Supplementary information

Shape-complementary co-assembly of concave nanocubes and nanospheres into binary superlattices

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Experimental Section

Materials. Cetyltrimethylammonium bromide (CTAB, ≥ 98%), cetyltrimethylammonium chloride (CTAC, 25 wt.% in H_2O), thioacetamide (TAA, 99%), and sodium dodecyl sulfate (SDS, 99%) were purchased from Sigma-Aldrich, Co. Hydrochloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%) was obtained from Beijing Chemical Reagents Co. 4-Aminothiophenol (4-ATP, 96%) was obtained from Alfa Aesar China Chemical Co., Ltd. All the other chemicals are of analytical grade and used without further purification. The water was deionized. Silicon wafers were bought from Lijing Photoelectric Technology Co. Ltd. and washed with acetone, water and isopropanol solution sequentially before used for the assembly experiments.

Synthesis of gold nanospheres (GNSs). Monodisperse GNSs with varied sizes were synthesized following the reported three-step method[1] with minor modifications.

Synthesis of small gold nanoparticles. The small gold nanoparticles were synthesized by the seed-mediated method as follows. Briefly, a $HAuCl_4$ solution (0.01 M, 0.25 mL) was first mixed with a CTAB solution (0.1 M, 10 mL), followed by the rapid injection of a freshly-prepared, ice-cold $NaBH_4$ solution (0.01 M, 0.60 mL) under vigorous stirring, which was kept in 30℃ for 3 h. Then, 0.12 mL of the resultant seed solution was injected into a growth solution made of CTAB (0.1 M, 0.2 mL), water (3.8 mL), $HAuCl_4$ (0.01 M, 0.08 mL), and ascorbic acid (AA, 0.1 M, 0.3 mL). The reaction mixture was gently shaken and then left undisturbed overnight at 30℃. The resultant small gold nanoparticles were washed and concentrated by four times into water through repeated centrifugation and redispersion for further use.

Growth of gold nanopolyhedrons. The gold nanopolyhedrons were grown by the seed-mediated method using the small gold nanoparticles as seeds. Typically, a varying volume of the seed solution (typically, 1.0 mL) was first added into a CTAC solution (0.025 M, 10 mL). The seed solution was diluted four times with water before use. After the sequential addition of AA (0.1 M, 0.25 mL) and $HAuCl_4$ (0.01 M, 0.5 mL), the mixture solution was placed in 45℃ for 3 h. The obtained Au nanopolyhedrons were centrifuged and redispersed in a CTAC solution (1 mM, 10 mL). For the synthesis of GNSs with varied diameters, the added amount of the seed solution was varied (0.8~1.3 mL).

Preparation of GNSs. The large GNSs were produced by oxidizing the obtained Au nanopolyhedrons with $HAuCl_4$. The Au nanopolyhedrons in CTAB solutions were mixed with a $HAuCl_4$ solution (0.01 M, 0.1 mL). The resultant mixture solution was kept in 45℃ for 2 h. GNSs

were produced through the mild oxidation of the Au nanopolyhedrons in the presence of $HAuCl_4$ and CTAB. The obtained GNSs were centrifuged and redispersed in 1 mM CTAB solution for storage. The sizes of GNSs were adjusted by the addition amount of the seed solution during the growth of gold nanopolyhedrons.

Synthesis of concave gold nanocubs (cGNCs). Uniform cGNCs were synthesized following the reported seed-mediated method[2] with minor modifications. Au seeds were prepared by quickly injecting 0.60 mL of ice-cold, freshly prepared $NaBH_4$ (10 mM) into a rapidly stirred solution containing 0.25 mL of $HAuCl_4$ (10 mM) and 10.00 mL of CTAC (100 mM). The seed solution was stirred for 1 min and then left in 30℃ for 2 h. A growth solution was prepared by consecutively adding 0.50 mL of $HAuCl_4$ (10 mM), 0.10 mL of $AgNO_3$ (10 mM), 0.20 mL of HCl (1.0 M), then 0.10 mL of AA (100 mM) into 10.00 mL of CTAC (100 mM). The seed particle solution was diluted in 0.1 M CTAC to generate a solution 1/500 of the concentration of the original seed solution. A typical synthesis of concave nanocubes was initiated by the addition of 0.1 mL of the diluted seeds to the growth solution. The reaction was swirled immediately after the addition of the seeds and then left undisturbed in 30℃ until the reaction completed.

Purification of cGNCs. A depletion-induced flocculation process was employed to purify the cGNCs through separation from polyhedral impurities and to ensure a 1:1 number ratio of the cGNCs and GNSs. The as-synthesized cGNC solution (2 mL) was mixed with GNS solution (2 mL) in an aqueous solution of CTAC (4 mL, 200 mM) in a 10 mL centrifuge tube, allowing sedimentation of the GNSs and cGNCs due to depletion attraction at a high CTAC concentration of 100 mM. The solution was left undisturbed for 3 h until it turned light purple (with GNSs in excess). Then, the light purple supernatant mainly containing the impurity nanoparticles and excessive GNSs was carefully removed. The sediment at the bottom of the centrifuge tube was redispersed in 1 mM CTAC solution (0.5 mL), resulting in a blue colloid solution.

Synthesis of PbS nanospheres (NSs). Uniform PbS NSs were produced by the synthesis of PbS nanooctahedrons in a mixed CTAB-SDS solution[3] and the subsequent conversion to PbS NSs via hydrothermal treatment. In a typical synthesis, 3.0 mL of water, 0.5 mL of 0.05 M CTAB, 0.1 mL of SDS (0.05 M), and 0.4 mL of acetic acid (1.0 M) were mixed at room temperature, followed by the addition of 0.2 mL of $Pb(OAc)_2$ (0.5 M) and 0.2 mL of TAA (0.5 M) under stirring, giving concentrations of 5.7 mM and 1.1 mM for CTAB and SDS, respectively. The resultant translucent solution was thermostated at 80 ℃ for 3 h under static conditions, resulting in a brown colloid solution. The colloidal particles were collected by centrifugation, washed with 1 mM CTAB solution. The transformation of PbS octahedrons to nanospheres was achieved by moderate hydrothermal treatment. The as-synthesized PbS octahedrons in 1 mM CTAB solution were placed in a 70 ℃ water bath for 4 h, resulting in the formation of PbS NSs.

Co-assembly of cGNCs with NSs into binary superlattices (SLs). A droplet evaporation method was used to prepare the GNS-cGNC binary SLs and PbS NS-cGNC binary SLs.

Co-assembly of GNS-cGNC binary SLs. Typically, a 10 μL droplet containing purified GNSs and cGNCs with a 1:1 number ratio was placed on a silicon wafer. The sample was then transferred into a humidity chamber with a humidity of 90±5% and a temperature of 30℃, where the evaporation rate is much slower so that the nanoparticles had enough time to assemble. The

whole evaporation process took about 48 h.

Co-assembly of PbS NS-cGNC binary SLs. Our preliminary experiments showed that the addition of the as-synthesized cGNC and PbS NS solutions with a volume ratio of 3:1 resulted in a co-assembled structure with a particle number ratio of ~ 1:1. Therefore, such a recipe was adopted for the preparation of the mixture solution for co-assembly. Typically, 18 μL of cGNC solution and 6 μL of PbS NS solution was mixed and added on a silicon wafer. The sample was then transferred into a humidity chamber with a humidity of 90 ± 5% and a temperature of 30℃ for evaporation-induced co-assembly, in a similar way to case of the GNS-cGNC binary system.

Selective etching of PbS NS-cGNC binary SLs. Selective etching of PbS in the PbS NS-cGNC binary SLs with HCl solution resulted in the formation of checkerboard SLs of cGNCs. Typically, 30 μL of 1 M HCl solution was dropped onto the surface of the co-assembled PbS NS-cGNC binary SLs on the silicon substrate, ensuring complete coverage of the SLs. The HCl solution was left for 20 min to fully etch away the PbS component.

Characterizations. The as-synthesized GNSs and cGNCs were characterized by UV-vis absorption (PerkinElmer Lambda 950). The reflection spectra of GNSs, cGNC and GNS/cGNC superlattices were also characterized by PerkinElmer Lambda 950. The morphology and structure of the GNSs and cGNCs and the superlattices on various substrates were characterized with SEM (Hitachi S-4800, acceleration voltage 5–10 kV, acceleration voltage 5 kV). The sample on amorphous carbon-covered TEM grid was characterized by TEM (FEI Tecnai T20, acceleration voltage 200 kV and FEI Tecnai F30, acceleration voltage 300 kV).

Surface-enhanced Raman scattering (SERS) measurements. The SERS measurements were carried out using Raman spectrum (Horiba, LabRAM HR-800) with an excitation laser wavelength of 633 nm (laser power of 0.2 mW) and a laser spot diameter of 1 μm. All Raman spectra were recorded by fine-focusing a 100× (Numerical aperture, 0.9) microscope objective using a data acquisition time of 5 s.

Measurement of SERS enhancement factor (EF) of various SLs The strong a1-type Raman band of probe molecule 4-ATP at around 1082 cm^{-1} was used to calculate the EF values of various SLs. For the Raman test, the SLs were assembled on a bare Si wafer. The Si substrate-supported SLs were first UV/ozone-treated for 20 min and then submerged into 0.15 mL of ATP-ethanol solution (10^{-6}~10^{-13} M) and left undisturbed for 6 h. The samples were rinsed with ethanol and dried before testing.

The measured EF was calculated using the following equation:[4]

$$EF = \frac{I_{SERS}}{N_{SERS}} \times \frac{I_{ref}}{N_{ref}}$$

where I_{SERS} and I_{ref} correspond to the integrated SERS and reference 4-ATP Raman intensities, respectively. N_{SERS} is the number of adsorbed 4-ATP molecules on the substrate containing nanocrystal assemblies within the laser spot, and N_{ref} is the number of 4-ATP molecules within the illumination volume of laser in a bulk sample.

Test of detection limit of cGNC-GNS binary SLs. The SERS performance of the 2D cGNC-GNS binary SLs was evaluated by employing crystal violet (CV) as a probe molecule. Typically, 20 μL of CV (10^{-6} ~ 10^{-13}M) solution was drop-casted on the cGNC-GNS binary SLs

sample. The SERS spectra were obtained with an excitation laser wavelength of 633 nm (laser power: 0.2 mW). To check the reproducibility, the measurements were repeated at randomly selected SL substrates.

Electromagnetic simulations. The optical properties of various gold nanocrystals and 2D SLs were numerically performed with COMSOL Multiphysics software based on the finite element method (FEM).[5] For the simulations, the narrowest nanogap size between adjacent nanoparticles in the SLs was set as 1 nm. The permittivity of gold was taken from the example data,[6] and a minimum mesh size of 0.1 nm was used to refine the tip area of the nanoparticles. In all simulations, the plane wave normally interacting with these structures was used. To get unpolarized results, we performed two separate simulations, with the incident electric field polarized along the y axis and z axis, respectively. Then, the unpolarized electric field was extracted with $E^2_{\text{unpolarized}} = 1/2E^2_{\text{y}} + 1/2E^2_{\text{z}}$. All electric fields represented in this study have been normalized to the incident electric field.

References

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Figures

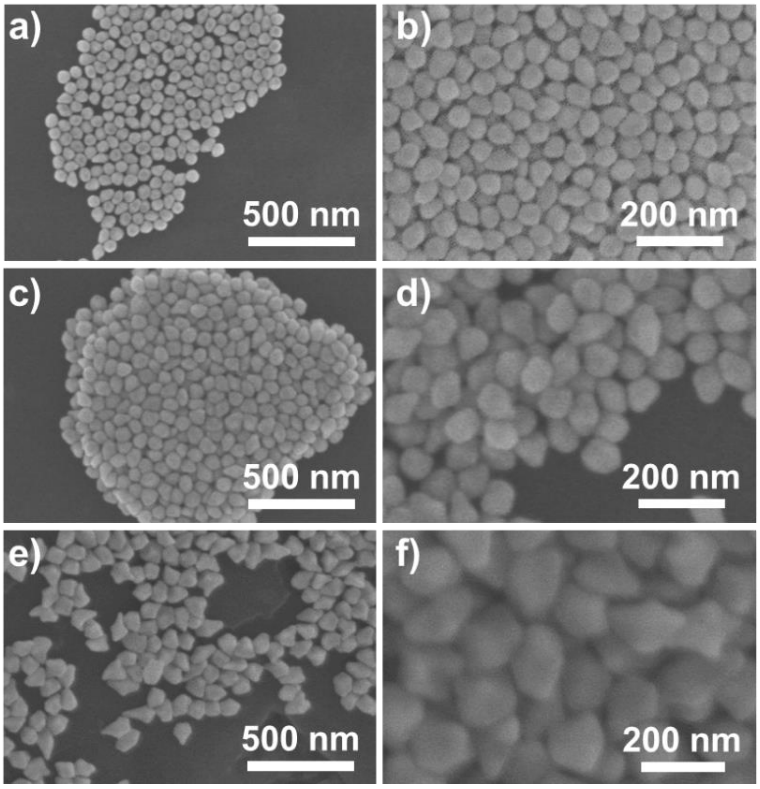

Figure S1. SEM images of GNSs before polishing with $HAuCl_4$. Amount of seed added: (a,b) 1.3 mL, (c,d) 1.0 mL, (e,f) 0.8 mL.

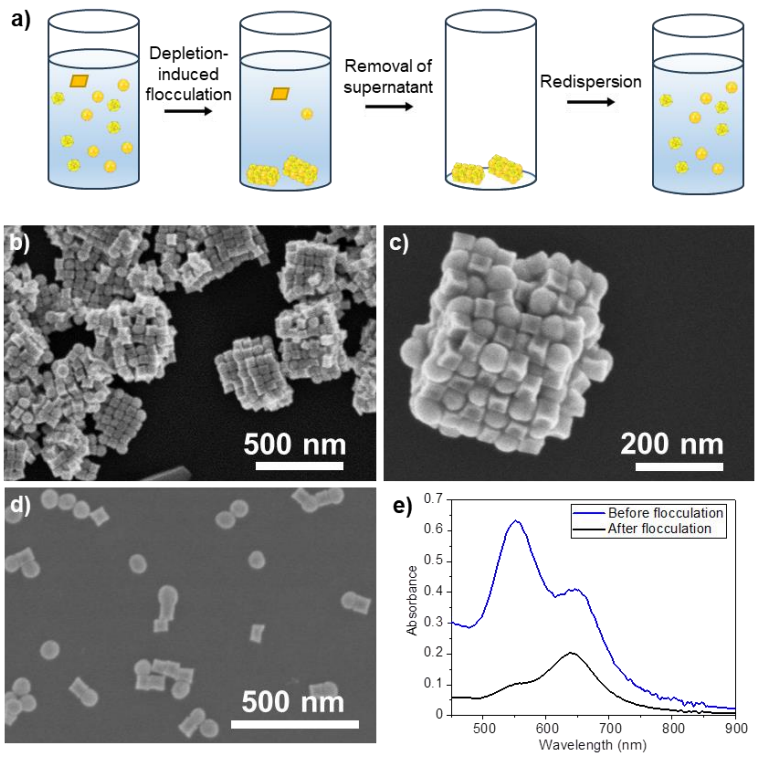

Figure S2. (a) Schematic showing purification process through depletion-induced flocculation of cGNCs and GNSs. (b,c) SEM images of flocculates of cGNCs and GNSs. (d) SEM image of re-dispersed cGNCs and GNSs after flocculation. (e) Absorption spectra of dispersions of mixed cGNCs and GNSs before and after flocculation.

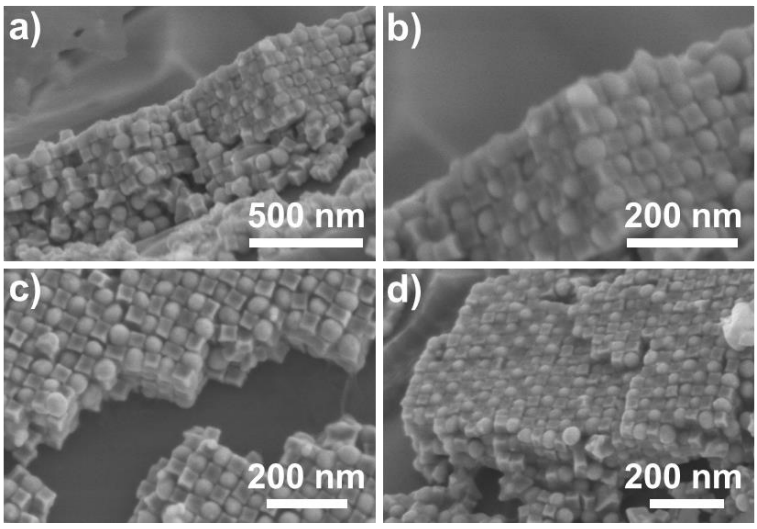

Figure S3. Side-view SEM images of 3D binary SLs of GNSs and cGNCs.

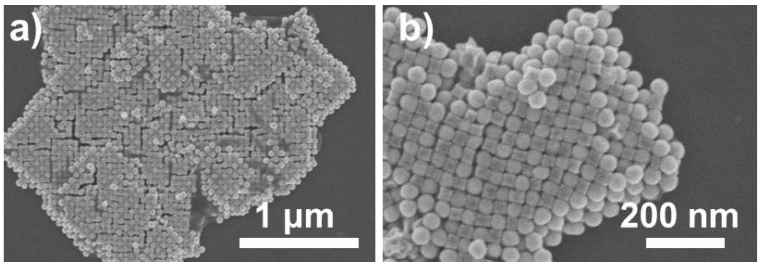

Figure S4. SEM images of binary SLs consisting of (a,b) 60 nm GNSs and 60 nm cGNCs with a GNS/cGNC number ratio of ~ 1.2.

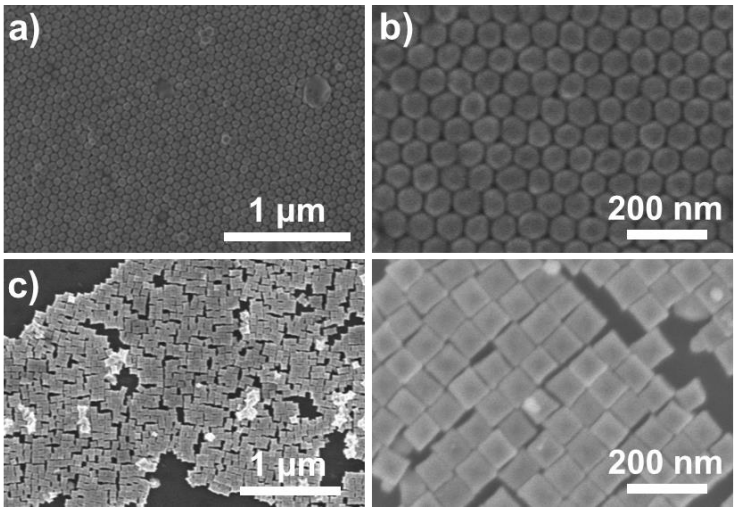

Figure S5. SEM images of 2D SLs of (a,b) GNSs and (c,d) cGNCs.

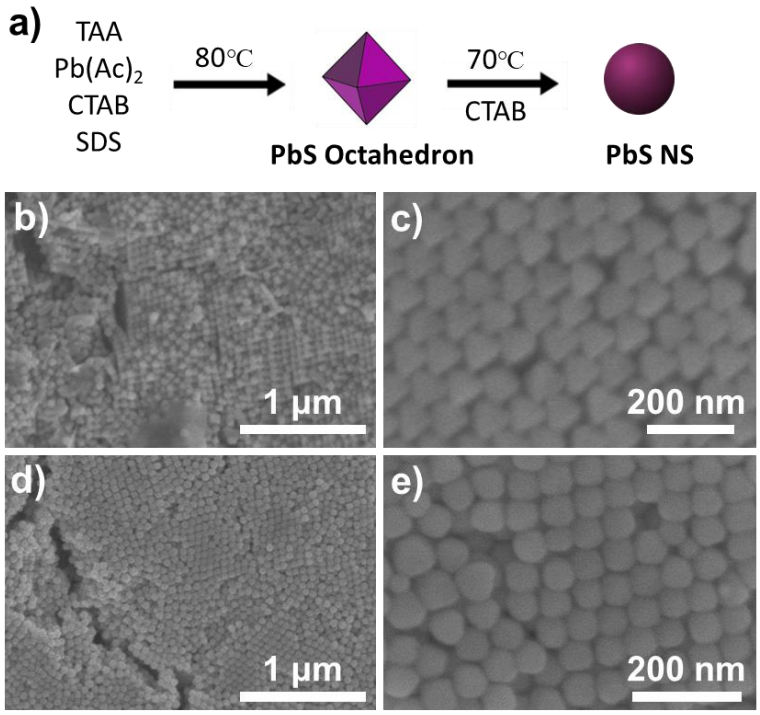

Figure S6. (a) Schematic synthesis of PbS nanooctahedrons and NSs. SEM images of PbS (b,c) nanooctahedrons and (d,e) nanospheres.