{5k}-SH (M_w/M_n = 1.15), PS_{12k}-SH (M_w/M_n = 1.09), and PS_{22k}-SH (M_w/M_n = 1.01) were purchased from Polymer Source, Inc. Other chemicals were supplied by Beijing Chemical Factory. All of the materials were used directly without further purification. The glasswares used to synthesize the gold nanocubes (AuNCs) in our experiment were cleaned by aqua regia and rinsed with deionized water for a dozen times.

Synthesis of AuNCs. The previously reported seed-mediated growth method was used to synthesize AuNCs.[1,2] To synthesize seed solution, 7.5 mL of CTAB (0.1 M) and 0.25 mL of $HAuCl_4 \cdot 3H_2O$ (0.01 M) were first mixed in a vial. Subsequently, a freshly ice-cold $NaBH_4$ aqueous solution (0.01 M, 0.6 mL) was quickly injected into the above solution, followed by vigorous stirring for 2 min. The resulting seed solution was kept at 25 °C for 1 h before use. To synthesize growth solution, 3.2 mL of CTAB (0.1 M), 0.4 mL of $HAuCl_4 \cdot 3H_2O$ (0.01 M) and 1.9 mL of ascorbic acid (0.1 M)

aqueous solution were sequentially added into deionized water (16 mL). Then, the seed solution was diluted 10 times with deionized water. To fabricate the AuNCs, 0.012 mL of the diluted seed solution was added to the growth solution with gentle inversion. The mixture solution was left undisturbed overnight at 27 °C. Afterwards, the AuNCs were purified by twice centrifugation (10,000 rpm, 8 min) and then redispersed in deionized water.

Surface modification of AuNCs. The surface of AuNCs was modified by PS-SH ligands through two-step ligand-exchange approach.[3,4] Typically, the 0.5 mL of the concentrated AuNCs aqueous solution was added into 10 mL of PS-SH (mole ratio Au:SH=1:0.1) solution in THF. Then, the mixture solution was sonicated for 2 h and incubted for 24 h. The resulting PS-tethered AuNCs were collected by centrifugation (10,000 rpm, 8 min) and redispersed in THF solution. Subsequently, PS-SH in THF was added into the resulting PS-tethered AuNCs solution again (mole ratio Au:SH=1:0.05), followed by the same sonication, incubation and centrifugation process to fabricate PS-tethered AuNCs. In order to remove the CTAB surfactant and free PS-SH, PS-tethered AuNCs were precipitated from the solution induced by adding ethanol. Afterwards, the PS-tethered AuNCs were separated by centrifugation (10,000 rpm, 8 min) and redispersed in THF solution. The same purified process was then repeated for 4-5 times. The resulting PS-tethered AuNCs were redispersed in chloroform and stored at -20 °C.

Preparation of AuNC hollow colloidosomes. The AuNC hollow colloidosomes were prepared through the confined assembly of PS-tethered AuNCs at emulsion interface. In a typical experiment, AuNCs@PS and HD were dissolved in chloroform solution at a concentration of 30 mg/mL and 10 mg/mL, respectively. Then, the AuNCs@PS solution and HD solution were mixted together at various volume ratios (AuNCs@PS : HD = 8:2, 6.5:3.5, or 5:5). Subsequently, 0.1 mL of the above mixed solution was emulsified with 1.0 mL of PVA aqueous solution (3 mg/mL) by magnetic stirring for 3 min at 850 rpm. The chloroform was then allowed to slowly evaporate at room temperature for 3 days without disturbing. Finally, the obtained AuNC hollow colloidosomes were separated by repeated centrifugation (10,000 rpm, 6 min) to

remove the PVA surfactant. In order to investigate the formation mechanism of the hollow colloidosomes, Nile Red (1 μL, 10 mg/mL) was dissolved in the AuNCs@PS chloroform solution and emulsified together with AuNCs@PS and HD chloroform solution in surfactant aqueous solution.

Characterization. Transmission electron microscopy (TEM) measurements were performed on JEOL JEM-1011 operated at an accelerating voltage of 100 kV. Scanning transmission electron microscopy (STEM) and Energy Dispersive X-ray Detector (EDX) elemental mapping were performed on an FEI Tecnai G^2 S-Twin instrument with the operation voltage of 200 kV. Several drops of the sample soultion were deposited on the TEM copper grid precoated with a thin carbon film for the preparation of TEM samples. The samples were then dried at room temperature. The shapes and surface morphology of the AuNCs and colloidosomes were characterized by a Zeiss Merlin scanning electron microscope (SEM). The SEM samples were prepared by dropping the sample soultion onto a silicon wafer, and then were dried at room temperature. The evolution of the emulsion droplets was observed by confocal laser scanning microscopy (CLSM) with a Carl Zeiss LSM 700 imaging system and optical microscope (Olympus, XDS-1). 10 μL of the freshly prepared emulsion droplets was quickly transformed onto a glass sheet to observe their evolution. Thermogravimetric analysis measurement was conducted on TGA (TA Co., Q50). Dry PS-tethered AuNC powder was placed in ceramic crucible and heated from room temperature to 800 ℃ at the rate of 10 ℃/min under dry flow of N_2.

Supporting Figures

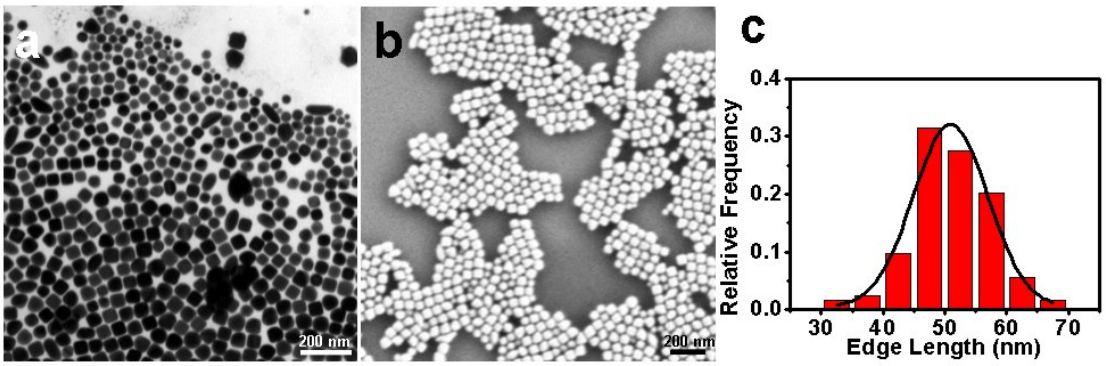

Figure S1. TEM (a) and SEM (b) images of the synthesized AuNCs, respectively. (c)

The edge length distribution histogram of AuNCs are obtained from the statistics of 100 AuNCs by TEM analysis software.

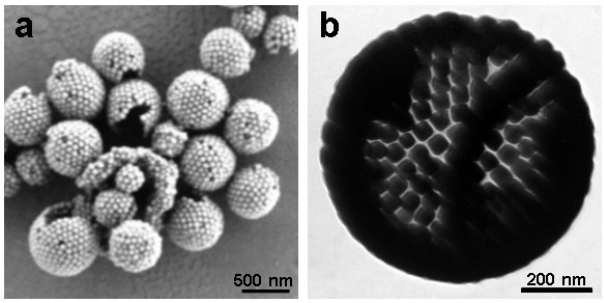

Figure S2. (a) SEM image of hollow AuNC colloidosomes at low magnification. (b) TEM image of the AuNC colloidosome.

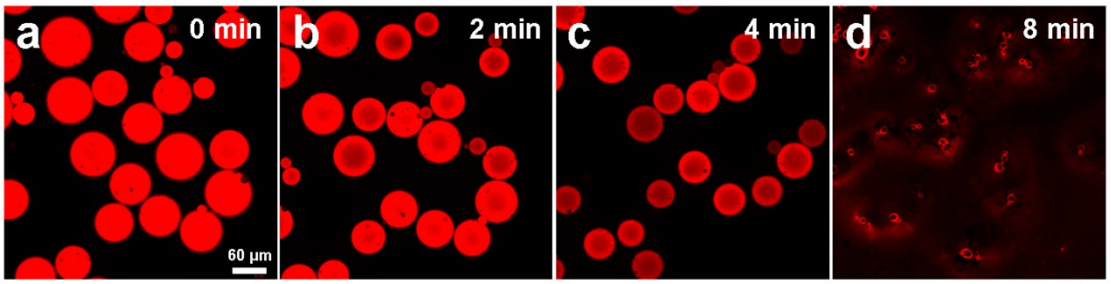

Figure S3. CLSM images at low magnification showing the size and morphology evolution of large amount of emulsion droplets during the evaporation of chloroform. Initial time (*i.e.*, 0 min) is regarded as the moment of capturing the droplet by CLSM after rapidly adding the freshly prepared emulsion onto a glass sheet. Red-ring assemblies are formed within 8 min. The scale bar in the first image applies to the others.

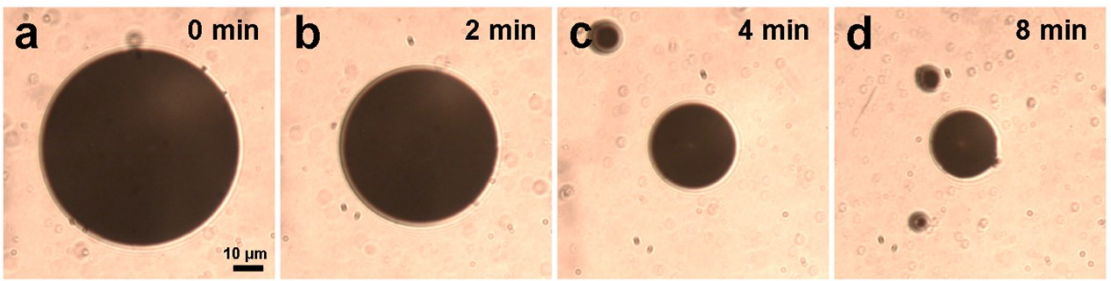

Figure S4. Optical microscopy (OM) images showing the size evolution of the emulsion droplets during the evaporation of chloroform. Initial time (*i.e.*, 0 min) is

regarded as the moment of capturing the droplet by OM after rapidly adding the freshly prepared emulsion onto a glass sheet. With the evaporation of emulsion droplets, the size of the droplets decreases dramatically. The scale bar in the first image applies to the others.

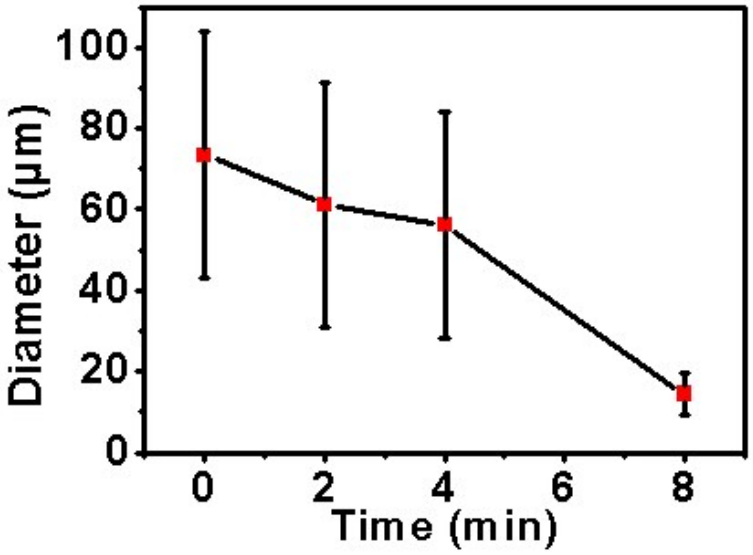

Figure S5. Plot displays the size evolution of the emulsion droplets during the evaporation process at different times.

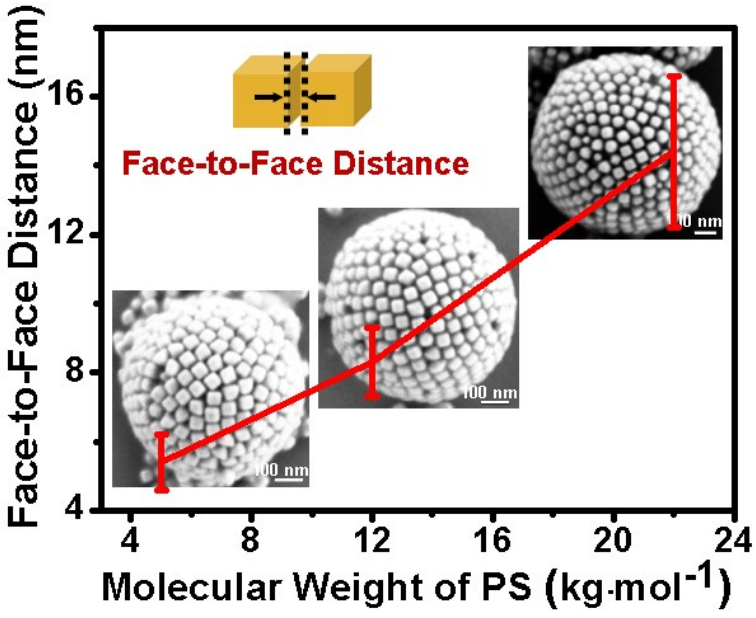

Figure S6. Plot displays dependence of the face-to-face distance between the adjacent AuNCs and M_n of tethered PS ligands. Insets are the representative SEM images for the data point.

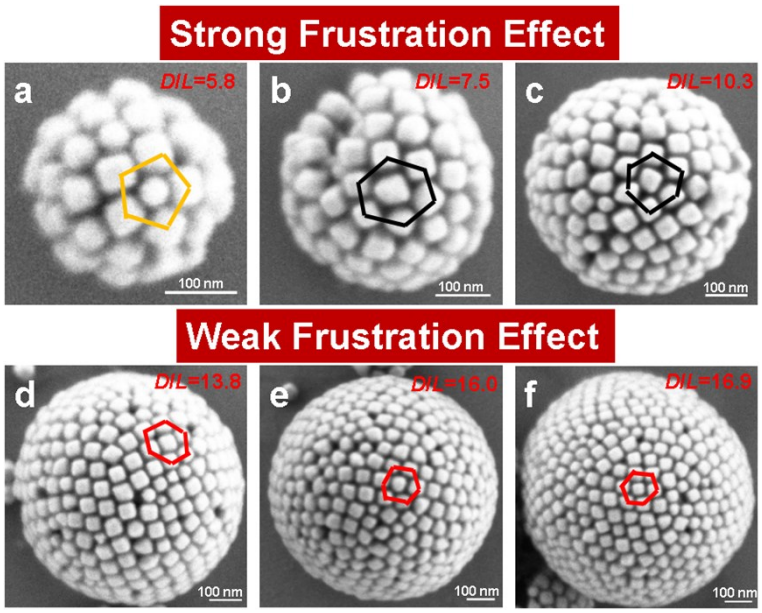

Figure S7. SEM images of representative AuNC colloidosomes fabricated under strong (a-c) and weak (d-f) frustration effect.

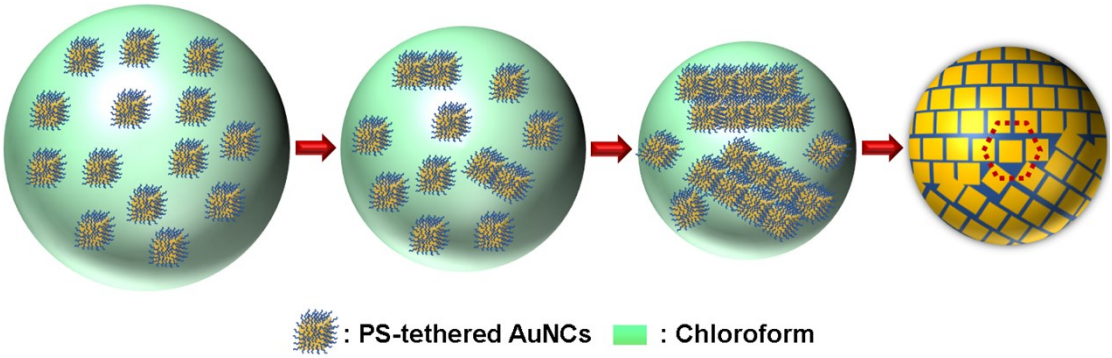

Figure S8. Schematic illustration of the hypothetical formation mechanism of the hexagonal configuration formed at the junction of the superstructures with different orientations during the chloroform evaporation process.

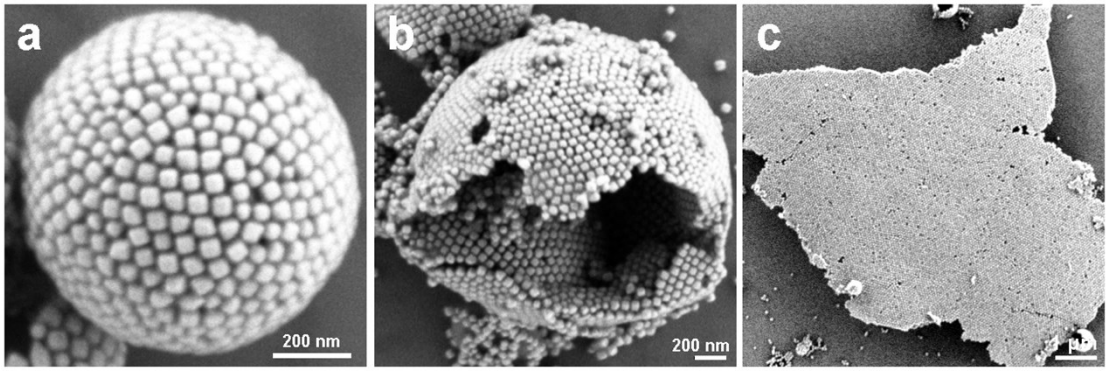

Figure S9. SEM images of the effect of the volume ratio of AuNCs@PS_{12k} solution to HD solution on the transformation in shape and dimension of the hierarchical superstructures. The volume ratios of the AuNCs@PS_{12k} solution to HD solution are (a) 8:2, (b) 6.5:3.5, and (c) 5:5.

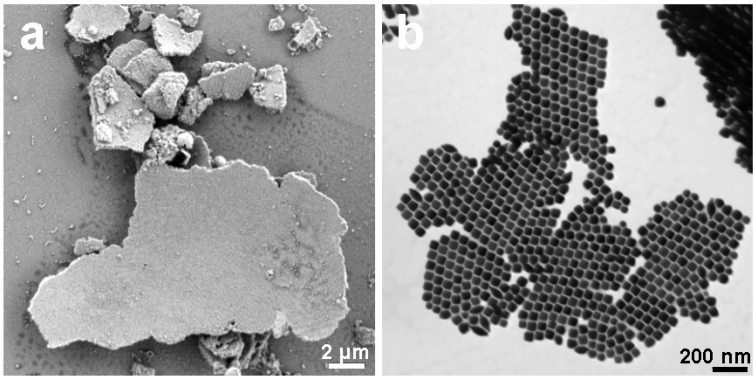

Figure S10. SEM (a) and TEM (b) images of 2D sheet-like superlattices at low magnification, respectively.

Table S1. Estimation of the graft density of PS_{12k} ligands grafted on the AuNCs.

PS ligands	W_{PS} vol%	$N_{\text{grafts per nanocube}}$	Graft density (chains/nm^2)
PS_{12k}	5.2	7170	0.43

Note: W_{PS} is the weight fraction of the polymer ligands. $N_{\text{grafts per nanocube}}$ is the average number of polymer ligands on per nanocube.

The size of an Au atom is 0.017 nm^3. The number of Au atom ($N_{\text{Au atom}}$) in AuNC (~52.8 nm) can be calculated using Equation S1, where L is the edge length of the AuNCs. The result is 8658703 gold atoms per nanocube and therefore the molar mass (M_{AuNC}) of the AuNC is 197 $N_{\text{Au atom}}$. The average number of polymer ligands can be calculated by

Equation S2, where, W_{AuNC} is the weight fraction of AuNC and M_{PS} is the molar mass of PS ligands. The graft density is calculated using Equation S3.

$$N_{\text{Au atom}} = \frac{V_{\text{AuNC}}}{V_{\text{Au atom}}} = \left(\frac{L^3}{V_{\text{Au atom}}} \right) \quad \text{Equation S1}$$

$$N_{\text{grafts per nanocube}} = \left(\frac{W_{\text{PS}} / M\text{n}_{\text{PS}}}{W_{\text{AuNC}} / M_{\text{AuNC}}} \right) \quad \text{Equation S2}$$

$$\text{Graft density} = N_{\text{grafts per nanocube}} / (6L^2) \quad \text{Equation S3}$$

References

1. Ming, T.; Kou, X.; Chen, H.; Wang, T.; Tam, H. L.; Cheah, K. W.; Chen, J. Y.; Wang, J. *Angew. Chem. Int. Ed.* **2008,** 47, 9685-9690.
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