Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Symmetrical and Asymmetrical Epitaxial Growth of Metals (Ag, Pd, and Pt) onto Au Nanotriangles: Effects of Reductants and Plasmonic Properties

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Contents of the Supporting Information

1 Chemicals

Chemicals used were: hydrogen tetrachloroaurate (III) 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), and CTAC solution (25wt% in water, Sigma-Aldrich). All chemicals were used as received without further purification. Also, de-ionized water with a resistivity of 18.2 MΩ·cm at 25 ℃ was used in the experiments.

2 Synthesis

2.1 Synthesis and purification of Au NTs

The Au NTs were synthesized by a modification of a previously reported synthesis.[1] (1) Au seeds@CTAC: 25 µL of 50 mM $HAuCl_4$ was mixed with 4.70 mL of 0.10 M CTAC solution in a 20 mL glass vial. Next, 300 µL of fresh prepared 10 mM $NaBH_4$ was injected into the above mixture while stirring. The seeds solution was strongly stirred for 2 min. After that, it was kept at room temperature for at least 2 hours. After 2 hours, 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 $HAuCl_4$, 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) 60.0 mL of deionized water was added into a 250 mL round-bottom flask. 60.0 mL of 0.1 M CTAC, 1.5 mL of 50 mM $HAuCl_4$, and 900 µL of 10 mM KI were injected into the deionized water. This solution was marked as solution-B. (4) 40 µL and 1.20 mL of 0.10 M AA solution were injected into solution-A and solution-B, respectively, while stirring. As both of A-solution and B-solution turned colorless, 100 µL of diluted Au seeds was injected into solution-A. Stirring continued for about one minute. All solution-A 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 mL of solution-B and 4.50 mL of 25 wt% CTAC were mixed in a 50 mL centrifuge tube, and then left undisturbed for 12 hours. The suspension was removed carefully, and the sediment was suspended in 35 mL of 0.01 M CATC and served as a stock solution for further use.

Determination of the concentration of Au NTs stock solution. The concentration of Au NTs solution was calculated by measuring the UV-VIS spectra and using the following equations ,[2]

$$\varepsilon = 1.6888 \times 10^{8} e^{5.1742 \times 10^{-3} \times \lambda_{max}} \qquad (1)$$

$$C = \frac{A}{\varepsilon l} \qquad (2)$$

where ε is extinction coefficient, λ_{max} is the wavelength of LSPR band of Au NTs, and A is the extinction intensity.

2.2 Synthesis of Au NT-Ag NPs

Using AA as reductant: Typically, 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 a temperature of 60 °C for 15 hours. The product was collected by centrifugation at 8000 rpm (Eppendorf Centrifuge 5424 R) for 10 min, and then washed by de-ionized water once, to remove excess CTAC. More details and the corresponding data are shown in **Table S1** 1-7.

Using SA as reductant: In general, 5.75 mL of de-ionized water and 3.50 mL of Au NTs stock solution were mixed in a 20 mL glass vial, then 150 µL of 10 mM $AgNO_3$ and 1.00 mL of saturated SA, respectively, were 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 deionized water once, to remove excess CTAC. More details and the corresponding data are shown in **Table S1** 8-13.

Table S1. The reaction conditions used for Au NT-Ag NPs growth

	Au NTs (µM)	**$AgNO_3$ (µM)**	**AA (µM)**	**SA (µM)**	**Temperature (Celsius)**	**Figure**
1	158	150	1000	/	60	Fig. 2 a-h Fig. S1a
2	158	150	1000	/	40	Fig. S1b
3	158	150	1000	/	20	Fig. S1c
4	158	200	1000	/	20	Fig. S3a
5	158	150	1000	/	20	Fig. S3b
6	158	100	1000	/	20	Fig. S3c
7	158	50	1000	/	20	Fig. S3d
8	158	150	/	1800	60	Fig. 2 i-p Fig. S1d
9	158	150	/	1800	40	Fig. S1e
10	158	150	/	1800	20	Fig. S1f
11	158	150	/	1800	60	Fig. S4a
12	158	100	/	1800	60	Fig. S4b
13	158	50	/	1800	60	Fig. S4c

2.3 Synthesis of Au NT-Pd NPs

Using AA as reductant: 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 de-ionized water once, to remove excess CTAC. More details and the corresponding data are shown in **Table S2** 1-12.

Using SA as reductant: In general, 5.75 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 Na_2PdCl_4 and 1.00 mL of saturated SA, respectively, were 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 de-ionized water once, to remove excess CTAC. More details and the corresponding data are shown in **Table S2** 13-18.

Table S2. The reaction conditions used for Au NT-Pd NPs growth

	Au NT (µM)	**Na_2PdCl_4 (µM)**	**AA (µM)**	**SA (µM)**	**Temperature (Celsius)**	**Figure**
1	158	150	1000	/	60	Fig. 4 a-h, Fig. S8a
2	158	150	1000	/	40	Fig. S8b
3	158	150	1000	/	20	Fig. S8c
4	158	200	1000	/	20	Fig. S6a
5	158	150	1000	/	20	Fig. S6b
6	158	100	1000	/	20	Fig. S6c
7	158	50	1000	/	20	Fig. S6d
9	158	50	1000	/	20	Fig. S7d
10	113	50	1000	/	20	Fig. S7c
11	79	50	1000	/	20	Fig. S7b
12	57	50	1000	/	20	Fig. S7a
13	158	150	/	1800	60	Fig. 4 i-p, Fig. S9a
14	158	150	/	1800	40	Fig. S9b, Fig S10
15	158	150	/	1800	20	Fig. S9c, Fig S11, Fig S12
16	158	150	/	1800	60	Fig. 5a, 5b

17	158	100	/	1800	60	Fig. 5c, 5d
18	158	50	/	1800	60	Fig. 5e, 5f

2.4 Synthesis of Au NT-Pt NPs

Using AA as reductant: Typically, 6.30 mL of de-ionized 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 100 μL of 0.10 M AA were added to 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 then washed by deionized water once to remove excess CTAC. More details and the corresponding data are shown in **Table S3** 1-6.

Using SA as reductant: In general, 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 de-ionized water once, to remove excess CTAC. More details and the corresponding data are shown in **Table S3** 8-12.

Table S3. The reaction conditions used for Au NT-Pt NPs growth

	Au NT (μM)	**K_2PtCl_4 (μM)**	**AA (μM)**	**SA (μM)**	**Temperature (Celsius)**	**Figure**
1	158	150	1000	/	60	Fig. 7 a-h, Fig. S15a
2	158	150	1000	/	40	Fig. S15b
3	158	150	1000	/	20	Fig. S15c, Fig S16
4	158	150	1000	/	60	Fig. 8a
5	158	100	1000	/	60	Fig. 8b
6	158	50	1000	/	60	Fig. 8c
7	158	150	/	1800	60	Fig. 7 i-p, Fig. S17a, b
8	158	150	/	1800	40	Fig S17c, d
9	158	150	/	1800	20	Fig S17e, f
10	158	150	/	1800	60	Fig. S14a
11	158	100	/	1800	60	Fig. S14b
12	158	50	/	1800	60	Fig. S14c

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, operated at 200 kV.

4 FDTD Simulations

The FDTD simulations were carried out using FDTD Solutions 8.11 developed by Lumerical Solutions. A total field scattered field source with a wavelength range of 300 nm to 900 nm was used to simulate the interaction between a propagating plane wave and the nanoparticles. The nanoparticle was surrounded by a virtual boundary with a size of 800 nm. A three-dimensional non-uniform mesh was used with a fine mesh grid size of 0.05 nm for calculating the extinction spectra of the nanoparticles. The refractive index of the surrounding medium was set as 1.33, namely water. The Au NT model was built as a triangular prism with an edge length of 65 nm and a thickness of 20 nm. The dielectric functions of metals were acquired by fitting to data of Johnson and Christy.[3]

5 Key physical parameters of bulk Au, Ag, Pd, and Pt

A number of physical parameters of Au, Ag, Pd, and Pt are summarized in Table S4, which include their lattice parameters, bond dissociation energy of same metal atoms (M-M) and between Au and another metal atom (Au-M), and the standard reduction potentials.[4-6]

Table S4. Key physical parameters of Au, Ag, Pd, and Pt

	Au	**Ag**	**Pd**	**Pt**
Lattice Parameters	4.078 Å	4.086 Å	3.891 Å	3.924 Å
Atomic Radius	1.442 Å	1.444 Å	1.376 Å	1.387 Å
Bond Dissociation Energy (M-M, kJ / mol)	226	160	100	307
Bond Dissociation Energy (Au-M, kJ / mol)	226	203	155	/
Standard Reduction Potentials (V)	+1.00 ($[AuCl]^{-}_{4}$)	+0.80 (Ag^+)	+0.59 ($[PdCl]^{2-}_{4}$)	+0.76 ($[PtCl]^{2-}_{4}$)

6 Supporting Figures

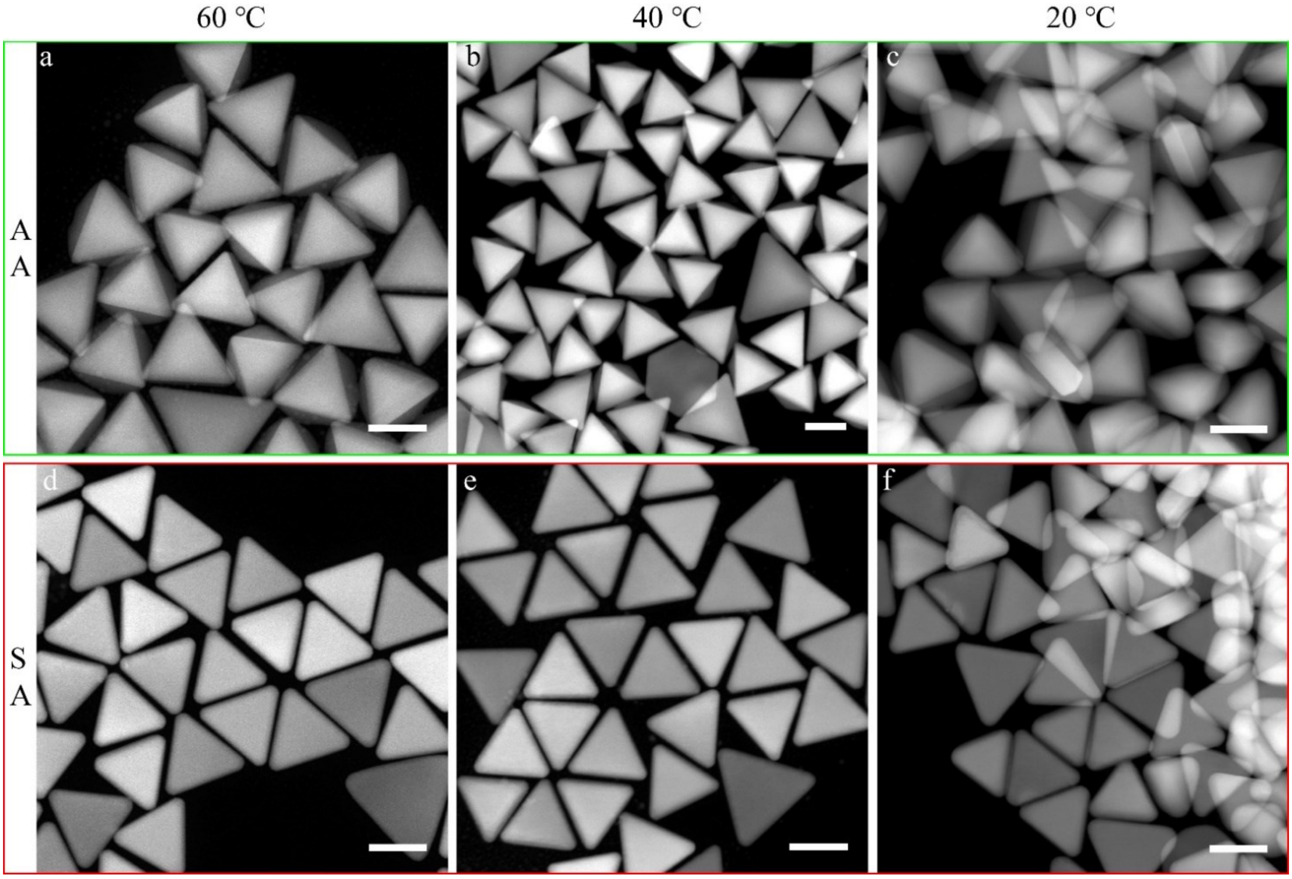


Figure S1. Shape evolution of Au NT-Ag NPs synthesized at different temperatures indicated on top. The scale bar of the STEM images indicates 50 nm.

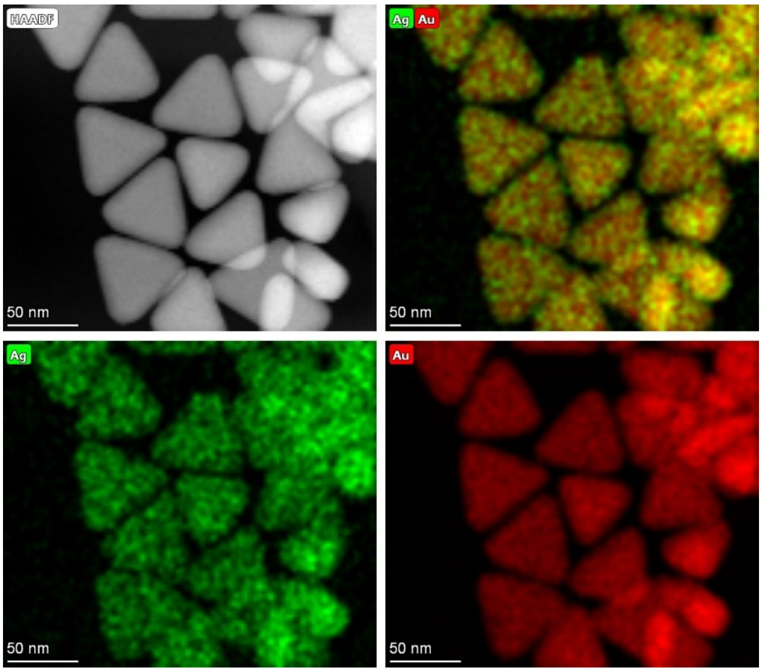


Figure S2. EDS mapping of Au NT@Ag synthesized at 20 °C using SA as reductant.

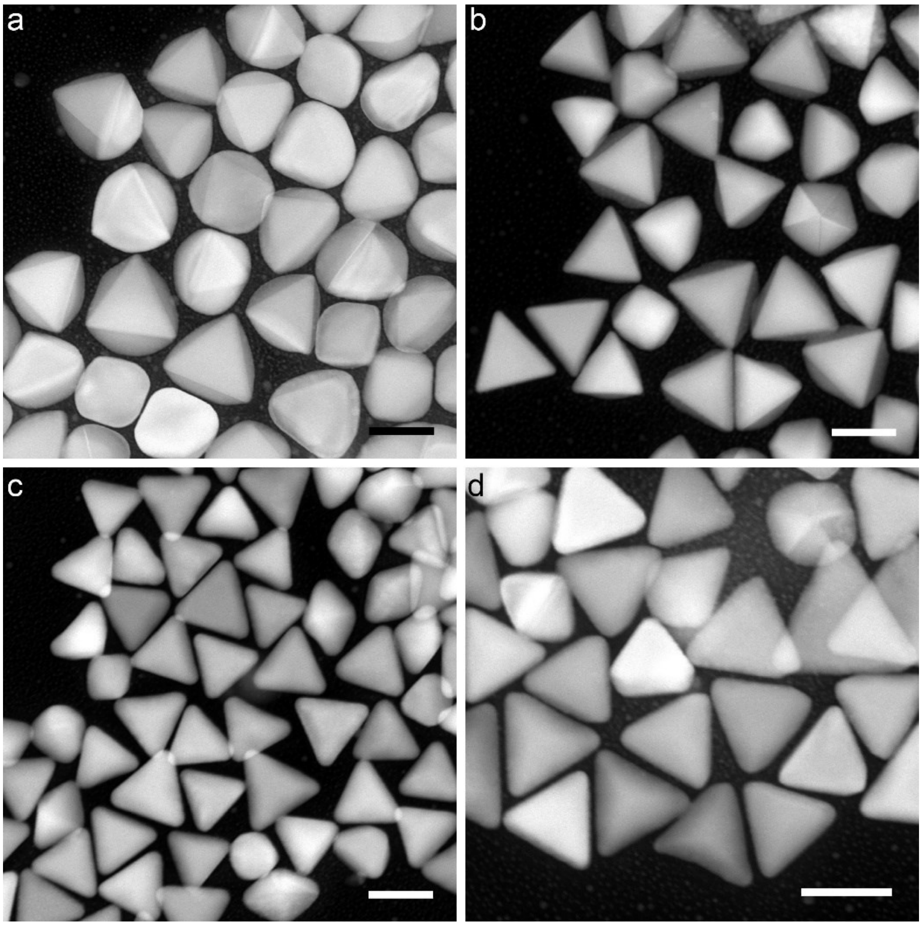


Figure S3. Morphology evolution of Au NT-Ag NPs synthesized using AA as reductant when changing the concentration of $AgNO_3$. The concentration of $AgNO_3$ is: a) 200 µM, b) 150 µM, c) 100 µM, and d) 50 µM. The scale bar of STEM images is 50 nm.

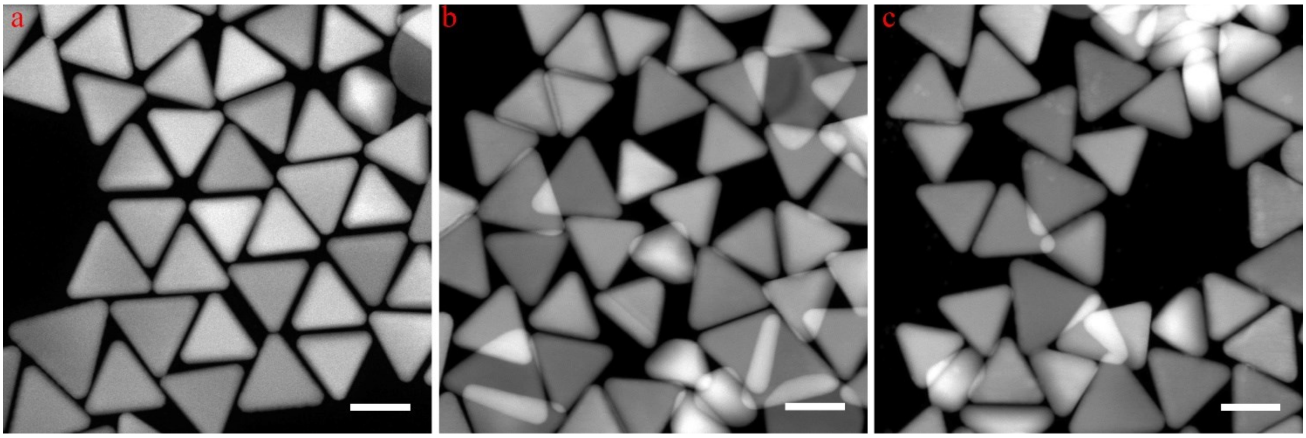


Figure S4. Morphology evolution of Au NT-Ag NPs synthesized using SA as reductant when changing the concentration of $AgNO_3$. The concentration of $AgNO_3$ is: a) 150 µM, b) 100 µM, c) 50 µM. The scale bar of STEM images is 50 nm.

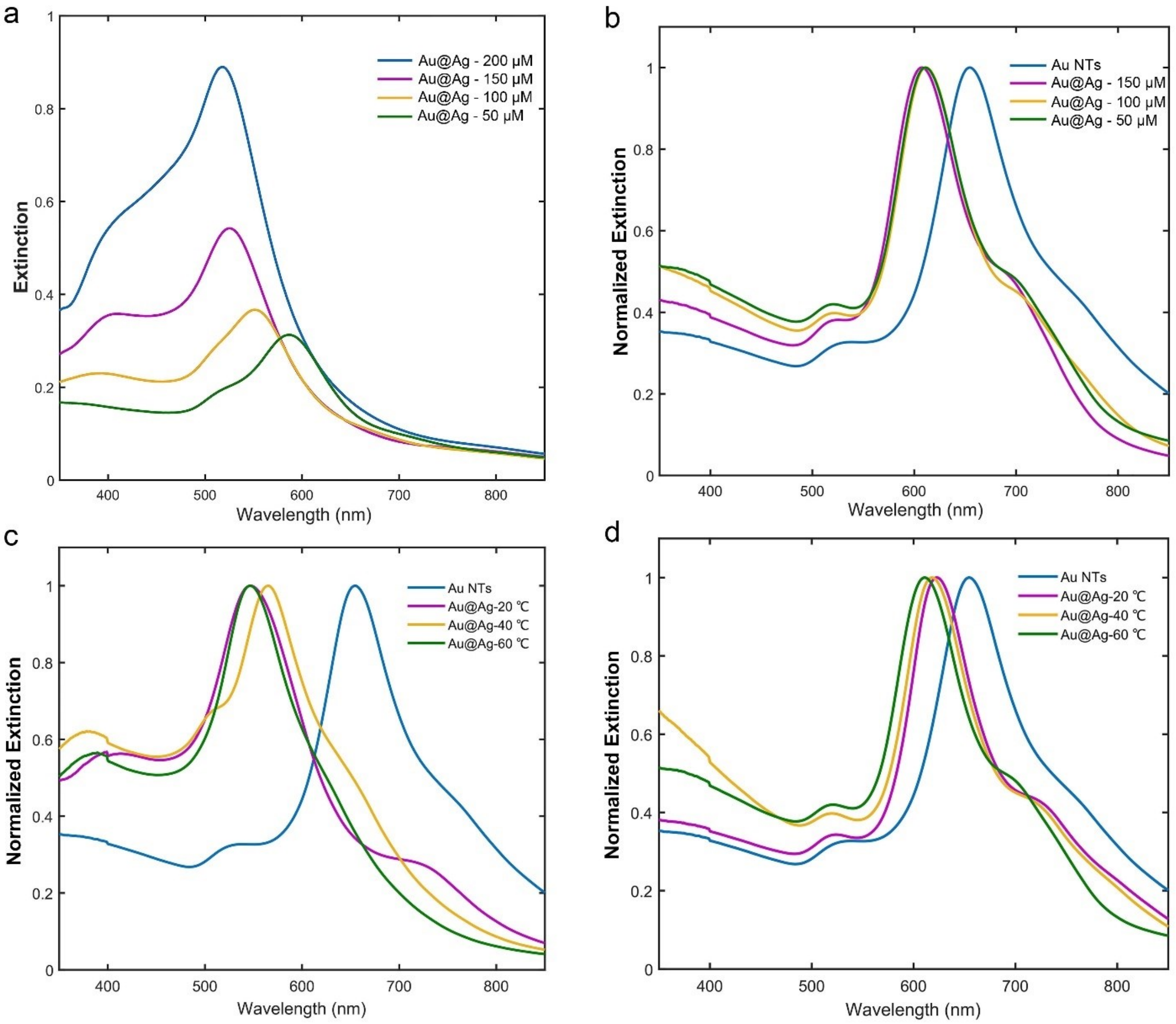


Figure S5. UV-VIS spectrum of Au NT-Ag NPs synthesized at different conditions. (a) Using AA and changing the concentration of $AgNO_3$; (b) Using SA and changing the concentration of $AgNO_3$ (μM); (c) Using AA and changing reaction temperature; (d) Using SA and changing reaction temperature.

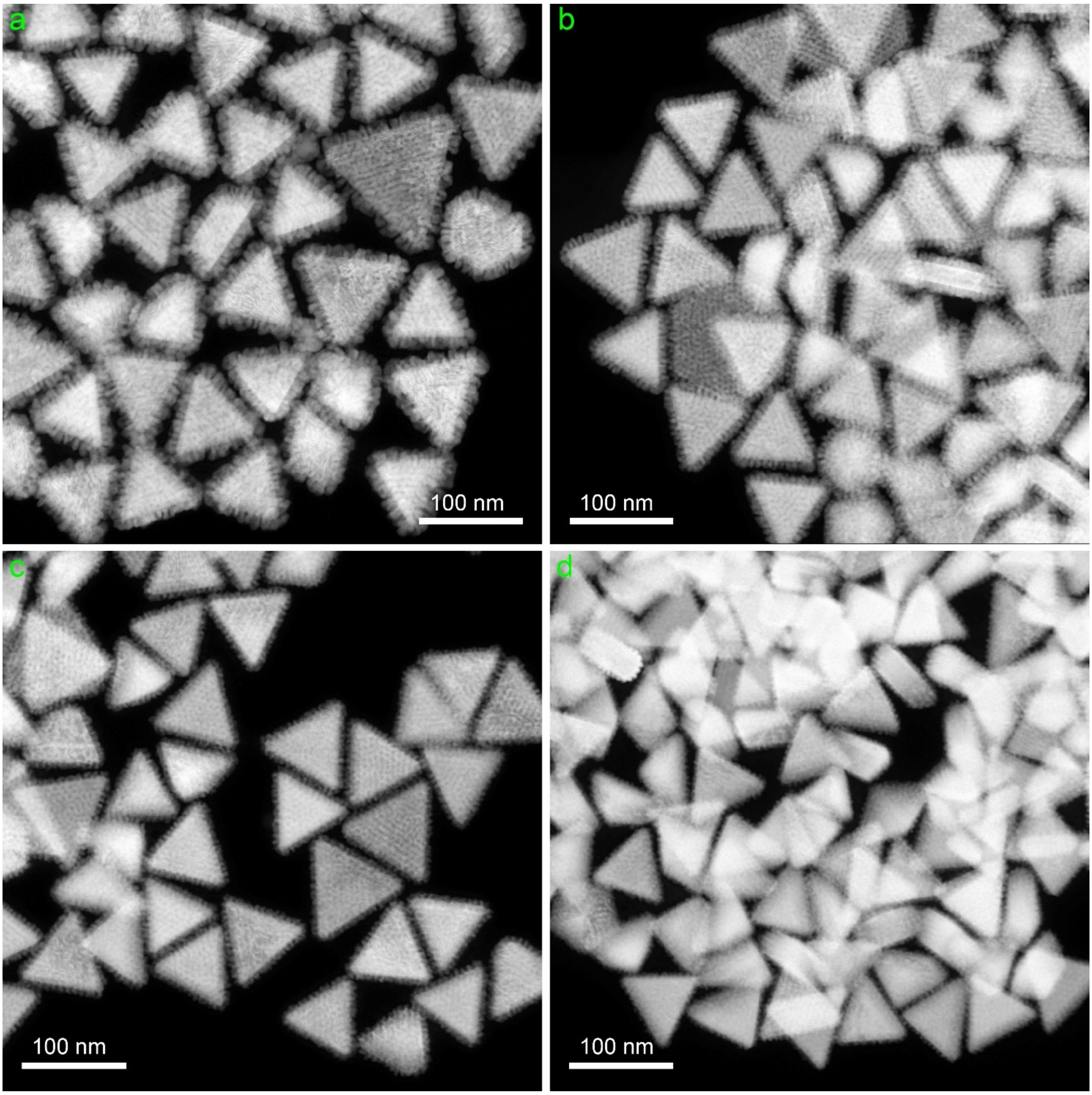


Figure S6. Morphology evolution of Au NT-Pd NPs synthesized using AA as reductant when changing the concentration of Na_2PdCl_4. The concentration of Na_2PdCl_4 is: a) 200 µM, b) 150 µM, c) 100 µM, and d) 50 µM.

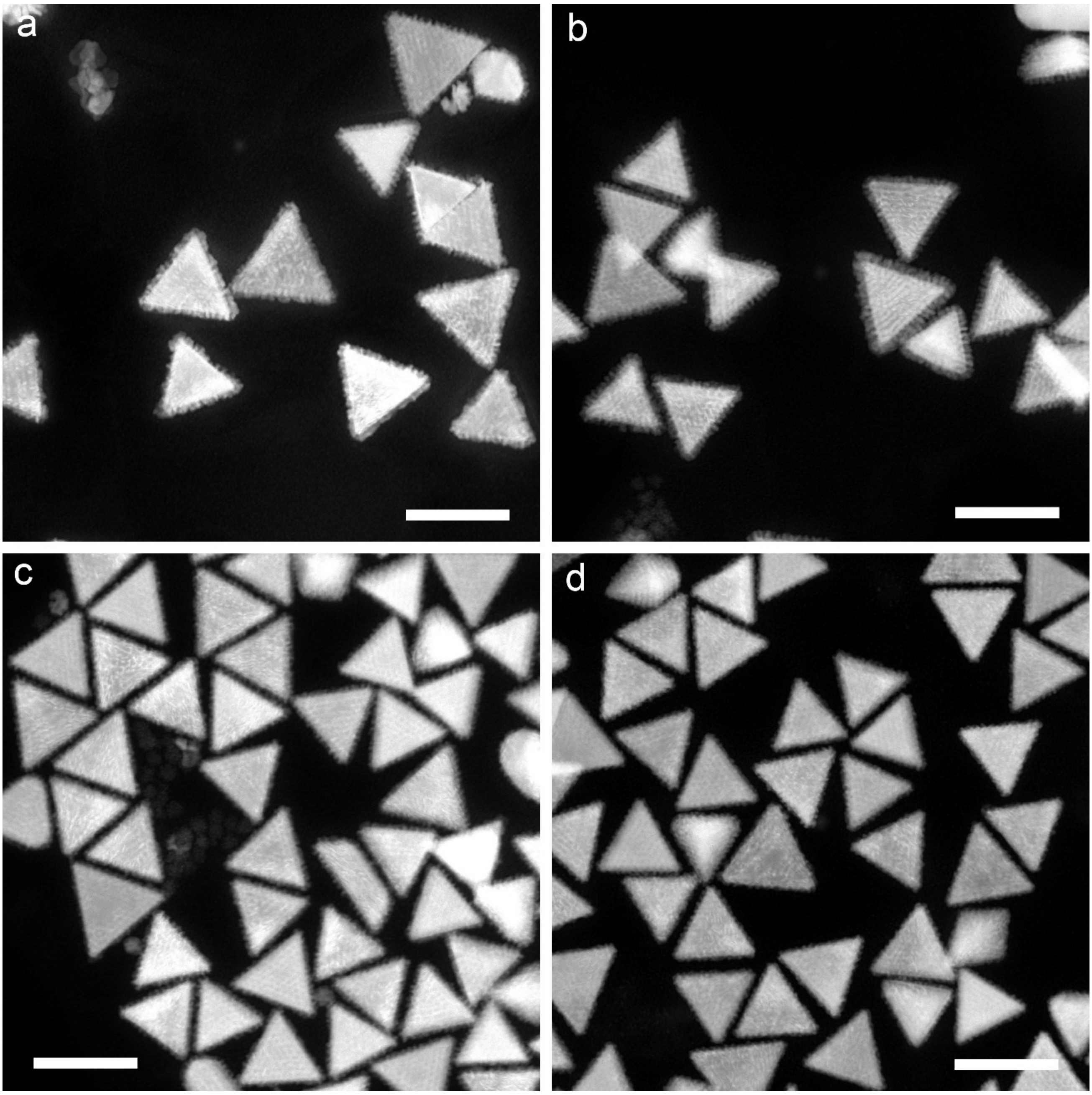


Figure S7. Morphology evolution of Au NT-Pd NPs synthesized using AA as reductant when changing the concentration of Au NTs. The details of Au NTs added are shown in table S2 9-12. The scale bar in all STEM images is 100 nm.

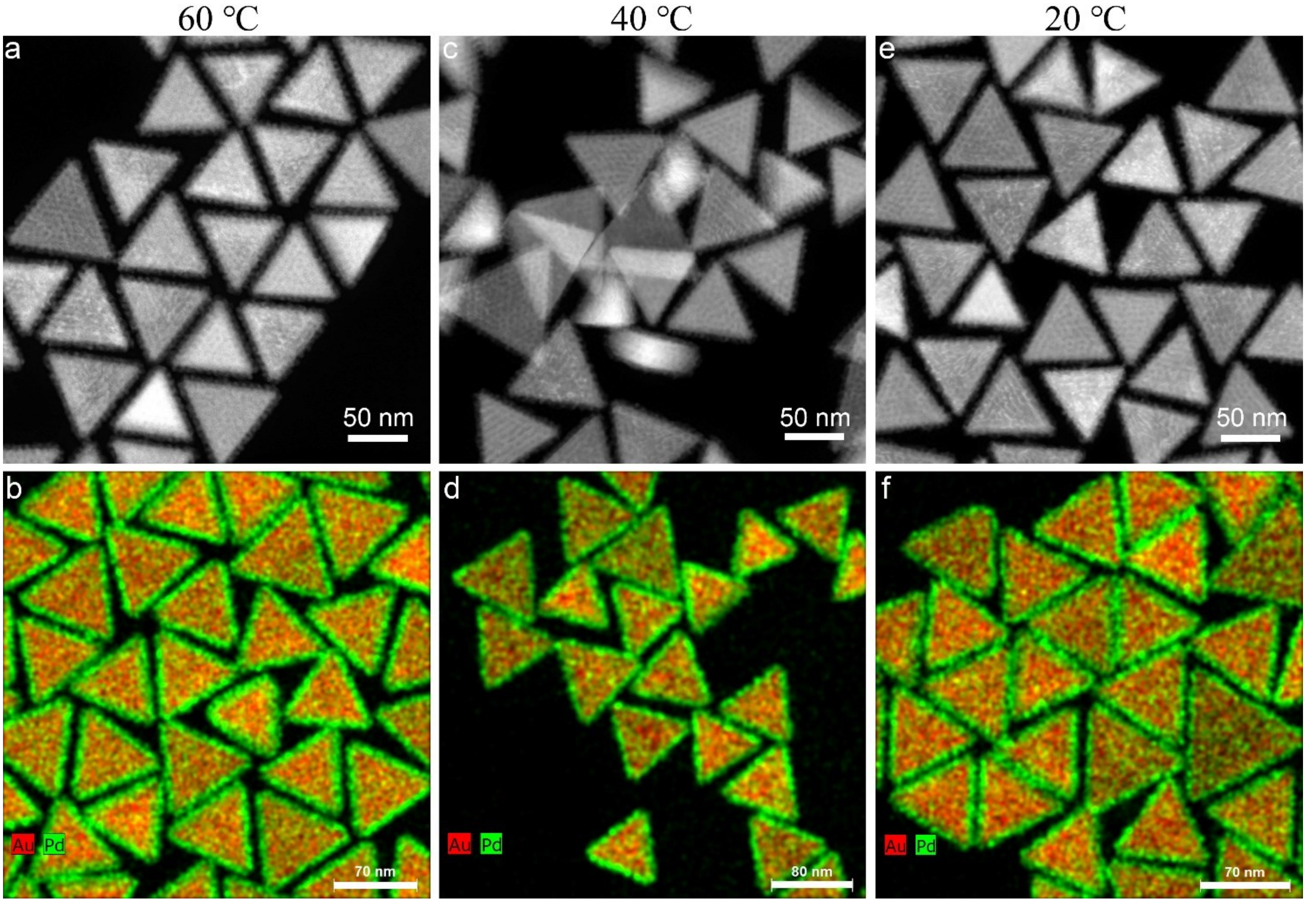


Figure S8. Shape evolution of Au NT-Pd NPs synthesized at different temperatures using AA as reductant.

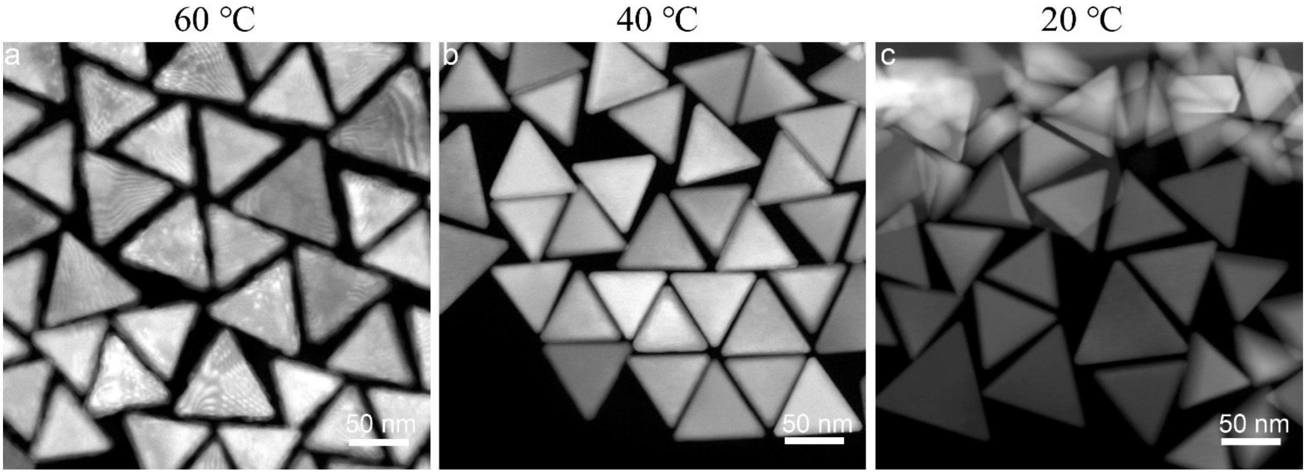


Figure S9. Shape evolution of Au NT-Pd NPs synthesized at different temperatures using SA as reductant.

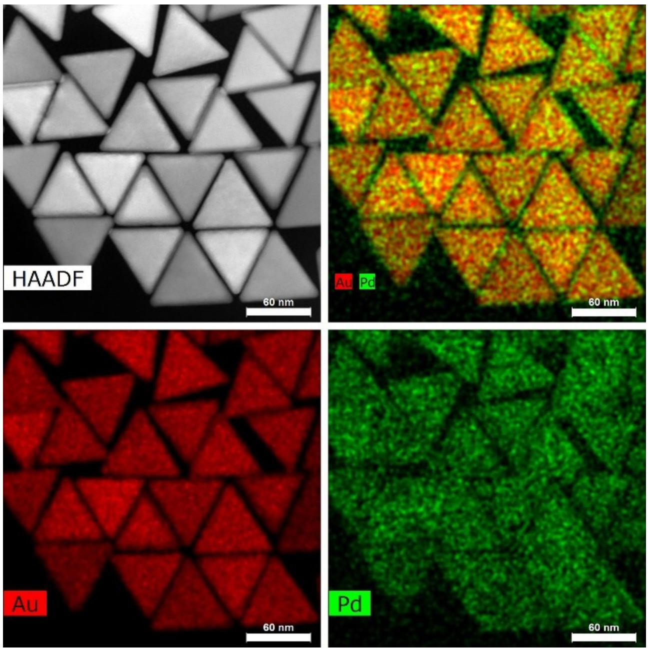


Figure S10. EDS maps of Au NT-Pd NPs synthesized at 40 °C using SA as reductant.

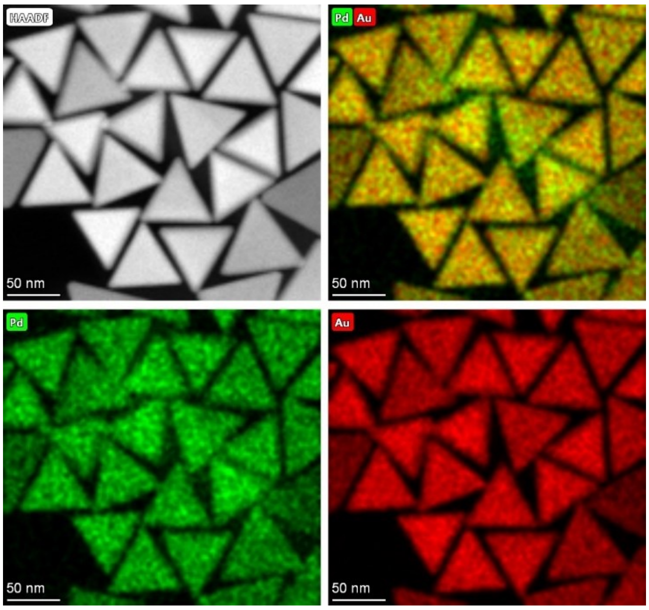


Figure S11. EDS maps of Au NT-Pd NPs synthesized at 20 °C using SA as reductant.

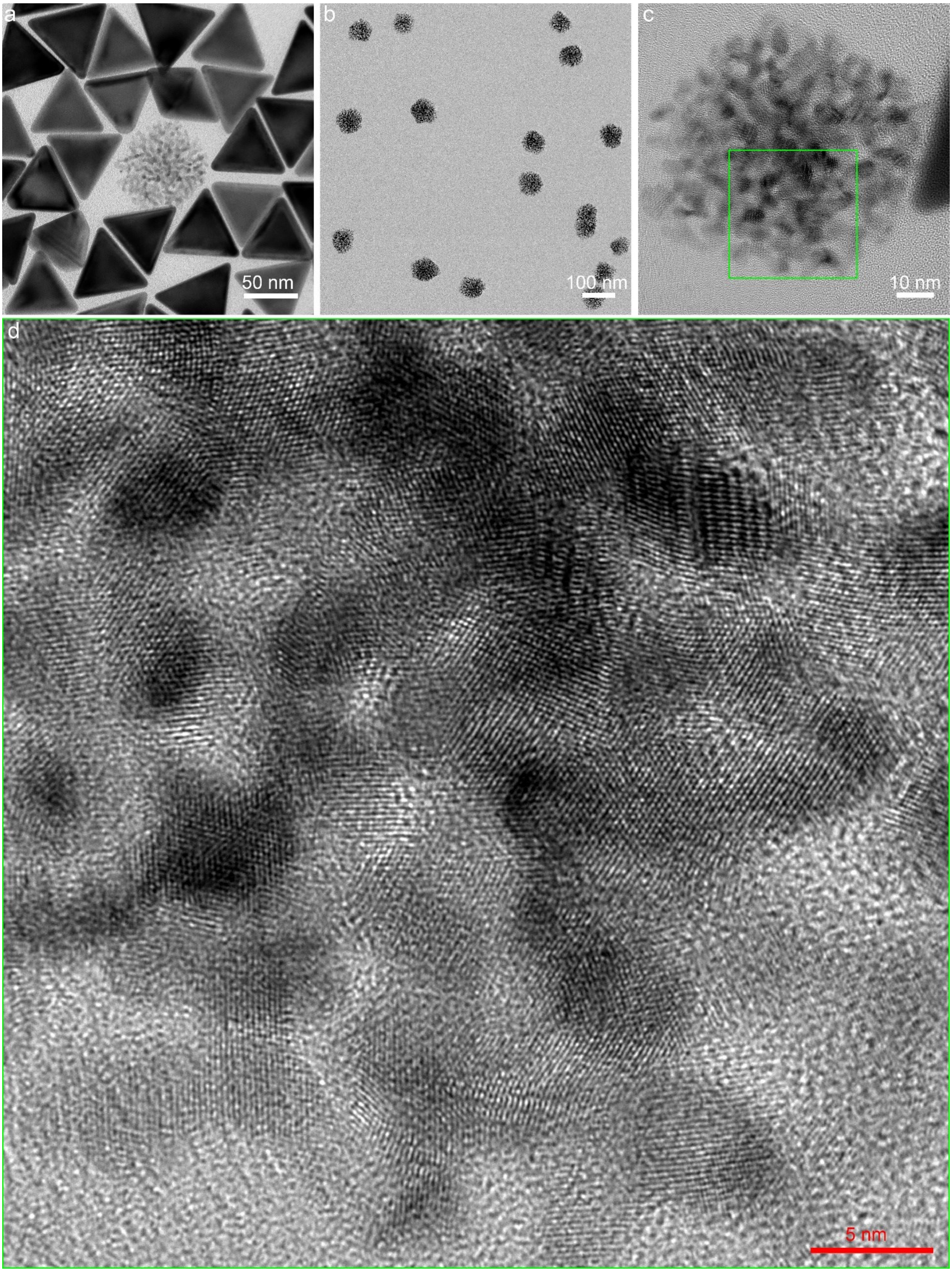


Figure S12. By-productions of Au NT-Pd NPs synthesized at 20 °C using SA as reductant.

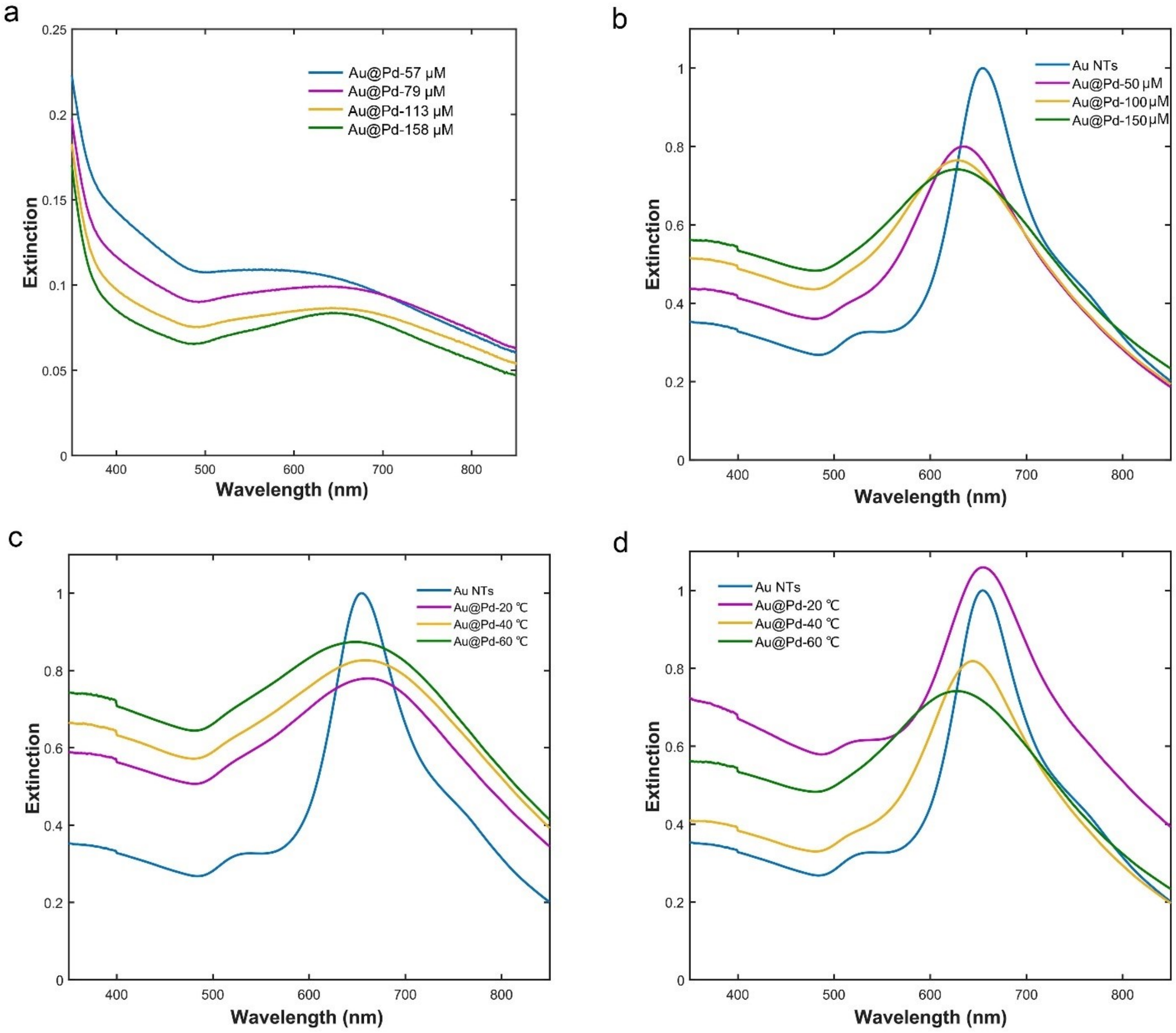


Figure S13. UV-VIS spectrum of Au NT-Pd NPs synthesized at different conditions. (a) Using AA and changing the concentration of Na_2PdCl_4; (b) Using SA and changing the concentration of Na_2PdCl_4 (μM); (c) Using AA and changing reaction temperature; (d) Using SA and changing reaction temperature.

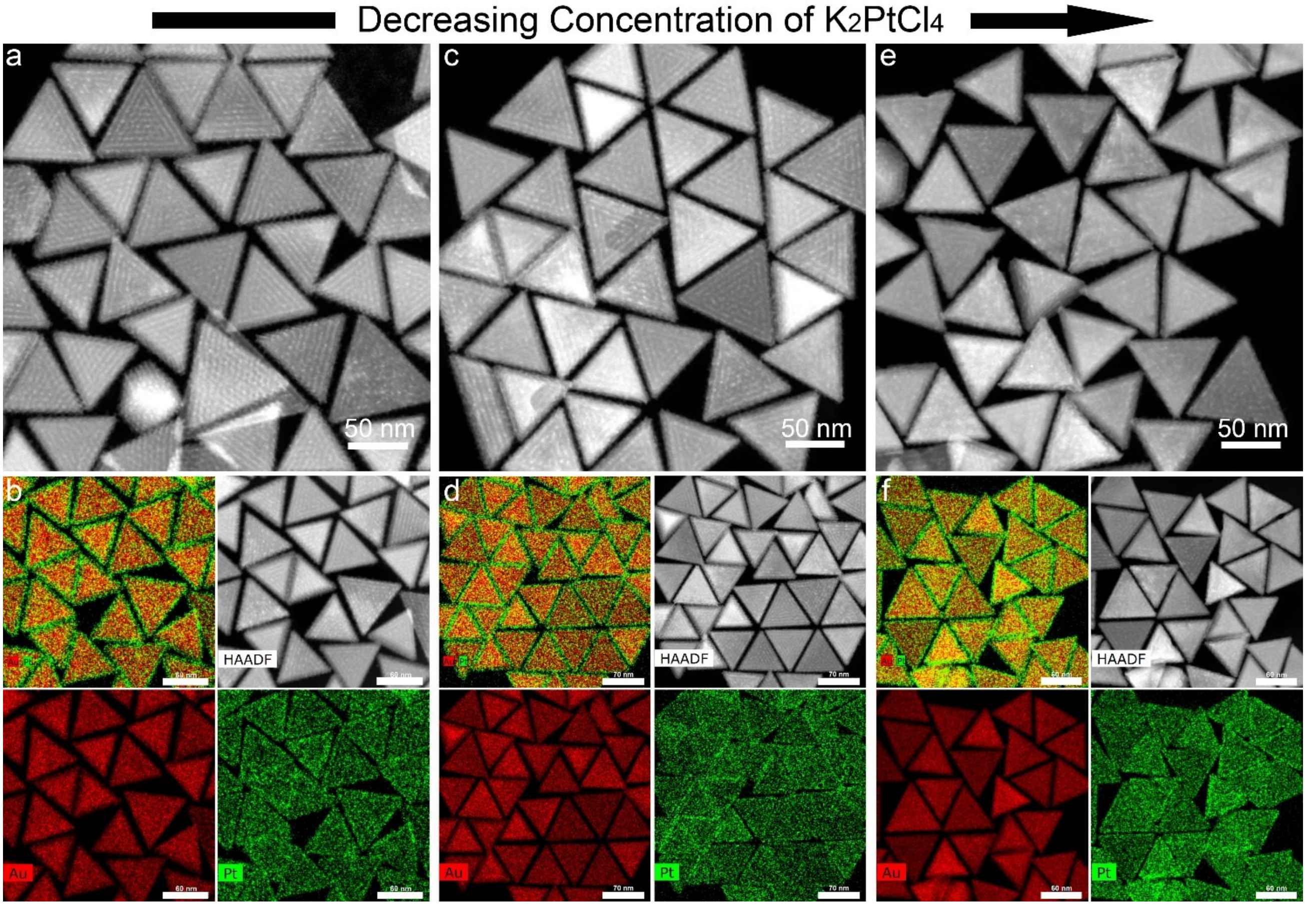


Figure S14. Morphology evolution of Au NT-Pt NPs synthesized using SA as reductant when changing the concentration of K_2PtCl_4. The scale bar in (b) & (f) is 60 nm, in (d) is 70 nm.

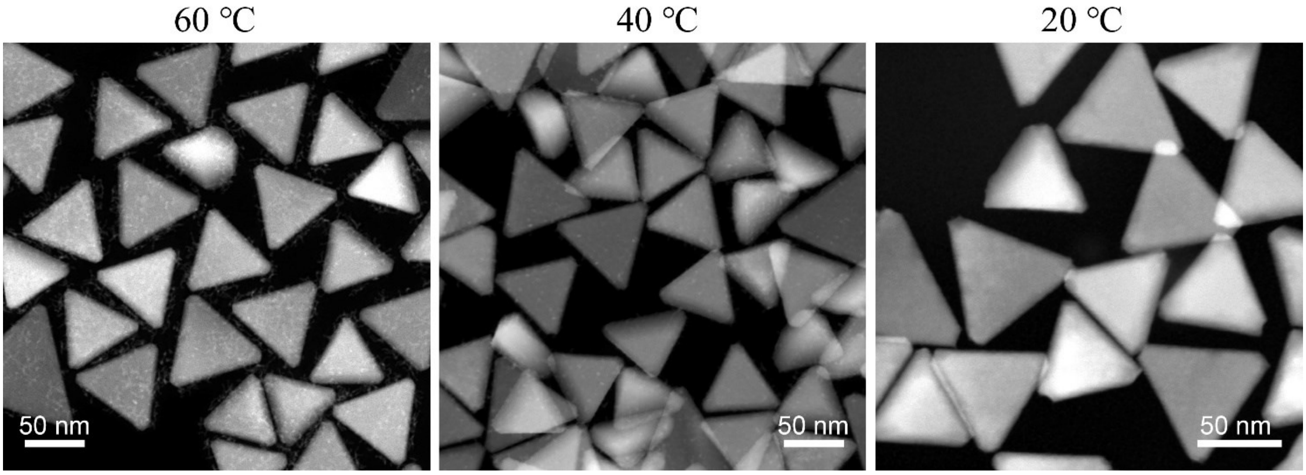


Figure S15. Shape evolution of Au NT-Pt NPs synthesized at different temperatures (indicated on top) using AA as reductant.

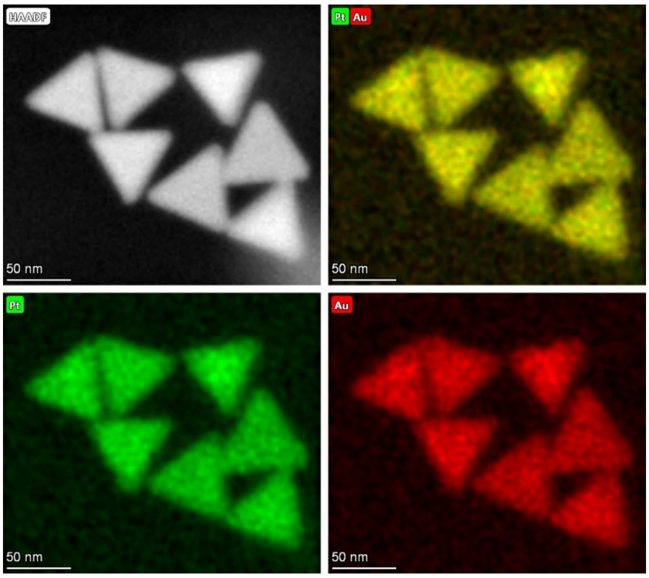


Figure S16. EDS maps of Au NT-Pt NPs synthesized at 20 °C using AA as reductant.

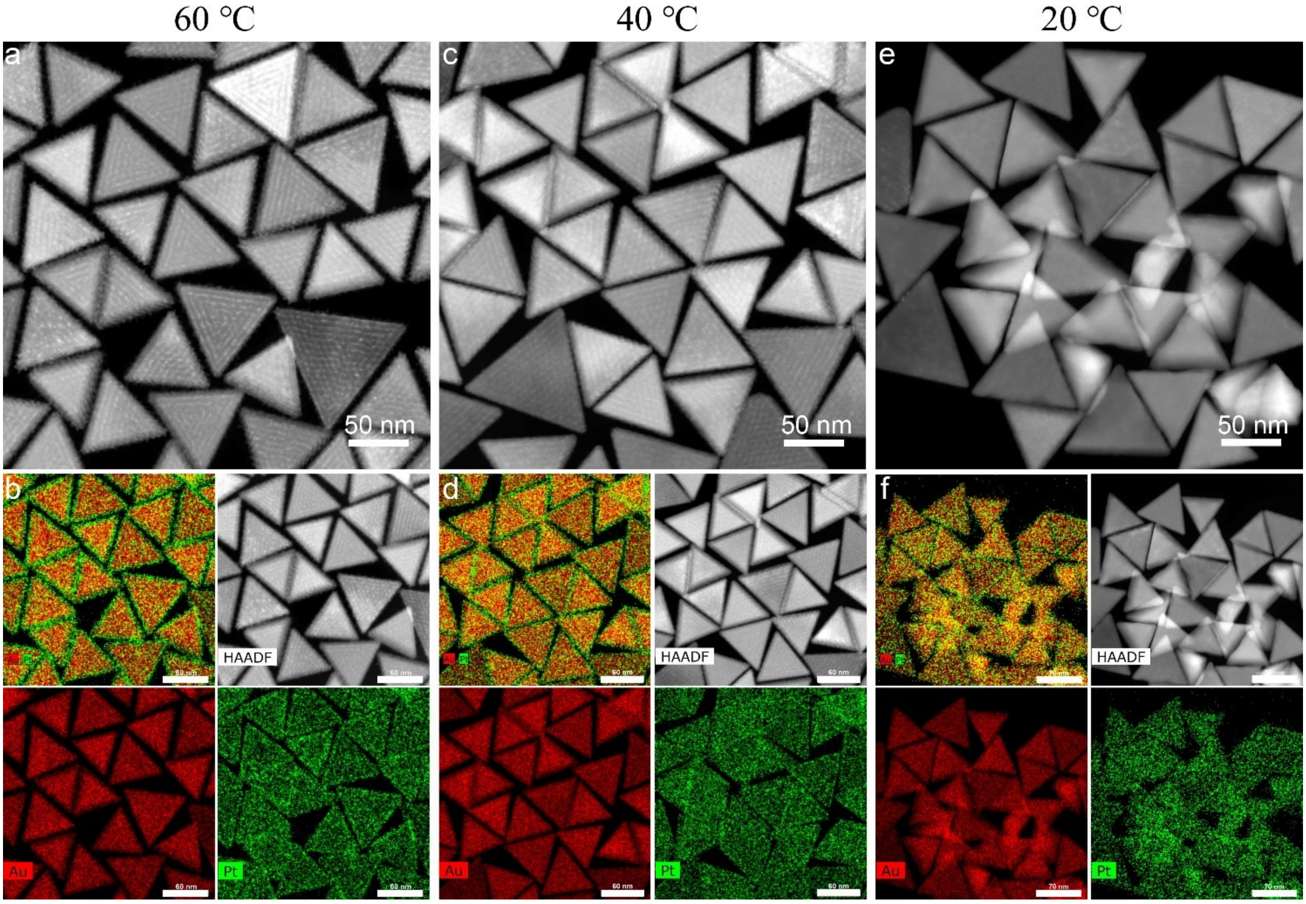


Figure S17. Shape evolution of Au NT-Pt NPs synthesized at different temperatures using SA as reductant. The scale bar in (b) & (d) is 60 nm, in (f) is 70 nm.

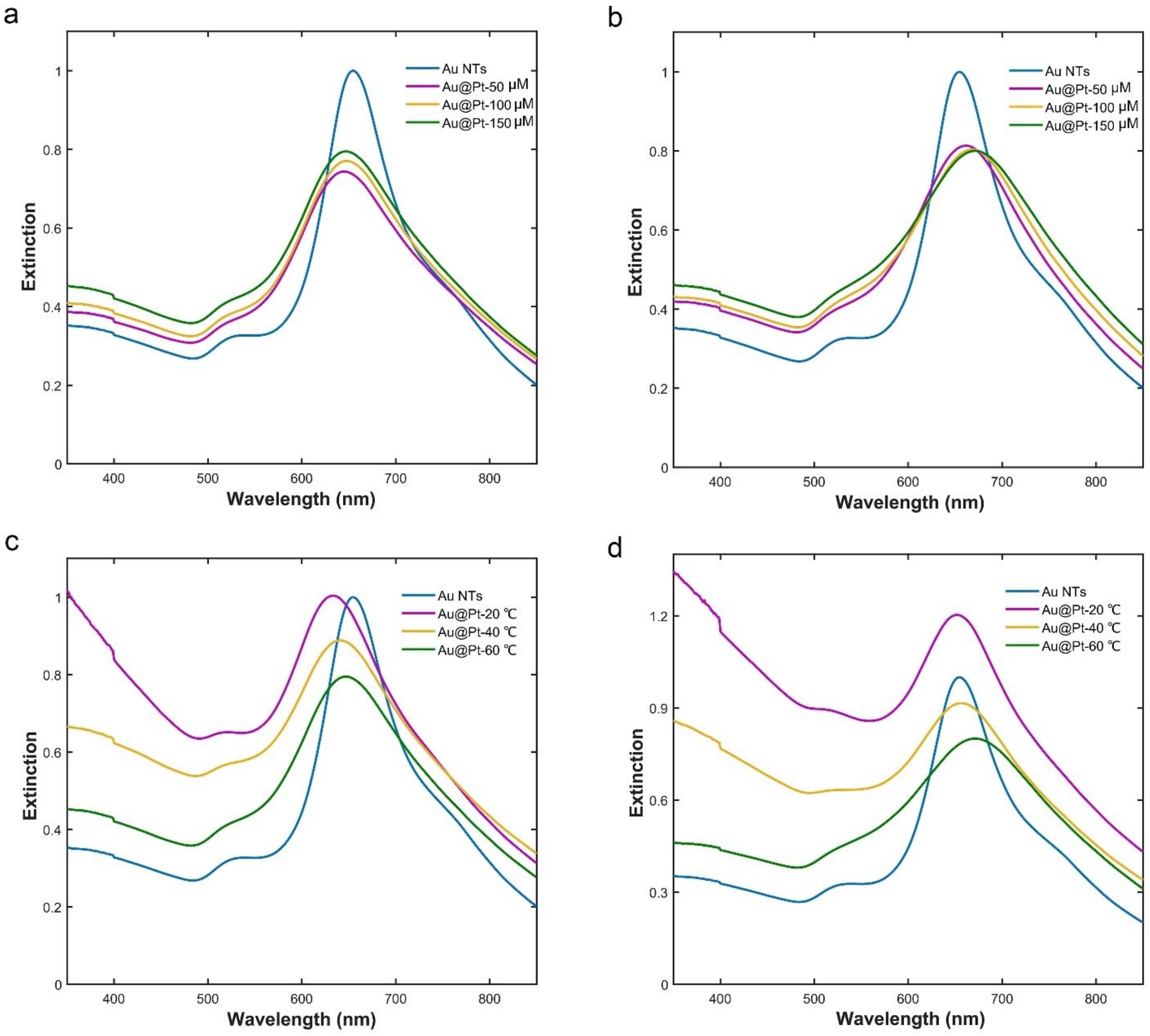
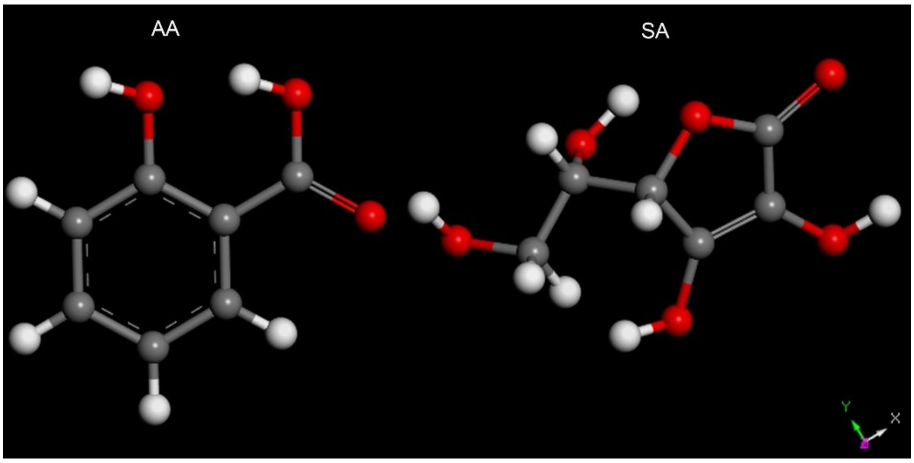


Figure S18. UV-VIS spectrum of Au NT-Pt NPs synthesized at different conditions. (a) Using AA and changing the concentration of K_2PtCl_4 (μM); (b) Using SA and changing the concentration of K_2PtCl_4 (μM); (c) Using AA and changing the reaction temperature; (d) Using SA and changing the reaction temperature.



Scheme S1. Molecule structure of AA and SA. Gray ball: carbon atom, red ball: oxygen atom, and white ball: hydrogen atom.

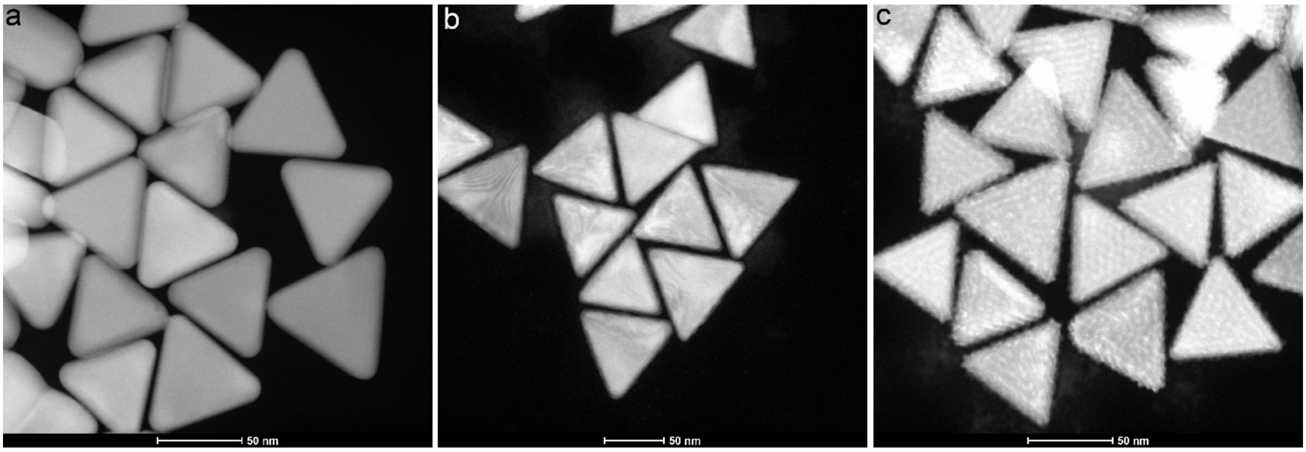


Figure S19. STEM images of Au NT-M NPs synthesized using SA as reductant. The concentration of SA in each reaction was 900 µM. a) Au NT@Ag, b) Au NT@Pd, and c) Au NT@Pt.

References:

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