- Electronic Supplementary Information –

Liquid-on-Solid Heterogeneous Nucleation for a General Synthesis of Yolk-Shell Nanostructures

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Materials and Methods

Materials：

Tetraethyl orthosilicate (TEOS), hydroxypropyl cellulose (HPC, Average Mn ~10,000), polyvinylpyrrolidone (PVP, Average Mw 55,000), glucose (D-(+)-glucose, GC), Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), L-Glutathione (L-GSH, ≥98%), hexadecyltrimethylammonium bromide (CTAB, ≥ 99.0%), L-ascorbic acid (AA, ≥ 99.0%), silver(I) nitrate ($AgNO_3$, ≥99.0%), sodium borohydride ($NaBH_4$, ≥98.0%), Diethylenetriamine (99.0%), Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ≥99%), 1-Propanethiol (1-PAT, 98%) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, ≥98.0%) was purchased from J&K, Potassium iodide (KI, ≥99.0%) was purchased from Macklin, Sodium citrate (dihydrate, ≥99.0%) was purchased from Leyan Reagent, ethanol (anhydrous, AR) was purchased from Sinopharm Chemical Reagent. 4-Ethynyl-benzoic acid methyl ester (4-EBA, 97%), Mercaptoacetic acid (MAA, 90.0%), 11-Mercaptoundecanicacid (MUA, 98.0%), 16-Mercaptohexadecanoicacid (MHA, 95.0%), 3-Mercaptobenzoic acid (3-MBA, 95.0%), 3-Mercaptopropionic acid (3-MPA, 99.0%) were purchased from Aladdin. Dimercaptosuccinic acid (DMSA, 98.0%), 2-Mercaptonicotinic acid (2-MNA, 98.0%), 6-Mercaptonicotinic acid (6-MNA, 97.0%) were purchased from Energy Chemical. 4-Mercaptobenzoic acid (4-MBA, 99.0%) was purchased from TCI. 2-Mercapto-5-benzimidazolecarboxylic acid (MBIA, 97.0%) was purchased from Alfa Aesar. 2,2'-Dithiodibenzoic acid (DTSA, 95.0%) was purchased from Bidepharm. All chemical reagents were purchased and used without further purification.

Methods：

Typical synthesis of Au@Syrup@Silic yolk shell nanostructures

Preparation of 40 nm gold nanoparticles (AuNPs): 0.25 mL $HAuCl_4$ solution (10 mg. mL^{-1}) was added to 25 mL H_2O in a 500 mL round bottle flask equipped with a condenser. The mixture was

refluxed for 30 min in an oil bath, followed by the addition of 0.375 mL sodium citrate solution (1 wt%). The color of the reaction solution changed quickly from light yellow to dark gray and black, then to purple. About 10 min later, the solution changed to red. Monodispersed AuNPs in 40 nm diameter formed at this point.

Preparation of the syrup with AuNPs as the phase separation initiator: The 1mL (0.5mL or 1.5mL) AuNP solution was centrifuged, and the supernatant was removed. Then the glucose aqueous solution was added to make a mixed aqueous solution of 0.5M (2M, 1M, 0.25M) glucose and nanoparticles. The sample was allowed to stand for 6 h, and then centrifuged, water-washed, and dispersed into ethanol.

Preparation of Au@Syrup@Silica: 250 μL of 4% HPC (w/w) ethanol solution was diluted by 750 μL of ethanol, then 1.25 μL of 1 M sodium hydroxide aqueous solution was added into the mixture. Under vortex, the above syrup initiator (0.25M or 1M or 2M, 62.5 μL) with AuNPs was introduced. 30 s later, 6 μL of TEOS was added under vortex. The mixture was allowed to stand for 6 h, and then centrifuged, water-washed, and dispersed into ethanol.

Capturing of early-stage droplets by adding TEOS at the very beginning

250 μL of 4% HPC ethanol solution was diluted by 750 μL of ethanol, then 1.25 μL of 1 M sodium hydroxide aqueous solution was added into the mixture. Then 6 μL of TEOS was added under vortex. 2 minutes later, under vortex, the syrup initiator (0.5M, 62.5 μL) was introduced. The sample was allowed to stand for 6 h, and then centrifuged, water-washed, and dispersed into ethanol.

Confirmation of liquid-on-solid HON by decoupling the formation of droplet and the addition of seeds

Preparation of ethanol dispersion of AuNPs: 1ml AuNP solution was centrifuged and the supernatant was removed. Then 50 μL of ethanol was added to disperse it.

Experiment when the formation of droplet and the addition of seeds were decoupled: 250 μL of 4% HPC ethanol solution was diluted by 700 μL of ethanol, then 1.25 μL of 1 M sodium hydroxide aqueous solution was added into the mixture. Under vortex, the syrup initiator (0.5M, 62,5 μL) WITHOUT AuNP was introduced, then the ethanol dispersion of AuNPs was added to the mixture after 10 seconds. Finally, 6 μL of TEOS was added under vortex. The mixture was allowed to stand

for 6 h, and then centrifuged, water-washed, and dispersed into ethanol.

Interchangeability test of AuNPs dispersed in ethanol: 250 μL of 4% HPC ethanol solution was diluted by 750 μL of ethanol, then 1.25 μL of 1 M sodium hydroxide aqueous solution was added into the mixture. 1 ml AuNP solution was centrifuged, and the supernatant was removed. Then it was dispersed by the above ethanol solution. Under vortex, (0.5M, 62.5 μL) glucose solution was introduced. Then in 30 seconds, 6 μL of TEOS was added under vortex. The mixture was allowed to stand for 6 h, and then centrifuged, water-washed, and dispersed into ethanol (Figure S1e, f).

Ligand exchange of nanostructures

10μL of 5 mM ethanol solution of a specific ligand (Figure S3) was added to 1mL specific nanostructures (AuNPs, silver nanostructure amalgam, silver nanowires, gold nano-badges, *vide infra*) solution under vigorous vortex. The resulting mixture was incubated at 60 °C for 2 h. Then centrifuge and ready to be dispersed in syrup initiators.

Preparation of 80 nm AuNPs: The experiment was carried out following the preparation of 40nm AuNPs described above. After reflux for another 15 min, 25 mL boiled water was added into the red AuNPs solution, followed by the dropwise addition of 50 mL 6.6 mg mL-1 NaOH solution and then quick addition of 0.25 mL sodium citrate solution (1 wt%) and 0.25 mL $HAuCl_4$ solution (10 mg. mL-1). The mixture was heated for 20 min to completely reduce the $HAuCl_4$ and form Au layer on the seed NP surface. In the third cycle, 50 mL H_2O, 0.1 mL NaOH, 0.5 mL sodium citrate and 0.5 mL $HAuCl_4$ were added in sequence via the same way. The above cycle was repeated for three times, after which the AuNPs in 80 nm diameter were obtained.

Preparation of silver nanostructure amalgam: In this procedure, Ag NPs were synthesized by a classic method in a 100 mL quantity. 1.7 mL of 1% $AgNO_3$ aqueous solution was added to a 100 mL of water in a three-necked round bottom flask equipped with a reflux condenser and the mixture was brought to boiling by a heating mantle for 15 min. Next, 2 mL of 1% citrate solution was added to the reaction solution. The reaction solution was kept reflux with vigorously mechanical stirring for 1 h and cooled to room temperature.

Preparation of PVP-stabilized silver nanowires (Ag NWs): 0.300 g of PVP and 0.200 g of $AgNO_3$ were dissolved in 50 mL of ethylene glycol. A small amount of $FeCl_3{\cdot}6H_2O$ (0.100 mg, 12.5 μM) was added, and the mixture was stirred at room temperature until it was fully dissolved. Then,

the solution was transferred to an oil bath and reacted at 130 °C and 800 rpm for 8 h.

The as-synthesized Ag NWs were cleaned twice with acetone: First, 5 mL of acetone was added to 1 mL of the as-synthesized Ag NW solution, and the mixture was shaken up and down, let stand, and removed of the supernatant. Then, 3 mL of acetone was added to the Ag NWs again, and the mixture was shaken up and down, let stand, and removed of the supernatant. Finally, the obtained Ag NWs were dispersed in ethanol and used as a stock solution.

Preparation of PVP-stabilized AuNPs: In a typical synthesis, Au seeds with an average diameter of ~3 nm were prepared by a direct reduction method using sodium borohydride as the reducing agent and trisodium citrate dihydrate (TSC) as the capping agent. More specifically, 1 mL of $HAuCl_4$ (5 mM) and 1 mL of TSC (5 mM) were mixed with 18 mL of H_2O in a flask. Under vigorous stirring, 0.6 mL of freshly made $NaBH_4$ solution (0.1 M) was quickly injected into the solution, leading to an immediate color change to yellowish red. After stirring for 4 h, the solution was collected as the seed solution for subsequent seeded growth. Again under vigorous stirring, a predetermined amount of the seed solution (1–1600 μL) was then quickly injected into a freshly prepared growth solution of Au containing 500 μL of PVP (5 wt%), 250 μL of L-ascorbic acid (0.1 M), 200 μL of KI (0.2 M), 60 μL of $HAuCl_4$ (0.25 M), and 2 mL of H_2O. After 10 min， the AuNPs formed were collected by centrifugation and redispersed in water. The size of the AuNPs can be facilely tuned by injecting different amounts of the seed solution in a defined typical synthesis.

Preparation of CTAB-stabilized AuNPs: The small Au NPs were obtained by a seed-mediated growth method. Briefly, a $HAuCl_4$ solution (0.01 M, 0.25 mL) was first mixed with a CTAB solution (0.1 M, 9.75 mL), followed by the rapid injection of a freshly-prepared, ice-cold $NaBH_4$ solution (0.01 M, 0.60 mL) under vigorous stirring. The resultant solution was kept under gentle stirring for 3 h at room temperature. 0.12 mL of the as-prepared seed solution was injected into a growth solution made of CTAB (0.1 M, 9.75 mL), water (190 mL), $HAuCl_4$ (0.01 M, 4 mL), and ascorbic acid (0.1 M, 15 mL). The reaction mixture was gently shaken and then left undisturbed overnight at room temperature. The resultant Au NPs sample was washed and concentrated by four times into water by centrifugation and redispersion for further use.

Preparation of chiral gold nano-badges

Preparation of triangular gold nanoplates were synthesized following literature (Nanoscale, 2014,6, 6496-6500). The as synthesized triangular gold nanoplates with a side length of 150 nm was used without any further treatment.

Preparation of chiral gold nano-badges: CTAB (0.8 mL, 100 mM), $HAuCl_4$ (10 mM, 0.2 mL) and H_2O (3.95 mL) were placed into a 20 ml vial. Then 0.1 M, 0.475mL AA were added to the above solution quickly. After shaking the vial to mix the reactant, color of the mixture changes quickly from yellow to colorless. Then 40 µL GSH solution (1.5 mg GSH powder dispersed in 10 mL water) and 100 µL triangular gold nanoplates were added to the above solution for the second time growth. The growth was maintained at 30 °C for 1 h.

Characterization:

TEM images were collected by using Transmission Electron Microscopy operated at 100 kV (HITACHI HT7800). SEM images were collected on Gemini 450 Analytical Field Emission Scanning Electron Microscope operated under 5 kV (Gemini 450). Raman and SERS spectra were collected from the as-synthesized sample solutions in a quartz cuvette (pathlength = 1.00 cm) on a portable Raman analyzer (Accuman SR-510 Pro) equipped with 785 nm red LED laser. Dynamic light scattering (DLS) data were collected from the BI-200SM/Nano-Brook Zeta-PALS/BI-DNDC machine.

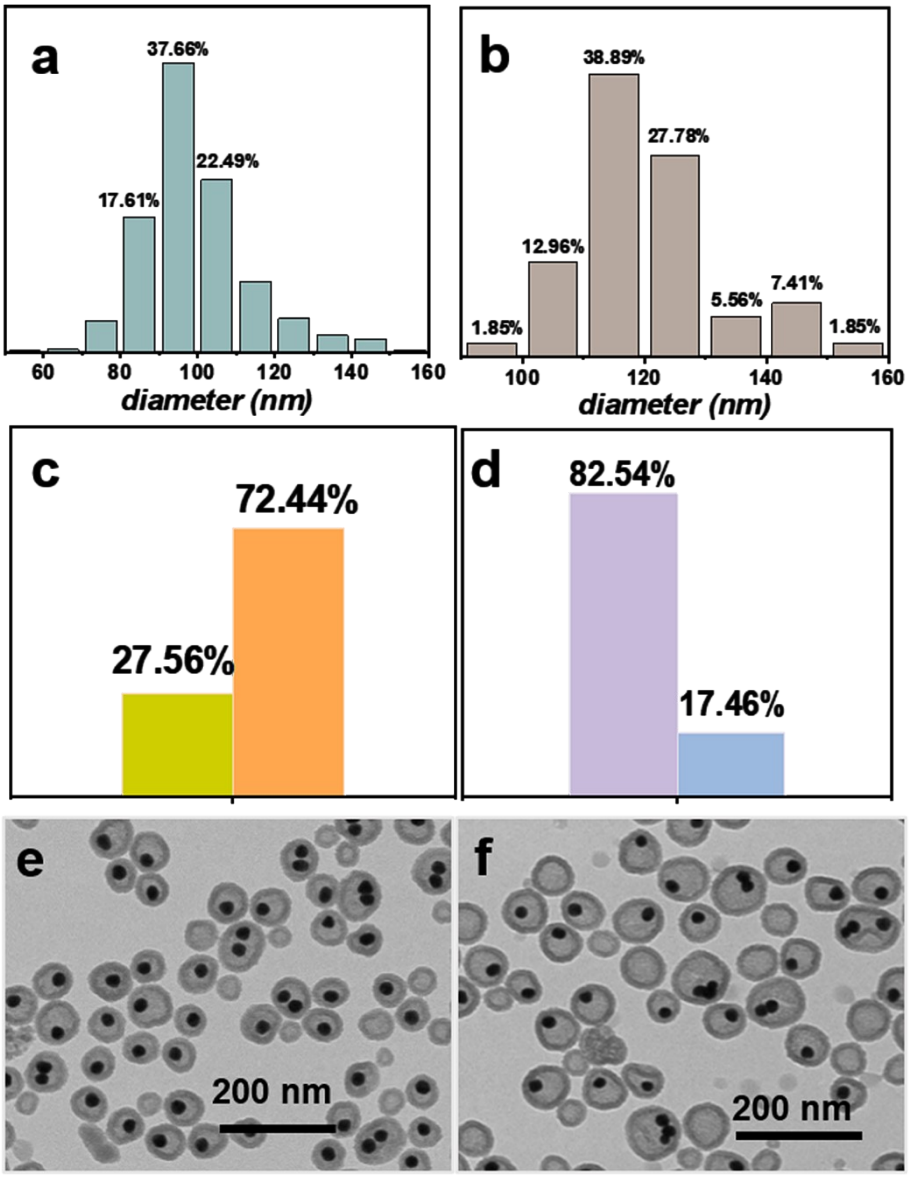

Figure S1 (a) The particle size distribution of Au@Syrup@Silica; (b) The particle size distribution of Au_N@Syrup@Silica; (c) The percentage of empty nanoshells (yellow) and Au@Syrup@Silica (orange); (d) The proportion of Au_2@Syrup@Silica (purple) and Au_N@Syrup@Silica (N > 2) (blue); (e) TEM image of the sample obtained by introducing AuNPs from the ethanol phase; (f) TEM image of the sample obtained by introducing AuNPs from the aqueous phase.

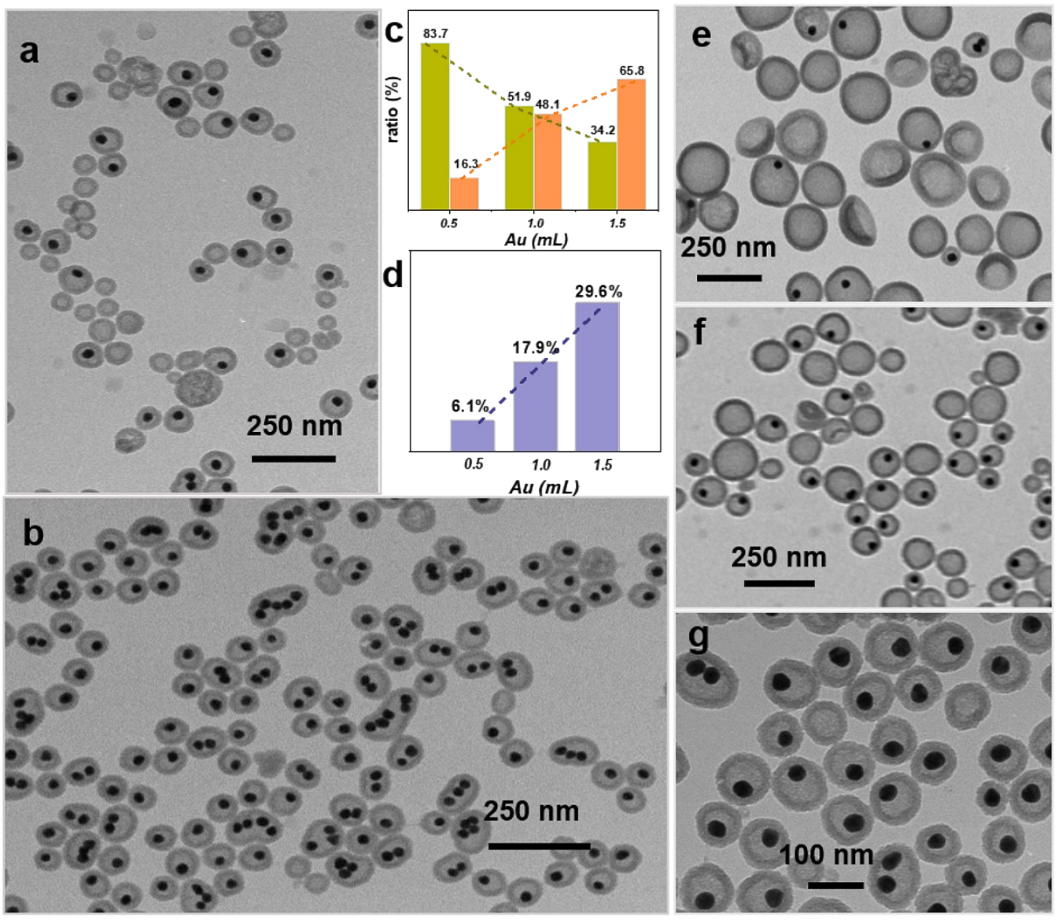

Figure S2 (a, b) TEM images of introducing different amounts of AuNPs: a-0.5ml; b-1.5ml. (c) Percentage statistics of empty nanoshells (yellow) and Au@Syrup@Silica (orange) in the non-purified samples as the amount of gold seeds increases. (d) Percentage statistics of Au_N@Syrup@Silica structures as the amount of gold seeds increases. (e-g) TEM images of the samples obtained by changing the glucose concentration: e-2M, f-1M, g-0.5M.

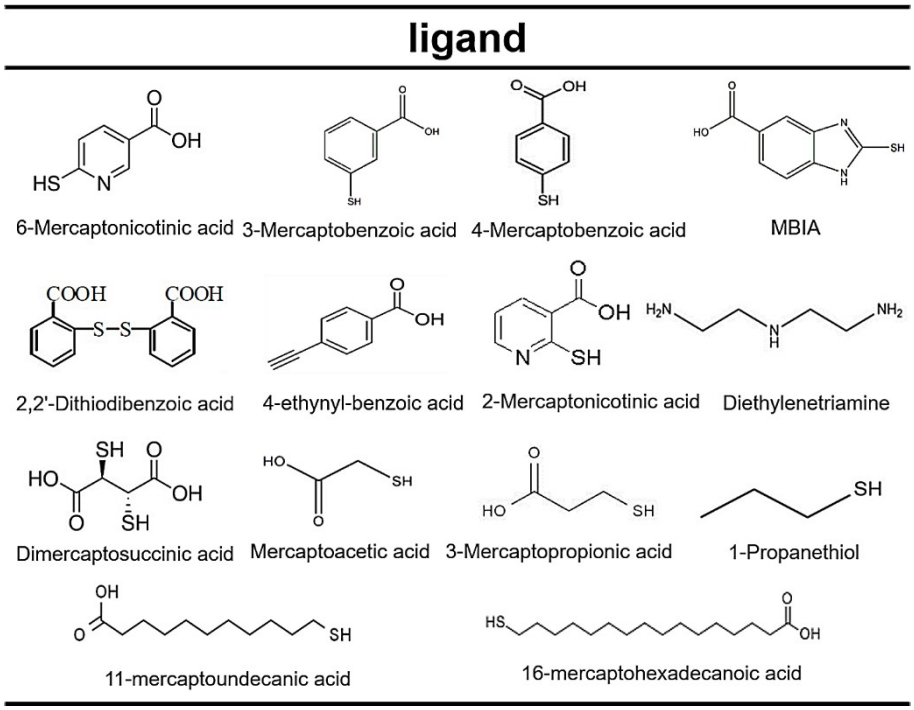

Figure S3 Ligand molecules with different hydrophilicities tested.

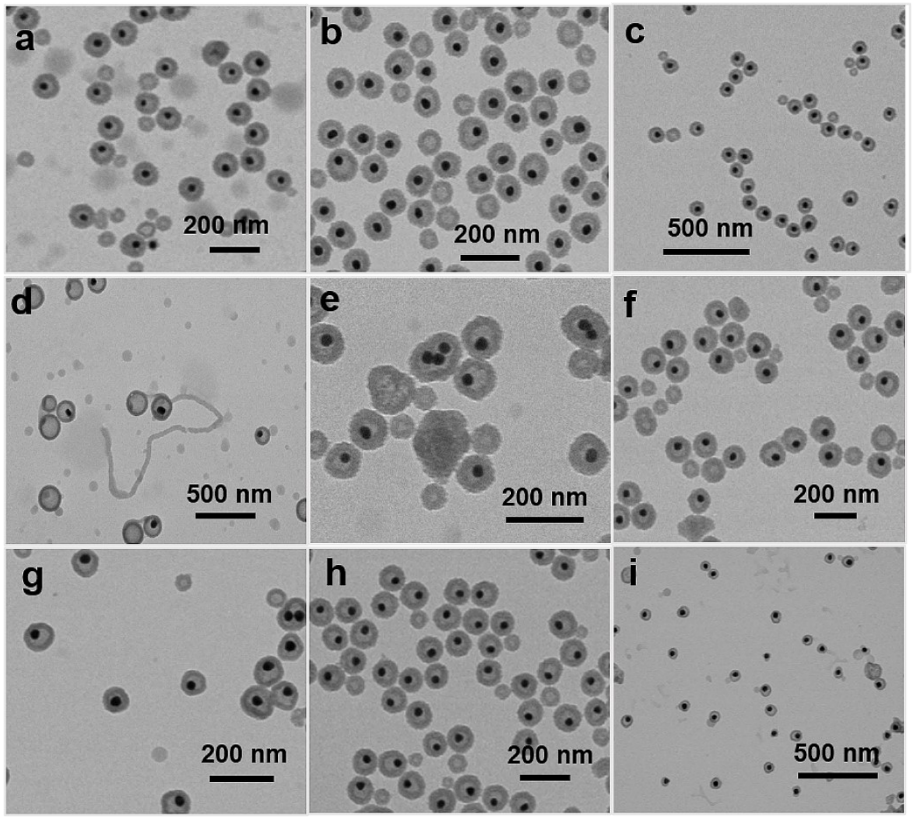

Figure S4 The yolk-shell structure of Au NPs characterized by TEM: (a) 3-MBA; (b) DMSA; (c) MAA; (d) MBIA; (e) 4-MBA; (f) 1-PAT; (g) 11-MUA; (h) 2-MNA; (i) Sodium citrate.

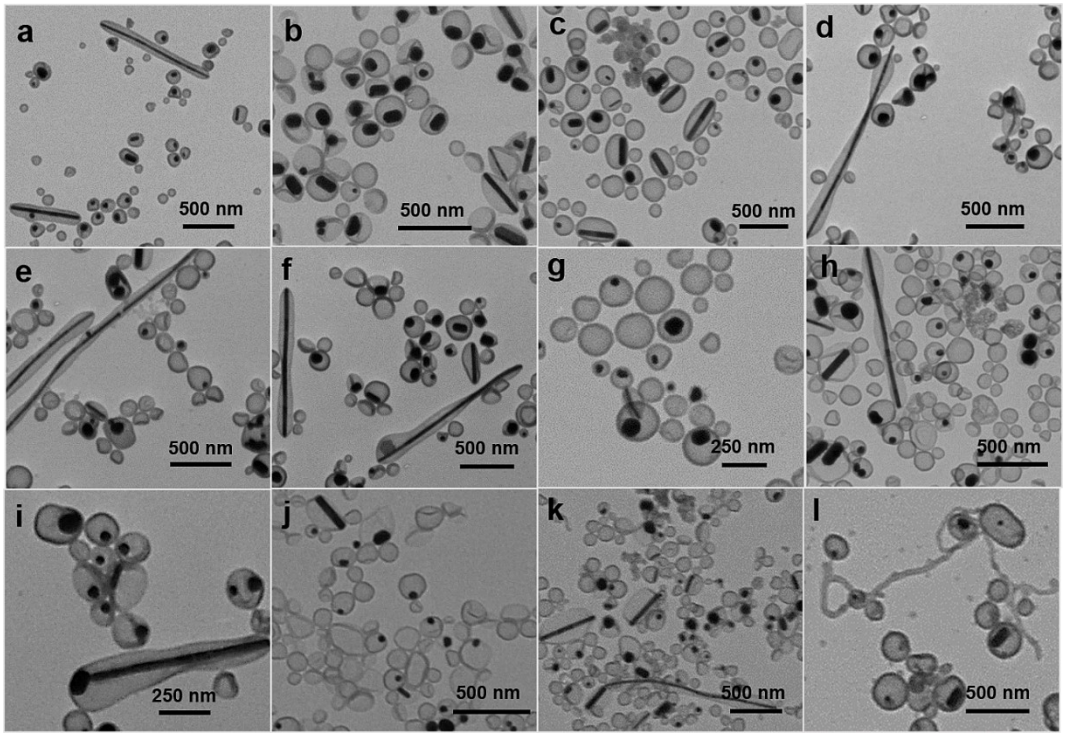

Figure S5 The yolk-shell structure of silver nanostructure mixture characterized by TEM: (a) Sodium citrate; (b) Diethylenetriamine; (c) 16-MHA; (d) 3-MBA; (e) 4-MBA; (f) 3-MPA; (g) 11-MUA; (h) DMSA; (i) 1-PAT; (j) 4-EBA; (k) 2-MNA; (l) MBIA.

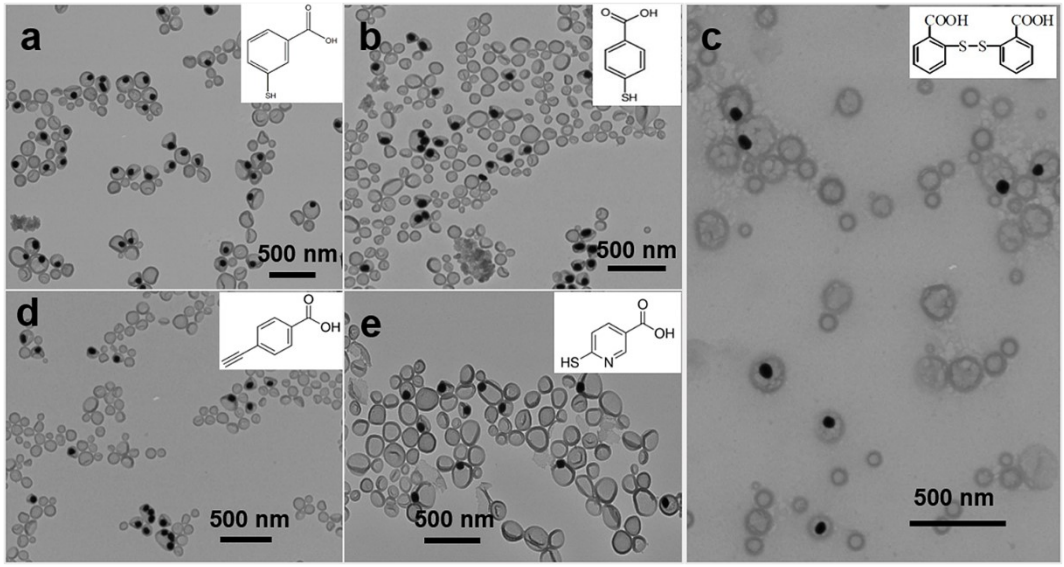

Figure S6 The yolk-shell nanostructure of AuNPs obtained by incubating ligand molecules with SERS signals: (a) 3-MBA; (b) 4-MBA; (c) DTSA; (d) 4-EBA; (e) 6-MNA.

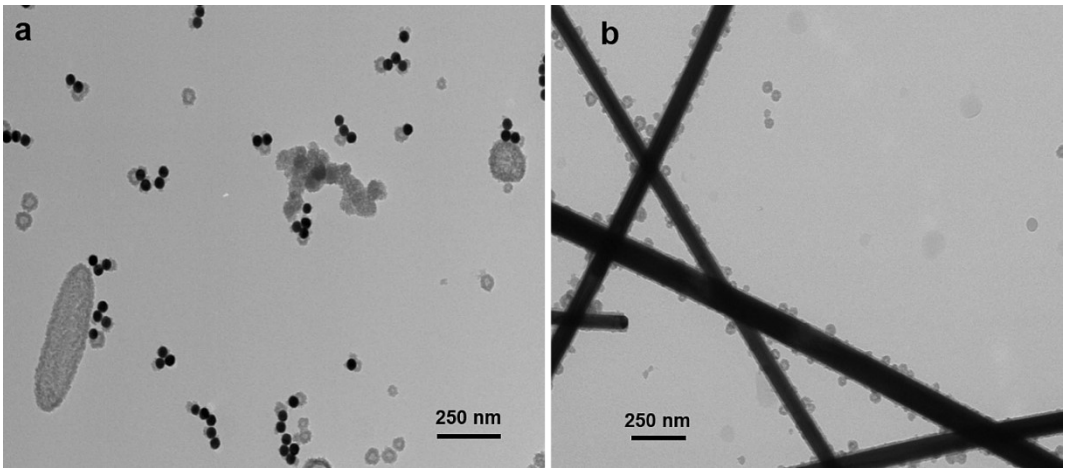

Figure S7 (a) AuNPs stabilized with CTAB and (b) Ag NWs stabilized with PVP coated directly without replacement of ligands.

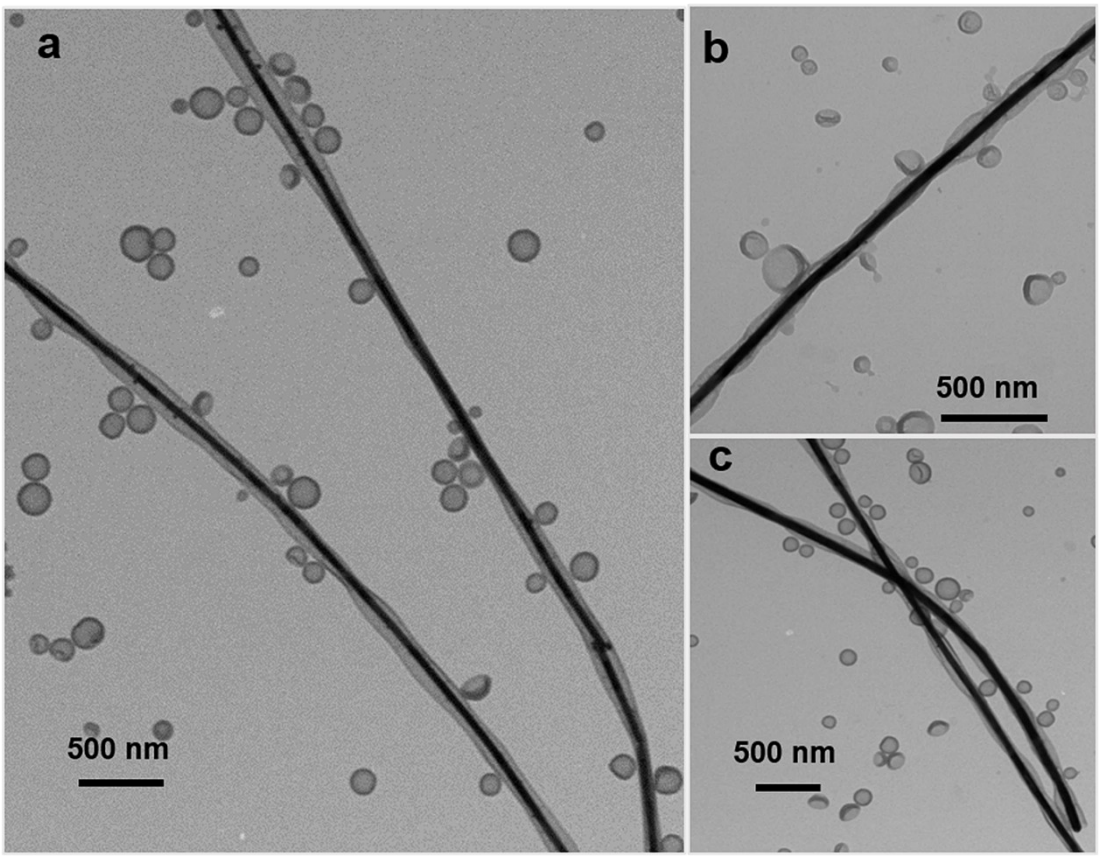

Figure S8 Yoke-shell nanostructures of Ag NWs with exchanged ligands: (a) DMSA; (b) MAA; (c) 1-PAT.

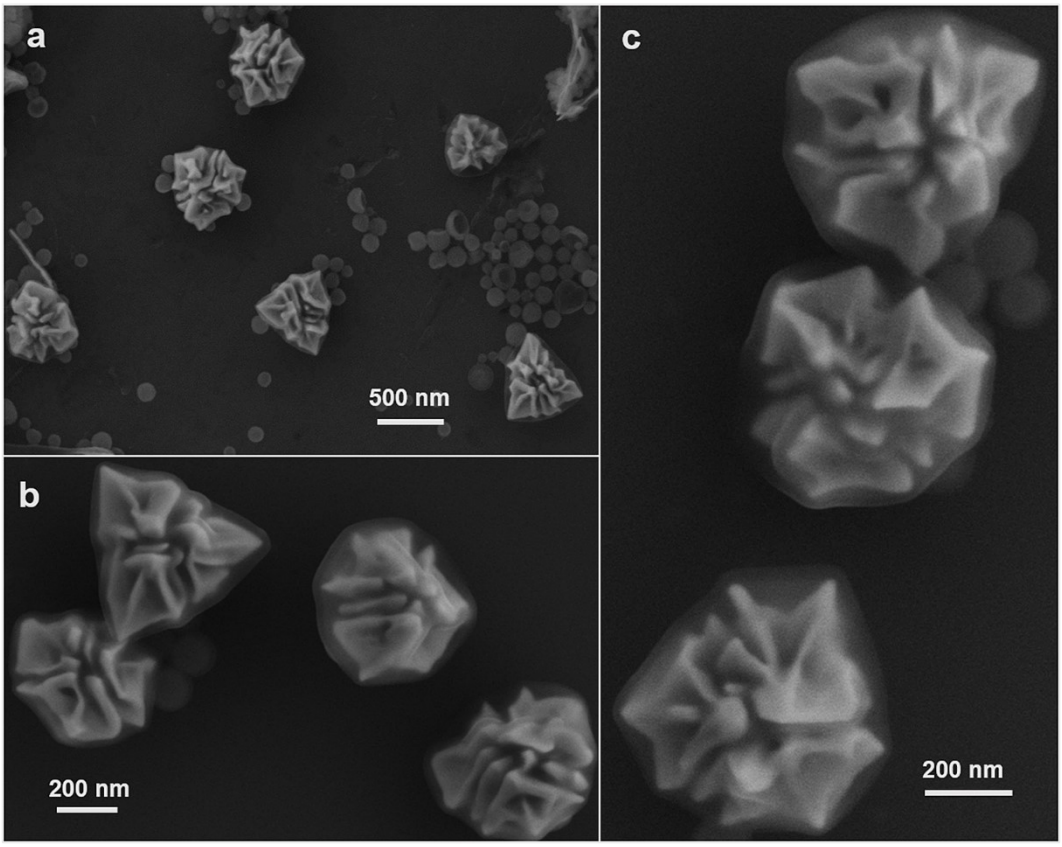

Figure S9 Yoke-shell nanostructures of chiral gold nano-badges with exchanged ligands: (a) DMSA; (b) MAA; (c) 1-PAT.

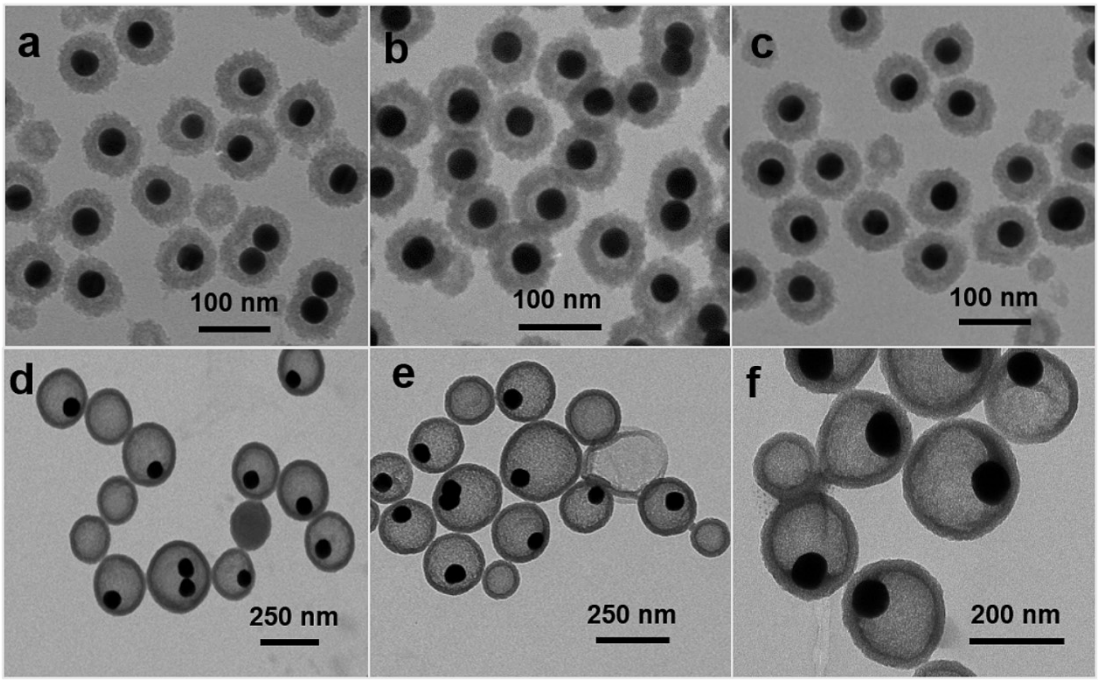

Figure S10 Au@Syrup@Silica through the exchange of ligands with (a-c) CTAB-stabilized AuNPs and (d-e) PVP-stabilized Ag NWs.: a, d. DMSA; b, e. MAA; c, f. 1-PAT.