Supporting Information

Single-Step Coating of Mesoporous SiO_2 onto Nanoparticles: Growth of Yolk-Shell Structures from Core-Shell Structures

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Contents of the Supporting Information

1. Chemicals

Chemicals used were: Hydrogen tetrachloroaurate hydrate ($HAuCl_4$, 99.9%, Sigma), Sodium borohydride ($NaBH_4$, 96%, Sigma), Silver nitrate ($AgNO_3$, ≥99.9%, Sigma), Sodium tetrachchloropalladium (II) (Na_2PdCl_4, 99.95%, Sigma), Potassium tetrachchloroplainate (II) (K_2PtCl_4, 99.95%, Sigma), L-ascorbic acid (AA, 99.98%, Sigma), Salicylic acid (SA, 99.9%, Sigma), Cetyltrimethyl-ammonium chloride (CTAC, ≥99%, Sigma), CTAC solution (25wt% in water, Sigma-Aldrich), Cetyltrimethyl-ammonium bromide (CTAB, ≥99%, Sigma), Tetraethyl orthosilicate (TEOS, Sigma), Sodium hydroxide (NaOH, 98%, Aldrich), Methoxypolyethylene glycol thiol (PEG-SH, Sigma, 99%) Polyvinyl Pyrrolidone (PVP, 10000, 99%, Aldrich) Methanol (100%, Aldrich), Ethanol (100%, Aldrich). All chemicals were used as received without further purification. Also de-ionized water with a resistivity of 18.2 MΩ·cm at 25 °C was used in the experiments.

2. Synthesis

2.1 Synthesis and purification of Au NTs

The Au NTs were prepared by a modification of a previously reported synthesis.[1] (1) Au seeds@CTAC: 25 µL of 50 mM $HAuCl_4$ were mixed with 4.70 mL of 0.10 M CTAC solution in a 20 mL glass vial. Next, 300 uL of fresh prepared 10 mM $NaBH_4$ was injected into the above mixture while stirring. The seeds solution was strongly stirred for 2 min. Thereafter, it was kept at room temperature for at least 2 hours. Next, the Au seeds solution was diluted 10 times by mixing 0.50 mL of Au seeds and 4.50 mL of 0.10 M CTAC. (2) 1.60 mL of 0.10 M CTAC, 40 µL of 50 mM, and 30 µL of 10 mM KI were added into 8.00 mL of de-ionized water in a 20 mL glass vial one by one. This solution was marked as solution-A. (3) 60 mL of deionized water was added into a 250 mL round-bottom flask. 60 mL of 0.10 M CTAC and 900 µL of 10 mM KI were injected into the deionized water. This solution was marked as solution-B. (4) 40 uL and 1.20 mL of 0.10 M AA solution were injected into solution-A and solution-B, respectively, while stirring. When both the solution-A and solution-B had turned colorless, 100 µL of diluted Au seeds was injected into solution-A. Stirring continued for about one minute. All solution-B was added into solution-B while stirring. After the two solutions were well mixed, it was left undisturbed for about 2 hours, which allowed growth of the Au nanocrystals. (5) Purification: After allowing growth for about 2 hours, 34.0 mL of the mixed solution and 4.50 mL of 25 wt% CTAC were mixed in a 50 mL tube, and then left undisturbed for 12 hours. The excess CTAC in the form of micelles caused depletion aggregation of the Au NPs causing them to sediment to the bottom of the tube. The suspension was removed carefully, and the sediment was resuspended in 35 mL of 0.01 M CATC and served as a stock solution for further use.

2.2 Synthesis of Au nanorods

The Au NRs were synthesized via a seed-mediated growth method which is a modification of the protocols reported by Lintao Cai`s group.[2-3] (1) Au seeds@CTAB solution: 5.00 mL of 0.20 M CTAB solution was mixed with 0.25 mL of 10 mM $HAuCl_4$ and 4.75 mL of deionized water in a 20 mL glass vial. 0.600 mL of 10 mM ice-cooled $NaBH_4$ was injected into this mixture while stirring, followed by strong stirring for 2 min. After that, it was kept at room temperature for at least 2 hours before being used. (2) Growth of the Au NRs: CTAB solution (10.00 mL, 0.20 M) was added to 0.40 mL of 4 mM $AgNO_3$ with 9.6 mL of deionized water in a 40 mL glass vial. Then, 1.00 mL of 10 mM $HAuCl_4$ was added to above mixture, and 140 µL of 0.078 M AA was injected into the solution. Finally, 24 µL of Au seeds was added to the growth solution. The solution was kept under magnetic stirring at 30 ℃ for 12 hours. Au NRs were collected by centrifuging with a speed of 10,000 rpm for 10 minutes. After removing the suspension, the sediment was dissolved in 20 mL of 0.010 M CTAB solution by sonicating for about 1 minute and served as a storage solution.

2.3 Synthesis of Au nanocubes

The Au NCs were prepared using a seed-mediated method reported by Michael H. Huang`s group,[4] modified as follows. (1) Au seeds@CTAC: 0.45 mL of 10 mM ice-cold $NaBH_4$ solution was injected into 10.0 mL of aqueous solution containing 0.25 mM $HAuCl_4$ and 0.10 M CTAC with stirring. After stirring for 2 minutes, the seed solution was aged for 2 hours before being used. (2) Two 20 mL glass vials were marked as A and B. 9.625 mL of 0.10 M CTAC aqueous solution, 250 µL of 10 mM $HAuCl_4$, and 10 µL of 10 mM NaBr were mixed in the two glass vials. 90 µL of 0.04 M AA was injected into solution-A and solution-B under stirring. 25 µL of Au seeds was added to the solution-A. After stirring for about 1 minute, 50 µL of solution-A was added into solution-B. solution-B was kept undisturbed in a 30 ℃ water bath for 1 hour. The Au NCs were collected by centrifuging solution-B with 8000 rpm for 10 minutes. After removing the supernatant, the sediment was dissolved in 10 mL of 0.01 M CTAC solution by sonicating for about 1 minute and served as a storage solution.

2.4 Synthesis of Au NT@Metals (Ag, Pd, & Pt) core-shell nanoparticles

The Au NT@Metals core-shell nanoparticles (NPs) were synthesized using our previously reported synthesis.[5]

Au NT-Ag NPs: 6.30 mL of de-ionized water and 3.50 mL of Au NTs stock solution were mixed in a 20 mL glass vial, next 150 µL of 10 mM $AgNO_3$ and 100 µL of 0.10 M AA were added to the above mixture with magnetic stirring. It was left to react at room temperature for 15 hours. The product was collected by centrifugation at 8000 rpm for 10 min, and then washed by 5 mL de-ionized water once, to remove excess CTAC.

Au NT-Pd NPs: 6.30 mL of de-ionized water and 3.50 mL of Au NTs stock solution were added to a 20 mL glass vial, after which 150 µL of 10 mM Na_2PdCl_4 100 µL of 0.10 M AA were added into the above mixture with magnetic stirring. After reacting at 60 °C for 15 hours, the product was collected by centrifugation at 8000 rpm for 10 min and washed by 5 mL de-ionized water once, to remove excess CTAC.

Au NT-Pt NPs: 5.75 mL of deionized water and 3.50 mL of Au NTs stock solution were mixed in a 20 mL glass vial, then 150 µL of 10 mM K_2PtCl_4 and 1.00 mL of saturated SA were subsequently injected into the above mixture under magnetic stirring. The reaction took place at 60 °C, with a stirring speed of 400 rpm for 15 hours. The product was collected by centrifuging at 8000 rpm for 10 min and then washed by 5 mL de-ionized water once, to remove excess CTAC.

2.5 Typical protocol of synthesis of Au NT@hollow-mSiO$_2$

A volume of 10 mL of Au NTs storage solution was centrifuged at 9000 rpm for 10 minutes. After centrifuging, the suspension was removed and the sediment was suspended in 10 mL of deionized water and transferred into a 20 mL glass vial. 150 µL of 0.1 M CATC and 100 µL of 0.10 M NaOH were added into above Au NTs solution. Lastly, 200 µL of 20 vol% TEOS in methanol was injected into the above solution in one shot under stirring. The solution was stirred for 45-48 hours. More details of changing the reaction conditions synthesis and their corresponding figures are shown in Table S1.

2.6 Ligands exchange of Au NT-CTAC

The method of ligand exchange was modified from previous report.[6] A volume of 10 mL of Au NTs storage solution was centrifuged at 9000 rpm for 10 minutes. After centrifuging, the supernatant was removed and the sediment was suspended in 3 mL of 0.05 M CTAB, or 10 mg/mL PVP, or 1 mg/mL PEG-SH, sonicating for 2 minutes in 37 °C water, and then kept in water bath at 30 °C for overnight. The solution was further centrifuged at 9000 rpm for 10 minutes, the suspension was removed and the sediment was suspended in 10 mL of deionized water.

Table S1 The reaction conditions used for synthesis of Au NT@mSiO$_2$

	Au NTs Solution	**0.10 M CTAC**	**0.10 M NaOH**	**TEOS in MeOH**	**Figure**
1	10 mL	150 µL	100 µL	20 vol %, 200 µL	Figure 1
2	10 mL	150 µL	100 µL	20 vol %, 200 µL	Figure 2a
3	10 mL	150 µL	100 µL	15 vol %, 200 µL	Figure 2b
4	10 mL	150 µL	100 µL	10 vol %, 200 µL	Figure 2c

5	10 mL	150 µL	100 µL	5 vol %, 200 µL	Figure 2d
6	10 mL	10 µL	100 µL	20 vol %, 200 µL	Figure S2a
7	10 mL	50 µL	100 µL	20 vol %, 200 µL	Figure S2b
8	10 mL	150 µL	100 µL	20 vol %, 200 µL	Figure S2c
9	10 mL	200 µL	100 µL	20 vol %, 200 µL	Figure S2d
10	10 mL	300 µL	100 µL	20 vol %, 200 µL	Figure S2e
11	10 mL	500 µL	100 µL	20 vol %, 200 µL	Figure S2f
12	10 mL	150 µL	100 µL	20 vol %, 67 µL	Figure S3a
13	10 mL	150 µL	100 µL	20 vol %, 67 + 67 µL	Figure S3b
14	10 mL	150 µL	100 µL	20 vol %, 67 + 67 + 66 µL	Figure S3c
15	10 mL	150 µL	100 µL	20 vol %, 124 µL	Figure S3d
16	10 mL	150 µL	100 µL	20 vol %, 200 µL	Figure S3e
17	10 mL	150 µL	100 µL	20 vol %, 200 µL	Figure S4a
18	10 mL	150 µL	200 µL	20 vol %, 200 µL	Figure S4b
19	10 mL	150 µL	300 µL	20 vol %, 200 µL	Figure S4c
20	10 mL	150 µL	400 µL	20 vol %, 200 µL	Figure S4d

3. Characterization

Ultraviolet-Visible (UV-VIS) spectroscopy was performed with a Lambda 750 UV-Vis spectrograph (Perkin Elmer). Transmission electron microscopy (TEM) images and high angular annular dark field scanning transmission electron microscopy (HAADF-STEM) images were acquired with a FEI Talos F200X, operating at 200 kV and equipped with a ChemiSTEM EDS detector that was used for the EDS maps displayed in Figures S12-S14.

4. Liquid-cell experiments

***Sample preparation**:* 10.0 mL of as-prepared Au NT@mSiO$_2$ yolk-shell NPs were centrifuged at 9000 rpm for 10 minutes. After centrifuging, the supernatant was carefully removed and washed by deionized water twice. Finally, the sediment was suspended in 2.0 mL of deionized water for further use.

***Assembly of LC-TEM chips**:* (1) The LC-TEM chips were pretreated using 20 seconds of Ar/O$_2$ (20 vol% of O$_2$) plasma treatment. (2) A bottom chip was put on LC-TEM holder and 2.0 µL of above Au NT@mSiO$_2$ yolk-shell NPs was dropped on a liquid-cell bottom chip. (3) A top chip was carefully put onto the bottom chip and seal the chips.

***Recording TEM images and videos**:* The experiments were performed on a FEI Tecnai F20 TEM, operating at 200 kV. The videos were recorded by TIA software using preview mode and a recording speed of 2 fps. The final videos shown in Supporting Information were processed by ImageJ software and are displayed 3 times faster than real time.

5. Supporting Figures

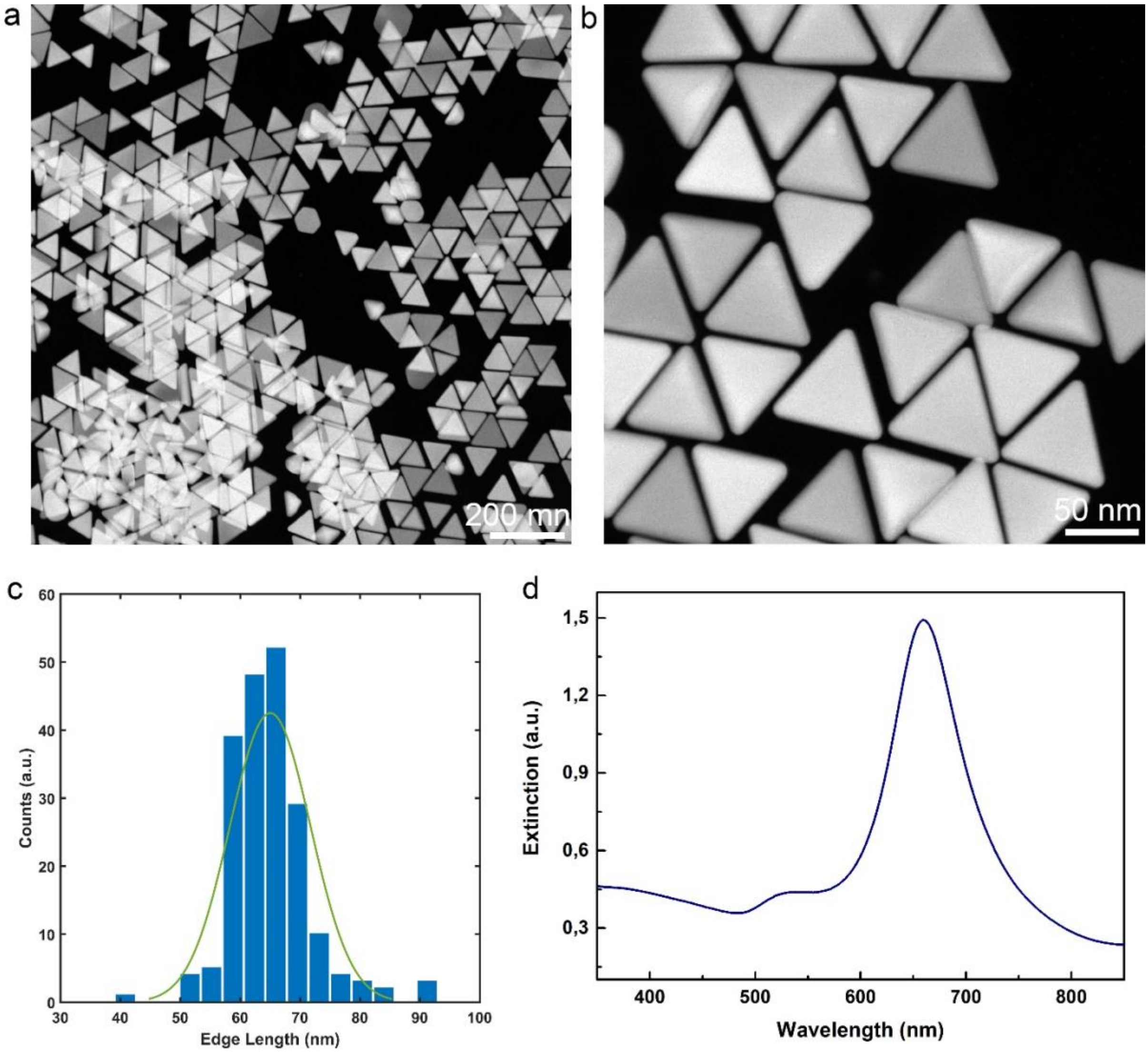

Figure S1: Morphology and size distribution of the Au NTs: a) & b) STEM image of Au NTs, C) histogram of edge length of Au NTs, D) UV-VIS spectrum of Au NTs.

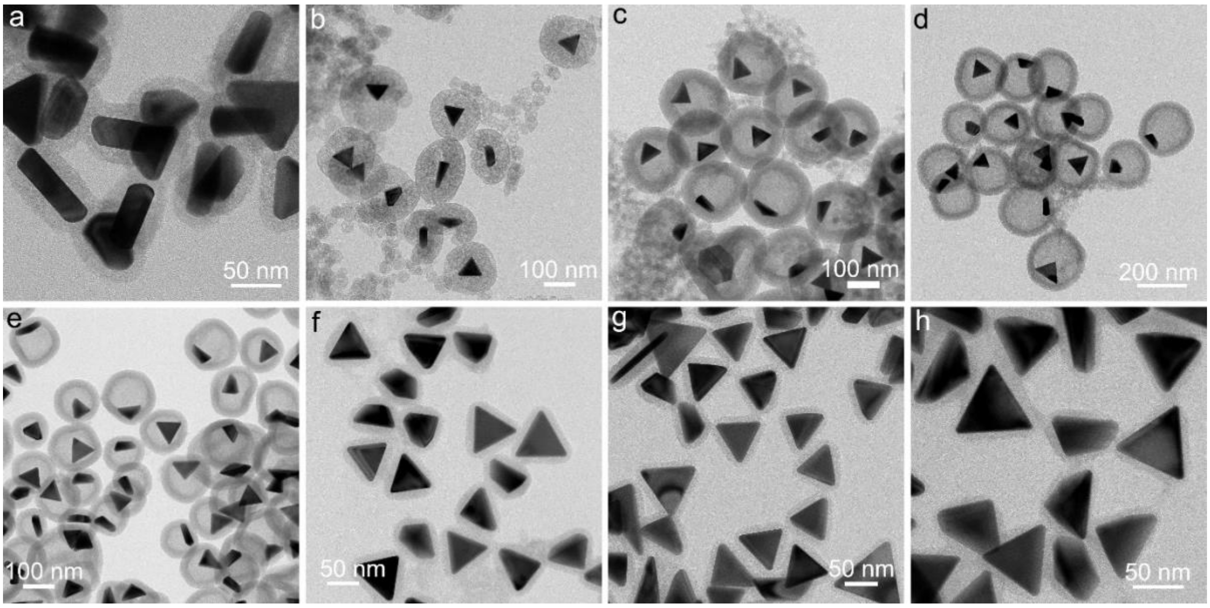

Figure S2: Morphologies of Au NT@mSiO_2 NPs obtained by changing the concentration of CTAC for the reactions. The corresponding concentration of CTAC used for synthesizing the NPs shown in the TEM images above are: a) 1.5 mM, b) 2.0 mM, c) 2.5 mM, d) 3.0 mM, e) 3.5 mM, f) 4.0 mM, g) 4.5 mM, and h) 5.0 mM.

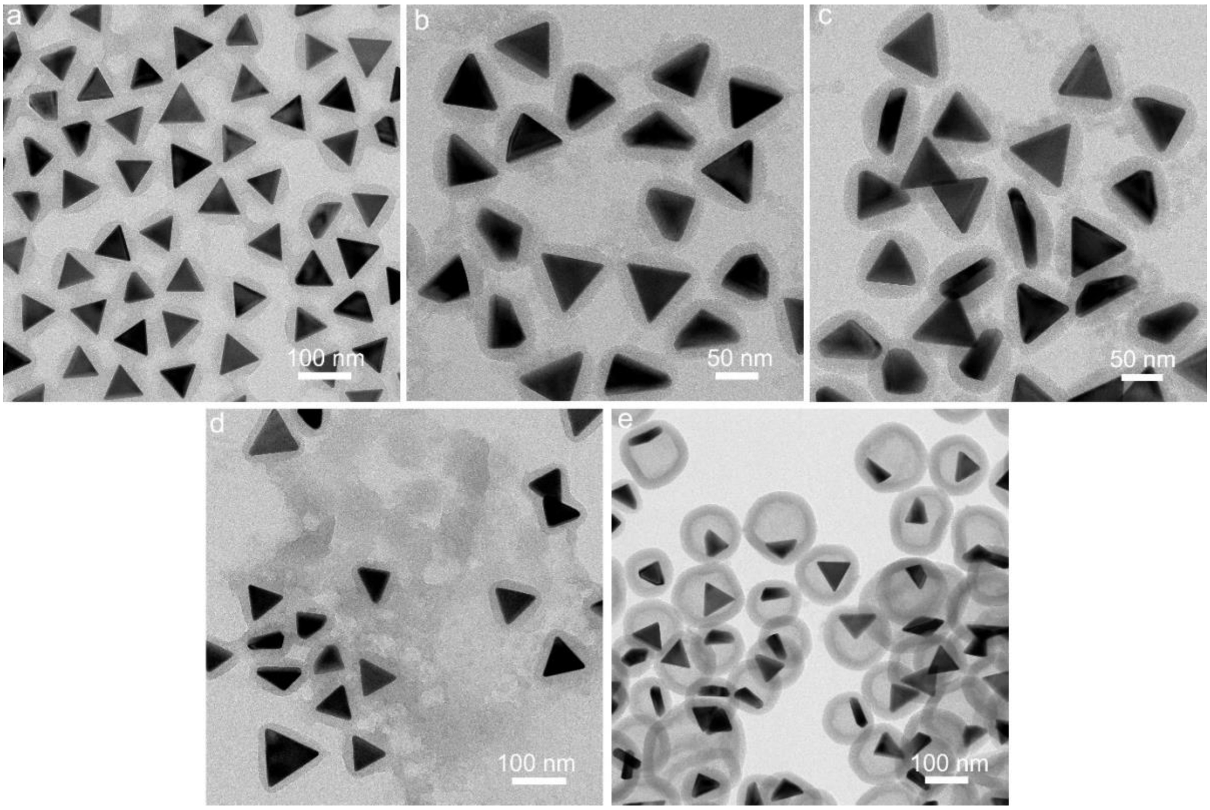

Figure S3: Morphologies of Au NT@mSiO_2 NPs obtained by changing the procedure of adding 20 vol% TEOS for the reactions. The corresponding ways of adding TEOS for synthesizing the NPs shown in above TEM images are: a) 67 µl, b) 67 µl + 67 µl, c) 67 µl + 67 ul + 67 µl, d) 134 µl, and e) 200 µl.

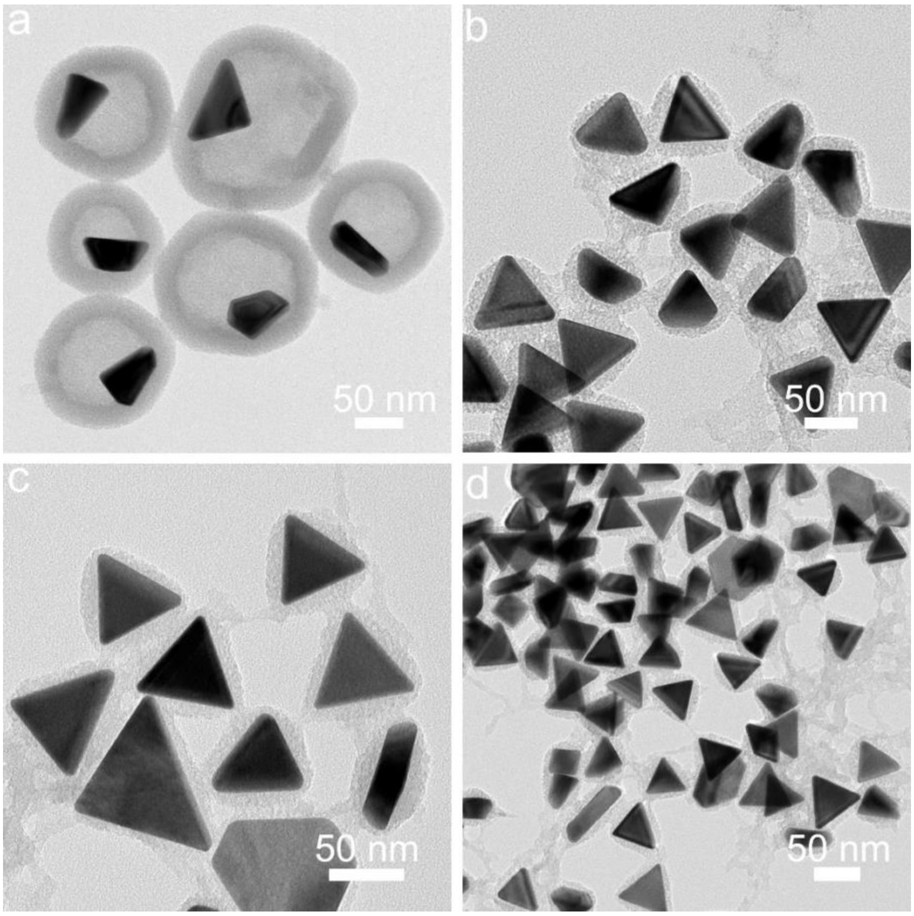

Figure S4: Morphologies Au NT@mSiO$_2$ NPs obtained by changing the concentration of NaOH for the reactions. The corresponding concentration (in the reaction solution) of NaOH used for synthesizing the NPs shown in above TEM images are: a) 1.0 mM, b) 2.0 mM, c) 3.0 mM, and d) 4.0 mM.

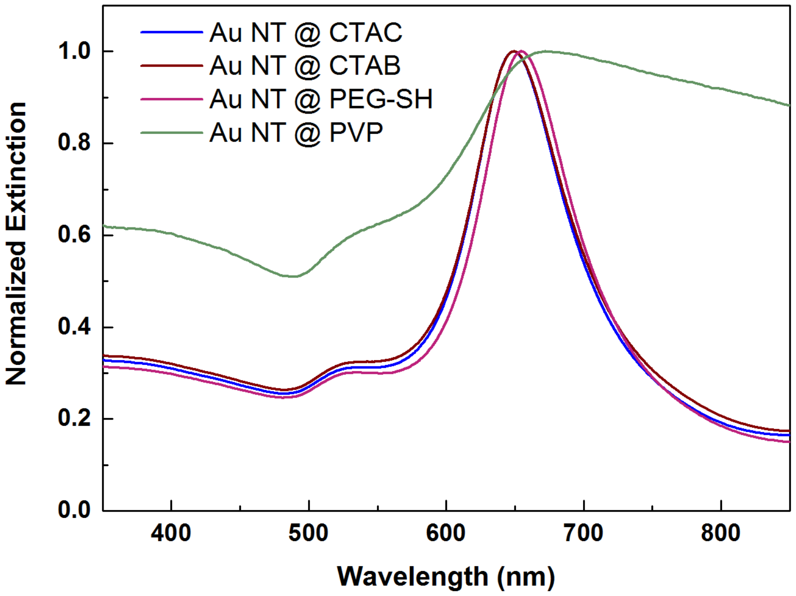

Figure S5: UV-VIS spectra of Au NTs covered by different ligands. PVP (Mol. Wt. 10000), PEG-SH (Mol. Wt. 10000).

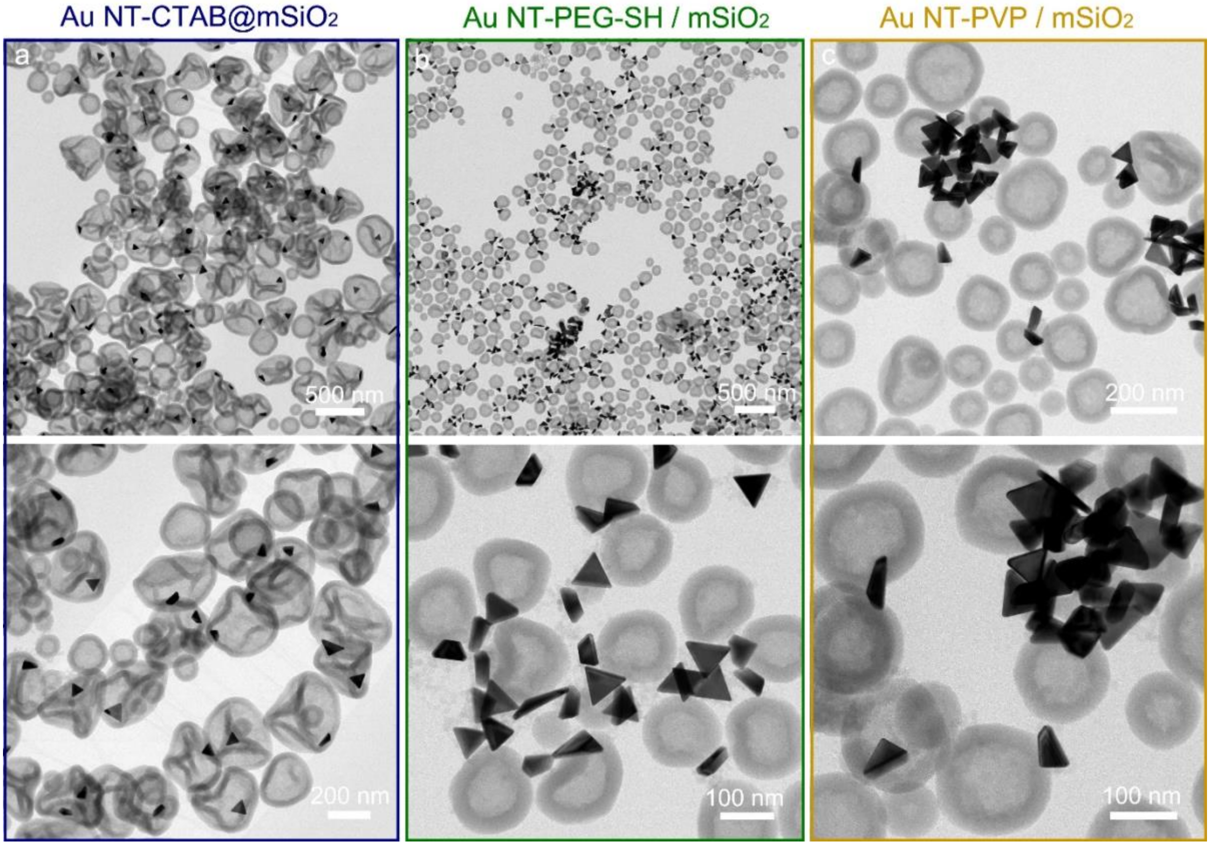

Figure S6: TEM images of Au NT-mSiO$_2$ products synthesized using Au NTs covered with different ligands, as indicated on top.

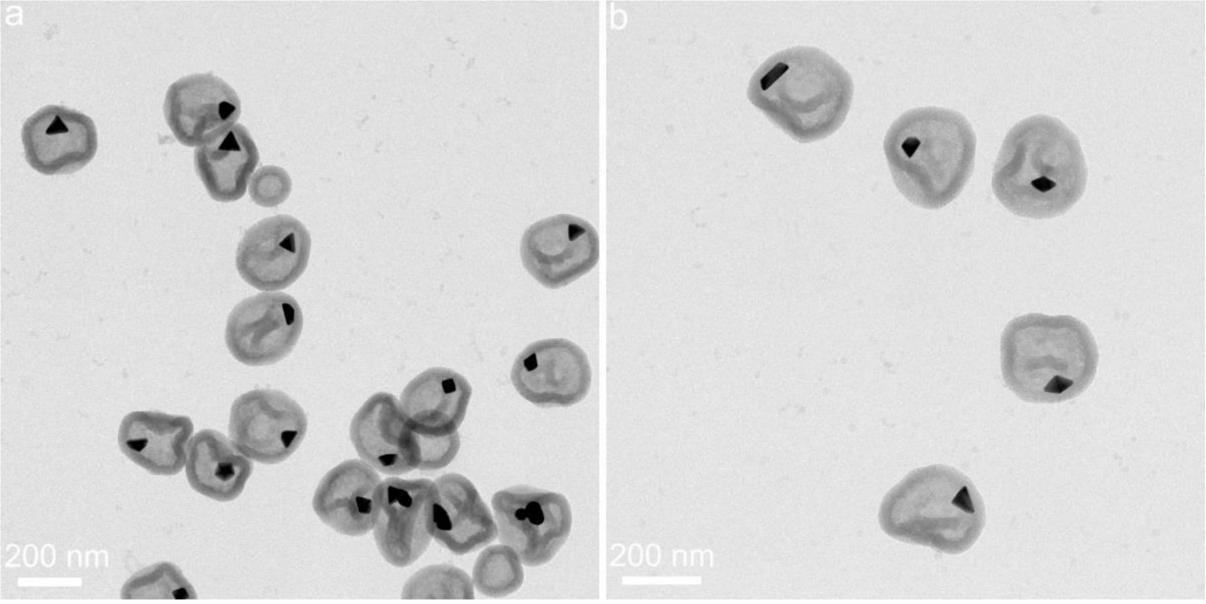

Figure S7: TEM images of Au NT-mSiO$_2$ products from a scaled-up synthesis.

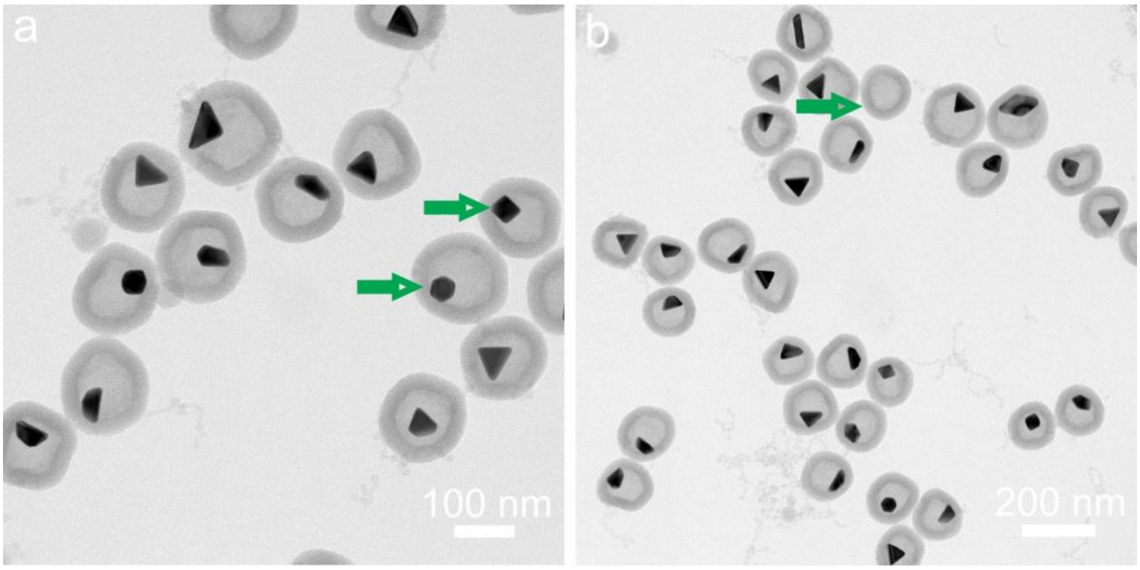

Figure S8: TEM images showing examples of Au NPs with a different morphology found in Au NT@hollow-mSiO$_2$ NPs syntheses.

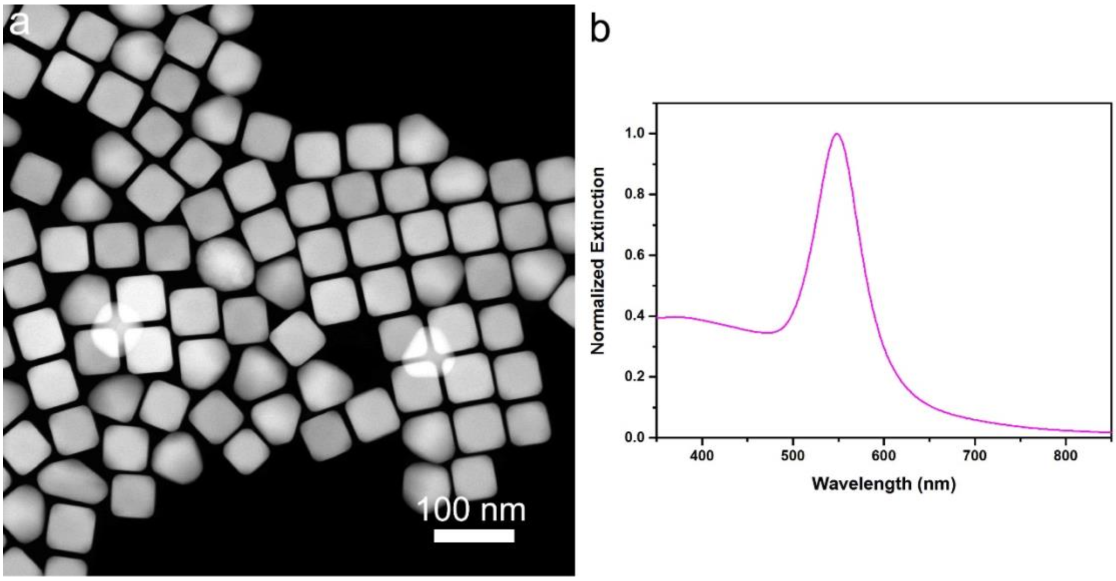

Figure S9: a) STEM image of Au nanocubes, b) UV-VIS spectrum of Au nanocubes.

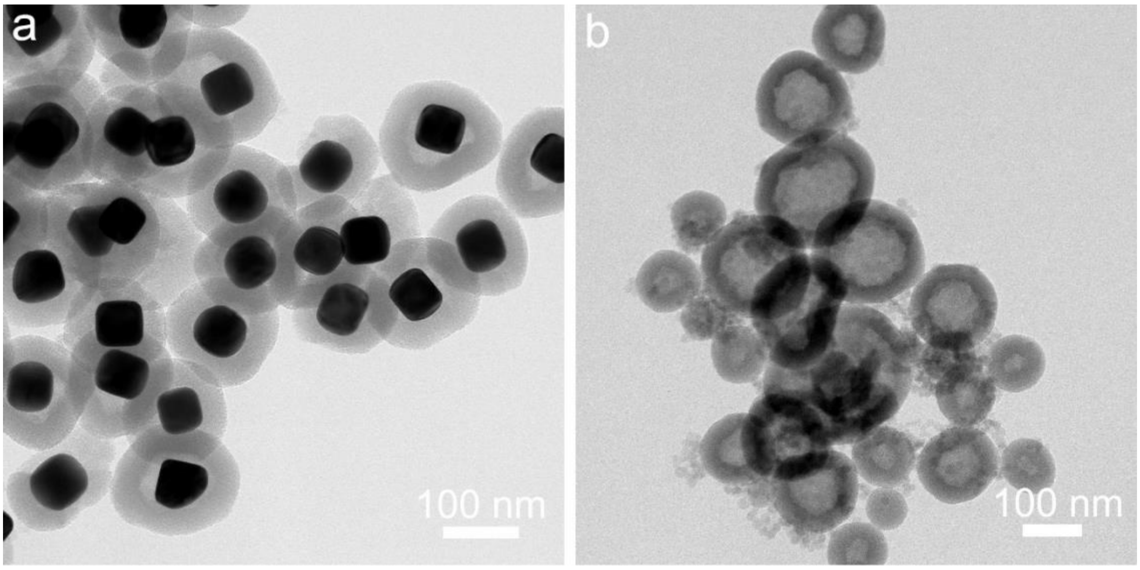

Figure S10: TEM images showing the morphology of a) Au NC@hollow-mSiO_2 yolk-shell NPs and b) hollow mSiO_2 nanospheres.

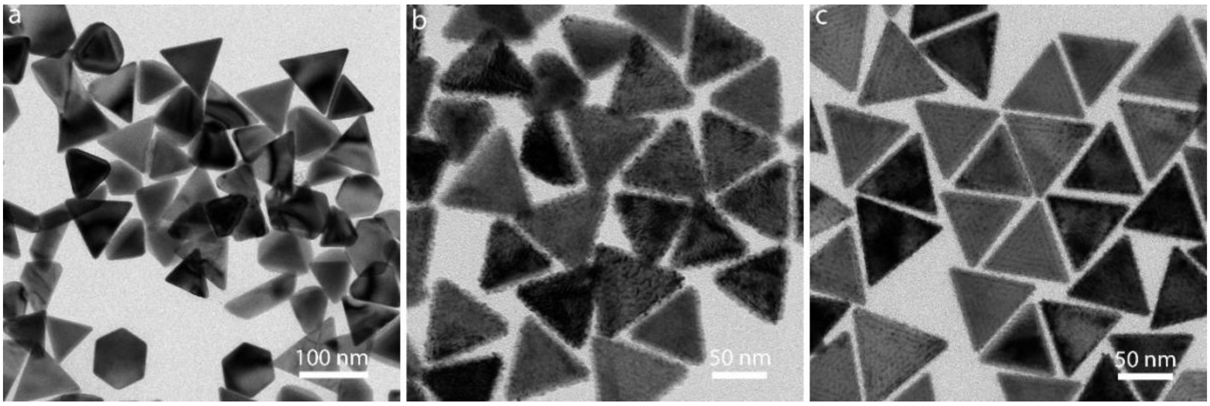

Figure S11: Morphology of Au NT@M (Ag, Pd,& Pt) nanoparticles (NPs). a) Au NT@Ag NPs, b) Au NT@Pd NPs, and c) Au NT@Pt NPs

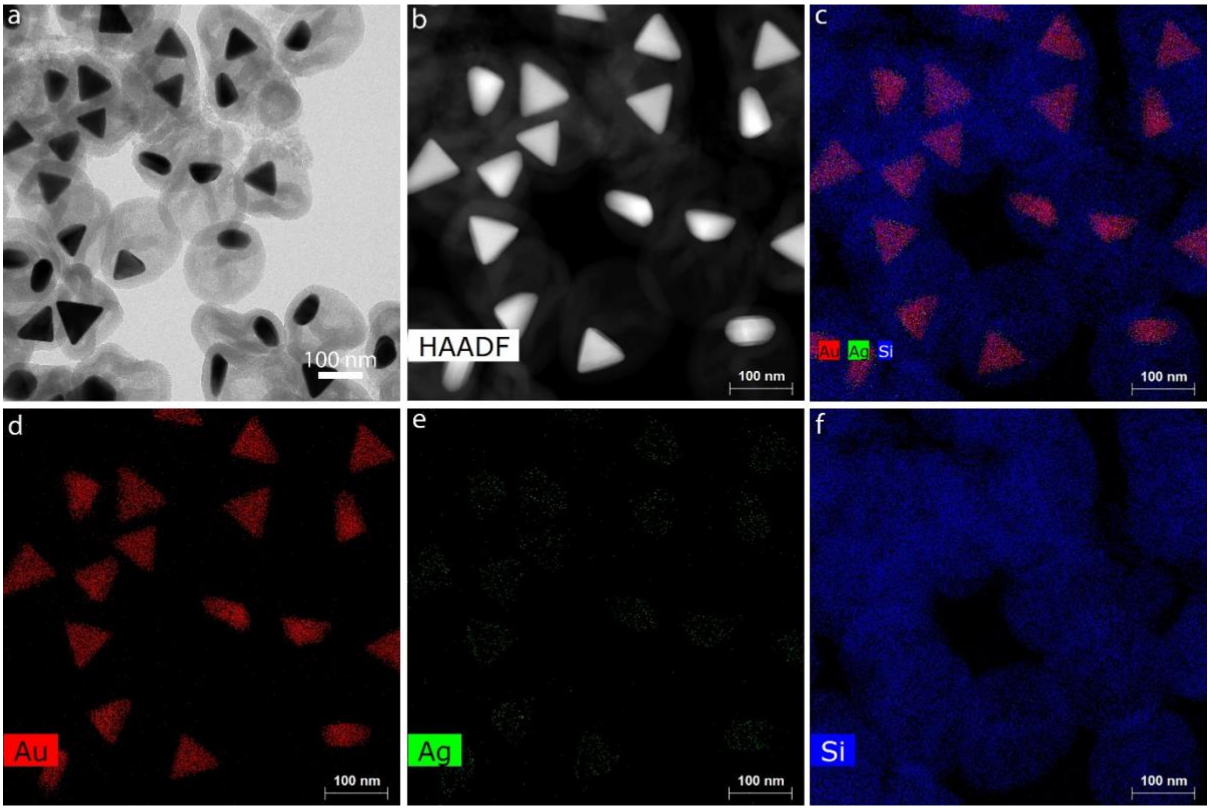

Figure S12: a) TEM image, b) STEM image, and c-f) EDS maps of Au NT@Ag@hollow-mSiO_2 yolk-shell NPs.

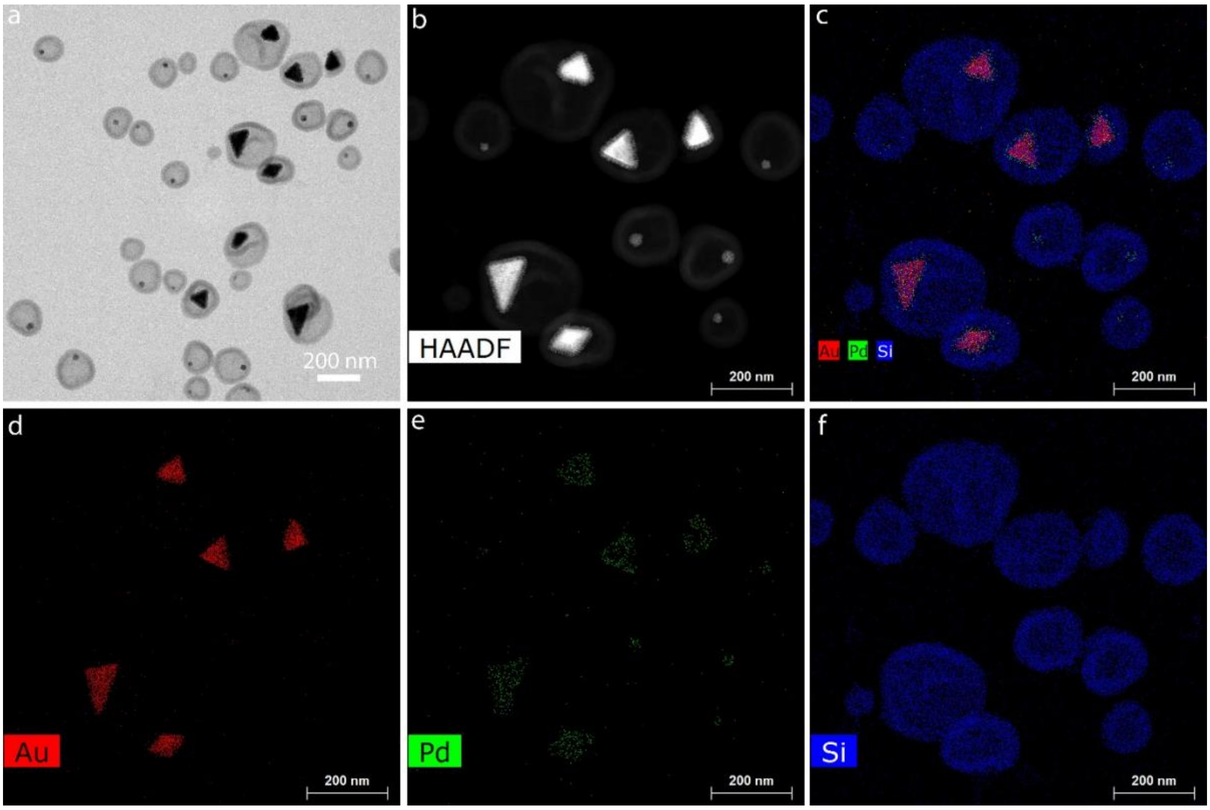

Figure S13: a) TEM image, b) STEM image, and c-f) EDS maps of Au NT@Pd@hollow-mSiO$_2$ yolk-shell NPs.

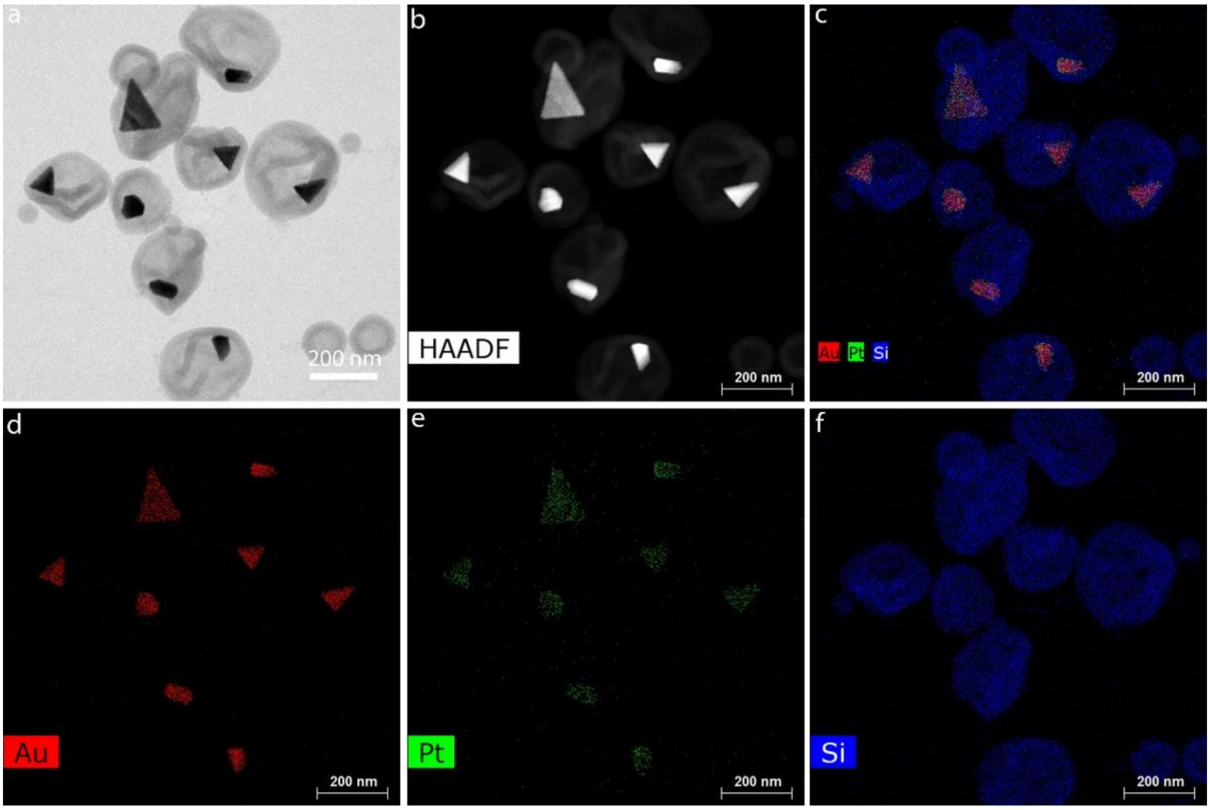

Figure S14: a) TEM image, b) STEM image, and c-f) EDS maps of Au NT@Pt@hollow-mSiO$_2$ yolk-shell NPs.

6. Supporting Movies Information

Movie S1: LC-TEM movie showing the motion of Au NT@hollow-mSiO_2 particles recorded at a relatively low electron dose rate of 215 e^-/nm^2/s. The movie is accelerated by a factor of 3 with respect to real time.

Movie S2: LC-TEM movie showing the motion of Au NT@hollow-mSiO_2 particles recorded at a relatively high electron dose rate of 3940 e^-/nm^2/s. The movie is accelerated by a factor of 3 with respect to real time.

References

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6. Thierry, B.; Ng, J.; Krieg, T.; Griesser, H. J., A robust procedure for the functionalization of gold nanorods and noble metal nanoparticles. *Chem. Commun. (Camb)* **2009,** (13), 1724-6.