

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

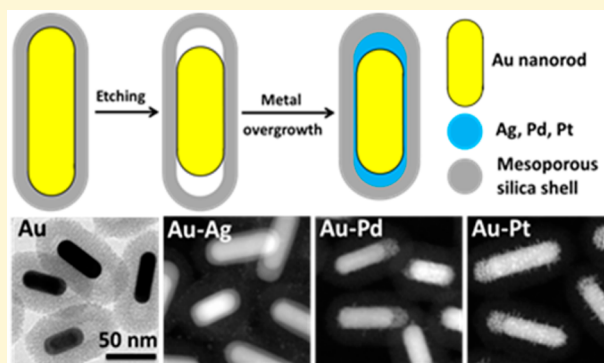
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Supporting Information

ABSTRACT: Composite noble metal-based nanorods for which the surface plasmon resonances can be tuned by composition and geometry are highly interesting for applications in biotechnology, imaging, sensing, optoelectronics, photovoltaics, and catalysis. Here, we present an approach for the oxidative etching and subsequent metal overgrowth of gold nanorods, all taking place while the nanorods are embedded in mesoporous SiO₂ shells (AuNRs@meso-SiO₂). Heating of the AuNRs@meso-SiO₂ in methanol with HCl resulted in reproducible oxidation of the AuNRs by dissolved O₂, specifically at the rod ends, enabling precise control over the aspect ratio of the rods. The etched-AuNRs@meso-SiO₂ were used as a template for the overgrowth of a second metal (Ag, Pd, and Pt), yielding bimetallic, core-shell structured nanorods. By varying the reaction rates of the metal deposition both smooth core-shell structures or gold nanorods covered with a dendritic overlayer could be made. This control over the morphology, including metal composition, and thus the plasmonic properties of the composite rods were measured experimentally and also confirmed by Finite-Difference Time-Domain (FDTD) calculations. The presented synthesis method gives great control over tuning over both plasmonic properties and the particle stability/affinity for specific applications.



INTRODUCTION

Gold nanorods (AuNRs) possess two different surface plasmon resonances, one associated with a longitudinal and the other with a transverse mode of oscillations of the conduction electrons. The transverse surface plasmon resonance (TSPR) is in the visible spectrum with a wavelength around 510–540 nm, whereas the longitudinal surface plasmon resonance (LSPR) can be varied from the visible (~600 nm) to near-infrared wavelength range (>1200 nm), depending on the aspect ratio of the nanorod.^{1–4} The tunable properties of the LSPR and the strong local electromagnetic field enhancements that can be realized close to the nanoparticle make AuNRs useful for a broad range of application fields that include sensing, such as in surface-enhanced Raman scattering (SERS)^{5,6} or through changes in refractive index,⁷ plasmon enhanced fluorescence,^{8–10} optoelectronics,¹¹ data storage,¹² photothermal therapy,^{13,14} (in vivo) imaging,^{15–17} and biomedicine.^{18,19} For the present work, it is important to mention that for the different applications, sometimes even opposite requirements are optimal with respect to the plasmonic properties of the particles. For instance, excessive damping of the plasmon resonance is detrimental for many applications in optoelectronics and plasmon field enhancement methodologies (such as in SERS and plasmon enhanced fluorescence), while the

generation of heat out of plasmon induced by light absorption is what makes certain imaging¹⁷ and medical applications^{13,14} possible. For some applications, like catalysis and SERS, a rough metal interface is often measured or predicted to be advantageous. For other applications like in a femtosecond-light-pulse that induces a change in the aspect ratio of AuNRs which has been used in a data storage application,¹² a smooth defect free AuNR is optimal. For almost all applications, control over the actual position of the LSPR is important as well. For pure AuNRs, this tuning is possible through the aspect ratio. If composite particles, as studied in the present article, are an option, the composition in combination with the morphology provide an even wider spectrum of possibilities to tune the plasmonic properties.²⁰

In principle, the aspect ratio of the AuNRs can be controlled during synthesis and/or via postselective-etching afterward. Presently, AuNRs are usually synthesized via a so-called seed-mediated growth method,^{21–23} under the influence of the shape directing and stabilizing surfactant hexadecyltrimethylammonium bromide (CTAB) and shape inducing agent Ag, whereby

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the aspect ratio of the AuNRs can roughly be controlled by tuning the acidity of the growth solution. However, selective etching²⁴ after particle growth allows for more precise control of the aspect ratio. This has already been successfully shown for mild oxidation by cyanide,²⁵ Au(III),²⁶ O₂,²⁷ and H₂O₂.²⁸ The etching preferentially takes place at the ends of the nanorods,^{26–28} leaving the diameter unchanged. Thus, the AuNRs are selectively shortened, enabling more precise control over the aspect ratio. So far, these etching processes were performed in AuNRs solutions with high CTAB concentrations as stability with metal particles is always an issue at higher ionic strengths because of the large Hamaker constants and thus van der Waals forces for these systems. However, the toxicity of CTAB is problematic when using bare AuNRs for *in vivo* studies.^{18,19} Also in applications such as catalysis, the presence of a dense surfactant layer on the particles is undesirable, for it makes the Au metal surface inaccessible for reactants.²⁹ Therefore, a different stabilizing mechanism based on a nontoxic mesoporous silica layer^{30,31} overcomes these problems with CTAB, as the silica coating significantly reduces the van der Waals forces, and is compatible with almost any solvent by surface modification, while keeping the AuNR accessible for surrounding molecules.³² For example, Zhang et al.¹⁵ demonstrated that multilayer-coated AuNRs (with a dyed SiO₂ shell and polymer layer) exhibited ultrahigh colloidal stability and excellent tunability, which makes them suitable for *in vivo* fluorescence imaging, SERS detection, and photothermal therapy. Apart from many developed coating schemes, an SiO₂ coating has also advantages in chemical and mechanical stabilities (including increased stability against temperature induced shape changes of AuNRs³²), a tunable porosity, and optical transparency.^{33,34} A thin SiO₂ shell also can act as a “spacer” to control the coupling distance between metal particles with other metal particles and molecules, and thus can be used to optimize SERS³⁰ and plasmon enhanced fluorescence.³⁵ In addition, the benefits of a silica shell in the growth of bimetallic nanorods were already demonstrated^{36,37} in at least two papers. In the first paper, Au nanoparticles grown inside empty silica shells were used to seed the growth of other metals within the rod-like silica shells.³⁶ In ref 37, patchy silica layers were grown around AuNRs at the particles’ ends or midsections. Subsequently, the noncoated regions could be overgrown by another metal. Such bimetallic AuNR-metal nanostructures have unique plasmonic properties^{37,38} and catalytic activities,^{39,40} both caused by unique combinations of the properties of the two metals.

Here, we report a novel approach in which we oxidatively etched monodisperse AuNRs within meso-SiO₂ shells by dissolved O₂ at the tips of the nanorods only, enabling a precise control over the aspect ratio. The oxidation speed could be varied by changing the acid concentration and/or temperature. Furthermore, we show that it is possible to overgrow the resulting AuNRs by several noble metals in the mesoporous shells. The plasmonic properties of the AuNRs-metal nanostructures were studied both experimentally and by means of FDTD calculations.

RESULTS AND DISCUSSION

AuNRs were synthesized using a modified seed-mediated method⁴¹ and coated with a meso-SiO₂ shell.³¹ For oxidative etching, the AuNRs@meso-SiO₂ in methanol was mixed with certain amounts of HCl dissolved in water and then kept at a specific increased temperature under gentle stirring (for

experimental details, see [Experimental Section](#) and [Supporting Information](#) (SI)). The etching process was monitored by measuring the extinction spectra as a function of the oxidation time after quenching the reaction to room temperature by dilution in methanol. Digital photographs and transmission electron microscopy (TEM) images were also taken at different oxidation times. [Figure 1a](#) shows the extinction spectra

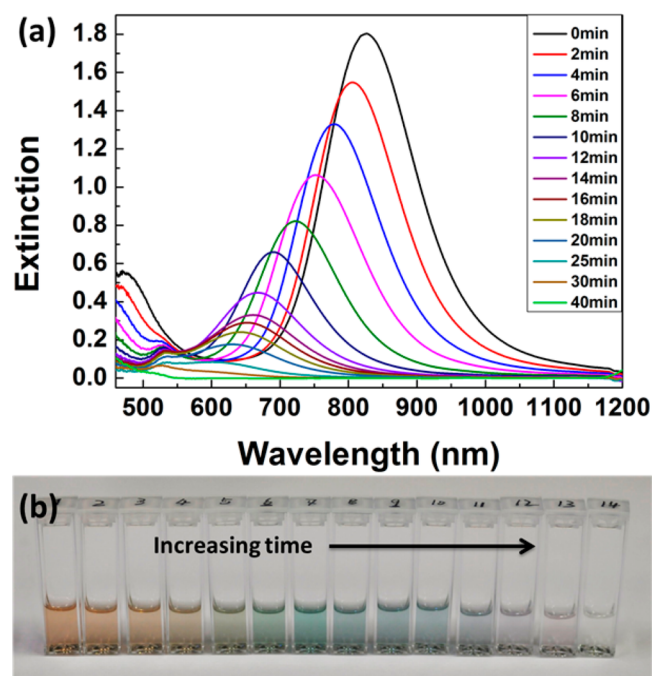


Figure 1. AuNRs were oxidatively etched by adding 0.2 mL of HCl to 10 mL of AuNRs@meso-SiO₂ methanol solution at 70 °C. (a) Extinction spectra acquired with increasing etching time. The LSPR peak blue-shifts, and the intensity decreases during oxidation due to “shortening” of the rods. (b) A digital photograph of the samples taken out with varying oxidation time for extinction spectra measurements. The shift in the LSPR peak caused a continuous color change during etching.

measured at different times after the oxidation was started by the addition of HCl solution in water. The LSPR peak of the AuNRs@meso-SiO₂ before etching was found at 827 nm with intensity 1.80 in a 1.0 cm cuvette. We estimate (see [SI](#)) a particle concentration of $2.0 \times 10^{11} \text{ mL}^{-1}$. The LSPR peak was found to blue-shift, and the intensity was found to decrease during the oxidation as expected by the decreasing aspect ratio, while the TSPR peak stayed at $\sim 520 \text{ nm}$ and decreased in intensity. Finally, after 40 min the AuNRs were oxidized completely, as indicated by the disappearance of any extinction peak and almost zero intensity. [Figure 1b](#) shows a digital photograph of the appearance of the dispersions of the etched-AuNRs@meso-SiO₂ at different stages. The color of the solution changed due to the varying LSPR peak. After complete oxidation of the AuNRs, the solution turned yellowish, indicating that the final oxidation product is Au(III) as Au(I) is colorless, a result that will be discussed in more detail later.

[Figure 2a](#) shows the AuNRs coated with a meso-SiO₂ shell before etching. The size parameters of initial AuNRs were $75.3 \pm 9.4 \text{ nm}$ in length (L), $17.6 \pm 2.1 \text{ nm}$ in diameter (D), and thus had an aspect ratio (AR) of 4.3 ± 0.7 . Note that for the size parameters not the error in the measurement but the standard deviation (which is related to the width of the

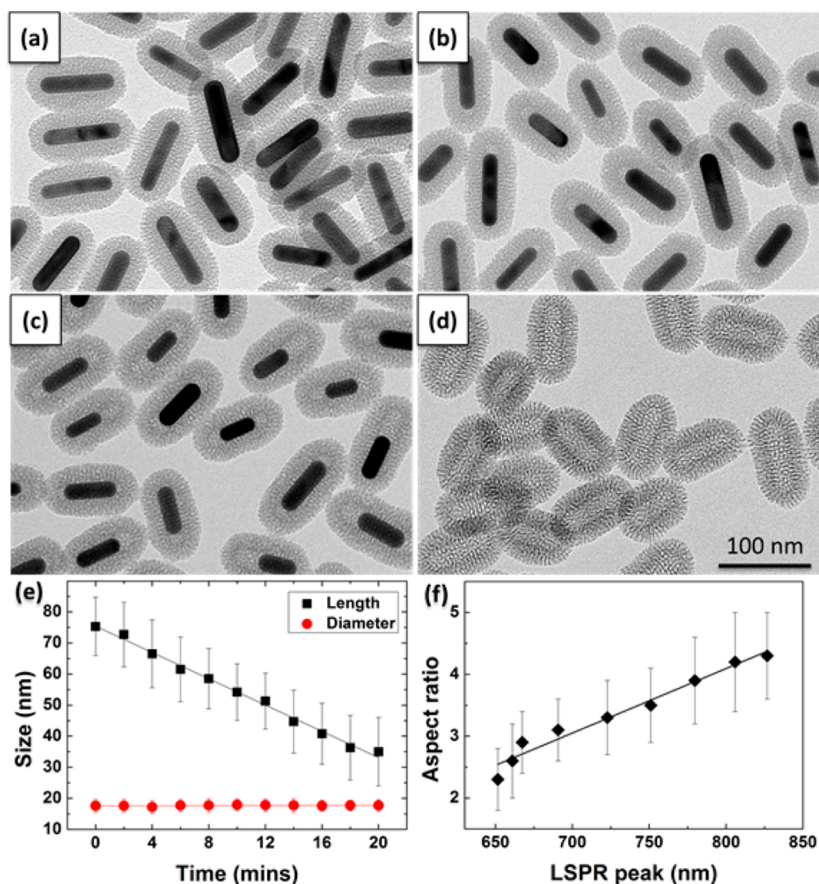


Figure 2. TEM images of AuNRs@meso-SiO₂ at different etching stages (a) $t = 0$ min, LSPR = 827 nm, $L = (75.3 \pm 9.4)$ nm, $D = (17.6 \pm 2.1)$ nm, and $AR = 4.3 \pm 0.7$; (b) $t = 8$ min, LSPR = 723 nm, $L = (58.5 \pm 9.7)$ nm, $D = (17.7 \pm 2.2)$ nm, and $AR = 3.3 \pm 0.6$; (c) $t = 14$ min, LSPR = 661 nm, $L = (44.7 \pm 10.1)$ nm, $D = (17.7 \pm 2.2)$ nm, and $AR = 2.6 \pm 0.6$; and (d) $t = 40$ min, complete etching. Scale bar for a–d is shown on the bottom-right of panel d. (e) Changes of lengths and diameters of AuNRs versus etching time. With increase of the oxidation time, the length of AuNRs decreased while the diameter of AuNRs remained nearly constant. (f) The plot of aspect ratios versus LSPR peaks during etching. The line is a linear fit.

distribution or polydispersity (see S1) and was based on 200–400 particle measurements) is given. It can be seen in Figure 2e that the AuNRs were etched exclusively at the ends of nanorods (see also Figure 2b and c). After complete oxidation, only empty meso-SiO₂ shells were left due to dissolution of the AuNR cores (Figure 2d). A full set of TEM images at different etching stages are given in Figure S1. As mentioned, during the oxidation process, the diameter of nanorods remained nearly constant (Figure 2e) during the etching. Such selective etching of bare AuNRs has been reported before,^{26–28} whereby oxidizing agents such as Au(III), O₂, and H₂O₂ were used. Here, we realized selective etching of the AuNRs within meso-SiO₂ shell. A plot of the aspect ratio versus the LSPR peak shows an approximately linear relationship (Figure 2f), in agreement with previous results.^{1–4} In addition, the polydispersities of the etched-AuNRs in length and diameter were comparable to those of the starting AuNRs (Figure 2e), suggesting fine control of the aspect ratio of AuNRs during etching.

It was found that the oxidation speed of the AuNRs could be controlled by the HCl concentration and/or the temperature (Figure 3 and Figures S2–S4). In both cases, the initial blue-shift of the LSPR peaks was approximately linear with oxidation time. Therefore, the slope of the LSPR position with time can be used to estimate the etching speed. At fixed temperature (70 °C), the oxidation speed was found to increase with increasing

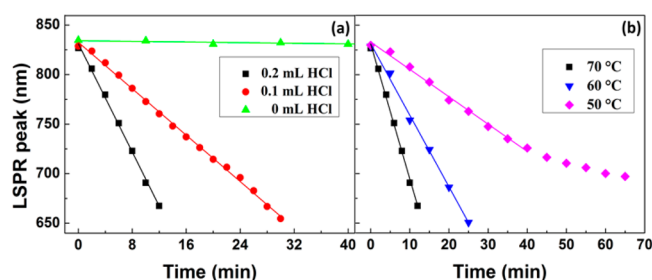


Figure 3. Etching rate of AuNRs@meso-SiO₂ could be controlled via the (a) HCl concentration and (b) temperature. The line is a linear fit. The slopes (etching rates) are <0.01 nm/min, 5.9 nm/min, and 13.7 nm/min for 0 mL of HCl, 0.1 mL of HCl, and 0.2 mL of HCl, respectively, and 7.2 nm/min and 2.8 nm/min for 60 and 50 °C, respectively.

HCl concentrations. For HCl amounts of 0 mL, 0.1 mL, and 0.2 mL, the oxidation speeds were <0.01 nm/min, 5.9 nm/min, and 13.7 nm/min, respectively. The negligible oxidation rate in the absence of HCl indicates that acidic conditions are required for oxidative etching at the conditions of our experiments. The oxidation speed could also be tuned by varying the temperature. At fixed HCl concentration (0.2 mL) but temperatures equal to 60 and 50 °C, the oxidation rates measured were 7.2 nm/min and 2.8 nm/min, respectively. Full extinction spectra

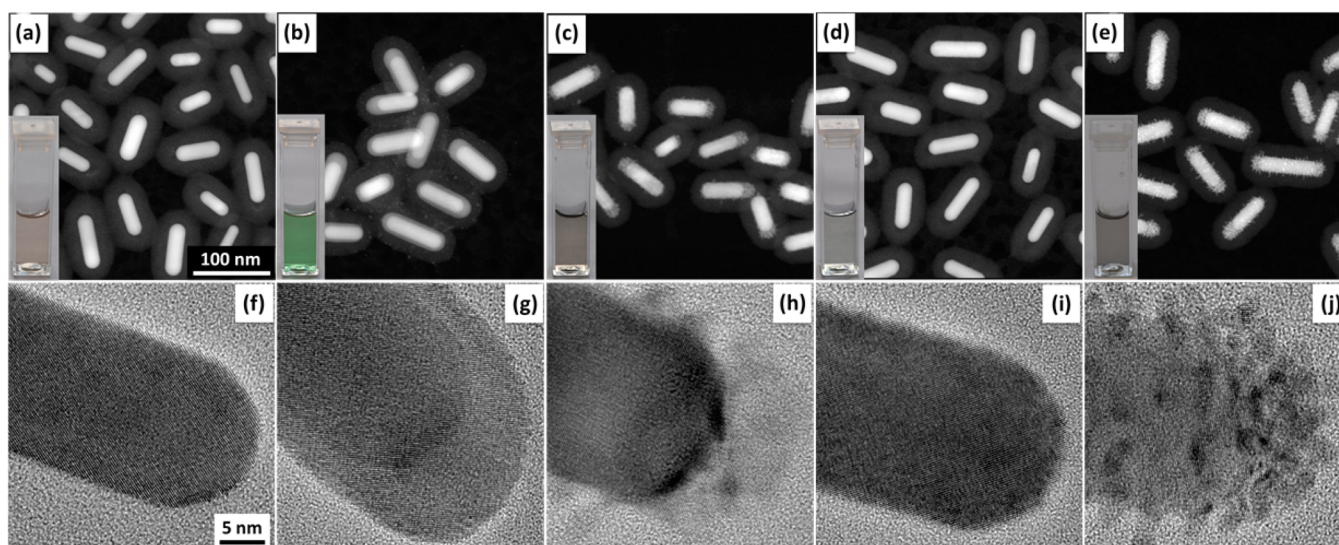
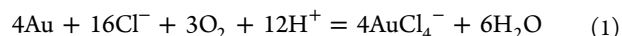


Figure 4. HAADF-STEM and HRTEM images of (a,f) etched-AuNRs@meso-SiO₂, (b,g) AuNRs-Ag@meso-SiO₂, (c,h) AuNRs-Pd@meso-SiO₂, (d,i) AuNRs-Pt-smooth@meso-SiO₂, and (e,j) AuNRs-Pt-rough@meso-SiO₂. The HRTEM images are shown at full resolution in Figure S10. The insets on the bottom-left of a–e are optical images of the samples for extinction spectra measurements.

and digital photographs are shown in Figures S2–S4. As expected (results not shown in detail), the etching speed was also found to depend on the exact details (thickness and pore volume-sizes) of the mesoporous layer. However, for similar conditions etching speeds were reproducible. For this reason, the concentrations of dissolved O₂ were not determined or controlled as also these will vary with many of the parameters used in the etching solution such as amount of water, temperature, and pH. Thus, for fine-tuning the aspect ratio of a particular dispersion of AuNRs@meso-SiO₂, it suffices to determine the initial speed and from this stop at the required aspect ratio by a temperature quench (see also below).

To investigate the oxidative reaction mechanism of the AuNRs in meso-SiO₂ shells in more detail, we performed several control experiments (Figures S5–S9). First, we determined that metallic Au(0) was oxidized to Au(III) in the following way: after the reaction was completed, the solution was mixed with a certain amount of CTAB aqueous solution. The peak that appeared around 400 nm coloring the solution a clear yellow (Figure S5, inset) was caused by the metal–ligand charge transfer absorption of AuBr₄[−],^{26,28} which suggests that Au was present as Au(III) (Figure S5). Second, the presence of O₂ in the air above the etching solution is required for the complete dissolution of the AuNRs. When the oxidation reaction was performed under inert N₂ atmosphere, there was only minimal etching of the AuNRs. After etching for 2 h, the LSPR peak was found to blue-shift only 43 nm (Figure S6), indicating that the oxidation speed was much slower and incomplete under the N₂ atmosphere strongly suggesting that O₂ is the oxidizing agent and is replenished by dissolution from the air above the dispersion. Third, it was found that heating is not required for AuNR oxidation. At room temperature (~20 °C), the oxidation also proceeded. The reaction speed was relatively slow (<3 nm/h), but the oxidation reaction could be completed in 200 h (Figure S7). The appearance of the peak at around 400 nm again suggested that the final state was Au(III) (Figure S7, inset). Fourth, the porosity of the meso-SiO₂ shell was found to influence the oxidation speed. To illustrate this point in a dramatic way, before etching, a Stöber SiO₂ shell⁴² was grown onto the AuNRs@meso-SiO₂ (total ~25 nm shell

thickness after growth). The LSPR peak blue-shifted only 5 nm after etching for 2 h (Figure S8), suggesting that the accessibility for the dissolved O₂ to reach the metal surface for a “normal” Stöber SiO₂ shell without a mesoporous pore is very poor and that such a layer can effectively prevent oxidation. This result is in complete agreement with those of Matijevic who could prevent the oxidation of metallic Fe with a Stöber layer of similar thickness.⁴³ Finally, CTAB is not required for the oxidation of the AuNRs. Before oxidation, CTAB was removed from the meso-SiO₂ shell by calcination of the AuNRs@meso-SiO₂ particles at 500 °C in air for 6 h. The AuNRs core was partially deformed to a lower aspect ratio of 1.9 ± 0.2, and the calcined particles were redispersed in methanol for the oxidation reaction. The oxidation could still be completed, but the speed was slower than the oxidation without calcination (Figure S9), most probably by a reduction in the pore volume and/or sizes. From the results obtained, we propose the following overall reaction for the oxidative etching process:



Here, H⁺ enhances the reduction potential of the O₂ half reaction from 0.401 to 1.229 V (vs a normal hydrogen electrode, NHE), while Cl[−] acts as complexing agent, which reduces the reduction potential of Au(0)/Au(III) from 1.52 to 1.002 V (vs NHE; see SI).²⁴

The etched-AuNRs@meso-SiO₂ were used for a second metal overgrowth. The etched-AuNRs core acts as a “seed” making the reduced metal salts specifically deposit on the AuNRs, with the meso-SiO₂ shell acting as “nanocapsule” which confines the shape and size of the final nanostructures. To illustrate the generality of this approach, we successfully completed the overgrowth of the noble metals (Ag, Pd, and Pt) on etched-AuNRs in a meso-SiO₂ shell. We found additionally that by varying the speed of growth both smooth layers and layers with very rough almost dendritic overlayers could be realized.

The etched-AuNRs@meso-SiO₂ particles were used for metal overgrowth by adding metal salt as precursor and ascorbic acid as reducing agent. The AuNRs-metal@meso-SiO₂

nanostructures were investigated by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and high-resolution transmission electron microscopy (HRTEM) imaging (Figure 4 and Figures S10 and S11). It is likely that part of the CTAB is removed from the mesopores in the silica shell so that precursor molecules can access the surface of the AuNRs. The openness of the pores likely influences the effectiveness of the overgrowth reaction. The meso-SiO₂ shell is accessible from all directions; therefore, a second metal can be grown on both the sides and the ends of the AuNRs. Because of the exclusive anisotropic etching at the ends only, there is more space at the ends of AuNR inside the SiO₂ shells, resulting in thicker metal overgrowth at the ends. Thus, the length was found to increase more than the diameter in the final AuNRs-metal structures. Figure 4a and f show the etched-AuNRs@meso-SiO₂ particles. The AuNRs are single crystals of face-centered cubic (fcc) structure, with one of the main cubic axes oriented along the length of the rod. In general, they are observed to lie on the grid either in a [110] or in a [100] orientation (Figure S10), in agreement with previous reports.^{44,45} The growth behavior varied for different metals. Ag could be epitaxially grown on the AuNR surface, forming an AuNRs-Ag core-shell structure with a single crystalline structure (Figure 4g). The epitaxial growth of Ag on Au is possible due to the small lattice mismatch and the low interface energy between Au and Ag. We also found line defects in some of the AuNRs-Ag structures (Figure S11), which might arise from a too fast growth speed. For Pd growth, epitaxial growth occurred only in a few atomic layers. Thereafter, Pd nanoparticles were grown on both the sides and ends of the AuNRs (Figure 4h and Figure S10c). For Pt overgrowth, the Pt layers could be either smooth or rough, depending on the speed of growth. When the growth speed is slow, the Pt layer is smooth (Figure 4i), and the morphology is similar to that of a single AuNR. The success coating of Pt was confirmed by elemental mapping (Figure S12). When the growth speed is faster, dendritic layers were obtained (Figure 4j), and the structure is similar to the AuNRs-Pd nanostructure. The insets in Figure 4a–e show obvious color changes after metal growth: from brown to green after Ag growth and from brown to dark brown after Pd and Pt growth. The different color changes are due to the differences in the plasmonic properties after the second metal overgrowth.

To investigate the plasmonic properties of the AuNRs-metal nanostructures in more detail, we compared measured extinction spectra with FDTD calculated spectra for single composite rods with different geometries and compositions. Figure 5a shows the experimental extinction spectra of the etched-AuNRs and AuNRs-metal structures. For the LSPR of the AuNRs-Ag nanostructures, the peak blue-shifted (from 741 to 709 nm), and the peak intensity increased dramatically. The blue-shift and intensity increase arise from the higher plasmonic resonance energy and decrease in plasmonic damping of Ag compared to Au.⁴⁶ However, for the AuNRs-Pd and AuNRs-Pt-rough nanostructures, the LSPR peak red-shifted, decreased in intensity, and broadened. The red-shift is due to a slight increase in aspect ratio, whereas the intensity reduction and broadening arise from plasmon damping due to the large imaginary part of both the Pd and Pt dielectric functions.^{37,38} For the AuNRs-Pt-smooth nanostructure, the LSPR did not show an obvious shift. This unchanged LSPR band is due to nearly the same aspect ratio after the Pt overgrowth. As mentioned, we performed FDTD simulations to calculate the

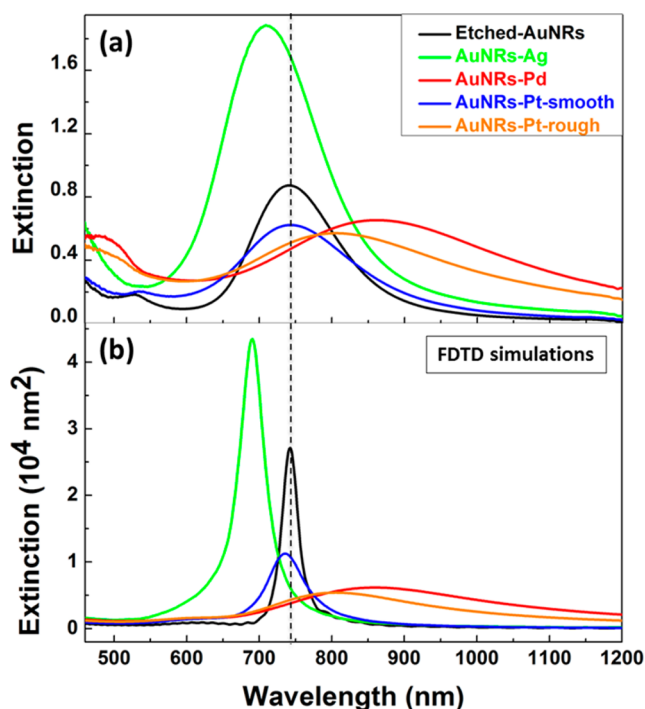


Figure 5. Experimental and simulated extinction spectra of AuNRs-metal nanostructures. (a) Experimental extinction spectra of etched-AuNRs@meso-SiO₂ (black, 70 °C, 0.2 mL of HCl in 10 mL of methanol, $t = 8$ min), AuNRs-Ag@meso-SiO₂ (green), AuNRs-Pd@meso-SiO₂ (red), AuNRs-Pt-smooth@meso-SiO₂ (blue), and AuNRs-Pt-rough@meso-SiO₂ (orange). (b) Extinction spectra obtained from FDTD simulations. The size parameters ($L \times D$) were set to be the same as the ones measured from the TEM images: 58.5 nm \times 17.7 nm for etched-AuNRs, 71.9 nm \times 26.3 nm for AuNRs-Ag, 78.6 nm \times 19.4 nm for AuNRs-Pd, 59.5 nm \times 18.7 nm for AuNRs-Pt-smooth, and 70.2 nm \times 20.2 nm for AuNRs-Pt-rough, respectively. Only LSPR was calculated by setting the polarization parallel to the long axis of the nanorod.

extinction cross-sections for different geometries of single AuNRs-metal nanostructures using the dielectric functions of the corresponding bulk materials (Figure 5b). We assumed a porosity of 63% in our mesoporous layer of silica⁴⁷ to which we assigned a refractive index of 1.45⁴⁸ and that the pores were filled with water solvent with a refractive index of 1.33 through a volume weighed average of the pores and silica. We obtained an effective index of refraction of 1.38, which we assumed to be valid for all wavelengths. We are aware of the fact that there is a small effect on the rod resonance frequency caused by the fact that the outer mesoporous layer encounters yet another index jump to the bulk water, but earlier work has shown this effect on the metal resonances to be quite small (only several nanometer shifts for our parameters).⁴⁹ We therefore ignored this effect in the calculations. The characteristics of the plasmonic properties after the metal overgrowth in the FDTD simulations are in good agreement with the experimental data. The only important difference is the width of the peaks, which is explained by the polydispersity of our systems which was not taken into account in the single particle calculations.

CONCLUSIONS

In summary, we have demonstrated a relatively simple approach to selectively control the dimensions of AuNRs@

meso-SiO₂ rods after synthesis via oxidative etching. The etching speed could be precisely controlled by the HCl concentration and/or temperature but is also dependent on the mesoporous layer characteristics. Additionally, the etched AuNRs@meso-SiO₂ particles can be used as seeds for a second metal overgrowth of the etched-AuNRs in their meso-SiO₂ shells. The growth only takes place inside the mesoporous silica shell, which stabilizes the rods both mechanically, against aggregation and against deformations induced by increased temperatures, while still keeping the metal surface available for applications like catalysis and sensing such as SERS. Overgrowth was shown for the metals: Ag, Pd, and Pt, but we expect the procedure to work for other metals as well. The morphology of the additionally grown metal layers could be tuned to be both smooth and rough depending on the speed of growth. This was shown for Pt overgrowth, but preliminary results have shown these limits to be accessible for the other metals as well, and work is in progress to find the exact conditions for different metals. Depending on the intended use of these composite metal nanostructures in, e.g., plasmonics, sensing, and catalysis, the ability to also fine-tune this part of the morphology is an important extra control parameter. As expected, depending on the dielectric responses of the metals used, the plasmonic responses of the composite particles could be either increased (Ag) or decreased (Pd and Pt resulting in more dissipation). Moreover, also the catalytic properties are expected to show similarly large differences in properties depending on the reaction and metal composite as well. Finally, work is in progress to investigate whether alloy formation in the composite structures can be induced before the structures resort back to a spherical shape as the alloys of the metals used have unique properties as well and to the best of our knowledge have not yet been realized for anisotropic particles.

EXPERIMENTAL SECTION

Materials. All chemicals were used as received without further purification. Hexadecyltrimethylammonium bromide (CTAB, >98.0%) and sodium oleate (NaOL, >97.0%) were purchased from TCI America. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O), sodium hydroxide (98%), and polyvinylpyrrolidone (PVP, average molecular weight 58000 g/mol, K29–32) were purchased from Acros Organics. L-Ascorbic Acid (BioXtra, ≥99%), silver nitrate (AgNO₃, ≥99%), sodium borohydride (NaBH₄, 99%), hydrochloric acid (HCl, 37 wt % in water), tetraethyl orthosilicate (TEOS, 98%), ammonium hydroxide solution (≥25 wt % in water), sodium tetrachloropalladate(II) (Na₂PdCl₄, 98%), and potassium tetrachloroplatinate(II) (K₂PtCl₄, 98%) were purchased from Sigma-Aldrich. Ultrapure water (Millipore Milli-Q grade) with resistivity of 18.2 MΩ was used in all of the experiments. All glassware for AuNR synthesis was cleaned with fresh aqua regia (HCl/HNO₃ in a 3:1 ratio by volume; *caution! Aqua regia is extremely corrosive and should be handled with extreme care!*) and rinsed with large amounts of water.

Oxidative Etching of AuNRs@meso-SiO₂. The oxidative etching of AuNRs in meso-SiO₂ shell was carried out by heating the AuNRs@meso-SiO₂ solution (10.0 mL in methanol) in a 40 mL glass vial to 70 °C in an oil bath. To start the etching, 0.20 mL HCl (37 wt % in water) was added. The cap of the glass vial was closed to prevent evaporation of HCl. With the increase of etching time, the color of the solution changed from brownish to green, blue, and finally yellowish (due to the formation of Au(III)). The amount of HCl (0.10 mL, 0 mL) or temperature (60 °C, 50 °C) was changed to control the etching speed. The oxidation process was monitored by measuring extinction spectra as a function of oxidation time in a 1.0 cm cuvette. The spectra were measured by taking samples from the etched-AuNRs@meso-SiO₂ solutions and mixing them with the same volume of methanol to rapidly cool down the temperature. The LSPR peak of

the AuNRs@meso-SiO₂ before etching was at 827 nm and had an intensity of 1.80.

Metal Overgrowth on Etched-AuNRs@meso-SiO₂. The AuNRs@meso-SiO₂ solution (15.0 mL in methanol) was mixed with HCl (37 wt % in water, 0.30 mL) and etched at 70 °C for 8 min. The etching was stopped by adding large amounts of cool methanol and centrifuging at 8000 rpm for 10 min. The precipitate was redispersed into PVP aqueous solution (molecular weight, 58000 g/mol, 1.1 wt %). Then, the solution was centrifuged again and redispersed into PVP solution (1.1 wt %, 10.0 mL) as a stock solution. The metals were grown on etched-AuNRs@meso-SiO₂ using the method from ref 37 with modifications. For the growth of AuNRs-Ag, AgNO₃ (0.01M, 0.03 mL) was added into the etched-AuNRs@meso-SiO₂/PVP stock solution (0.6 mL), followed by the addition of ascorbic acid (0.03 M, 0.04 mL). The mixture was gently shaken for 20 min. For the growth of AuNRs-Pd, the conditions are the same as those for the growth of AuNRs-Ag except for the use of Na₂PdCl₄ (0.01M, 0.03 mL) instead of AgNO₃. For the growth of AuNRs-Pt-smooth, K₂PtCl₄ (0.01 M, 0.03 mL) was added into the etched-AuNRs@meso-SiO₂/PVP stock solution (0.6 mL), followed by the addition of ascorbic acid (0.03 M, 0.04 mL). The mixture was gently shaken for 5 min and left undisturbed for 4 h. For the growth of AuNRs-Pt-rough, K₂PtCl₄ (0.01 M, 0.12 mL) was added into the etched-AuNRs@meso-SiO₂/PVP stock solution (0.6 mL), followed by the addition of ascorbic acid (0.1 M, 0.24 mL). The mixture was gently shaken for 5 min and left undisturbed for 4 h. Since the growth speed is much slower for the growth of AuNRs-Pt, more metal salt and ascorbic acid were added to obtain the AuNRs-Pt-rough structure. Also the reaction time was much longer for Pt overgrowth. The resulting particles were centrifuged at 8000 rpm for 10 min and redispersed in water. The results are shown in Figures 4–5 and Figures S10–S12.

Characterization. Extinction spectra were measured using a vertex 70 FT-IR spectrometer (BRUKER) and 1.0 cm cuvettes. To measure the Au(III) with a peak at ~400 nm, a PerkinElmer Lambda 950 spectrophotometer was used. TEM images were acquired with a Tecnai 12 microscope (FEI) operating at 120 kV. HAADF-STEM and HRTEM measurements on AuNRs-metal@meso-SiO₂ structures (Figures 4, S10, and S11) were performed using a cubed Titan microscope (FEI) with spherical aberration correction for bright-field imaging, and operating at 300 kV. A camera length of 115 mm was used to limit diffraction effects in HAADF-STEM imaging.⁵⁰ For the AuNRs-Pt-smooth@meso-SiO₂, EDX mapping was also performed. The particle sizes of etched-AuNRs were measured from TEM images, whereby 200–400 particles were measured for each sample. The mean (μ) and standard deviation (σ) of length (L), diameter (D), and aspect ratio were obtained by the following formula,

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \mu)^2}, \quad \text{where } \mu = \frac{1}{N} \sum_{i=1}^N x_i$$

Here, x_i is the length (or diameter) of measured particles or the aspect ratio obtained by (L/D), and N is the number of particles. The results shown in the article are $\mu \pm \sigma$.

FDTD Simulations. Finite difference time domain (FDTD) is a method for solving Maxwell's equations on a discretized spatial grid in complex geometries. The FDTD simulations were carried out with commercial software (Lumerical FDTD Solutions 8.11). A total field scattered field source was used to simulate a propagating plane wave interacting with the nanostructures, with a wavelength range of 450 to 1200 nm. Only LSPR was calculated by setting the polarization parallel to the long axis of AuNRs. A three-dimensional nonuniform mesh was used, and a grid size of 0.5 nm was chosen for the AuNRs-metal nanostructures and the immediate vicinity of the structures. For the dimensions of AuNRs-metal nanostructures, the average sizes as determined from TEM were used. The shape of the AuNR core was modeled as a cylinder capped with a hemisphere at each end. For the AuNRs-Ag core-shell structure, the Ag shell was modeled by wrapping the AuNR core with a Ag layer. For the AuNRs-Pd (or AuNRs-Pt) nanostructure, a few Pd (or Pt) atomic layers were epitaxially grown on the AuNR surface. Thereafter, additional Pd (or

Pt) deposition led to the formation of nanoparticles on both sides and ends of the AuNRs. Therefore, the model of AuNRs-Pd (or AuNRs-Pt) nanostructures consisted of an AuNR core wrapped by a 0.5 nm thick Pd (or Pt) layer and randomly distributed Pd (or Pt) nanoparticles (1–3 nm in diameter) on the outside. The dielectric functions of metals were obtained by fitting the points from the data of Palik, E. D. (Handbook of Optical Constants of Solids; Academic Press: Boston, MA, 1985). We assumed a porosity of 63% (f) in our mesoporous layer of silica⁴⁷ to which we assigned a refractive index of 1.45⁴⁸ (n_{SiO_2}) and that the pores were filled with water solvent with a refractive index of 1.33 ($n_{\text{H}_2\text{O}}$) through a volume weighed average of the pores and silica. We calculated an effective refractive index by

$$n_{\text{eff}} = \sqrt{n_{\text{H}_2\text{O}}^2 f + n_{\text{SiO}_2}^2 (1 - f)}$$

The obtained effective index of refraction is 1.38, which we assumed to be valid for all wavelengths.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.5b03749](https://doi.org/10.1021/acs.chemmater.5b03749).

More experimental details, full set of TEM images of etched-Au@meso-SiO₂, extinction spectra, TEM images and digital pictures of all control experiments, HRTEM images of AuNRs-metal nanostructures at full resolution, and EDX elemental mapping of AuNRs-Pt-smooth nanostructure (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

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

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Experimental Details

1. AuNRs synthesis

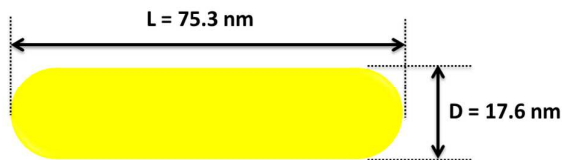
The AuNRs were synthesized using a modified seed-mediated method.^[1] The seed solution was prepared by the addition of HAuCl₄ (0.05 M, 50.0 μ L) into CTAB (0.1 M, 10.0 mL) in a 20 mL scintillation glass vial. A freshly prepared NaBH₄ solution (0.01 M, 0.60 mL) was then quickly injected into the Au(III)-CTAB 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

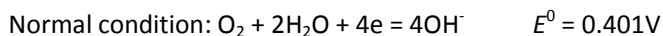
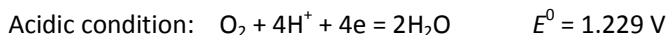
of the cuvette was closed, and sealed with several layers of parafilm. The oxidation process was monitored by measuring extinction spectra as a function of oxidation time. The measurements were repeated automatically with 1 h time intervals. The extinction spectra are shown in Figure S7.

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.

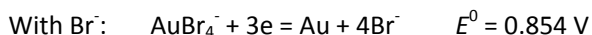
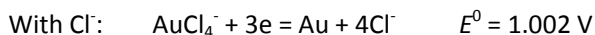
4.5 The role of CTAB in the meso-SiO₂ shells. To remove the CTAB from the meso-SiO₂ shell, the AuNRs@meso-SiO₂ methanol solution was dried at 70 °C overnight, and calcined at 500 °C for 6 h in air. After calcination, the AuNRs were partially deformed, but still anisotropic. The calcined particles were 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

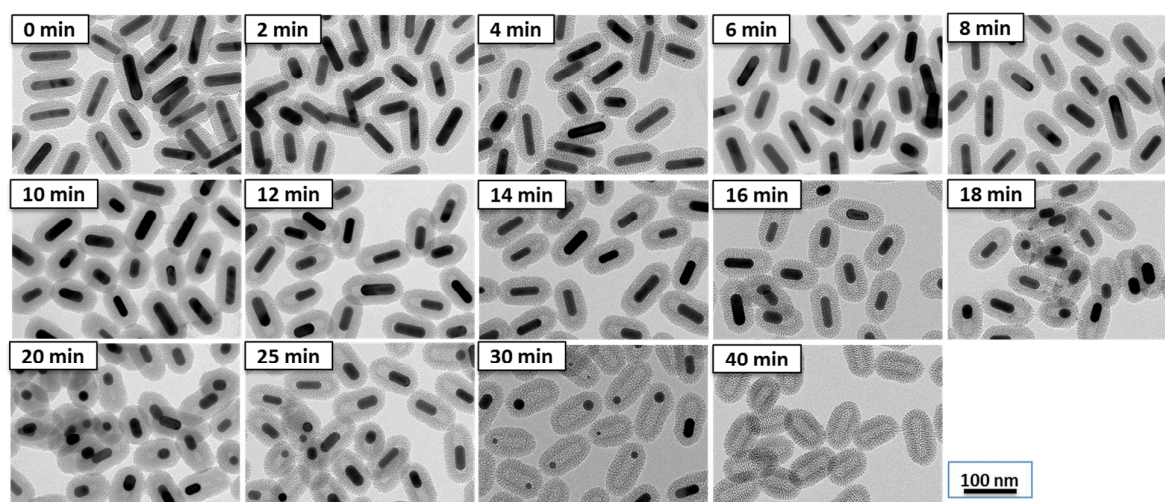


Figure S1. TEM images of AuNRs@meso-SiO₂ at different etching stages. The scale bar for all the images is shown in bottom-right of the image. The oxidation reaction was carried out at 70 °C and with 0.2 mL HCl per 10 mL methanol.

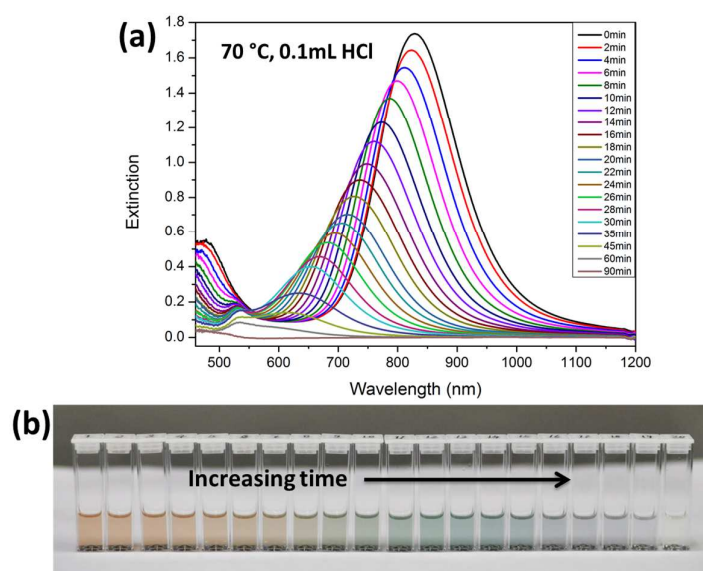


Figure S2. The extinction spectra (a) and the digital photograph (b) show the different stages during oxidative etching of AuNRs with less HCl. The oxidation reaction was carried out at 70 °C with 0.1 mL HCl in 10 mL methanol. The etching speed was 5.9 nm/min. The photograph shows the samples that were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

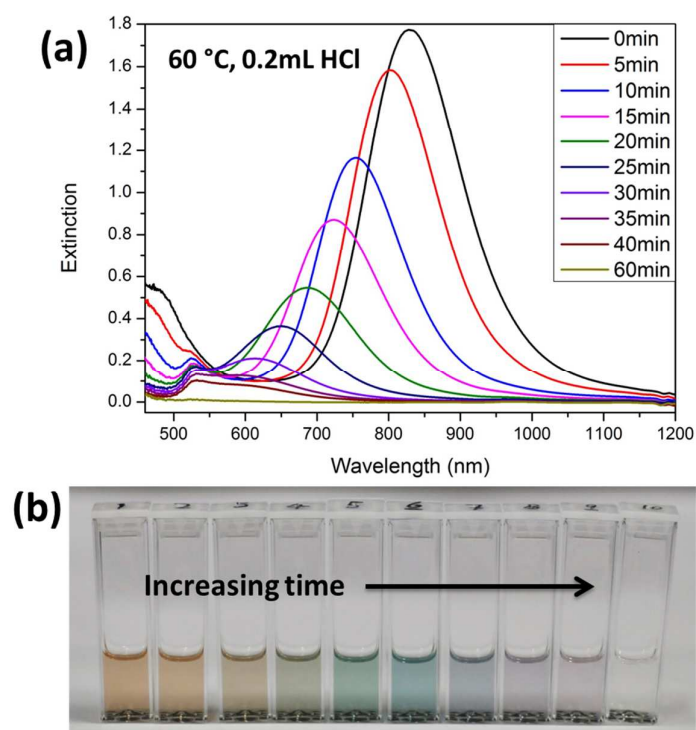


Figure S3. The extinction spectra (a) and the digital photograph (b) show the different stages during oxidative etching of AuNRs with lower temperature. The oxidation reaction was carried out at 60 °C with 0.2 mL HCl in 10 mL methanol. The etching speed was 7.2 nm/min. The photograph shows the samples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

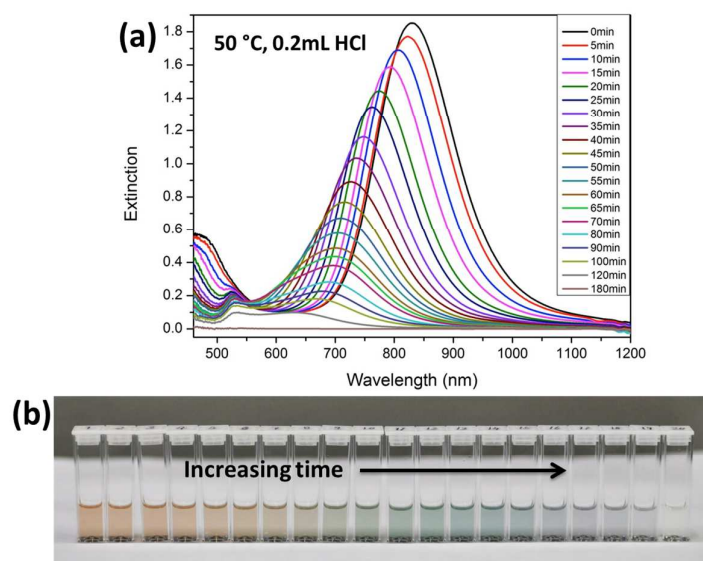


Figure S4. The extinction spectra (a) and the digital photograph (b) show the different stages during oxidative etching of AuNRs with lower temperature. The oxidation reaction was carried out at 50 °C with 0.2 mL HCl in 10 mL methanol. The etching speed was 7.2 nm/min. The photograph shows the samples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

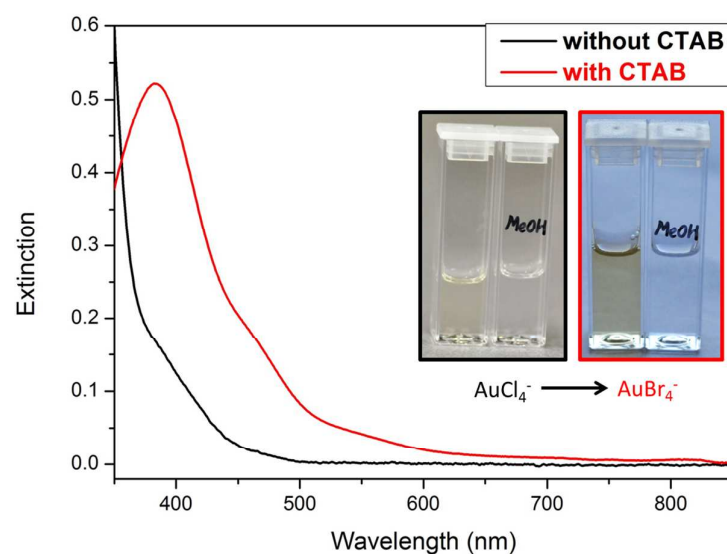


Figure S5. The extinction spectra and digital photographs (insets) show the final etching solution before and after mixing it with CTAB. The black curve was measured directly after the completion of the oxidation reaction, while the red curve was measured after mixing the final solution with certain 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.

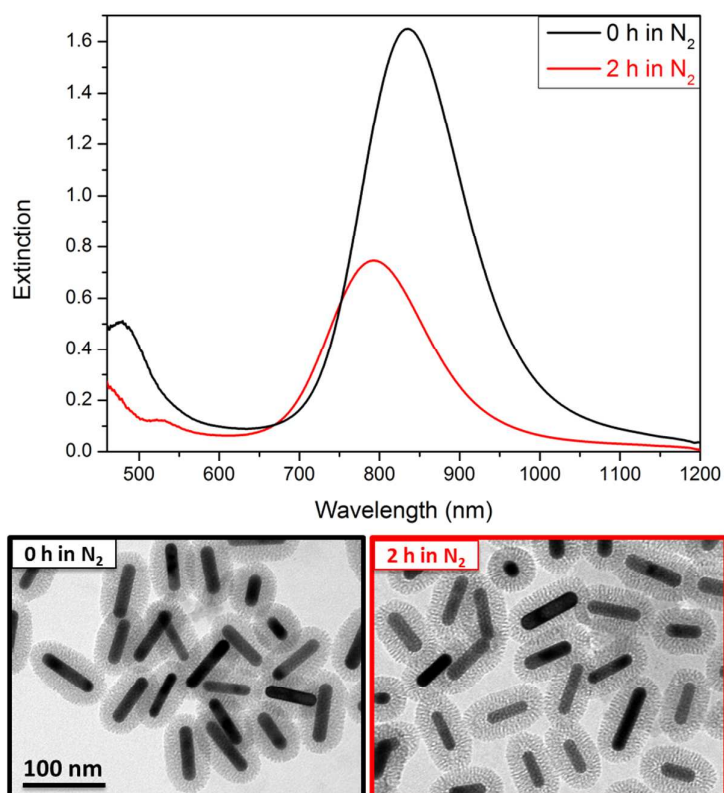


Figure S6. Oxidation in N₂ inert atmosphere. Oxidation reaction was carried out at 70 °C, 0.2 mL HCl in 10 mL methanol. LSPR peak only blue-shifts 43 nm after etching for 2 h. The oxidation speed is much slower than the oxidation in air, suggesting that O₂ is the oxidizing agent and necessary for completing 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.

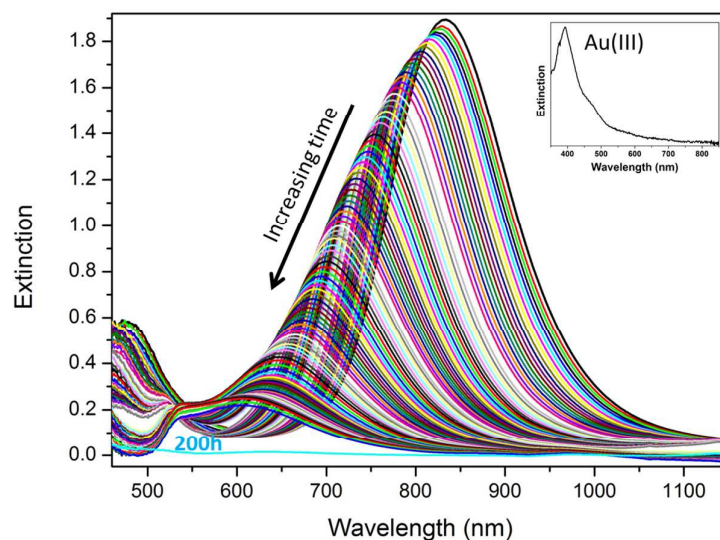


Figure S7. Oxidation at room temperature. Oxidation reaction was carried out at $\sim 20^\circ\text{C}$ in 0.2 mL HCl per 10 mL methanol. The oxidation could still proceed, but at much lower speed ($< 3\text{ nm/h}$). The oxidation was finished in 200 h, as indicated by the disappearance of extinction 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]

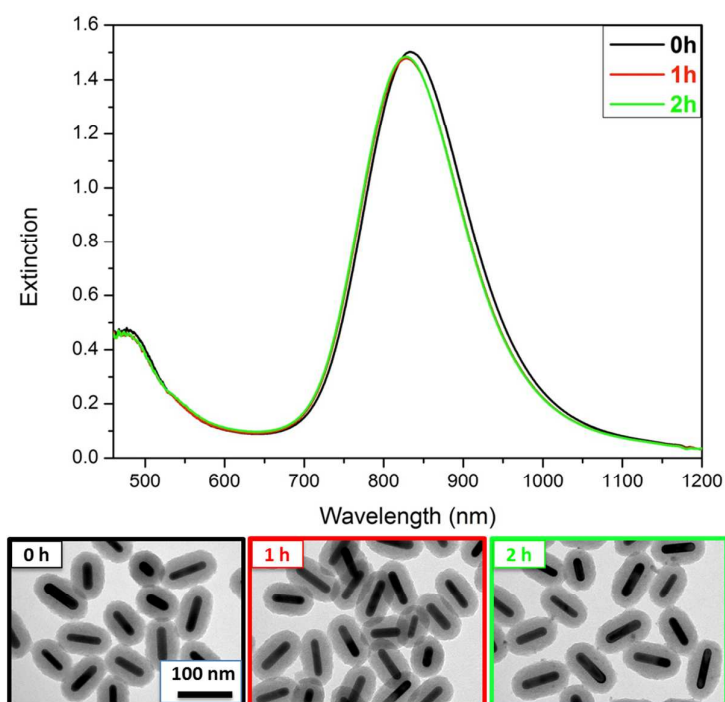


Figure S8. The extinction spectra (top) and TEM images (bottom) show that a Stöber SiO₂ shell coating can effectively prevent etching of AuNRs. The oxidation reaction was carried out at 70 °C, 0.2 mL HCl in 10 mL methanol. The LSPR peak only blue-shifts 5 nm after etching for 2 h, suggesting the accessibility 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.

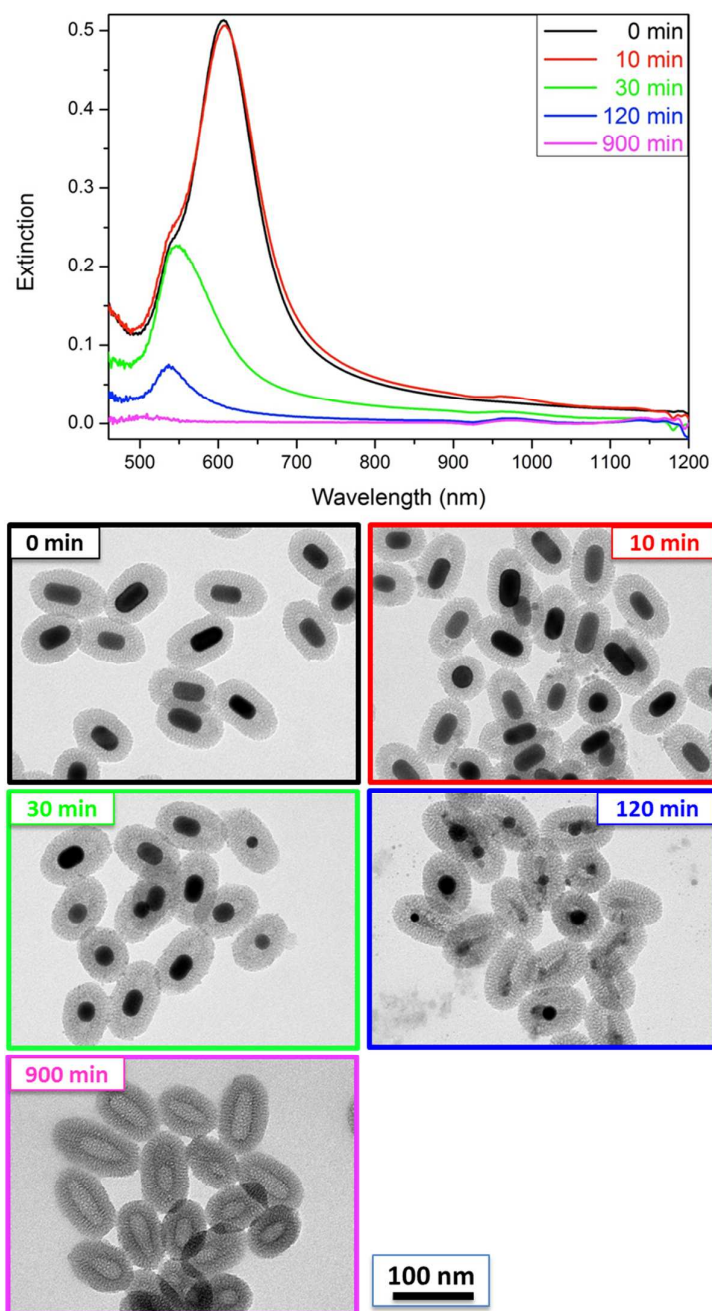


Figure S9. Oxidation after removal of CTAB in meso-SiO₂ shell. Before oxidation, CTAB from meso-SiO₂ shell was removed by calcination of the AuNRs@meso-SiO₂ particles at 500 °C for 6 h. The calcined particles were re-dispersed in methanol and oxidized at 70 °C in 0.2 mL HCl per 10 mL methanol. The oxidation 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.

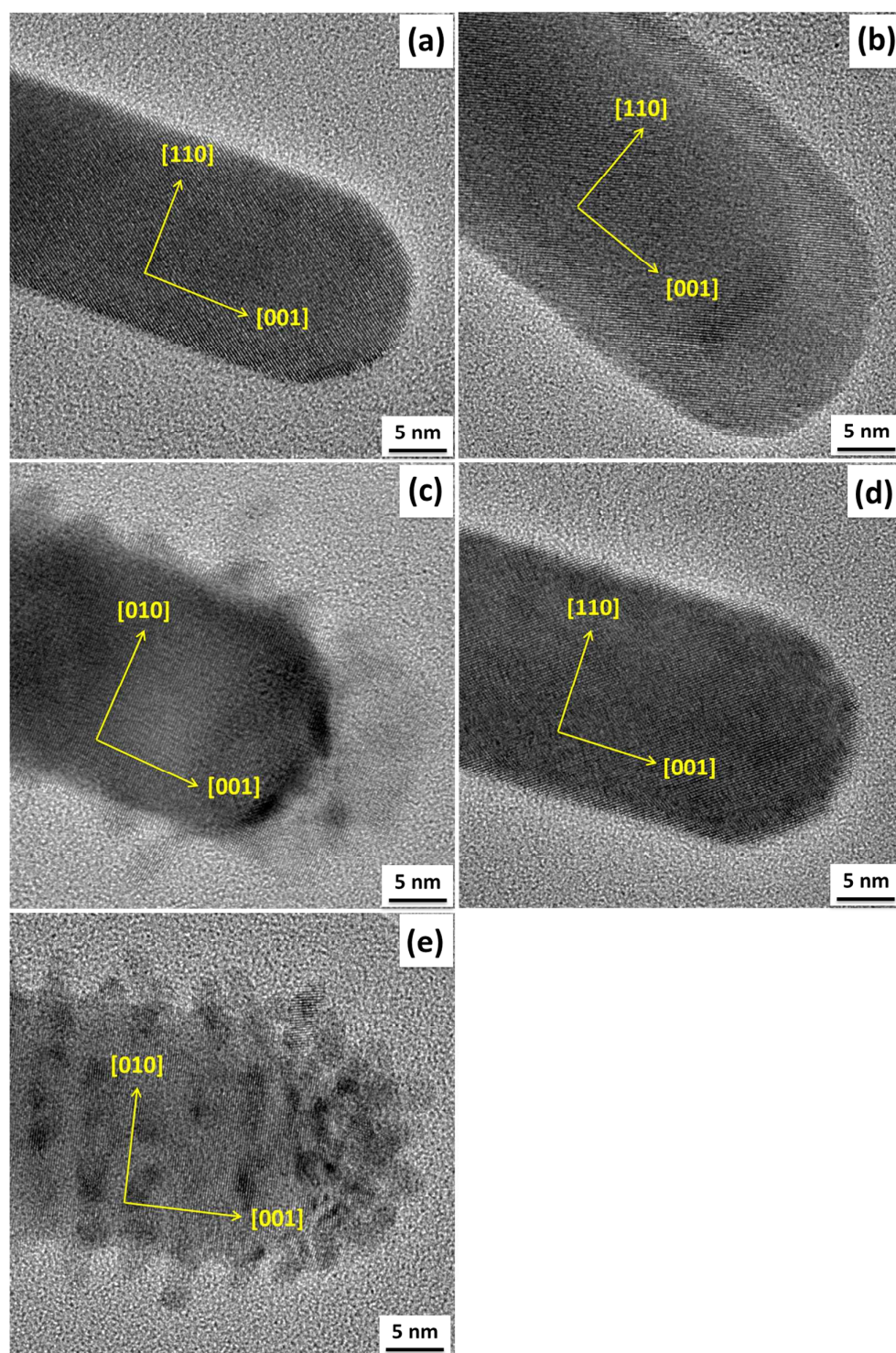


Figure S10. HRTEM images of nanostructures: (a) etched-AuNRs, (b) AuNRs-Ag, (c) AuNRs-Pd, (d) AuNRs-Pt-smooth, and (e) AuNRs-Pt-rough. All AuNRs have the crystallographic $\langle 001 \rangle$ direction along the length of the rod, and are observed to lie on the grid either in a $[110]$ projection (a,b,d), 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.

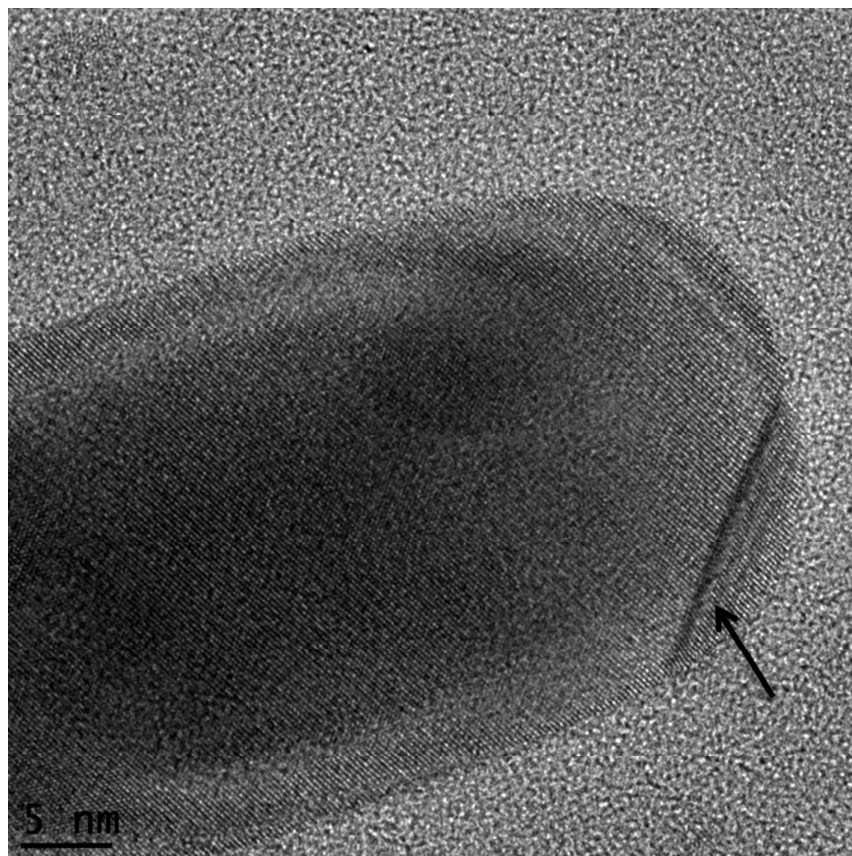


Figure S11. HRTEM image of a AuNRs-Ag nanostructure. A line defect is shown at the tip of the structure as indicated by the arrow.

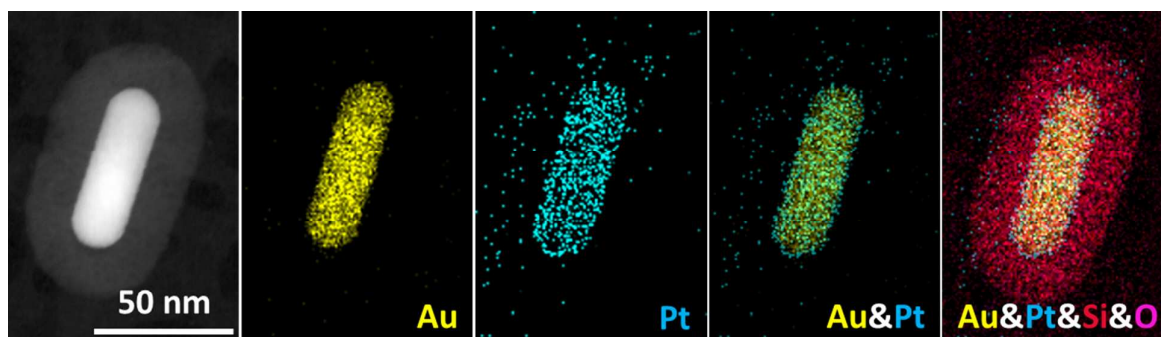


Figure S12. EDX mapping of a AuNRs-Pt-smooth nanostructure. The HAADF-STEM image, Au, Pt, Au&Pt, and Au&Pt&Si&O were illustrated sequentially from left to right.

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