

Supporting Information

Oxidative Etching and Metal Overgrowth of Gold Nanorods within Mesoporous Silica Shells

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Experimental Details

1. AuNRs synthesis

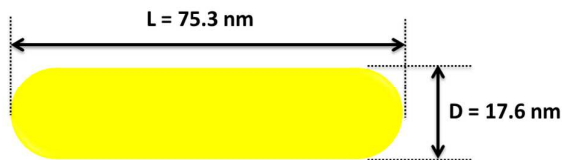
The AuNRs were synthesized using a modified seed-mediated method.^[1] The seed solution was prepared by the addition of HAuCl₄ (0.05 M, 50.0 μ L) into CTAB (0.1 M, 10.0 mL) in a 20 mL scintillation glass vial. A freshly prepared NaBH₄ solution (0.01 M, 0.60 mL) was then quickly injected into the Au(III)-CTAB solution under vigorous stirring (1200 rpm) for 2 min. The seed solution was kept at 30 °C for at least 30 min before usage. To grow AuNRs, CTAB (7.0 g) and NaOL (1.234 g) were dissolved in warm water (~50 °C, 250 mL). Then the solution was allowed to cool down to 30 °C and AgNO₃ solution (0.01 M, 7.2 mL) was added. The solution was left

undisturbed for 15 min, followed by the addition of HAuCl_4 solution (1 mM, 250 mL). The solution was kept stirring for 90 min (400 rpm), and then HCl (37 wt. % in water, 2.1 mL) was added and stirred (400 rpm) for another 15 min. After that, ascorbic acid (0.064 M, 1.25 mL) was added and the solution was stirred vigorously for 30 s. Finally, the seed solution (0.80 mL) was injected into the growth solution. The solution was stirred for 1 min and left undisturbed for 12 h at 30 °C for AuNR growth.

2. Meso-SiO₂ coating

Before meso-SiO₂ coating, the as-synthesized AuNRs solution (400 mL) was centrifuged at 6000 rpm for 30 min followed by removal of the supernatant. The precipitate was re-dispersed in water and centrifuged again. Then the precipitate was re-dispersed into a CTAB solution (120 mL, 1.5 mM). NaOH solution (0.1 M, 1.2 mL) was added while stirring (400 rpm), followed by three additions of TEOS solution (20 v% in methanol, 0.36 mL) at 60 min intervals. The reaction was allowed to continue while stirring for 2 days, resulting in a meso-SiO₂ shell thickness of ~18 nm. The resulting particles were washed with water and methanol, and dispersed in methanol (200 mL) for etching experiments.

3. Estimate the particle concentration



The shape of the nanorod was treated as a cylinder capped with two hemispheres at both ends. The volume thus can be calculated by the following formula: $V_{rod} = \frac{1}{4}\pi D^2(L - D) + \frac{1}{6}\pi D^3$. The length and diameter were determined from TEM images. The gold nanorod is a single crystal with face-centered cubic (*fcc*) structure. The volume occupied by a single gold atom in *fcc* lattice can be calculated by using the lattice constant of Au crystal ($a = 0.408$ nm), that is, $V_{atom} = \frac{1}{4}a^3$. So each

nanorod contains $N = V_{rod}/V_{atom}$ of Au atoms. Finally, the number of particles in a unit volume (1 mL) can be calculated by $c_{particle} = \frac{\alpha \cdot c \cdot V \cdot N_A}{N}$, where α is a coefficient related to the conversion ratio of gold precursor, c is the molecular concentration of gold precursor (0.5 mM), V is 1 mL, N_A is Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$). We assume that all the ascorbic acid are reacted in the AuNRs synthesis, and 67% of gold precursor is converted into solid AuNRs, α is thus set to be 0.67. The particle concentration was calculated to be $2.0 \times 10^{11} \text{ mL}^{-1}$. This value is slightly higher than the real value, due to incomplete reaction in the synthesis and loss of particles during multi washing steps.

Etched-AuNRs@meso-SiO₂ from intermediate stages were separated from the etching solution by centrifugation and re-dispersed into methanol solution to prevent further etching. The results are shown in Figures 1-3 and Figures S1-S4.

4. Control experiments on the oxidative etching of AuNRs@meso-SiO₂

4.1 The final product after complete oxidation. To prove that the final product was Au(III), an equal volume of 0.1 M CTAB solution was mixed with the final solution, and extinction spectra were measured with and without CTAB (Figure S5).

4.2 The role of O₂ – as oxidant. The setup for etching under an inert N₂ atmosphere was composed of a 50 mL two-neck round bottom flask with a water cooled condenser, connected to a Schlenk line via which dry N₂ and vacuum could be introduced to the system. First, the round bottom flask was made water free, by putting it in an oil bath at 70 °C and applying multiple vacuum/N₂ cycles. Next, 6.0 mL of AuNRs@meso-SiO₂ in methanol were added under a N₂ flow. To remove all O₂ from the system, 10 vacuum/N₂ cycles were performed at room temperature. Before adding 0.12 mL of HCl (37 wt. % in water), the AuNRs@meso-SiO₂ solution was kept under N₂ for 45 minutes. Thereafter, the connection to the Schlenk line was closed to prevent HCl to evaporate out of the system, and the round bottom flask was put in an oil bath at 70 °C under stirring (400 rpm) for 2 h. The extinction spectra and TEM images before and after etching are shown in Figure S6.

4.3 Etching at room temperature. 40.0 μL HCl (37 wt. % in water) was added into 2.0 mL AuNRs@meso-SiO₂ methanol solution in a cuvette. The cuvette was gently shaken for 10 s. The cap

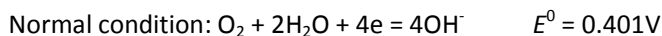
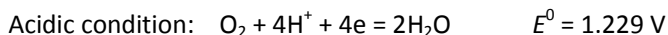
of the cuvette was closed, and sealed with several layers of parafilm. The oxidation process was monitored by measuring extinction spectra as a function of oxidation time. The measurements were repeated automatically with 1 h time intervals. The extinction spectra are shown in Figure S7.

4.4 Porosity of the silica shell. To reduce the porosity of the mesoporous silica layer to the ultra-microporous regime (pores less than 0.3 nm),^[2] a Söber silica layer was grown over the mesoporous shell. To grow this layer the mesoporous silica-coated nanoparticles were dispersed in a mixture of 9.0 mL of methanol, 0.50 mL water and 0.50 mL ammonium solution. Three injections of TEOS (20 v% in methanol, 30.0 μ L) with 60 min intervals were conducted and the reaction was allowed to continue for 1 day under stirring. The resulting particles were washed with water and methanol, and dispersed in methanol for the etching experiments. The oxidation etching was carried out in 10.0 mL methanol solution with 0.20 mL HCl (37 wt. % in water) at 70 °C for 2 h. The extinction spectra and TEM images during varied etching stages are shown in Figure S8.

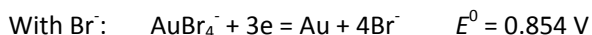
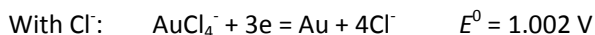
4.5 The role of CTAB in the meso-SiO₂ shells. To remove the CTAB from the meso-SiO₂ shell, the AuNRs@meso-SiO₂ methanol solution was dried at 70 °C overnight, and calcined at 500 °C for 6 h in air. After calcination, the AuNRs were partially deformed, but still anisotropic. The calcined particles were re-dispersed in methanol for etching experiments. The etching was carried out in 10.0 mL methanol solution with 0.20 mL HCl (37 wt. % in water) at 70 °C for 15 h. The extinction spectra and TEM images during varied etching stages are shown in Figure S9.

5. Standard reduction potentials (E^0 , vs the normal hydrogen electrode (NHE)) of half reactions^[3]

O₂ half reaction



Au(0)/Au(III) reaction



Supported Figures

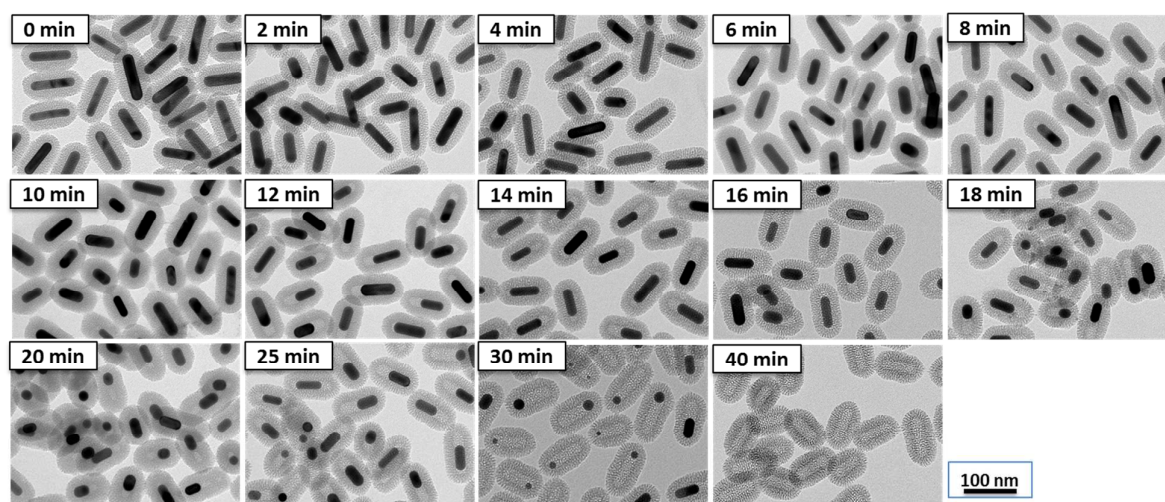


Figure S1. TEM images of AuNRs@meso-SiO₂ at different etching stages. The scale bar for all the images is shown in bottom-right of the image. The oxidation reaction was carried out at 70 °C and with 0.2 mL HCl per 10 mL methanol.

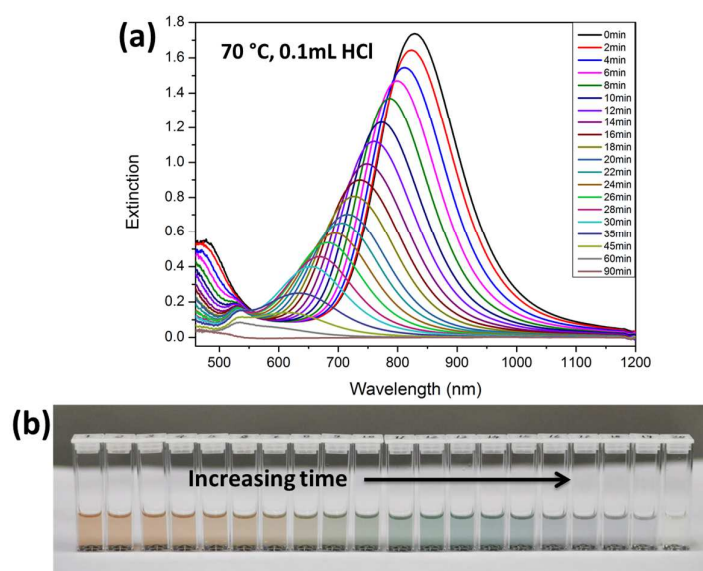


Figure S2. The extinction spectra (a) and the digital photograph (b) show the different stages during oxidative etching of AuNRs with less HCl. The oxidation reaction was carried out at 70 °C with 0.1 mL HCl in 10 mL methanol. The etching speed was 5.9 nm/min. The photograph shows the samples that were taken from the etching solution at different oxidation times.

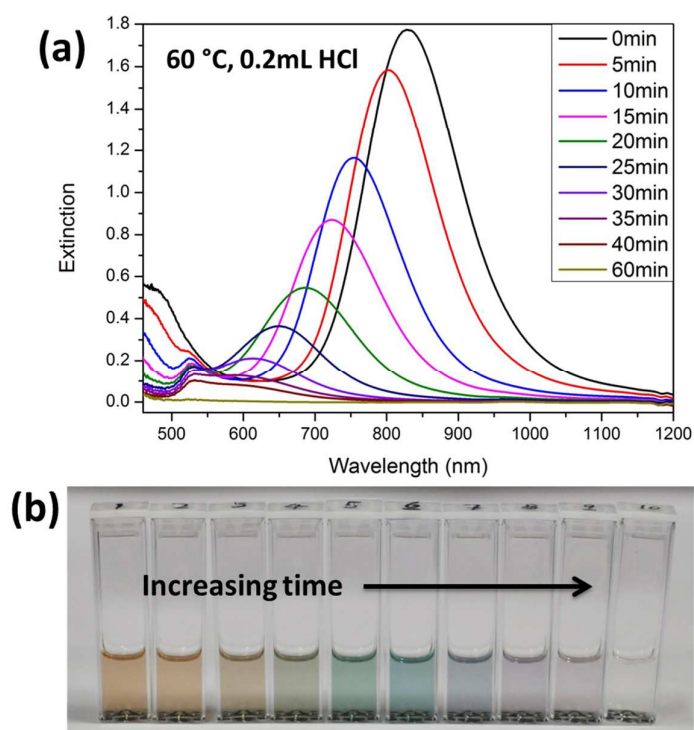


Figure S3. The extinction spectra (a) and the digital photograph (b) show the different stages during oxidative etching of AuNRs with lower temperature. The oxidation reaction was carried out at 60 °C with 0.2 mL HCl in 10 mL methanol. The etching speed was 7.2 nm/min. The photograph shows the samples that were taken from the etching solution at different oxidation times.

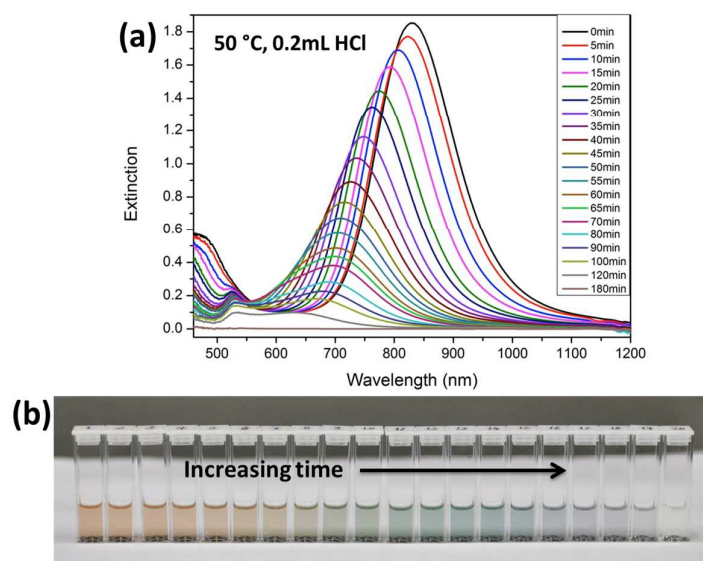


Figure S4. The extinction spectra (a) and the digital photograph (b) show the different stages during oxidative etching of AuNRs with lower temperature. The oxidation reaction was carried out at 50 °C with 0.2 mL HCl in 10 mL methanol. The etching speed was 7.2 nm/min. The photograph shows the samples that were taken from the etching solution at different oxidation times.

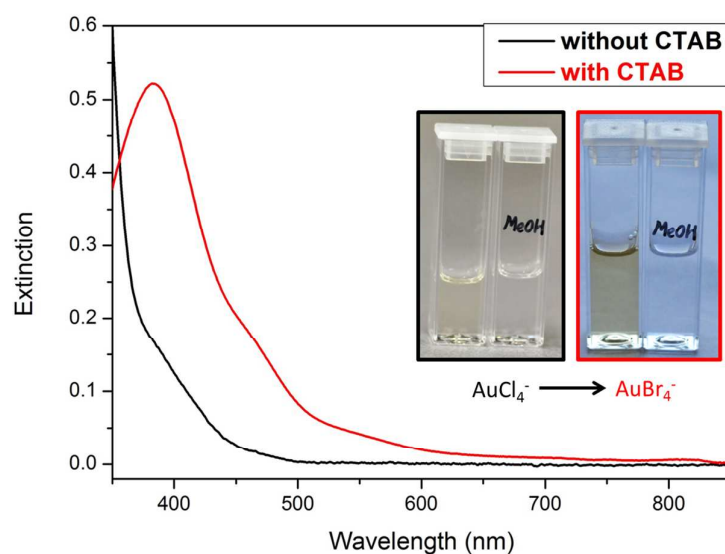


Figure S5. The extinction spectra and digital photographs (insets) show the final etching solution before and after mixing it with CTAB. The black curve was measured directly after the completion of the oxidation reaction, while the red curve was measured after mixing the final solution with certain amount of 0.1 M CTAB solution. The red curve has a peak at ~ 400 nm, which is caused by the metal-ligand charge transfer absorption of the AuBr_4^- complex.^[4] Directly after the oxidation reaction, the solution was a little yellowish, but changed to dark yellow in presence of CTAB.

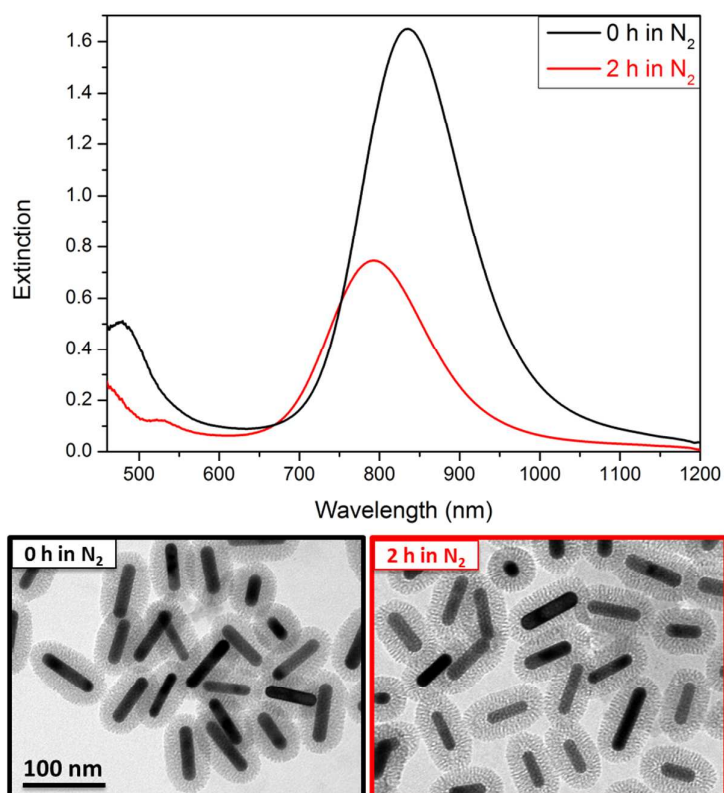


Figure S6. Oxidation in N₂ inert atmosphere. Oxidation reaction was carried out at 70 °C, 0.2 mL HCl in 10 mL methanol. LSPR peak only blue-shifts 43 nm after etching for 2 h. The oxidation speed is much slower than the oxidation in air, suggesting that O₂ is the oxidizing agent and necessary for completing for the reaction. The TEM images show the AuNRs@meso-SiO₂ before (black) and after etching (red). After etching for 2 h, the AuNRs were partially dissolved, as shown in the image. For both TEM images, the scale bar is shown in bottom left of the image.

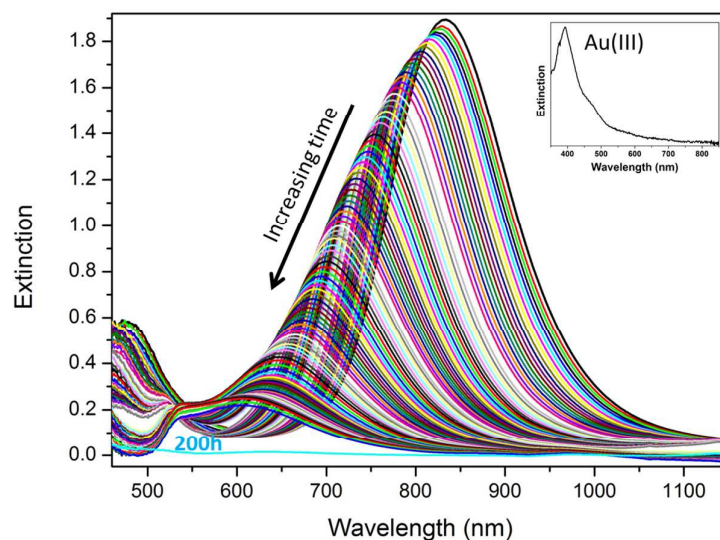


Figure S7. Oxidation at room temperature. Oxidation reaction was carried out at $\sim 20^\circ\text{C}$ in 0.2 mL HCl per 10 mL methanol. The oxidation could still proceed, but at much lower speed ($< 3\text{ nm/h}$). The oxidation was finished in 200 h, as indicated by the disappearance of extinction peak and almost zero in intensity. This suggests that heating is not required for complete oxidation. The inset shows the extinction spectrum after mixing the final etching solution with CTAB. The appearance of the peak at around 400 nm shows that Au(III) is the final oxidation product.^[4]

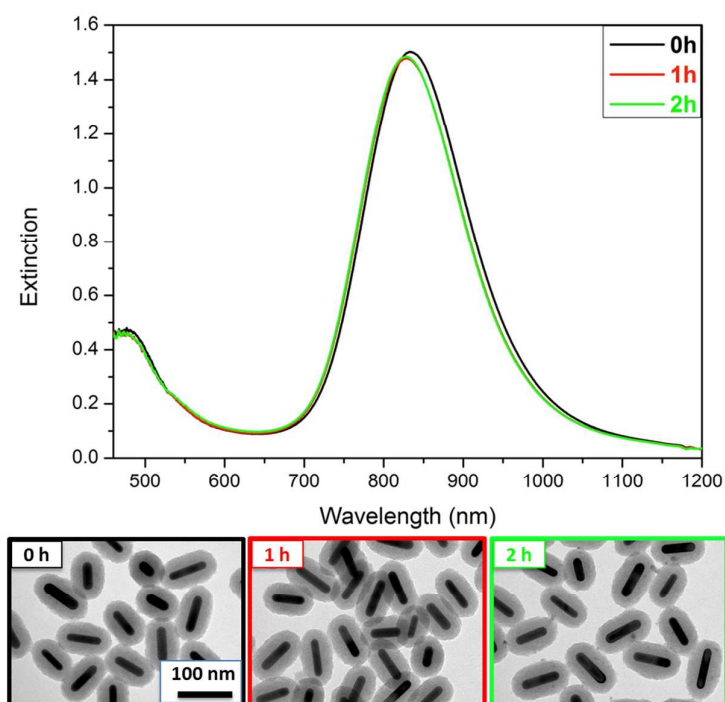


Figure S8. The extinction spectra (top) and TEM images (bottom) show that a Stöber SiO₂ shell coating can effectively prevent etching of AuNRs. The oxidation reaction was carried out at 70 °C, 0.2 mL HCl in 10 mL methanol. The LSPR peak only blue-shifts 5 nm after etching for 2 h, suggesting the accessibility of the AuNR in a Stöber SiO₂ shell is very limited. Thus, the meso-porosity of the SiO₂ shell is mandatory for oxidative etching of AuNRs. Also the TEM images of AuNRs@meso-SiO₂ before and after etching show no obvious etching. The scale bar is shown in bottom-left of the image.

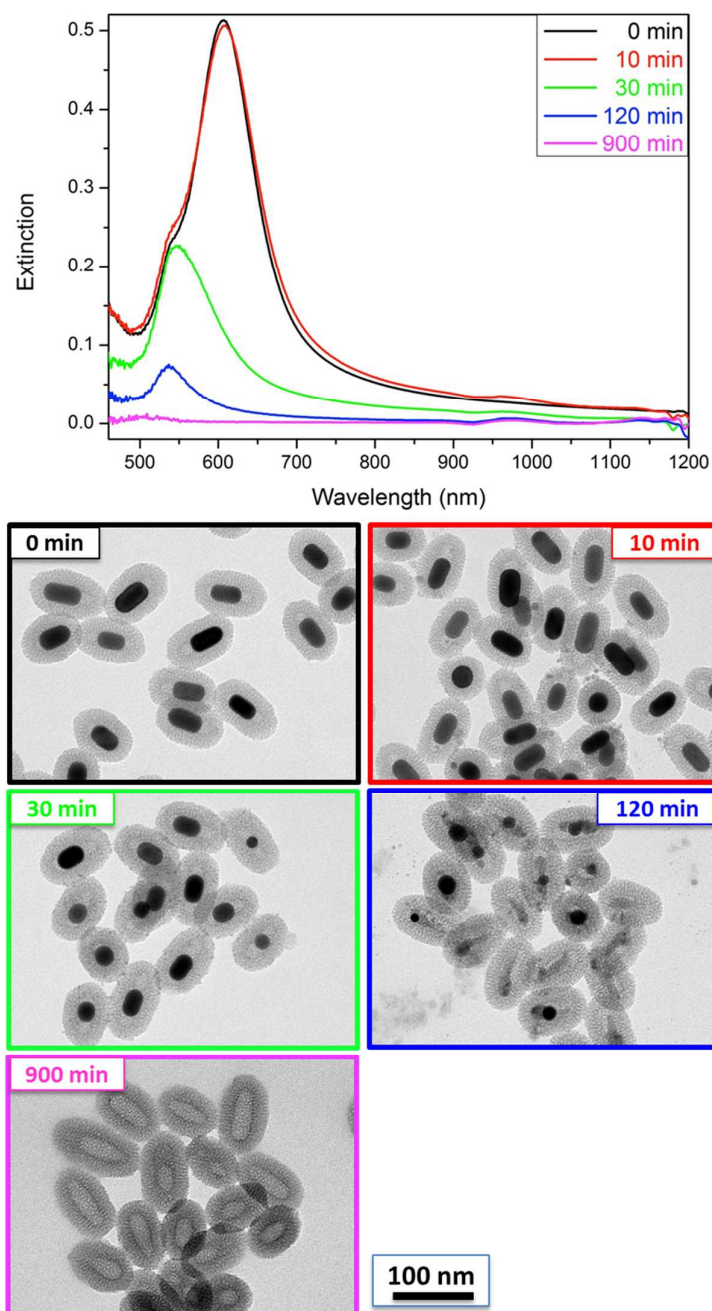


Figure S9. Oxidation after removal of CTAB in meso-SiO₂ shell. Before oxidation, CTAB from meso-SiO₂ shell was removed by calcination of the AuNRs@meso-SiO₂ particles at 500 °C for 6 h. The calcined particles were re-dispersed in methanol and oxidized at 70 °C in 0.2 mL HCl per 10 mL methanol. The oxidation was completed but slower than for the un-calcined AuNRs. The scale bar for all TEM images is shown in bottom-right of the figure.

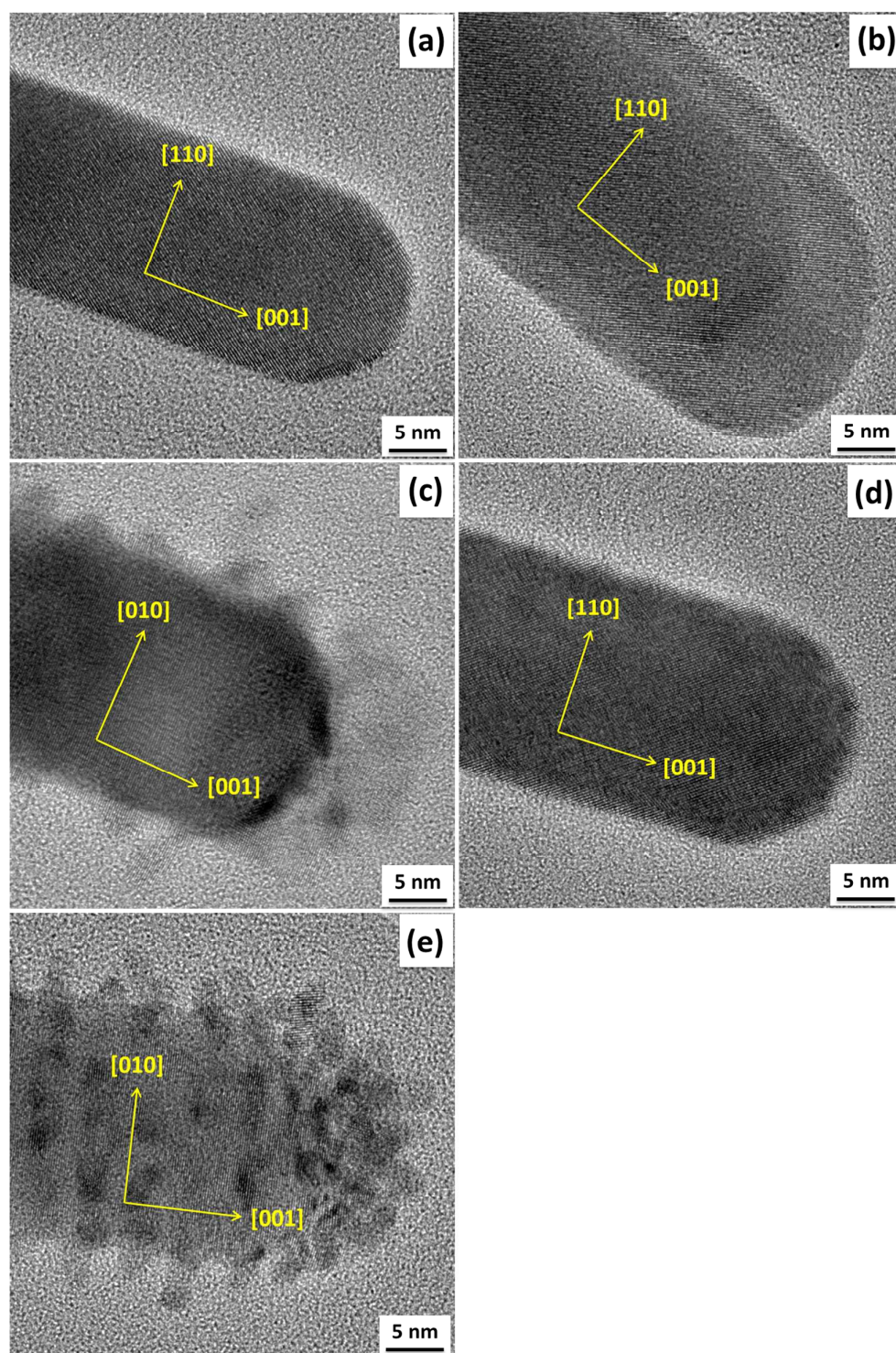


Figure S10. HRTEM images of nanostructures: (a) etched-AuNRs, (b) AuNRs-Ag, (c) AuNRs-Pd, (d) AuNRs-Pt-smooth, and (e) AuNRs-Pt-rough. All AuNRs have the crystallographic $\langle 001 \rangle$ direction along the length of the rod, and are observed to lie on the grid either in a $[110]$ projection (a,b,d), or in a $[100]$ projection (c,e). Ag can be epitaxially grown on AuNR surface, while only a few atomic layers of Pd (or Pt) were epitaxially grown on AuNR, and then Pd (or Pt) nanoparticles were grown on both the sides and ends of the AuNRs.

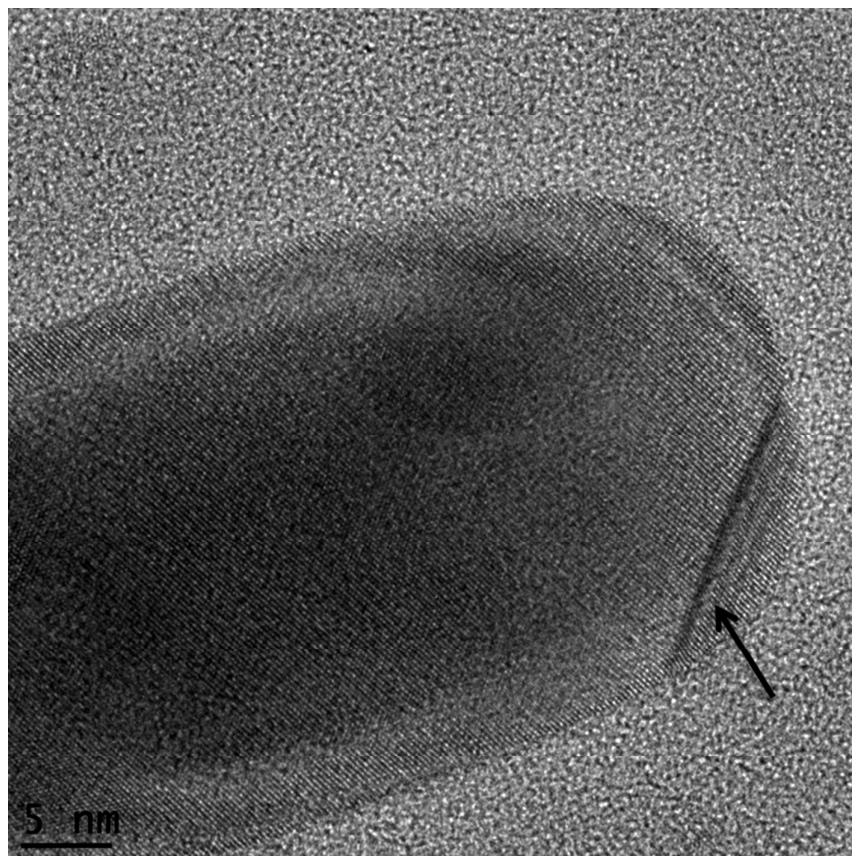


Figure S11. HRTEM image of a AuNRs-Ag nanostructure. A line defect is shown at the tip of the structure as indicated by the arrow.

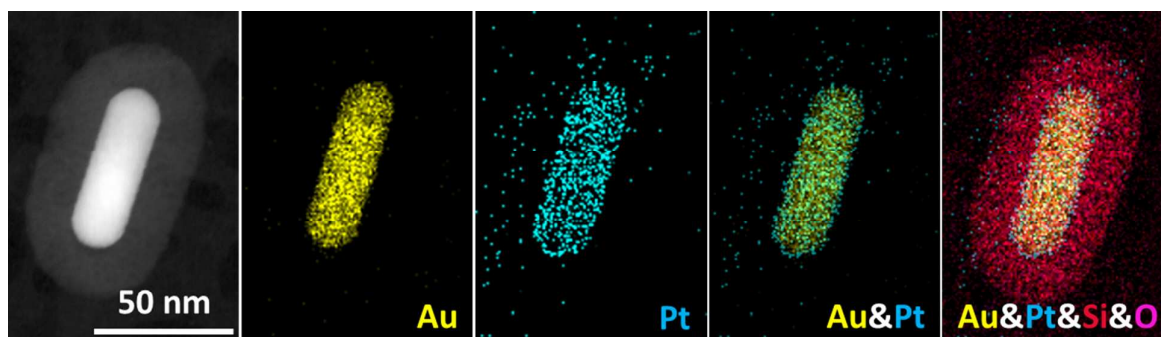


Figure S12. EDX mapping of a AuNRs-Pt-smooth nanostructure. The HAADF-STEM image, Au, Pt, Au&Pt, and Au&Pt&Si&O were illustrated sequentially from left to right.

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