Supporting Information

Mass-determining role in the electrophoresis separation of colloidal plasmonic nanoparticle oligomers

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Experimental section

Materials

Chloroauric acid ($HAuCl_4$, 99.9%), ethylene glycol (EG, >99.5%), silver nitrate ($AgNO_3$, >99.8%), 1,4-benzenediol, sodium hydrogen carbonate ($NaHCO_3$), L-ascorbic acid (AA, >99.7%), agarose, sucrose, tris(hydroxymethyl)aminomethane (Tris, >99.9%), boric acid (>99.8%), ethylenediamine tetraacetic acid (EDTA, >99.5%) were obtained from Sinopharm Chemical Reagent Corporation. Poly (diallyldimethylammonium) chloride (PDDA, Mw=100 000-200 000, 20 wt% in water), fish sperm DNA (FSDNA) were purchased from Sigma-Aldrich. The deionized water (DI water, 18.2 MΩ cm resistivity at 25 °C) was produced by a Milli-Q integral water purification system. All chemicals and solvents were directly used as received without any further treatment.

Preparation of gold nanospheres

The gold nanospheres with uniform size were synthesized by suing a polyol-reduction method.[1] Briefly, EG (60 mL), $HAuCl_4$ (1 M, 30 μL), PDDA (1.2 mL), $AgNO_3$ aqueous solution (0.1M, 12 μL) were added to the glass vial in turn. The mixture solution was stirred vigorously for 3 min at room temperature and put into the oil bath at 220 °C for 2 h without stirring. The final products were centrifuged at 10 000 rpm for 20 min after cooling to the room temperature, and rinsed with DI water for three times. Then the gold nanospheres were re-dispersed in the 100 μL DI water and used for further assembly.

Preparation of Au/Ag core-shell nanocubes

For a typical process of preparing Au/Ag core-shell nanocubes, $NaHCO_3$ (1M, 600 μL), $AgNO_3$ (1M, 120 μL), AA (1M, 600 μL) were added into the gold nanosphere seeds (60 mL).[2] Then the mixture solution was reacted at 75 °C for 2h. When the color of the reaction solution changed from wine red to brownish yellow, it indicated that the Au/Ag core-shell nanocubes had been successfully synthesized. The Au/Ag core-shell nanocubes were centrifuged at 10, 000 rpm for 20 min and rinsed repeatedly with DI water for three times. The final products were dispersed into 100 μL of DI water for next assembly.

Preparation of gold bipyramids

Gold bipyramids were synthesized by seed growth method.[3] The gold decahedron seeds were obtained by the following typical polyol-reduction method, EG (60 mL), $HAuCl_4$ (1 M, 15 μL), PDDA (1.2 mL), $AgNO_3$ aqueous solution (2M, 48 μL) were introduced to the glass vial. Subsequently, the mixture solution was put into the oil bath at 220 °C for 4 h. The color of the solution changed from bright yellow to wine red, indicating that gold decahedron seeds of uniform size were successfully prepared. After the gold decahedron seeds were cooled to room temperature, 1,4-benzenediol (0.25 M, 480 μL) and $HAuCl_4$ (0.1 M, 600 μL) were added into the gold decahedron seeds colloid solution. Then the mixture solution was reacted at 50 °C for several hours. The final products were centrifuged at 10, 000 rpm for three times and re-dispersed into 100 μL of the DI water for subsequent assembly.

Synthesis and separation of nanoparticle oligomers

Building blocks (gold nanoshperes, Au/Ag core-shell nanocubes, gold bipyramids) were dispersed in FSDNA aqueous solution (5 mg/mL), then the mixture solution was slightly shaken for one minute to make it evenly mixed. Under the action of van der Waals force and electrostatic force, the nanoparticles were assembled and reached an equilibrium state within several seconds. The mixture nanoparticles solution was loaded in a 1% agarose gel and run in 0.5×TBE buffer at 100 V for 1 hour. Different quality oligomers moved toward the positive electrode of the electrophoresis instrument under the action of the electric field force, and divided into different bands. The sample bands were carefully cut and soaked in DI water for 12 hours.[4]

Simulation

A 2D model was employed to qualitatively simulate the movements of the particles during gel electrophoresis. The simulation was conducted in COMSOL Multiphysics [COMSOL Multiphysics® v. 6.0. cn.comsol.com. COMSOL AB, Stockholm, Sweden.]. The qualitative model covers a 100 um * 10 um area. The Navier-Stokes equations were solved for flow field. And the electrostatic field was attached for offering the driving force. The particle tracing module with drag force was applied to simulate the interaction between the particles and the flow field. The complex collision and interaction between the particles and the gel was simplified as periodically resetting the velocity of the particle to zero. To accelerate the simulation, the electric potential between the top side and the bottom side was set as 180 V. The viscosity of liquid was set as 0.07 Pa*s.[5] And the density of liquid was approximated as the density of water.

2.6 Characterizations

The morphology of the final products was characterized by a field emission scanning electron microscope (SEM, SU 8020) and a TEM (JEOL-2010). The optical spectrum of the final products was record by a spectrophotometer (FX 2000). The optical photographs of the samples were recorded by a digital camera.

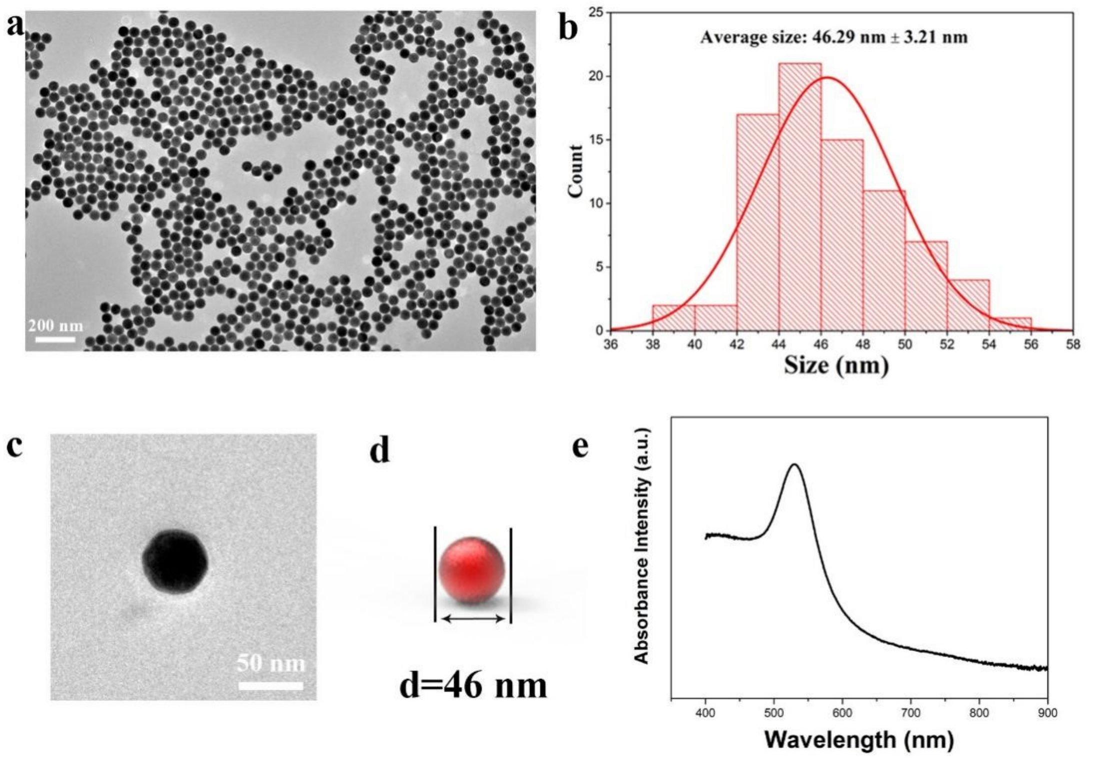

Fig. S1 (a) Low-magnification TEM image of the small gold nanospheres. (b) The histogram of particle size statistics of the small gold nanospheres. (c) High-magnification TEM image of the small gold nanosphere. (d) The model of the small gold nanosphere. (e) The absorbance spectrum of the small gold nanospheres.

Calculation of the mass of small nanosphere multimers

Monomer

$$M_{Monomer} = \rho V = \rho \frac{4}{3}\pi\left(\frac{d}{2}\right)^3$$

Here, $M_{monomer}$ is the mass, ρ is the density of gold nanosphere, d is the diameter of the nanosphere.

In this model, the value of ρ is 1.932×10^4kg/m^3, the value of d is 46 nm.

Therefore

$$M_{monomer} = 9.84 \times 10^{-16} g$$

In the same way, the masses of dimer, trimer, and tetramer can be calculated as 19.68×10^{-16} g, 29.52×10^{-16} g and 49.63×10^{-16} g.

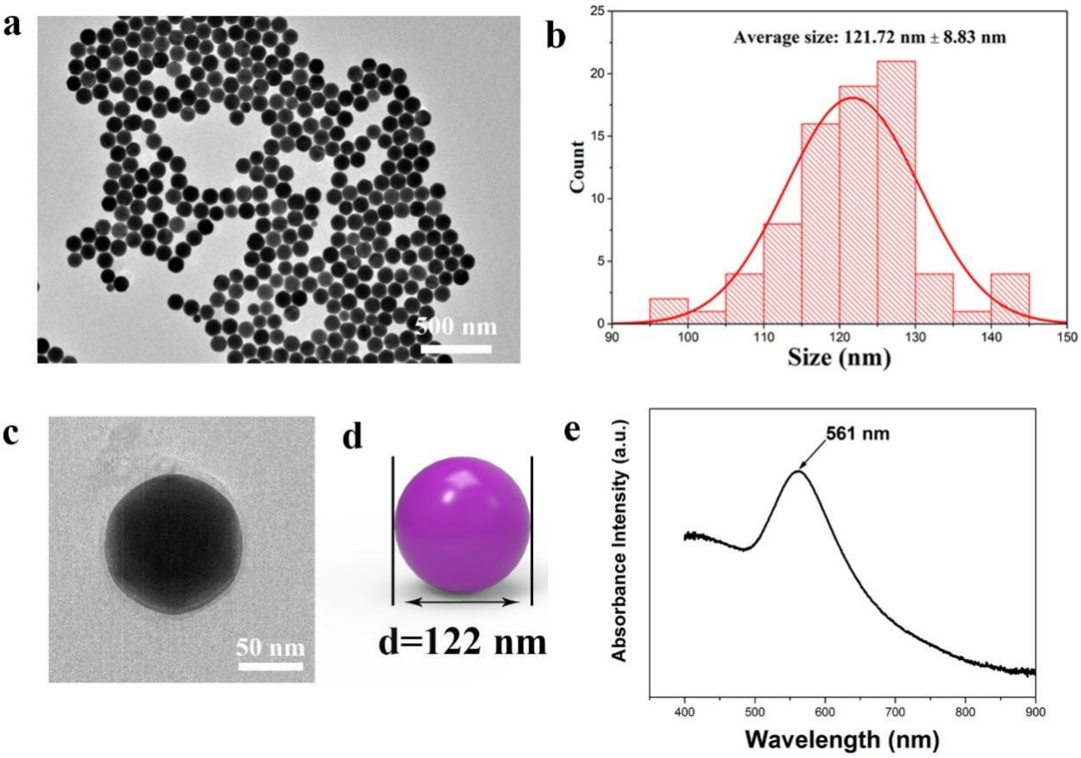

Fig. S2 (a) Low-magnification TEM image of the large gold nanospheres. (b) The histogram of particle size statistics of the large gold nanospheres. (c) High-magnification TEM image of the large gold nanosphere. (d) The model of the large gold nanosphere. (e) The absorbance spectrum of the large gold nanospheres.

Calculation of the mass of large nanosphere multimers

Monomer

$$M_{Monomer} = \rho V = \rho \frac{4}{3} \pi \left(\frac{d}{2} \right)^3$$

Here, $M_{monomer}$ is the mass, ρ is the density of gold nanosphere, d is the diameter of the nanosphere.

In this model, the value of ρ is 1.932×10^4kg/m^3, the value of d is 122 nm.

Therefore

$$M_{monomer} = 183.6 \times 10^{-16} g$$

Heterodimer

$$M_{Heterodimer} = M_{S-Monomer} + M_{B-Monomer}$$

$$M_{Heterodimer} = 193.44 \times 10^{-16} g$$

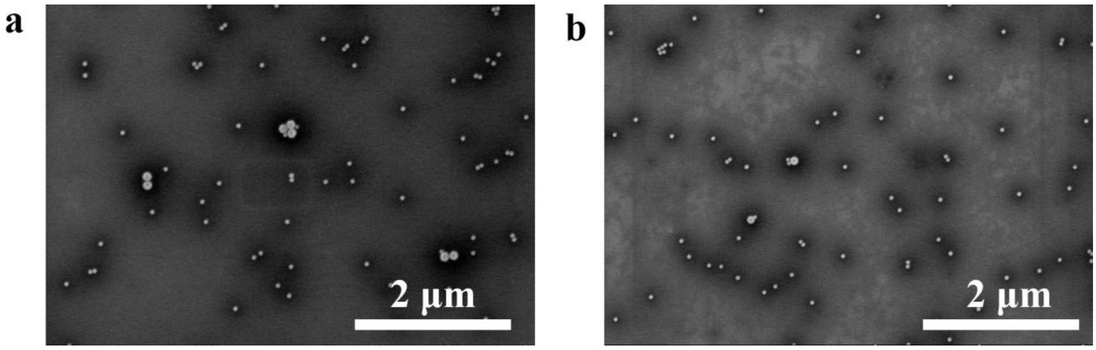

Fig. S3 (a)-(b) SEM images of the colloidal mixture containing serials of gold oligomers.

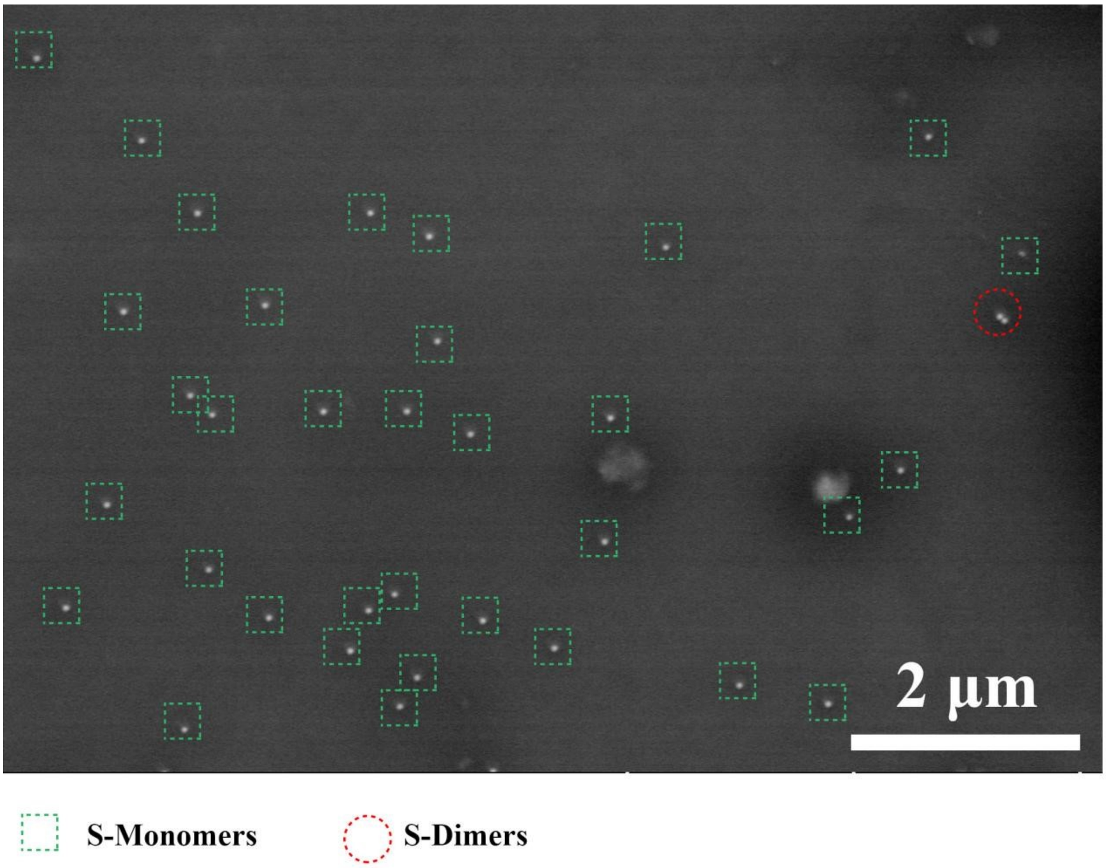

Fig.S4 Low magnification SEM image of the oligomers recovered from the band I.

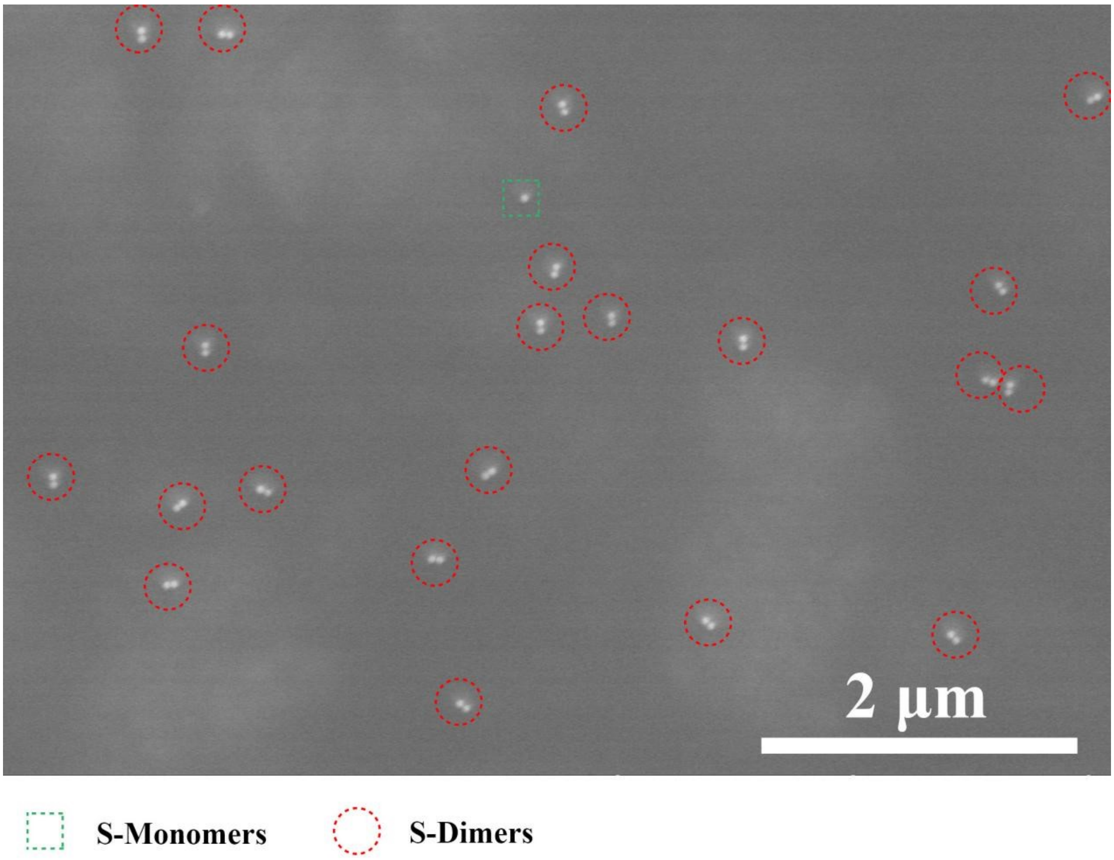

Fig. S5 Low magnification SEM image of the oligomers recovered from the band II.

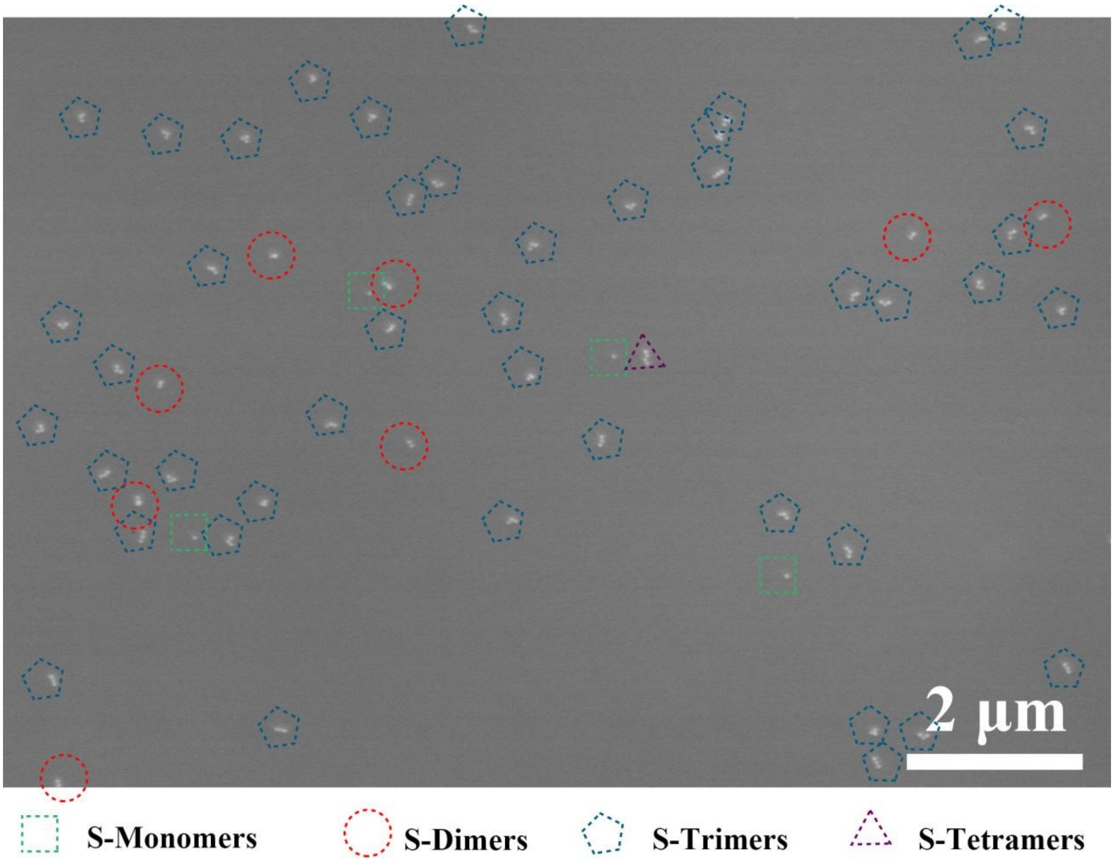

Fig. S6 Low magnification SEM image of the oligomers recovered from the band III.

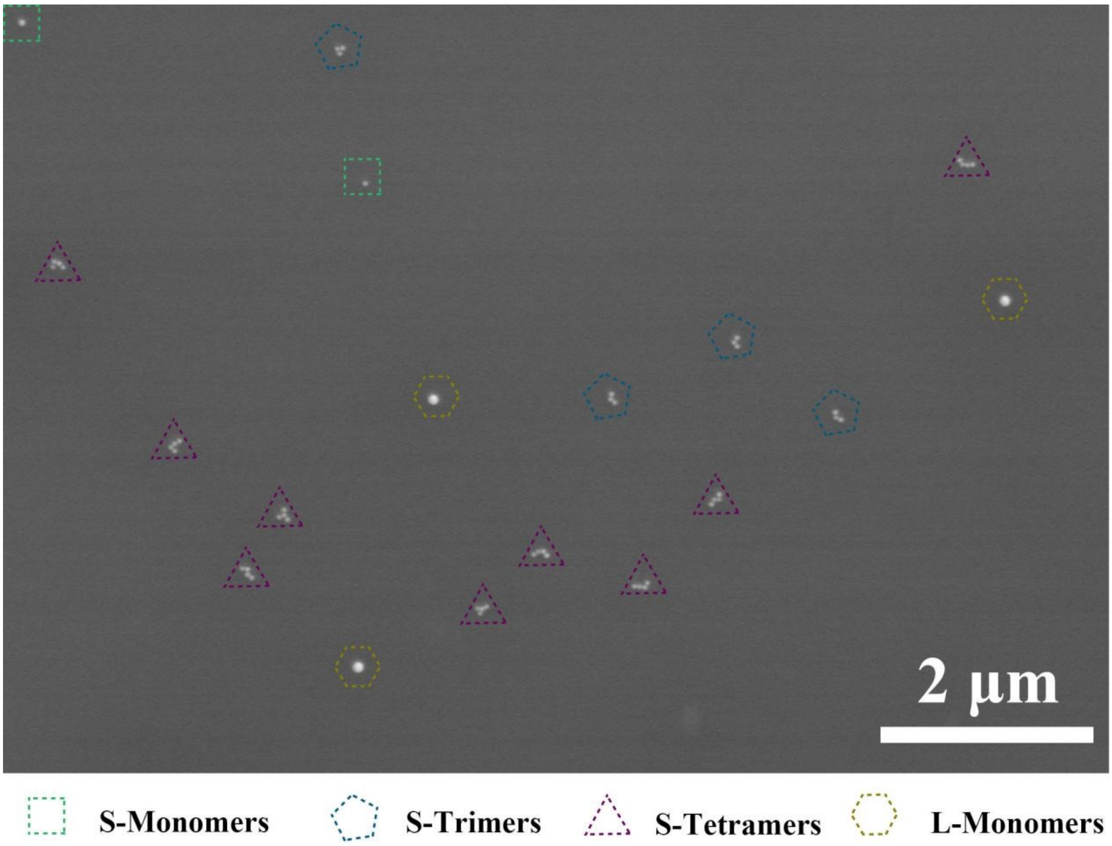

Fig. S7 Low magnification SEM image of the oligomers recovered from the band IV.

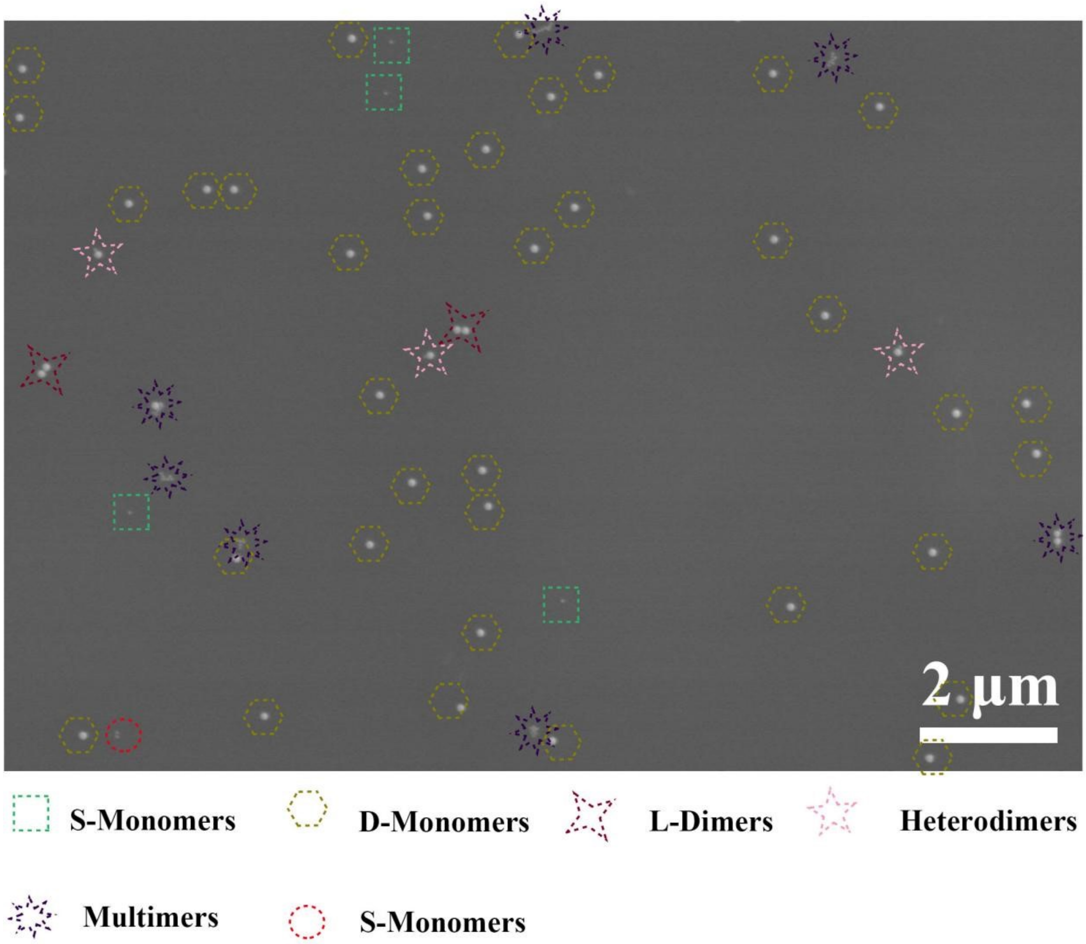

Fig. S8 Low magnification SEM image of the oligomers recovered from the band V.

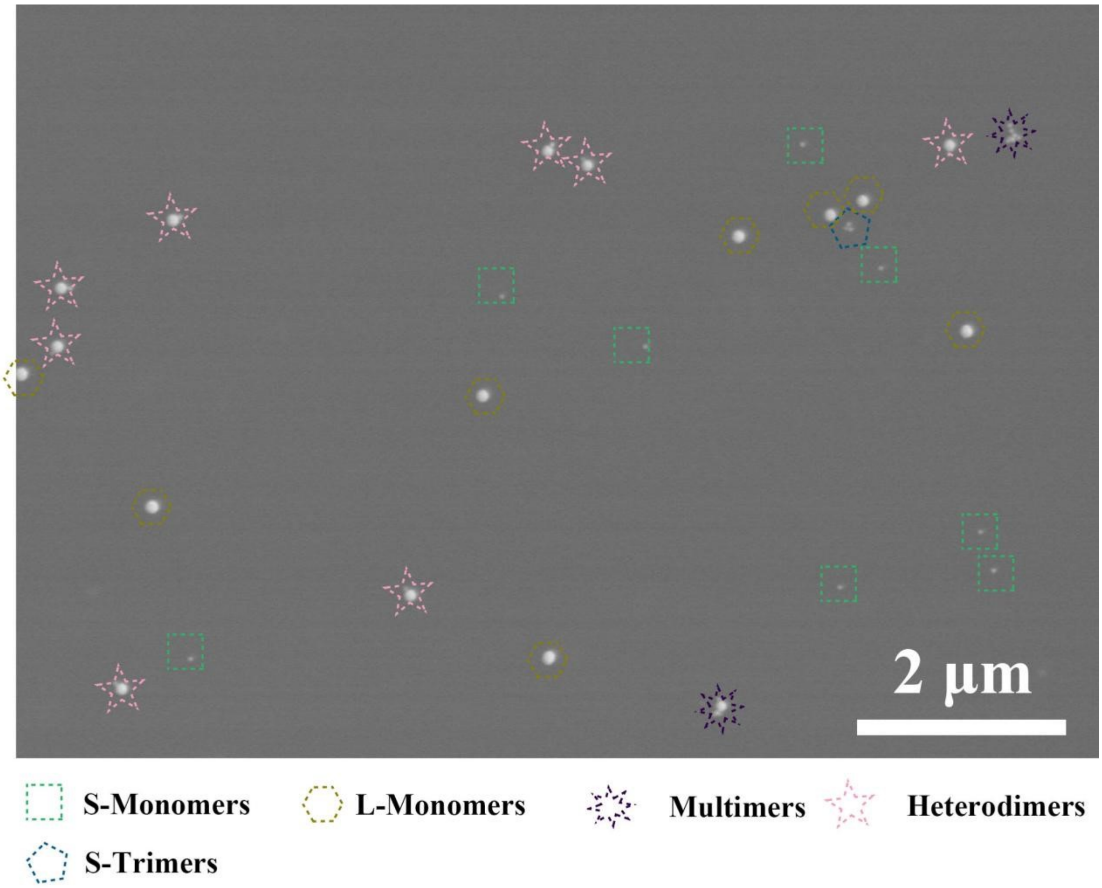

Fig. S9 Low magnification SEM image of the oligomers recovered from the band VI.

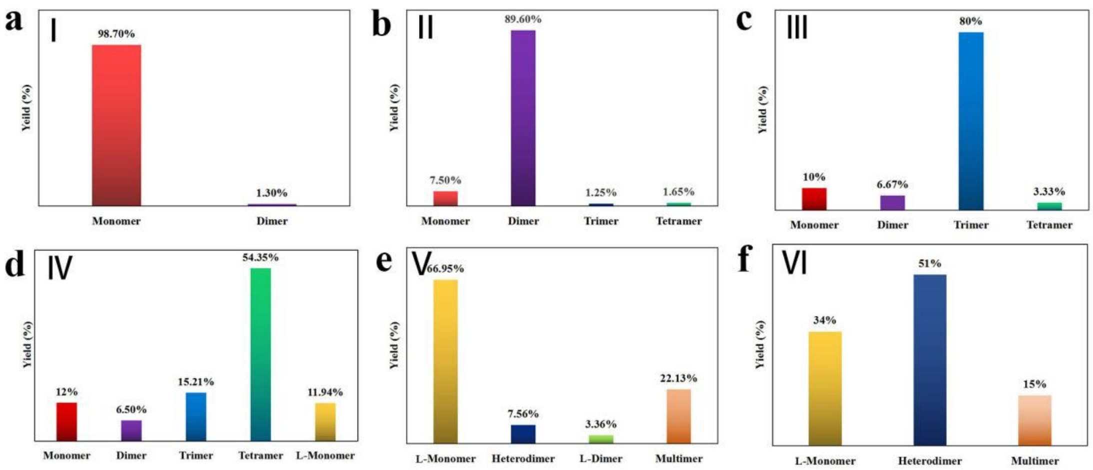

Fig. S10 (a)-(f) The yield of the oligomers recovered from the band I- VII.

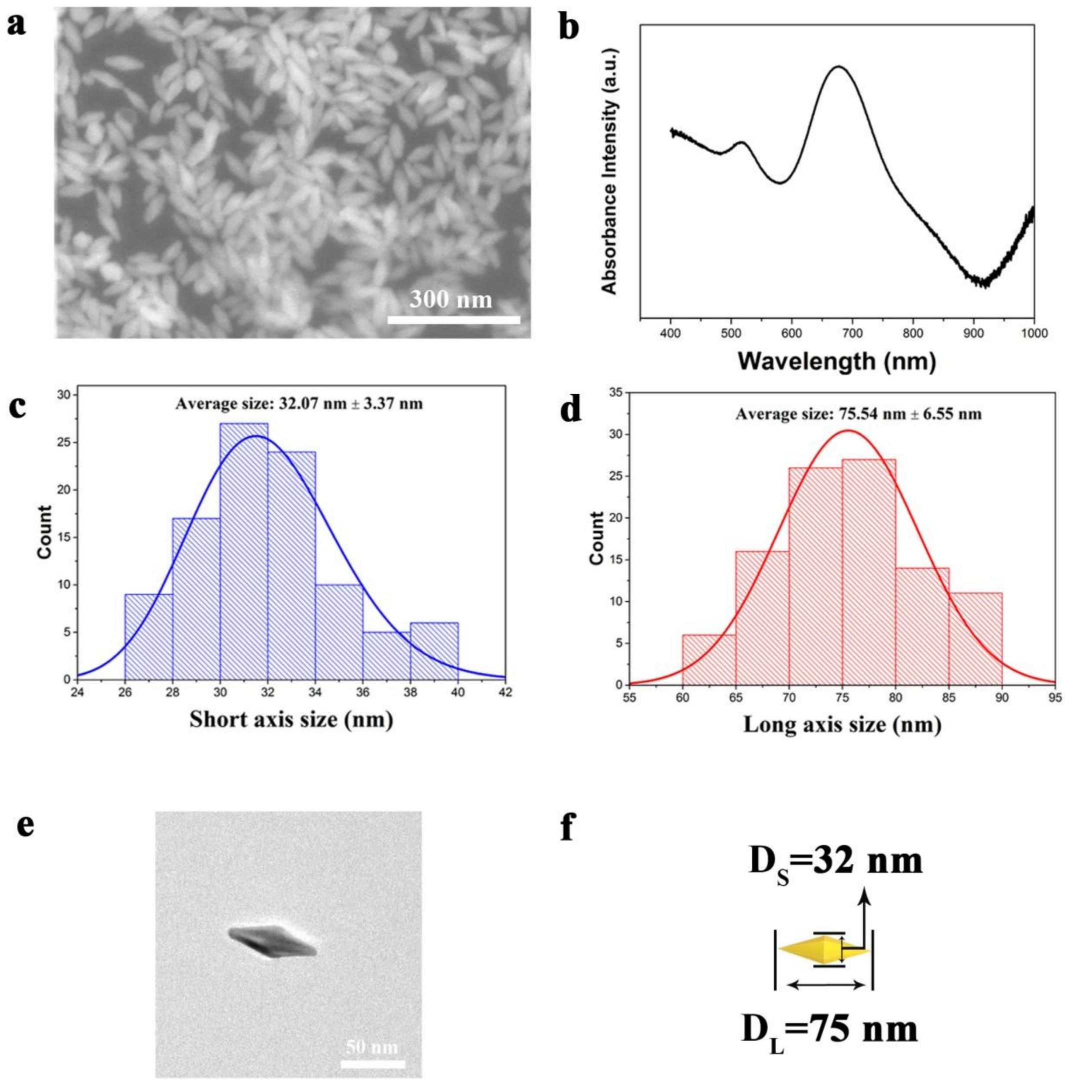

Fig. S11 (a) The SEM image of the small gold bipyramids. (b) The absorbance spectrum of the small gold bipyramids. (c-d) The histogram of particle size statistics of the small gold nanospheres. (e) The TEM image of the small gold bipyramid. (f) The model of the small gold bipyramid.

Calculation of the mass of the small gold bipyramid

In this experiment, the gold bipyramid is approximated as a splicing of two cones.

Therefore

$$V = 2 \times \pi \times \left(\frac{D_S}{2} \right)^2 \times \frac{D_L}{2} \times \frac{1}{3}$$

$$M = \rho V$$

Here, V is the volume of the small gold bipyramid, D_S is the diameter of short shaft short axis of the gold bipyramid, D_L is the diameter of long shaft short axis of the gold bipyramid. ρ is the density of the small gold bipyramid.

Therefore

$$M = 3.86 \times 10^{-16} \text{ g}$$

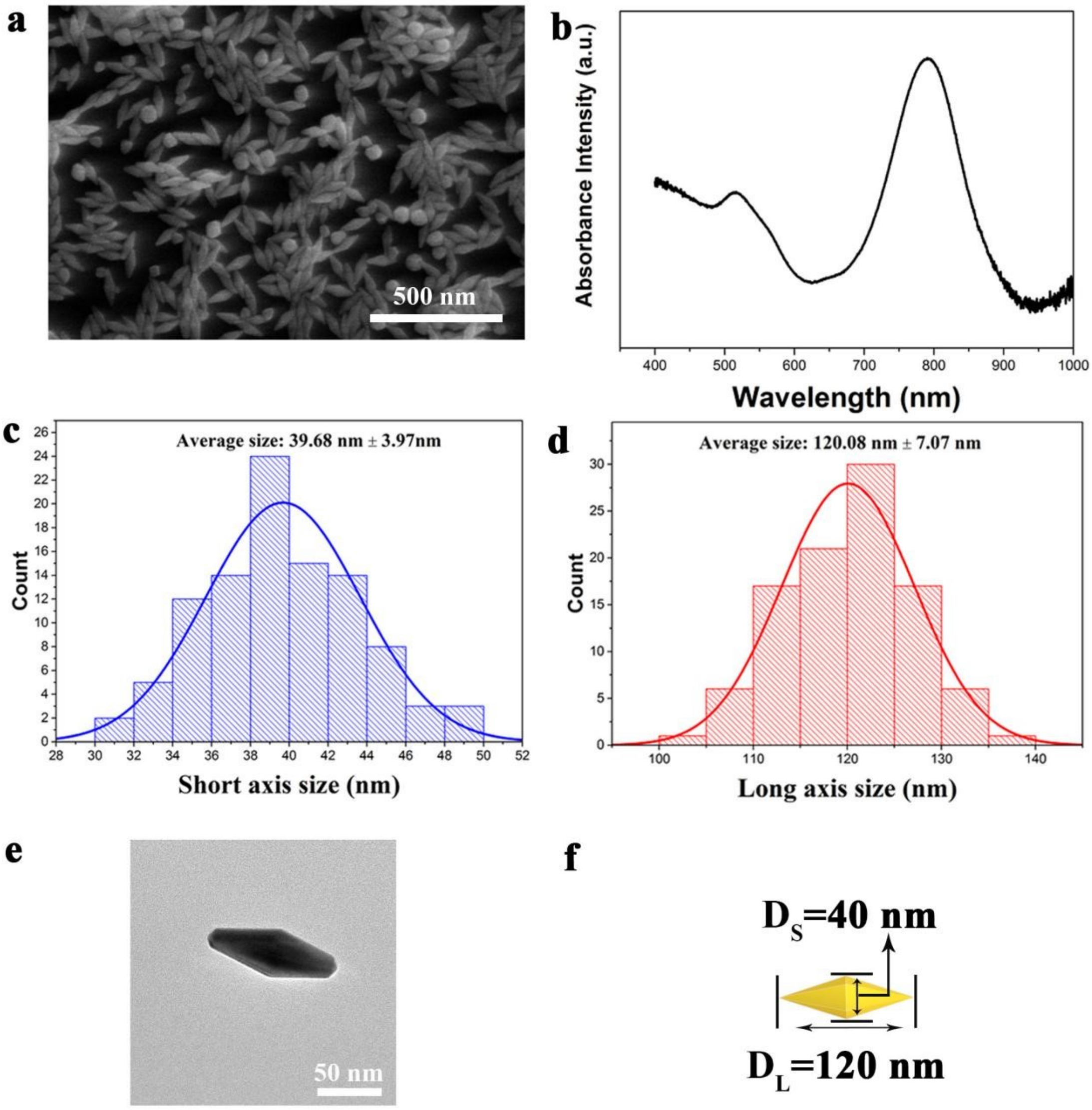

Fig. S12 (a) The SEM image of the medium gold bipyramids. (b) The absorbance spectrum of the medium gold bipyramids. (c-d) The histogram of particle size statistics of the medium gold nanospheres. (e) The TEM image of the medium gold bipyramid. (f) The model of the medium gold bipyramid.

Calculation of the mass of the medium gold bipyramid

$$V = 2 \times \pi \times \left(\frac{D_S}{2} \right)^2 \times \frac{D_L}{2} \times \frac{1}{3}$$

$$M = \rho V$$

Therefore

$$M = 9.7 \times 10^{-16} \text{ g}$$

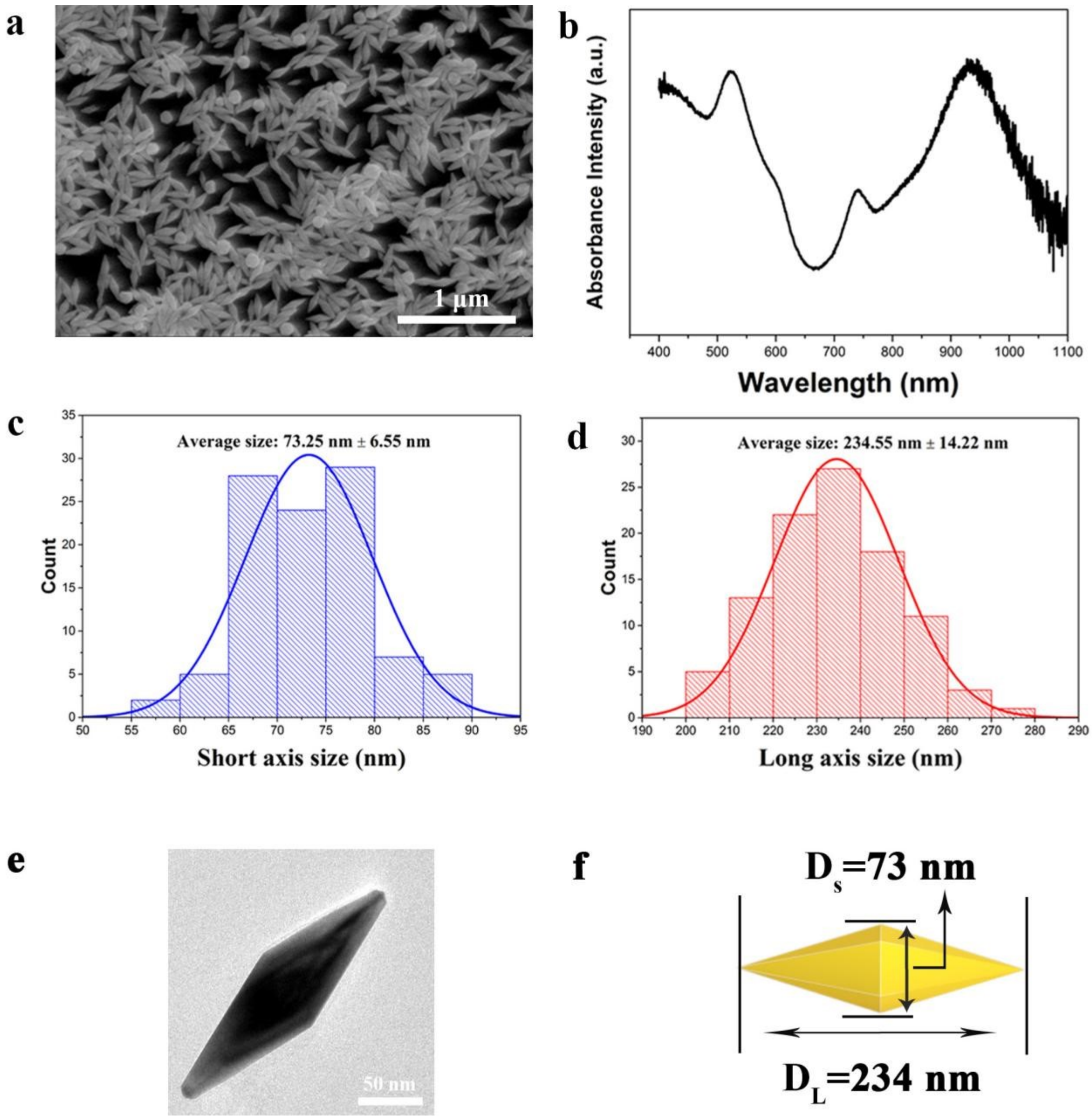

Fig. S13 (a) The SEM image of the large gold bipyramids. (b) The absorbance spectrum of the large gold bipyramids. (c-d) The histogram of particle size statistics of the large gold nanospheres. (e) The TEM image of the large gold bipyramid. (f) The model of the large gold bipyramid.

Calculation of the mass of the large gold bipyramid

In this experiment, the gold bipyramid is approximated as a splicing of two cones.

Therefore

$$V = 2 \times \pi \times \left(\frac{D_S}{2}\right)^2 \times \frac{D_L}{2} \times \frac{1}{3}$$

$$M = \rho V$$

Here, V is the volume of the large gold bipyramid, D_S is the diameter of short shaft short axis of the gold bipyramid, D_L is the diameter of long shaft short axis of the gold bipyramid. ρ is the density of the large gold bipyramid.

Therefore

$$M = 64.78 \times 10^{-16} \text{ g}$$

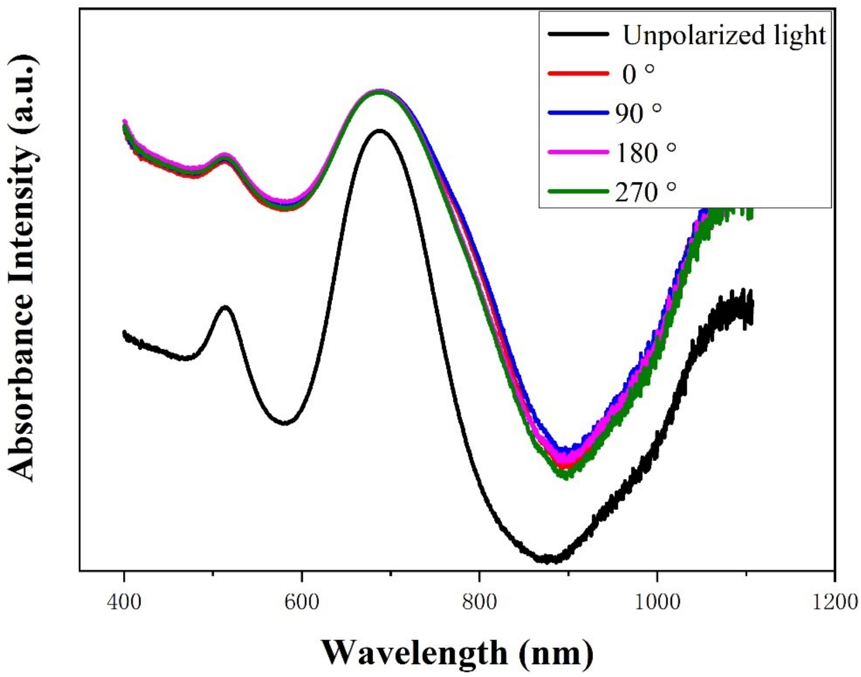

Fig. S14 The Absorption spectrum of band I in Figure 3b after adding polarizer.

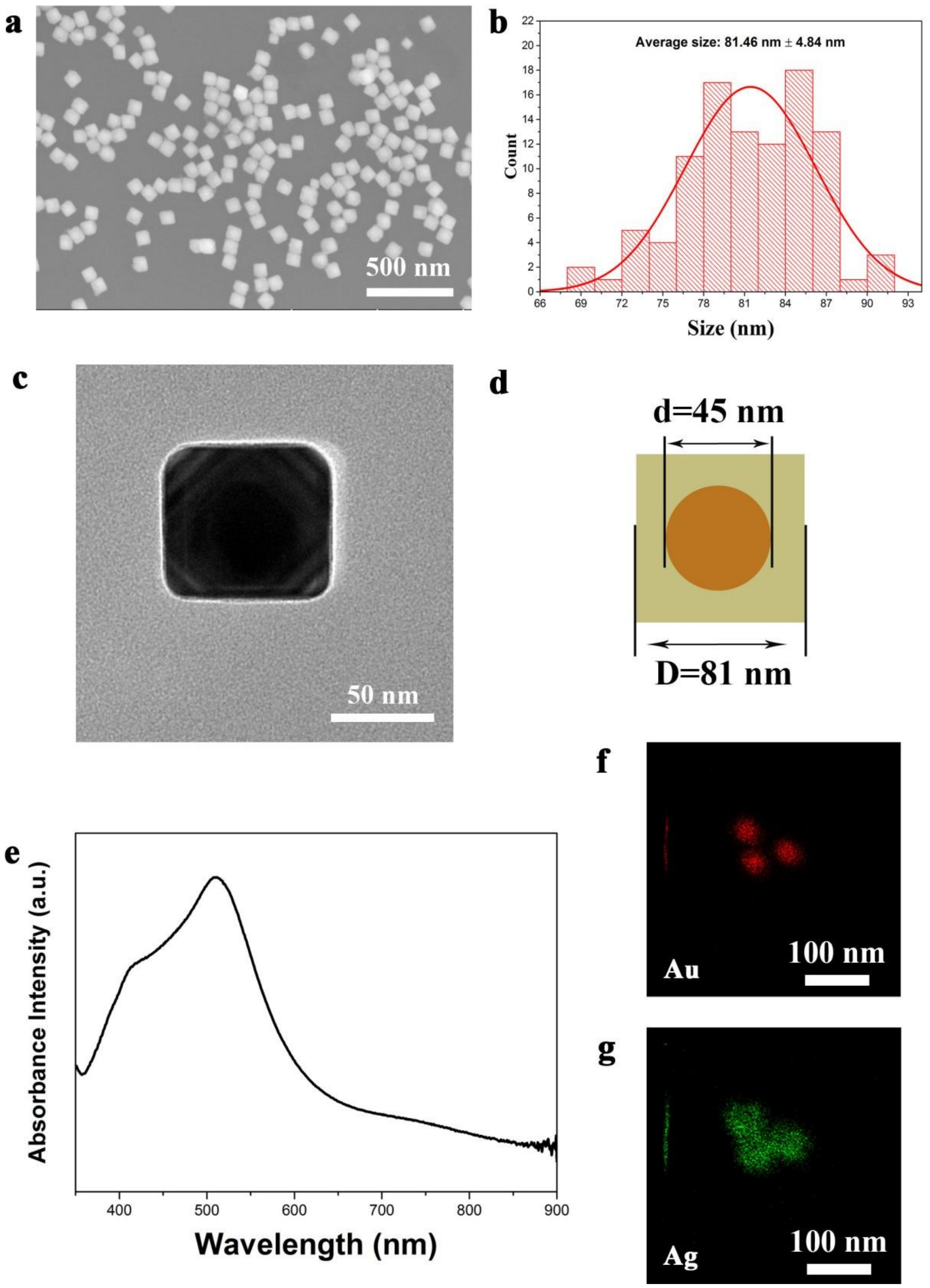

Fig. S15 (a) The SEM image of the Au/Ag core-shell nanocubes. (b) The histogram of particle size statistics of the Au/Ag core-shell nanocubes. (c) The TEM image of the Au/Ag core-shell nanocubes. (d) The model of the Au/Ag core-shell nanocubes. (e) The absorbance spectrum of the Au/Ag core-shell nanocubes. (f-g) EDS elemental mapping of Au and Ag, respectively.

Calculation of the mass and volume of the Au/Ag core-shell nanocubes

$$V_{cube} = D^3$$

$$V_{cube} = 531441 \text{ nm}^3$$

$$V_{sphere} = \frac{4}{3} \times \pi \times \left(\frac{d}{2}\right)^3$$

$$V_{sphere} = 47688 \text{ nm}^3$$

$$M_{cube} = M_{Au} + M_{Ag}$$

$$M_{cube} = \rho_{Au} V_{sphere} + \rho_{Ag} (V_{cube} - V_{sphere})$$

$$M_{cube} = 60 \times 10^{-16} \text{ g}$$

Here, V_{cube} is the volume of the Au/Ag core-shell nanocubes, V_{sphere} is the volume of the gold core nanosphere. M_{gold} is the mass of the gold. M_{Ag} is the mass of the Ag. M_{cube} is the mass of the Au/Ag core-shell nanocubes. ρ_{Au} is the density of the Au (1.932×10^4 kg/m^3). ρ_{Ag} is the density of the Ag (1.05×10^4 kg/m^3).

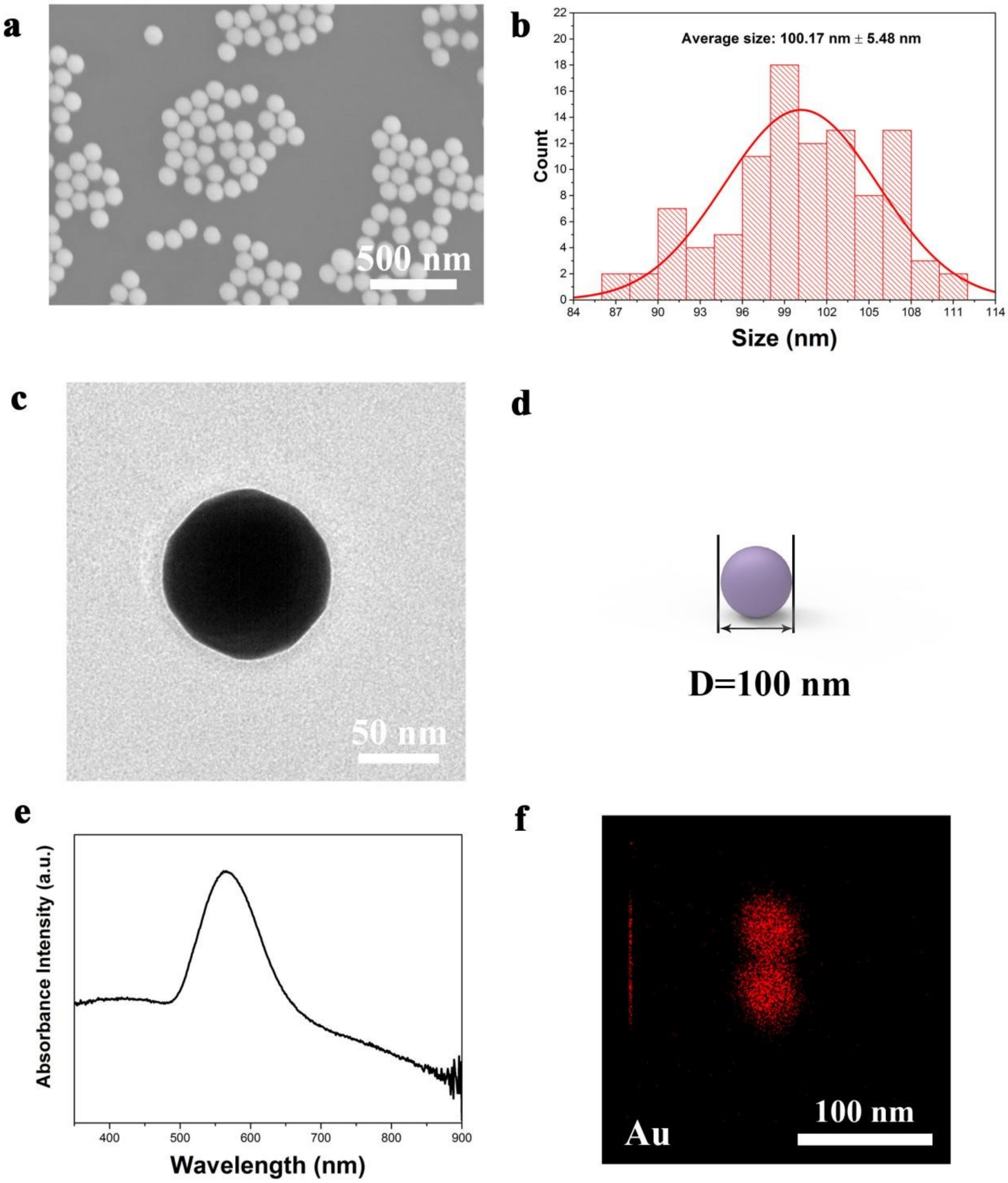

Fig. S16 (a) The SEM image of the medium gold nanospheres. (b) The histogram of particle size statistics of the medium gold nanospheres. (c) The TEM image of the medium gold nanosphere. (d) The model of the medium gold nanosphere. (e) The absorbance spectrum of the medium gold nanospheres. (f) EDS elemental mapping of gold.

Calculation of the mass and volume of the medium gold nanospheres

$$V = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3$$
$$M = \rho V$$

Here, M is the mass, ρ is the density of gold nanosphere (1.932×10^4kg/m^3), D is the diameter of the nanosphere. V is the volume of the gold nanosphere.

$$V = 523333\ \mathrm{nm}^3$$

$$M = 101.1\times10^{-16}\ \mathrm{g}$$

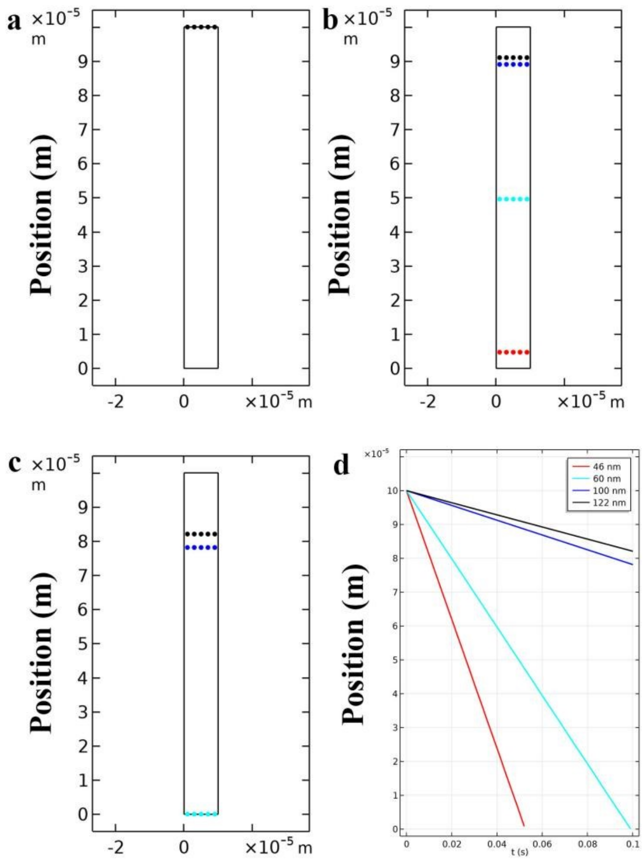

Fig. S17 The simulation screenshots of the position of the gold nanospheres with different diameter (46 nm, 60 nm, 100 nm and 122 nm) at (a) 0 s, (b) 36000 s and (c) 72000 s. (d) The position of the gold nanospheres as a function of time.

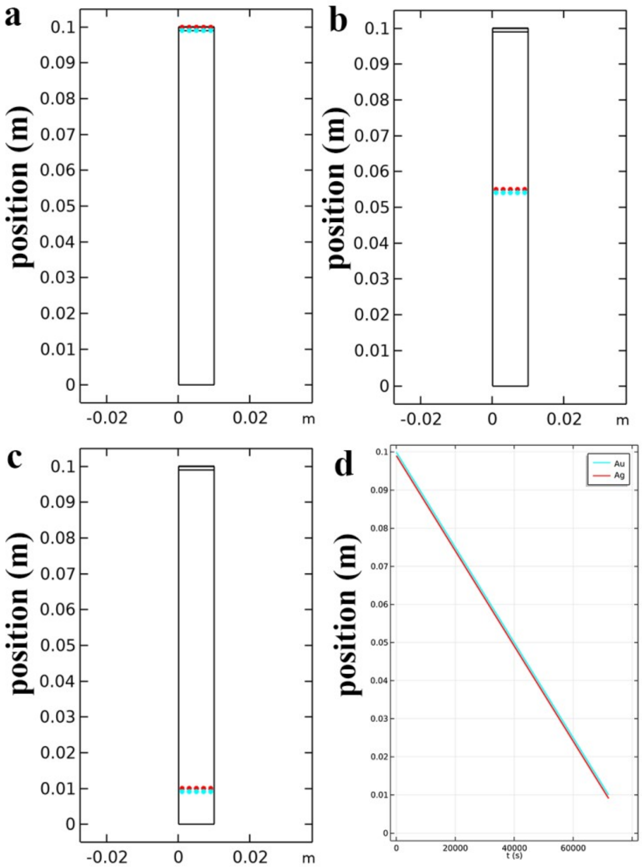

Fig. S18 The simulation screenshots of the position of the gold nanospheres and the Au/Ag core-shell nanocubes at (a) 0 s, (b) 36000 s and (c) 72000 s (no collision). (d) The position of the gold nanospheres and the Au/Ag core-shell nanocubes as a function of time (no collision).

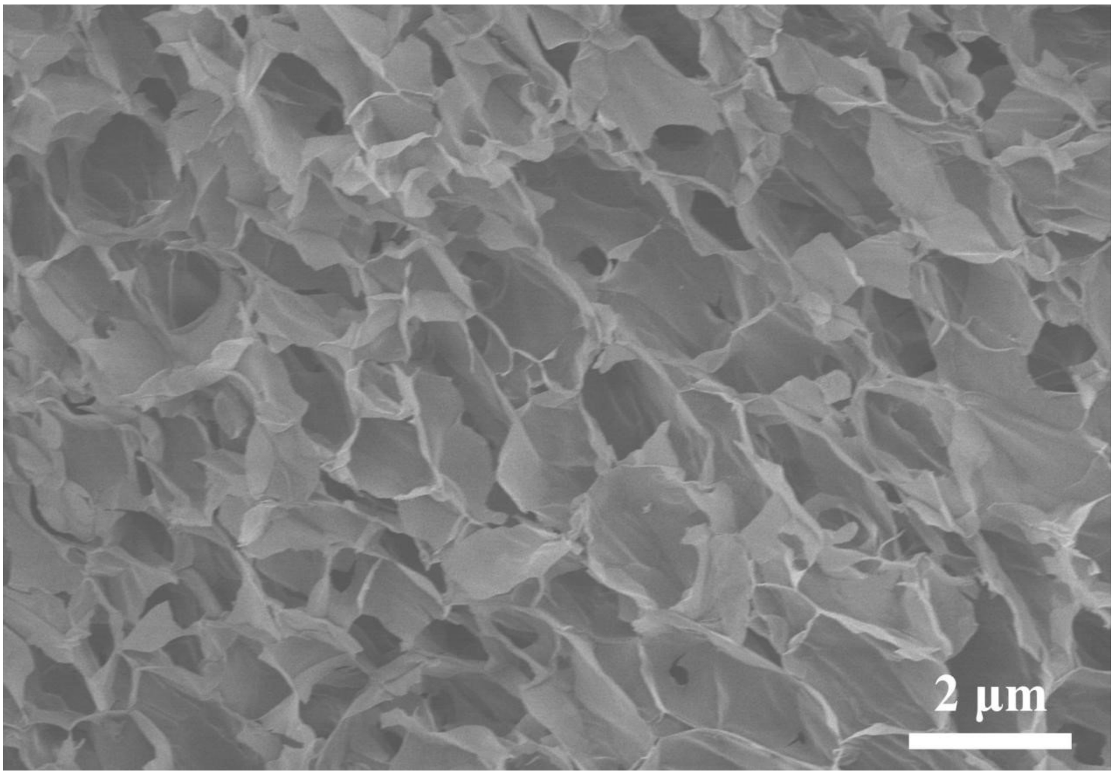

Fig. S19 SEM image of gel networks obtained by the freeze drying technique.

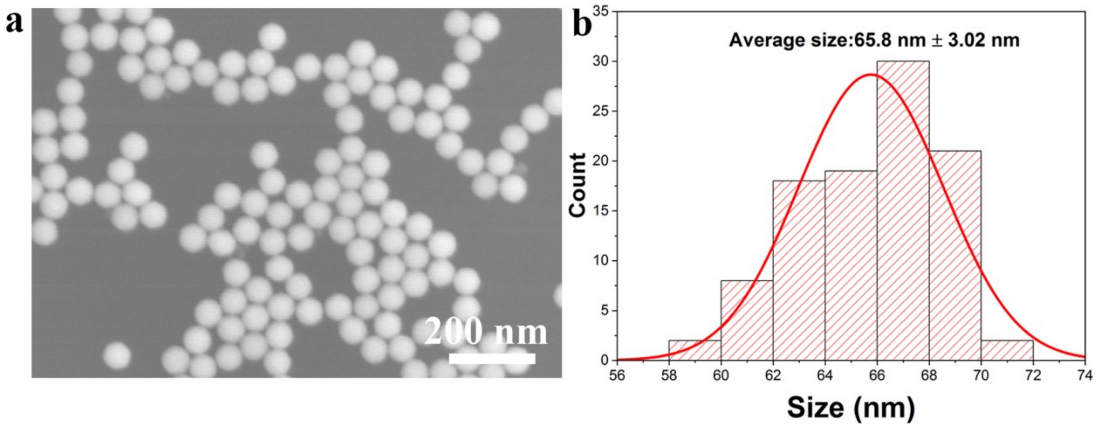

Fig. S20 (a) The SEM image of the gold nanospheres. (b) The histogram of particle size statistics of the gold nanospheres.

Calculation of the mass of the gold nanospheres

$$V = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3$$
$$M = \rho V$$

Here, M is the mass, ρ is the density of gold nanosphere (1.932×10^4 kg/m^3), D is the diameter of the nanosphere. V is the volume of the gold nanosphere.

$$V = 150456\,\mathrm{nm}^3$$

$$M = 29\times10^{-16}\,\mathrm{g}$$

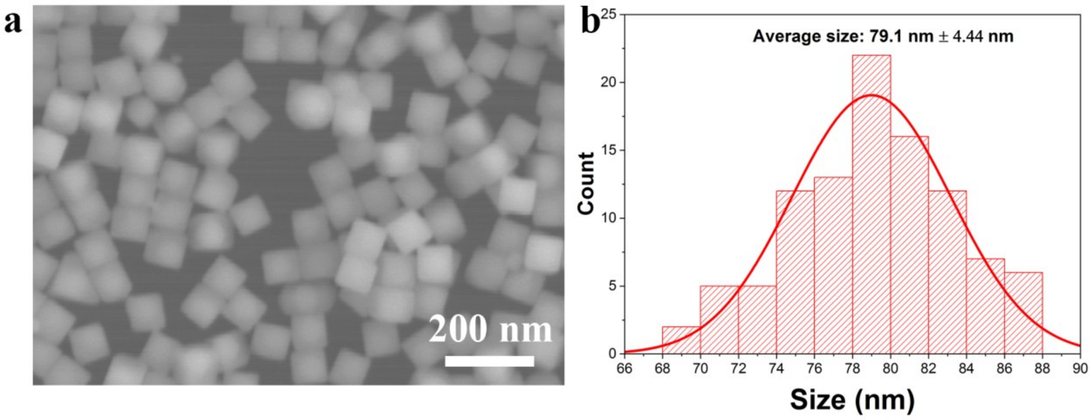

Fig. S21 (a) The SEM image of the Au/Ag core-shell nanocubes. (b) The histogram of particle size statistics of the Au/Ag core-shell nanocubes.

Calculation of the mass of the Au/Ag core-shell nanocube

$$V_{cube} = D^3$$

$$V_{cube} = 512000 \ \text{nm}^3$$

Since the Au/Ag core-shell nanocubes were grown from gold nanospheres (Figure S18) as seeds, therefore:

$$V_{sphere} = 150456 \ \text{nm}^3$$

$$M_{cube} = M_{Au} + M_{Ag}$$

$$M_{cube} = \rho_{Au} V_{sphere} + \rho_{Ag} \left(V_{cube} - V_{sphere} \right)$$

$$M_{cube} = 67 \times 10^{-16} \ \text{g}$$

Here, V_{cube} is the volume of the Au/Ag core-shell nanocube, V_{sphere} is the volume of the gold core nanosphere. M_{gold} is the mass of the gold. M_{Ag} is the mass of the Ag. M_{cube} is the mass of the Au/Ag core-shell nanocube. ρ_{Au} is the the density of the gold (1.932×10^4 kg/m^3). ρ_{Ag} is the the density of the Ag (1.05×10^4 kg/m^3).

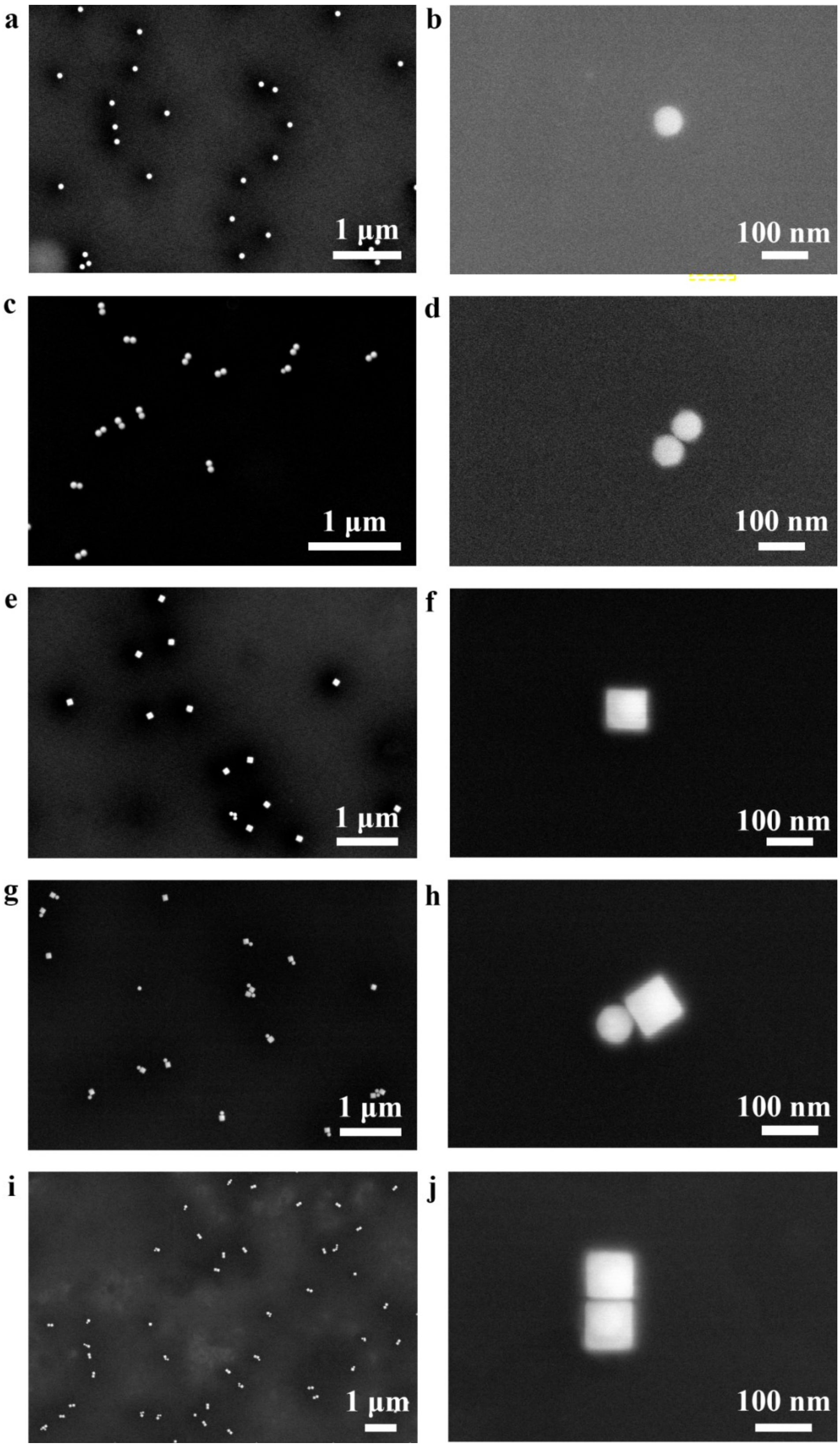

Fig. S22 (a-j) Low- and high- magnification SEM images of products recovered from the bands I-V.

Reference

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3 T. Zhang, X. Li, Y. Sun, D. Liu, C. Li, W. Cai and Y. Li, *Chem. Sci.*, 2021, **12**, 12631-12639.
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