Supporting Information for

Universal linker-free assembly of core-satellite hetero-superstructures

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Materials and experimental methods

1. Materials

Hexane (97%), palladium acetylacetonate (Pd(acac)₂,99%), nickel(II) acetylacetonate (Ni(acac)₂, 95%), tert-butylamine-borane complex (TBAB, 97%), benzyl alcohol, and cobaltic(III) acetylacetonate (Co(acac)₃,98%) were purchased from Meryer. n-Trioctylphosphine (TOP, 97%) and indium(III) acetate (99.99%) were purchased from Heowns. Sodium citrate, oleylamine (OA, 80-90%), oleic acid (OAc), octadecene (ODE) (>90%), 1,2,3,4-tetrahydronaphthalene (tetralin, 97%), and ferric(III) acetylacetonate (Fe(acac)₃, 98%) were purchased from MackLin. Silver nitrate (99.8%), lead(II) bromide (PbBr₂, 99.999%) and ethanol were purchased from Aladdin. Platinum acetylacetonate (Pt(acac)₂, 98%), trioctylphosphine oxide (TOPO, 90%), cesium carbonate (Cs₂CO₃, 99.95%), and polyvinylpyrrolidone (PVP, Mw~55000) were purchased from Sigma-Aldrich. The fixed rabbit erythrocytes were purchased from Zhengzhou Dening Biotechnology Co., Ltd. Hydrogen tetrachloroaurate (III) hydrate (HAuCl₄·xH₂O, 99.9%) was purchased from Alfa Aesar. Isopropanol, silver acetate (AgOAc), sulfur (99.5%), cadmium oxide (CdO, 99%), and benzyl ether were purchased from TCI, Innochem, Acros Organics, Energy chemical and Rhawn, respectively. 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE), 1,2dioleoyl-sn-glycero-3-phosphocholine (DOPC) and cholesterol were purchased from Avanti Polar Lipids. Cadmium chloride (CdCl₂, 99%), sodium perchlorate, ethylene glycol (EG, A.R.), hydrochloric acid (HCl, A.R.), ethylenediamine, acetonitrile (A.R.), acetone (A.R.), chloroform (A.R.), and liquid paraffin were purchased from Reagent supplier. THP1 cells were supplied by American Type Culture Collection (ATCC, USA). RPMI 1640 culture medium and fetal bovine serum (FBS) were purchased from BBI Life sciences. The sea shell was purchased from market. All chemical reagents were used as received without further purification.

2. Synthesis of nanoparticles

- 2.1 Synthesis of Au nanoparticles (Au NPs)
- (1) Synthesis of Au NPs with a mean diameter of ~80 nm

The 80 nm Au NPs were synthesized according to a reported method.¹ First, 150 mL of 2.2 mM sodium citrate was heated to 100 °C, and 1 mL of 25 mM HAuCl₄ was added to obtain \sim 10 nm Au seeds. The solution was then cooled down to 90 °C and 1 mL of 25 mM HAuCl₄ solution was

added. The mixture was kept at 90 °C for 30 min. This process was repeated for two times. Subsequently, 55 mL of solution was taken out and 2 mL of 60 mM sodium citrate and 53 mL of deionized water were added to keep the total volume unchanged. Then the whole process was repeated until Au NPs of 80 nm were obtained.

(2) Synthesis of Au NPs with a mean diameter of ~ 15 nm

The ~15 nm Au NPs were synthesized according to a reported method.² A mixture of 1 mL of 25 mM HAuCl₄ and 96 mL of water was heated to boiling. Subsequently, 3 mL of 1 wt% sodium citrate aqueous solution was injected, and the mixed solution was then kept at this temperature for 1 h to obtain ~15 nm Au NPs.

(3) Synthesis of Au NPs with a mean diameter of \sim 7.2 nm

The ~7.2 nm Au NPs were synthesized according to a reported method.³ Tetralin (10 mL), OA (10 mL) and HAuCl₄·3H₂O (100 mg) were mixed and magnetically stirred at 0 °C under N₂ gas flow for 10 min, and then a mixture of 0.5 mmol TBAB, 1 mL tetralin and 1 mL OA was injected to obtain Au seeds (~2.8 nm). The Au seeds were washed twice with hexane and ethanol, and then dispersed in hexane (10 mg mL⁻¹). Then the Au seed solution (1 mL) was added to OA (10 mL) containing 160 mg HAuCl₄·3H₂O. The resulting mixture was then heated at 60 °C for 10 h. Finally, the 7.2 nm Au NPs were washed twice with hexane and ethanol, and then dispersed in hexane for further use.

2.2 Synthesis of In₂O₃ nanoparticles (In₂O₃ NPs)⁴

0.6 mL OAc solution of indium acetate (0.2 mmol) were mixed with 0.8 mL OA and 5 mL ODE under vigorous stirring in a three-necked flask. The mixture was heated to 120 °C under a nitrogen atmosphere. This temperature was held for 20 min and then rapidly raised to 320 °C at a rate of 15 °C min⁻¹ and the system was vigorously stirred and refluxed under a nitrogen flow for 40 minutes. After cooling, absolute ethanol was added, the solution was centrifuged and the obtained In_2O_3 NPs were re-dispersed in hexane for further use.

2.3 Synthesis of AgNi nanoparticles (AgNi NPs)⁵

108 mg Ni(acac)₂, 20 mg AgNO₃ and 25 mg TOP were mixed with 7 mL OA under vigorous stirring in a three-neck flask. The mixture was degassed at 80 °C and heated to 190 °C under a nitrogen atmosphere. The resulting colloid was cooled down to room temperature after 2 h and

precipitated by adding ethanol. After being washed by ethanol and acetone sequentially, the precipitate was re-dispersed in 10 mL of hexane for further use.

2.4 Synthesis of CdS nanoparticles (CdS NPs)⁶

0.5 mmol CdCl₂ and 5 mmol OAc were added to 15 mL octylether in a three-neck flask. The mixture was heated to 220 °C at the rate of 20 °C min⁻¹ and stirred for 10 min under nitrogen atmosphere. The sample was washed by centrifugation after adding ethanol-chloroform mixture (v:v = 1:1), and the washing process was repeated twice. Finally, the product was dispersed in hexane for further use.

2.5 Synthesis of Ni nanoparticles (Ni NPs)⁷

First, 162 mg Ni(acac)₂, 2 mL TOP and 8 mL OA were mixed and stirred vigorously in a threenecked flask. Under a nitrogen atmosphere, the mixture was heated to 100 °C and kept for 30 min to remove air. Subsequently, the temperature was raised to 215 °C, during which the color of solution changed from blue to yellow, brown, and finally to black. It was kept for 40 min and allowed to cool naturally. After cooling, ethanol was added to the system and Ni NPs were obtained by centrifugation. The ~7 nm Ni NPs were washed with ethanol and acetone respectively, and finally dispersed in hexane for further use.

2.6 Synthesis of palladium nanoparticles (Pd NPs)⁷

100 mg Pd(acac)₂ and 1 mL TOP were mixed with 9 mL OA in a three-necked flask and stirred vigorously. The mixture was heated to 100 °C under N₂ atmosphere and maintained at this temperature for 30 min. Then the solution was rapidly heated to 250 °C at a heating rate of 10 °C min⁻¹, during which the solution changed from yellow to brown and finally to black. When the solution turned black, the mixture was kept at 250 °C for 30 min. After cooling to room temperature, 20 mL of ethanol was added, and ~5 nm Pd NPs were obtained after centrifugal separation. The NPs were washed with ethanol and acetone respectively, and then dispersed in hexane for further use.

2.7 Synthesis of Au-Ag core-shell nanoparticles (Au-Ag core-shell NPs)⁸

The ~40 nm Au NPs synthesized by the above seed growth method (2.1) were used as the core of this core-shell NPs. After heating the Au colloid to 100 °C, 4 mg of AgNO₃ was added to the above solution. Subsequently, 1 mL of 1% (w/w) sodium citrate solution was added dropwise and the solution was kept boiling for 1 h to obtain orange Au-Ag core-shell NPs.

2.8 Synthesis of Au nanopeanuts⁸

1 mL of 1% HAuCl₄ was diluted 100 times with water in a 250 mL three-necked flask. When the mixture was heated until boiling, 1 ml of 1% (w/w) sodium citrate solution was quickly injected to the system and then kept at this temperature for 20 min under magnetic stirring. Then 4 mg of AgNO₃ was added to the above solution, and subsequently, 1 mL of 1% (w/w) sodium citrate solution was added dropwise and kept boiling for 1 h to obtain orange Au-Ag core-shell NPs. For the growth step of nanopeanut, 1 mL 1% HAuCl₄ and 1 mL 1% (w/w) sodium citrate solution was core-shell NP suspension simultaneously. The resulting NPs suspension was cooled to room temperature after 20 min. Finally we obtained colloidal Au nanopeanuts.

2.9 Synthesis of CdS NanoWires (CdS NWs)9

2 mmol CdO, 2 mmol L-cysteine and 2 mmol sulfur powder were dissolved in 80 mL ethylenediamine and mixed well to form a clear solution. The mixture was then transferred to a 100 mL Teflon-lined autoclave and heated at 180°C for 12 h. After the reaction, the autoclave was cooled to room temperature, and a yellow precipitate was obtained by centrifugation. Then the yellow precipitate was alternately rinsed six times with ethanol and distilled water. The final centrifuged product was dried in a vacuum oven at 60 °C for 12 h.

2.10 Synthesis of Fe₃O₄ nanoparticles (Fe₃O₄ NPs)¹⁰

In a typical synthesis, Fe(acac)₃ (3 mmol) was mixed with 15 mL of benzyl ether and 15 mL of oleylamine in a three-necked flask and stirred vigorously. The mixture was heated to 110 °C under N₂ atmosphere and kept at this temperature for 1 h to remove air. Then the mixture was quickly heated to 300 °C at a rate of 20 °C min⁻¹ and kept at this temperature for 1 h. After cooling to room temperature, 50 mL of ethanol was added to collect Fe₃O₄ NPs by centrifugation. The obtained ~10 nm Fe₃O₄ NPs were washed with ethanol and acetone sequentially and then dispersed in hexane for further use.

2.11 Synthesis of CoO nanoparticles (CoO NPs)¹¹

 $Co(acac)_3$ (0.1g) and oleylamine (7.51g) were mixed in a three-necked flask, heated at 135 °C under N₂ atmosphere for 5 h. Then, the temperature was quickly raised to 250 °C and kept at this temperature for 3 h. After cooling down to room temperature, the CoO NPs were collected by centrifugation. After washing with ethanol and acetone respectively, the NPs were finally dispersed in hexane for further use.

2.12 Synthesis of AgPd nanoparticles (AgPd NPs)¹²

In a typical synthesis, 0.084 g of AgOAc (0.5 mmol) and 0.15 g of $Pd(acac)_2$ (0.5 mmol) were dissolved in a mixed solvent of 4.5 mL OAc, 0.5 mL OA and 10 mL ODE. The mixture was heated to 80 °C under N₂ atmosphere and degassed at this temperature for 1 h. The solution was then heated to 180 °C at a rate of 5-7 °C min⁻¹ and kept at this temperature for 20 min before cooling down to room temperature. After that 100 mL ethanol was added and the product was collected by centrifugation. The obtained NPs were washed with ethanol and acetone respectively, and finally the product was dispersed in hexane for further use.

2.13 Synthesis of Pt nanoparticles (Pt NPs)¹³

First, the formation of Pt-OA complex was achieved by dissolving 0.25 mmol of $Pt(acac)_2$ in 3 mL of OA at 70 °C overnight. Then, 10 mL of OA was heated to 250 °C under a N₂ atmosphere, and the above Pt-OA solution was injected into this system, which was kept heating for 1 h. After cooling down, 20 mL of ethanol was added and the NP sample was collected by centrifugation. The obtained Pt NPs were washed with ethanol and acetone respectively. Finally, the product was kept in hexane for further use.

2.14 Synthesis of Ag nanoparticles (Ag NPs)¹⁴

In a typical synthesis, 150 mg of AgNO₃ was added to a mixture of 20 mL liquid paraffin and 5 mL OA, and magnetic stirring was applied to make the mixture homogeneous. The mixture was degassed under a nitrogen atmosphere for 20 min. The reaction mixture was heated to 180 °C at a rate of 4 °C min⁻¹, then maintained at 180 °C for 2 h, and then aged at 150 °C for 8 h. During this process, the color of the suspension changed to bright orange, brown, and finally black. After the

mixture was cooled to room temperature, 50 mL of ethanol was added before centrifugation. The precipitate was washed with acetone and ethanol respectively, and finally the Ag NPs were dispersed in hexane for further use.

2.15 Synthesis of CsPbBr₃ quantum dots (QDs)¹⁵

In a typical synthesis, the mixture of 0.207 g PbBr₂, 15 mL ODE, 1.5 mL OA and 1.5 mL OAc was prepared as reaction solution. And the reaction solution was heated to 110 °C under N₂ atmosphere and degassed at this temperature for 40 min and then heated to 170 °C. 0.2035 g CsCO₃ was mixed with 10 mL of ODE and 1 mL of OAc in another three-necked flask and heated to 120 °C. 1.4 ml of the mixture of CsCO₃, ODE and OAc was quickly injected to the reaction solution, and after 5 s, the reaction solution was cooled by ice-water bath. The CsPbBr₃ QDs were washed by ethyl acetate and dispersed in hexane for further use.

2.16 Synthesis of Ag nanocube¹⁶

First 5 mL of EG in a 20 mL glass vial was preheated to 140 °C in an oil bath (stirring rate 360 rpm). After 1 h, 1 mL of 3 mM HCl was injected into the above solution. About 10 min later, 1 mL aqueous solution of 3 mM HCl was added. Then 3 mL EG solution of 94 mM AgNO₃ and 3 mL EG solution of 147 mM PVP were simultaneously injected into the glass vial at a rate of 45 mL h⁻¹. The vial cap was then loosened for 20 h and then tightened. After 8 h, the product was cooled down to room temperature.

2.17 Synthesis of polydopamine nanoparticles (PDA NPs)¹⁷

PDA NPs were generated by self-polymerization of dopamine under alkaline conditions. First, 3.3 mL 28-30% ammonia was mixed with 40 mL of ethanol and 90 mL of water at 25 °C. After stirring for 30 min, 10 mL of an aqueous solution containing 0.5 g of dopamine was added to the above mixture, and aged for 24 h. During the reaction, the color of the solution quickly changed from colorless to light yellow, then brown, and finally to black. After the reaction, the PDA NPs were collected by centrifugation, and washed four times with water before dispersed in 40 mL of water for further use.

2.18 Synthesis of liposome¹⁸

In a typical synthesis of liposomes, 200 μ L of 10 mM DOPE, 200 μ L of 10 mM DOPC and 200 μ L of 10 mM cholesterol were mixed with 5 mL of chloroform overnight. The mixture was rotavaporated 2 times (37 °C, 10 min) in order to remove the organic solvent and the formed lipid film was rehydrated in 1 ml of PBS with agitation for a minimum of 1 h. Small unilamellar vesicles were generated by sonication sequentially in a bath-sonicator for 40 min and a probe-sonicator for 5 min. After that, liposomes were extruded via an Avanti Mini-Extruder with a 100 nm polycarbonate nanoporous membrane. The resultant liposomes were stored at 4 °C for further use.

3. Assembly of core-satellite superstructures

3.1 Assembly of inorganic superstructures

In a typical assembly of superstructures using inorganic building blocks, the citrate-stabilized cores were redispersed in isopropanol, and the satellite NPs were dispersed in hexane. The concentration of Au NPs for assembly is about 4.9×10^{10} NPs/mL, and the corresponding satellite is about 8.3×10^{12} NPs/mL. Then, 1 mL hexane NP colloid was injected to 1 mL isopropanol colloid under ultrasonication. After 15 min, the superstructures were successfully synthesized. Then the product was centrifuged (200 g, 10 min) and dispersed in ethanol. For the assembly of Au@CsPbBr₃ perovskite superstructures, the Au cores were washed 2 times with ethyl acetate in order to remove the trace water in the colloid. Eventually the Au NPs dispersed in ethyl acetate were mixed with perovskite NPs dispersed in hexane under ultrasonication. After 15 min, superstructures were formed and then centrifuged (200 g, 10 min) and dispersed in ethyl acetate. For the assembly of PDA@SiO₂ superstructures, the PDA NPs and SiO₂ NPs were redispersed in ethanol and then hexane (1:1 v/v) was added into the mixture under ultrasonication. After 15 min, superstructures were formed and then centrifuged (200 g, 10 min) and redispersed in ethanol.

3.2 Assembly of liposome@Au superstructures

For assembly of liposome@Au core-satellite superstructures, the liposomes suspended in PBS buffer was diluted with water (3:100 v/v). The Au NPs dispersed in water were mixed with the liposomes under ultrasonication. And then a certain amount (1:20 v/v) of PBS buffer solution (1×)

was further added to the system in order to destabilize the Au colloid. After ~ 10 min, the obtained superstructures were centrifuged (600 g, 20 min) and then dispersed in water.

3.3 Assembly of red blood cell@Au superstructures

First, the red blood cells suspended in PBS buffer were diluted with water (3:100 v/v). Then Au NPs dispersed in ethanol were mixed with the red blood cells under ultrasonication. Then, a certain amount (1:50 v/v) of PBS buffer solution (1×) was further added to destabilize the Au colloid. After 10 min, the obtained nanostructures were collected and dispersed in ethanol. When preparing SEM sample, the superstructures were dehydrated in stages with 50%, 70%, 80%, 90%, and 100% ethanol solutions, and the sample was finally dropped on a silicon wafer and sprayed gold by ion sputtering for SEM characterization.

3.4 Assembly of THP1 live cell@PDA superstructures

For assembly of THP1 live cell@PDA superstructures, THP1 live cells were suspended in PBS buffer (1×) and PDA NPs were dispersed in diluted PBS solution ($0.25\times$) to maintain the colloidal stability of the PDA NPs. The live cells were mixed with PDA NPs on a temperature control shaker (37 °C, 300 rpm) and then a certain amount of PBS buffer solution (1×) was added into the mixture. After 30 min, the obtained superstructures were centrifuged and then dispersed in PBS. When preparing SEM sample, the superstructures were dehydrated in stages with 50%, 70%, 80%, 90%, and 100% ethanol solutions, and the sample was finally dropped on a silicon wafer. SEM characterization was performed after ion sputtering of gold on the dried sample.

3.5 Cell viability assay

Trypan blue dye was used to detect the viability of THP1 cells after assembly with PDA. The THP1@PDA superstructures are mixed with 0.4% trypan blue solution at a ratio of 9:1. Within three minutes, microscope images of THP1@PDA structures were collected. The dead cells were stained light blue, while live cells were not stained under the microscope.

3.6 Assembly of red blood cell@PDA, red blood cell@(Au+PDA) superstructures

For assembly of red blood cell@PDA superstructures, the fixed blood cells were suspended in diluted PBS buffer (3:100 v/v). PDA NPs dispersed in ethanol were mixed with the fixed cells

under ultrasonication. Then a certain amount (1:10 v/v) of PBS buffer solution was added. After 10 min, the obtained red blood cell@PDA superstructures were centrifuged and dispersed in ethanol. To assemble red blood cell@(Au+PDA) superstructures, the above red blood cell@PDA superstructures were re-dispersed in water and mixed with Au NPs in ethanol under ultrasonication. Then, a certain amount (1:50 v/v) of PBS buffer solution $(1\times)$ was further added to destabilize the Au colloid. After 10 min, the obtained red blood cell@(Au+PDA) superstructures were centrifuged and dispersed in ethanol.

4. Experimental characterizations

TEM images and elemental analysis of nanostructures were performed on a FEI Talos F200X G2 (AEMC) high-resolution transmission electron microscope, operating at a voltage of 200 kV. SEM characterizations were carried out on a ZEISS Gemini SEM 300 and JEOL JSM-7900F high-resolution scanning electron microscopes. A Bruker (TENSOR II) Fourier transform infrared spectrometer (FTIR) was used to record the IR spectra. X-ray photoelectron spectra (XPS) spectra of Au NPs before and after hexane treatment were collected through a Thermo Escalab Xi+ spectrometer. The real-time detection of the size and zeta potential of NPs before and after hexane treatment was performed on a Brookhaven's BI-200SM ZetaPALS potential analyzer. Extinction spectra were recorded on a SPECORD 2010 plus (analytikjena) UV-Vis absorption spectrometer. X-ray diffraction (XRD) measurements were performed on a Rigaku Miniflex600 Cu Kα radiation diffractometer. Atomic force microscopic (AFM) force curves were collected on a Bruker Dimension Fastscan. Ultrasonication was carried out on an elmasonic P 30H ultrasonic washer, and the condition for all samples is 100% power at 37 kHz.

5. AFM attractive force tests

AFM attractive force tests were carried out on Au NP monolayer films. The film was placed on a clean silicon wafer. A water droplet was placed on the film to simulate the liquid environment of colloidal NP assembly. After the initial state test, the water on the Au NP film was blotted by filter paper, and the film was soaked in a mixed solvent of hexane and isopropyl alcohol (1:1 v/v) for 10 min. After that, the film was gently soaked with isopropyl alcohol before AFM tests.

6. Application of superstructures

6.1 SERS spectra of 4-nitrophenylthiophenol (4-NTP) collected on single nanostructure The nanostructures dispersed in ethanol was dropped on a silicon wafer with etched mark. The location of single particle was first determined by SEM and then the silicon wafer was incubated with 4-NTP overnight. After several times of washing by ethanol in order to remove the free 4-NTP, SERS spectra were collected with 100× objective lens and 50% intensity of 633 nm laser.

6.2 Detection limit of 4-NTP and Crystal violet (CV) on Au@Au nanostructure

The nanostructures dispersed in ethanol was dropped on a silicon wafer and then the silicon wafer was immersed in different concentration 4-NTP/CV ethanol solutions to achieve the collection of SERS signals. SERS spectra were collected with 100× objective lens and 50% intensity of 633 nm laser.

6.3 In situ SERS measurement

SERS spectra were collected by Horiba HR-Evolution Raman microscope with an excitation wavelength of 633 nm, 50x objective and a Synapse EM-CCD in a spectroelectrochemical cell. To monitor the hydrogen evolution reaction by in situ SERS, Au@Pt superstructures were placed on glassy carbon electrodes with a Pt wire and an Ag/AgCl electrode serving as the counter and the reference electrodes.

6.4 Selective Oxidation of benzyl alcohol

CdS@Au superstructure was used to catalyze the oxidation of benzyl alcohol. Experiments in photocatalytic reaction were performed in a top-irradiation Pyrex flask. A 300 W Xe lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used as the irradiation light source. In a catalytic reaction, 5 mg of catalyst was suspended in the mixture of 10 μ L of benzyl alcohol and 4 mL of acetonitrile. The photocatalytic reaction was taken place in a quartz tube with a cooling water jacket to keep the whole reaction system at 25 °C. Samples were extracted from the system every half an hour for testing the conversion of reactant by gas chromatography (GC). As a control experiment, the Au NPs with the same diameter were loaded on the inert SiO₂ supporter to catalyze the oxidation reaction. And CdS nanowires is the same as Au NPs except for the load.

7. Density functional theory (DFT) calculation

All DFT calculations were performed using Vienna ab initio simulation package (VASP) in which a projector-augmented potential (PAW) method is implemented. The Perdew-Burke-Ernzerhof (PBE) exchange and correction functional at the generalized-gradient approximation (GGA) level was used at a plane-wave cutoff of 400 eV. The Monkhorst-Pack method of $3 \times 3 \times 1$ was used for Au (111). The convergence criteria for structure optimization and energy calculation were set to 1.0×10^{-4} eV/atom for energy and 0.02 eV/Å for maximum force. The Au surface was modeled using a $6 \times 6 \times 3$ Au (111) slab with the bottom 1 layers fixed. The van der Waals (vdW) interaction was included through the Grimme's semi-empirical DFT-D3 scheme of dispersion correction.

The adsorption energies, E_{ads1}, which means citrate coadsorption with hexane, were calculated by

E_{ads1}= E_{hexane-citrate-slab}- E_{hexane-slab}- E_{citrate}

And the E_{ads2}, which means citrate coadsorption with ethanol, were calculated by

E_{ads2}= E_{ethanol -citrate-slab}- E_{ethanol -slab}- E_{citrate}

where E_{solvent-citrate-slab}, E_{solvent-slab} and E_{citrate} are the total energies of the solvent and citrate coadsorbed slab, the solvent adsorbed slab, and cirate molecule, respectively.

8. DLVO formula calculation

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$$V_{tot} = V_{elec} + V_{vdW} + V_{Born}$$
$$V_{elec(h)} = \pi \varepsilon \varepsilon_0 \frac{r_1 r_2}{(r_1 + r_2)} [2\psi_1 \psi_2 \ln\left(\frac{1 + e^{-\kappa h}}{1 - e^{-\kappa h}}\right) + (\psi_1^2 + \psi_2^2) ln^{\frac{1}{100}} (1 - e^{-2\kappa h})]$$
(Eq S1)

In Eq S1, h is separation distance, r_1 and r_2 is the radius of small and large NPs, respectively. ψ is surface potential of NPs, and the relationship between ψ and zeta potential (ζ) is

 $\psi = \zeta(1 + \frac{z}{r_1})e^{\kappa z}$, where z =0.5 nm. The Debye-Huckel parameter (κ), which is the inverse of the diffuse layer thickness, was calculated with the following formula.

$$\kappa = [\frac{2IN_A 1000e^2}{\varepsilon \varepsilon_0 k_B T}]^{1/2}$$

where N_A is Avogadro's number (6.02×10²³), $\varepsilon \varepsilon_0$ is the dielectric constant of the solvent, k_B is Boltzmann constant (1.38×10⁻²³ J/K), I is the ionic strength was calculated with the following relationship. We obtained this data by consulting the published literature,¹⁹ and did not measure the ionic strength here.

$$I = \frac{1}{2} \sum c_i z_i^2$$

$$V_{vdW(h)} = -\frac{A}{12} \left(\frac{y}{r^2 + ry + r} + \frac{y}{r^2 + ry + r + y} + 2ln \frac{r^2 + ry + r}{r^2 + ry + r + y} \right) \quad \text{(Eq S2)}$$
In Eq (S2), $y = \frac{r_2}{r_1}, r = h/r_1, r_1$ is the radius of smaller particle.

$$V_{Born} = 4A \left(\frac{\sigma_c}{r_1} \right)^6 \left(\frac{4!}{10!} \right) \left(\frac{1}{R} \right) \left(\frac{-R^2 - 7(y - 1)R - 54}{(R - 1 + y)^7} + \frac{-R^2 + 7(y - 1)R - 54}{(R + 1 - y)^7} + \frac{R^2 + 7(y - 1)R + 726}{(R + 1 - y)^7} \right)$$
In Eq (S3), $R = \frac{h + r_1 + r_2}{2r_1}, \sigma_c$ is the Born collision parameter (usually $\sigma_c = 0.5$ nm).

9. Estimation of ΔG in assembly of Au@Pt and aggregation of Au NPs

The density of Au NPs is 19.32 g/cm³, and the volume of an 80 nm Au NP is

$$V(\text{Au}) = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (40 \times 10^{-9})^3 \text{ m}^3 = 2.68 \times 10^{-22} \text{ m}^3$$

The mass of an 80 nm Au NPs is

 $m_{\rm Au} = V_{\rm Au} \times \rho_{\rm Au} = 2.68 \times 10^{-22} \text{ m}^3 \times 19.32 \text{ }g/cm^3 = 5.18 \times 10^{-18} \text{ kg}$

Similar to the calculation of the mass of 80 nm Au NP, the density of Pt NPs is 21.45 g/cm⁻³, the mass of a 10 nm Pt NP is

 $m_{\rm Pt} = V_{\rm Pt} \times \rho_{\rm Pt} = 5.24 \times 10^{-25} \,\mathrm{m^3} \times 21.45 \,g/cm^3 = 1.12 \times 10^{-20} \,\mathrm{kg}$

According to the average kinetic energy of the colloid being 1.5^{KT} (3.7 kJ/mol), the move speeds of Au NPs and Pt NPs are calculated:

$$v_{\rm Au} = 0.04879 \text{ m/s}$$

 $v_{\rm Pt} = 1.050 \text{ m/s}$

During the collision, momentum is conserved. Therefore, for Au@Pt superstructure, during the collision of a single gold with many platinum NPs, the following formula is obtained. Among them, m_1v_1 represents the momentum of an Au NP, and the latter part represents the momentum of an Au@Pt nanostructures. The speed of the assembled nanostructure is represented by v_3 .

 $m_1 v_1 = (m_1 + 70m_2)v_3$ $v_3 = 0.04237 \text{ m/s}$

Loss of kinetic energy =
$$(\frac{1}{2}m_3v_3^2) - (\frac{1}{2}m_1v_1^2 + \frac{1}{2} \times 70 \times m_2v_2^2) = -4.330 \times 10^{-19} \text{ J}$$

Assuming all the loss of kinetic energy is converted into heat, therefore,

$$\Delta H_1 = -4.330 \times 10^{-19} J$$

$$\Delta G_{Au@Pt} = \Delta H_1 - T\Delta S_1 = -4.155 \times 10^{-19} J$$

Where $\Delta S_1 = K \times ln \frac{2}{W_1}$, W_1 and W_2 are the state numbers of the beginning and end states of the assembly process respectively. For aggregation of Au NPs:

 $m_1 v_1 = (m_1 + 6m_1)v_4$

$$v_4 = 0.006970 \ m/s$$

Loss of kinetic energy = $(\frac{1}{2} \times 7m_1v_4^2) - 7 \times (\frac{1}{2}m_1v_1^2) = -4.228 \times 10^{-20} J$

$$\Delta H_2 = -4.228 \times 10^{-20} J$$

$$\Delta G_{\rm Au - Au} = \Delta H_2 - T \Delta S_2 = -3.428 \times 10^{-20} \, \text{J}$$

From the above calculation, ${}^{\Delta G}_{Au@Pt} < {}^{\Delta G}_{Au-Au}$. Therefore, it is easier to form Au@Pt nanostructures during collision in this system.

Supporting Figures



Figure S1. (a) TEM image of Au NP building blocks. (b) Extinction spectrum of the Au NPs dispersed in isopropanol. TEM image (c) and extinction spectra (d) of Au NPs treated with hexane.



Figure S2. Zeta potential and hydrodynamic size change of Au NPs after treatment with hexane. During this testing process, hexane (1:1 v/v) was firstly added into Au NPs which dispersed in isopropanol, and the zeta potential and hydrodynamic diameter was collected immediately without stir until the end of the test.



Figure S3. TEM image (a) and XRD pattern (b) of In_2O_3 NPs. Scale bar (inset), 5 nm. (c) Extinction spectra of the assembly process of Au@In₂O₃ NPs core-satellite superstructures. (d) SEM image of Au@In₂O₃ core-satellite superstructures. (Inset) SEM image of a single superstructure. Scale bar (inset), 20 nm. (e) Content of different elements in the Au@In₂O₃ superstructure.



Figure S4. (a-b) TEM image (a) and XRD pattern (b) of Pt NPs. (c) EDS elemental mapping of a single Au@Pt core-satellite superstructure. (Inset) TEM image of the corresponding Au@Pt superstructure. Scale bar (inset), 20 nm. (d) TEM image of many Au@Pt superstructures. (e) Content of different elements in the Au@Pt superstructure.



Figure S5. (a-b) TEM image (a) and XRD pattern (b) of AgNi NPs. (c) EDS elemental mapping of a single Au@AgNi superstructure. (Inset) TEM image of the corresponding Au@AgNi superstructure. Scale bar (inset), 50 nm. (d) TEM image of many Au@AgNi superstructures. (e) Content of different elements in the Au@AgNi superstructure.



Figure S6. (a-b) TEM image (a) and XRD pattern (b) of CoO NPs. (c) EDS elemental mapping of a single Au@CoO superstructure. (Inset) TEM image of the Au@CoO superstructure. Scale bar (inset), 20 nm. (d) TEM image of many Au@CoO superstructures. (e) Content of different elements in the Au@CoO superstructure.

85.99

12.66

0.24

40.20

79

Au

L



Figure S7. (a-b) TEM image (a) and XRD pattern (b) of CdS NPs. (c) EDS elemental mapping of a single Au@CdS core-satellite superstructure. (Inset) TEM image of the corresponding Au@CdS superstructure. Scale bar (inset), 50 nm. (d) TEM image of several Au@CdS superstructures. (e) Content of different elements in the Au@CdS superstructure.

20.74

0.74

98.60

0.12

15.44

2.11

0.07

1.25

94.87

48

79

Cd

Au

L

L



Figure S8. (a-b) TEM image (a) and XRD pattern (b) of CsPbBr₃ perovskite nanoparticles. (c) EDS elemental mapping of Au@CsPbBr₃ core-satellite superstructure. (Inset) TEM image of the corresponding Au@CsPbBr₃ superstructure. Scale bar (inset), 20 nm. (d) TEM image of several Au@CsPbBr₃ superstructures. (e) Content of different elements in the Au@CsPbBr₃ superstructure.



Figure S9. (a-b) TEM image (a) and XRD pattern (b) of Au NP satellites. (c) EDS elemental mapping of a single Au@Au core-satellite superstructure. (Inset) TEM image of the corresponding Au@Au superstructure. Scale bar (inset), 20 nm. (d) TEM image of many Au@Au superstructures.



Figure S10. (a-b) TEM image (a) and XRD pattern (b) of AgPd NPs. (c) TEM image of a single Au@AgPd core-satellite superstructure. (d) Elemental mapping of many Au@AgPd superstructures. (e) Content of different elements in the Au@AgPd superstructure.



Figure S11. (a-b) TEM image (a) and XRD pattern (b) of Fe_3O_4 NPs. (c) EDS elemental mapping and corresponding TEM image (inset) of a single Au@Fe_3O_4 core-satellite superstructure. Scale bar (inset), 50 nm. (d) TEM image of many Au@Fe_3O_4 superstructures. (e) Content of different elements in the Au@Fe_3O_4 superstructure.



е	Ζ	Element	Family	Atomic	Atomic	Mass	Mass	Fit error
				Fraction	Error	Fraction	Error	(%)
				(%)	(%)	(%)	(%)	
	28	Ni	K	60.22	6.92	36.48	3.13	0.43
	47	Ag	L	18.87	2.81	21.00	2.69	0.38
	79	Au	L	20.91	3.08	42.52	5.34	0.38

Figure S12. (a-b) TEM image (a) and XRD pattern (b) of Ni NPs. (c) EDS elemental mapping and corresponding TEM image (inset) of a single Au-Ag@Ni core-satellite superstructure. Scale bar (inset), 50 nm. (d) TEM image of many Au-Ag@Ni core-satellite superstructures. (e) Content of different elements in the superstructure.



Figure S13. (a-b) TEM image (a) and XRD pattern (b) of Pd NPs. (c) EDS elemental mapping of a single Au nanopeanut@Pd core-satellite superstructure. (Inset) TEM image of the corresponding superstructure. Scale bar (inset), 20 nm. (d) TEM image of many Au nanopeanut@Pd superstructures. (e) Content of different elements in the Au nanopeanut@Pd superstructure.



Figure S14. (a) TEM image of CdS@Au core-satellite superstructures. (b) XRD pattern of CdS nanowires. (c) Content of different elements in the CdS@Au superstructure.

2.69

20.00

0.74

8.36

L

Au



Figure S15. (a) EDS elemental mapping of a single Ag nanocube@Au core-satellite superstructure. (Inset) TEM image of the corresponding superstructure. Scale bar (inset), 50 nm. (b) TEM image of many Ag nanocube@Au core-satellite superstructures. (c) Content of different elements in the Ag nanocube@Au superstructure.

11.90

1.45

1.05

6.89

L

Au

79

а	HAADF	C Si		0 nm	500 nm			
С	Ζ	Element	Family	Atomic	Atomic	Mass	Mass	Fit error
				Fraction	Error	Fraction	Error	(%)
				(%)	(%)	(%)	(%)	
	6	С	K	39.20	6.79	28.54	2.95	1.52
	8	0	K	43.74	11.61	42.42	9.59	2.44
	14	Si	K	17.06	4.41	29.04	6.34	1.13

Figure S16. (a-b) TEM images of PDA@SiO₂ core-satellite superstructures. (Inset) EDS elemental mapping of different element. Scale bar (inset): 200 nm. (c) Content of different elements in the PDA@SiO₂ superstructure.



Figure S17. (a) In situ UV-Vis spectra, (b) TEM image and Zeta potential (c)of Au NPs after addition of PBS solution. Inset of (b): HRTEM image of Au NPs after PBS buffer treatment. Scale bar: 20 nm. There is also a ligand layer on the surface of Au NP, which demonstrates the addition of PBS buffer weakens the repulsive force between the NPs by neutralizing the surface charge instead of removing the citrate ligands on Au NP.



Figure S18. (a-b) TEM images of liposome@Au core-satellite superstructures. (c) Content of different elements in the superstructure.



Figure S19. (a-b) SEM images of red blood cell@Au core-satellite superstructures.



Figure S20. (a-b) SEM images of THP1 live cell@PDA core-satellite superstructures. (Inset) Scale bar, 5 μ m. THP1@PDA superstructures before (c) and after (d) stain with trypan blue. The THP1cells were not stained after assembly, indicating the viability of assembled cells and the gentleness of the assembly methodology.



Figure S21. (a) DLS results and photographs of superstructures after different times. UV-Vis (d) spectra and TEM images (b,c,e,f) of Au@In₂O₃ superstructures in different conditions. The spectra have no distinct difference, which further demonstrates the stability of the superstructures. Ultrasonication was carried out by elmasonic P 30H, and condition for stability test is 100% power, at 37 kHz for 10 minutes.



Figure S22. Zeta potential of nanoparticles for assembly.



Figure S23. (a) Zeta potential of citrate-stabilized Au NPs and PVP-stabilized Ag nanocubes. (b) UV-Vis extinction spectra of Ag nanocube@Au core-satellite nanostructures. These results show that two kinds of NPs with the same surface charge can be assembled into a superstructure, indicating that electrostatic attraction is not the main driving force of the assembly.



Figure S24. UV-Vis extinction spectra of citrate-stabilized Au NPs after addition of hexane (a), isopropanol (b) and In_2O_3 NP colloid containing hexane (c). (d) UV-Vis extinction spectra of Au NPs and Au NPs mixed with In_2O_3 NPs in isopropanol. (Inset: Zeta potential of Au and In_2O_3 nanoparticles.)



Figure S25. FTIR spectra of the citrate-stabilized Au NPs before and after hexane treatment. The peaks at 1585 and 1373 cm⁻¹ can be assigned to the asymmetric COO⁻ stretching (v_{asy} (COO⁻)) and symmetric COO⁻ stretching (v_{sym} (COO⁻)) of citrate on Au surface. Compared with the COO⁻ of aliphatic hydrocarbons, the higher wavenumber of v_{asy} (COO⁻) may originate from the intermolecular hydrogen bonding.²⁰ The addition of a non-polar solvent results in a redshift of the peak from 1585 to 1558 cm⁻¹, indicating that hexane induces attenuation of the intermolecular hydrogen-bonds and disrupts the solvation of citrate molecules with isopropanol. At the same time, a new peak appeared at ~1572 cm⁻¹, which can be assigned to the asymmetric -COONa stretching. Therefore, the addition of non-polar solvent causes the ligand detachment from Au NPs and the formation of -COONa.



Figure S26. (a-b) XPS of Au NP surfaces before (a) and after (b) treatment with non-polar solvent. The binding energy peaks at 285.9, 287.6 and 289.4 eV were assigned to CH_2/COH , COO-Au and COO(H) of citrate adsorbed on Au NPs, respectively. Before the non-polar solvent was added, we could clearly distinguish these three peaks (a). However, after we treated the Au NPs with hexane, the intensity of the peaks from citrate molecules was seriously reduced, which is consistent with the results obtained by FTIR.



Figure S27. (a-b) SEM images of Pt coated tip before (a) and after (b) AFM attractive force test.



Figure S28. SEM image of a Au NP monolayer film. Scale bar, 200 nm.



Figure S29. (a-b) AFM force-distance curves measured on the Au NPs (film) before (a) and after (b) treatment with hexane.



Figure S30. (a, d) TEM image of $Au@In_2O_3$ core satellite superstructures prepared by adding toluene (a) and the corresponding UV-Vis extinction spectra (d) of Au NPs (black curve) and superstructures (red curve); (b, e) TEM image of $Au@In_2O_3$ core satellite superstructures prepared by adding cyclohexane (b) and the corresponding UV-Vis extinction spectra (e) of Au NPs (black curve) and superstructures (red curve); (c, f) TEM image of $Au@In_2O_3$ core satellite superstructures prepared by adding benzene (c) and the corresponding UV-Vis extinction spectra (f) of Au NPs (black curve) and superstructures (red curve).



Figure S31. (a-c) SERS spectra of 4-nitrothiophenol measured on a single Au@Au core-satellite superstructure (red) and the corresponding Au core (blue). (Inset) SEM images of a single superstructure (left) and a single Au core (right). Scale bar, 50 nm. The SEM images and optical photographs of corresponding location are shown in (d) and (e). Scale bar, 1 μ m.



Figure S32. SERS spectra of Au@Au core-satellite structures immersed in molecular ethanol solutions with different concentrations.



Figure S33. SERS spectra of adsorbed hydrogen species (Pt-H) on Au@Pt superstructure in 0.1 M NaClO₄ electrolyte at different potentials.



Figure S34. The photocatalytic stability of the CdS@Au at medium conversion of benzyl alcohol.

Video S1. One-step & one-minute assembly of core-satellite superstructures.

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