Supplementary Information

Controlled Etching and Tapering of AuNRs Using Cysteamine

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Experimental:

Materials

All glass containers were cleaned with freshly prepared Aqua Regia (HCl/HNO_3 3/1) and thoroughly rinsed with ultrapure water (18.2 MOhm) obtained from a Millipore Milli-Q system.

The gold chloride salt ($HAuCl_4 \cdot 3H_2O$) was purchased from Electron Microscopy Sciences (EMS) (Hatfield, PA). Tetraethylorthosilicate (99.999%), L-ascorbic acid (ACS reagent grade, ≥99%), and HCl (ACS reagent grade, 37%) were purchased from Sigma-Aldrich. Oleic acid (lab grade) and NaOH (2.00N) were purchased from Fisher Scientific. Cysteamine (98%), silver nitrate (99.5%, for analysis), and sodium borohydride (98+%) were purchased from Acros. Poly(ethylene glycol) (mPEG-SH, 5,000Da) was purchased from Laysan Bio, Inc. Cetyltrimethylammonium bromide (CTAB) (high purity grade) was purchased from Amresco. Ethanol (200 proof, anhydrous) was purchased from Pharmco-Aaper.

All UV-vis spectra were obtained using a Beckman Coulter DU730 Life Science UV/Vis spectrophotometer. Centrifugation was performed using a Servall Legend Micro 21R centrifuge or a Beckman Coulter Avanti J-E centrifuge with a Beckman JA-20 rotor for volumes greater than 10 mL.

If not otherwise indicated, the reactions were carried out at room temperature (22°C).

Methods

AuNRs Synthesis. Gold nanorods of 75 nm x 26 nm were synthesized following a procedure adapted from Ye *et al*.[1] This synthetic method involves both a seed solution as well as a growth solution.

The seed solution was prepared by mixing 5 mL of 0.20 M CTAB and 5 mL of 0.5 mM $HAuCl_4$ in a 25 mL round bottom flask, and then adding 0.60 mL of 10 mM $NaBH_4$ while stirring. After 2 minutes, stirring was stopped and the seed solution was allowed to age for 30 minutes before use.

The growth solution was prepared in a 50 mL round bottom flask by dissolving 0.70 g CTAB and 0.128 mL oleic acid in 25 mL of water under vigorous stirring and heating to 50°C. The reaction was then cooled to 30°C and the stirring was stopped before adding 0.800 mL of 4 mM $AgNO_3$. After 15 minutes, 25 mL of 1 mM $HAuCl_4$ was added and the reaction was left to sit undisturbed. After 90 minutes, 0.300 mL HCl (37%) was added under slow stirring. After 15 minutes, stirring was increased for the addition of 0.125 mL 64 mM ascorbic acid and 0.050 mL seed solution. After 30 seconds, the stirring was stopped and the reaction was left to sit overnight. All AuNRs were purified through 3x centrifugation at 10,000 g for 20 min at room temperature to remove unreacted starting materials and redispersed in 5 mM CTAB for storage.

AuNR Etching. AuNR etching was carried out on a 2 mL scale using purified AuNRs dispersed in 5 mM CTAB. A stock solution of cysteamine was prepared by dissolving approximately 0.015 g of cysteamine in 1 mL of ultrapure water, and the corresponding volume of cysteamine stock solution was added to the 2 mL AuNRs to bring the final concentration to 5 mM cysteamine. (Other concentrations were also tested and are mentioned in the Results/Discussion section). For heated samples, the solution was heated in an oil bath to the desired temperature (50, 60, 70 or 80°C) before adding cysteamine. During all trials, the longitudinal surface plasmon position was monitored by transferring the solution to a cuvette at regular intervals and measuring its absorption, then returning it to the vial.

Silica coating of AuNRs. Three types of silica coating were performed on the AuNRs: side-coating, end-coating and full coating.

Side-coating of AuNRs was accomplished following the protocol reported by Hinman *et al*.[2] First, the ends of AuNRs were functionalized with polyethylene glycol (PEG) disulfide (MW 5,000 Da) by adding 10 mg of the PEG to 10 mL of AuNRs in 5 mM CTAB and stirring overnight in a 25 mL glass vial. This solution was purified through centrifugation (10,000 g, 10 minutes, 20°C) and the pellet was redispersed in 1 mL of 0.3 mM CTAB. The silica coating reaction was carried out in a 5 mL glass vial. 0.133 mL of the AuNR-PEG solution was added to 1 mL of 0.3mM CTAB, followed by the addition of 35 µL of 77 mM TEOS in ethanol and 24 µL of 0.1 M NaOH. The solution was gently stirred overnight, then purified through two rounds of centrifugation (7,000 rpm, 20 minutes, 20°C) and redispersed in ethanol.

End-coating of AuNRs was accomplished following the protocol reported by Wang *et al*.[3] 3 mL of AuNRs were centrifuged (10,000 g, 10 minutes, 20°C) and redispersed in 3 mL of 10 mM CTAB. To this, 100 µL of 75 mM TEOS in ethanol was added, followed by 30 µL of 0.1 M NaOH. The solution was gently stirred overnight, then centrifuged (7,000 rpm, 20 minutes, 20°C) and redispersed in ethanol twice to remove excess silica.

Complete shells of silica were formed on the AuNRs by centrifuging 10 mL AuNRs (10,000 g, 10 minutes, 20°C), redispersing AuNRs in 10 mL ultrapure water, then adding 300 µL of 75 mM TEOS in ethanol followed by 100 µL of 0.1M NaOH and stirring slowly overnight. The particles were then centrifuged (7,000 rpm, 20 minutes, 20°C) and redispersed in ethanol twice to remove excess silica.

Etching of silica-coated AuNRs. All etching trials were performed on 2 mL samples of AuNRs coated with silica, and trials were performed in triplicate for each morphology described above (end-coated, side-coated, complete shell). Purified AuNRs in ethanol were heated to 60°C and cysteamine stock solution was added to bring the concentration to 5 mM cysteamine. The reaction was monitored at hourly

intervals. At the end of the reaction, the etched AuNRs were purified by centrifugation (10,000 g, 10 minutes, 20°C).

Hydrogen Peroxide Assay. The presence of H_2O_2 was detected using a an iodometric assay, following the protocol of DeLong*, et al*.[4] All solutions were prepared and kept under N_2 gas for the duration of the test. A 1:1 (v/v) solution of methanol and glacial acetic acid was prepared. A second solution of KI (10% w/v) and EDTA (1 mg/mL) in methanol was also prepared. The assay solution was prepared by mixing 1.2 mL of the methanol/acetic acid solution with 1.8 mL of the KI solution in a cuvette. To this cuvette, 100 μL of the solution to be tested was added. To test for the formation of H_2O_2 by cysteamine, a 5 mM solution of cysteamine in water was prepared and heated to 60°C for 6 hours to simulate conditions used during etching. This sample was added to the test cuvette and the absorption was monitored at 360 nm.

TEM imaging. Samples were deposited onto 300 mesh formvar/carbon grids (EMS), allowed to sit for 20 minutes, then rinsed with ultrapure water and air dried prior to imaging. Imaging was performed using an FEI Morgagni M268 TEM instrument equipped with a Gatan Orius CCD camera. The voltage was set to 100 kV. Between 100-200 AuNRs were measured from several TEM images of the same sample using Sigmascan to obtain mean sizes before and after etching.

Correlated single-particle measurements. A reflection-mode dark-field objective (Nikon NA 0.9 100x) was used to both illuminate and collect scattered light from the AuNR particles. Illumination was provided by a halogen lamp. Spectra were measured using a grating spectrometer (Acton SpectraPro 500i) equipped with a CCD camera (Princeton Instruments Pixis 400). The acquisition time was set to be 20 seconds. For each particle measured, a reference spectrum was taken simultaneously from a nearby location on the sample that contains no particles. The constant background due to dark counts was measured and subtracted from both the signal and reference spectra. The reference spectrum was then used to normalize the measured single-particle scattering spectrum. The position of each measured nanoparticle relative to the corner of the TEM grid was determined using a closed-loop sample positioning stage on the microscope, and a map was generated of all the positions of the AuNRs. A Nova NanoSEM 450 microscope from FEI was used for scanning transmission electron microscopy (STEM). The pressure of the chamber during imaging was approximately 10^{-6} Torr. The electron beam energy was set to 30 keV and the spot size to 1 (instrument units).

Simulations. The experimental sharpened AuNR was measured to be 66.6 nm long and 26.4 nm wide. A simulated sharp AuNR of the same size was approximated as a cylinder, two truncated cones and two ellipsoids, the ellipsoids being located at the tips of the cones. The ratio of the tip ellipsoid along the long axis of the rod versus the other two directions was set as 0.3. The overall length of the truncated cone and the ellipsoid was equal to the width of the rod. This geometry matched the STEM image. The thickness of the silica shell was set as 15 nm.

The spectra and the electromagnetic fields were calculated using COMSOL (finite element method). Using the wave-optics module, we performed calculations in the frequency domain. The scattering was calculated by integrating the scattered flux around a surface enclosing the rod, and the scattering spectrum was generated by sweeping the optical frequency. A second calculation was performed for a particle of the same length and width but without sharp tips, approximated as one cylinder and two ellipsoids. The axis of the ellipsoid along the long axis of the rod is 0.77 times the other two axes of the ellipsoid.

The dielectric function of gold used in the calculations was obtained from tabulated data.[5] The dielectric function of silica was obtained from the built-in library of COMSOL. The medium surrounding the silica-coated rod was assumed to have a refractive index of 1.25, to approximate the effect of the high-dielectric-constant substrate (silicon nitride) used for the measurement. The field strength was calculated at the plasmon resonance frequency for each case. The field enhancement was determined by integrating inside a virtual sphere of 2 nm in diameter at the ends of the rods.

Figures:

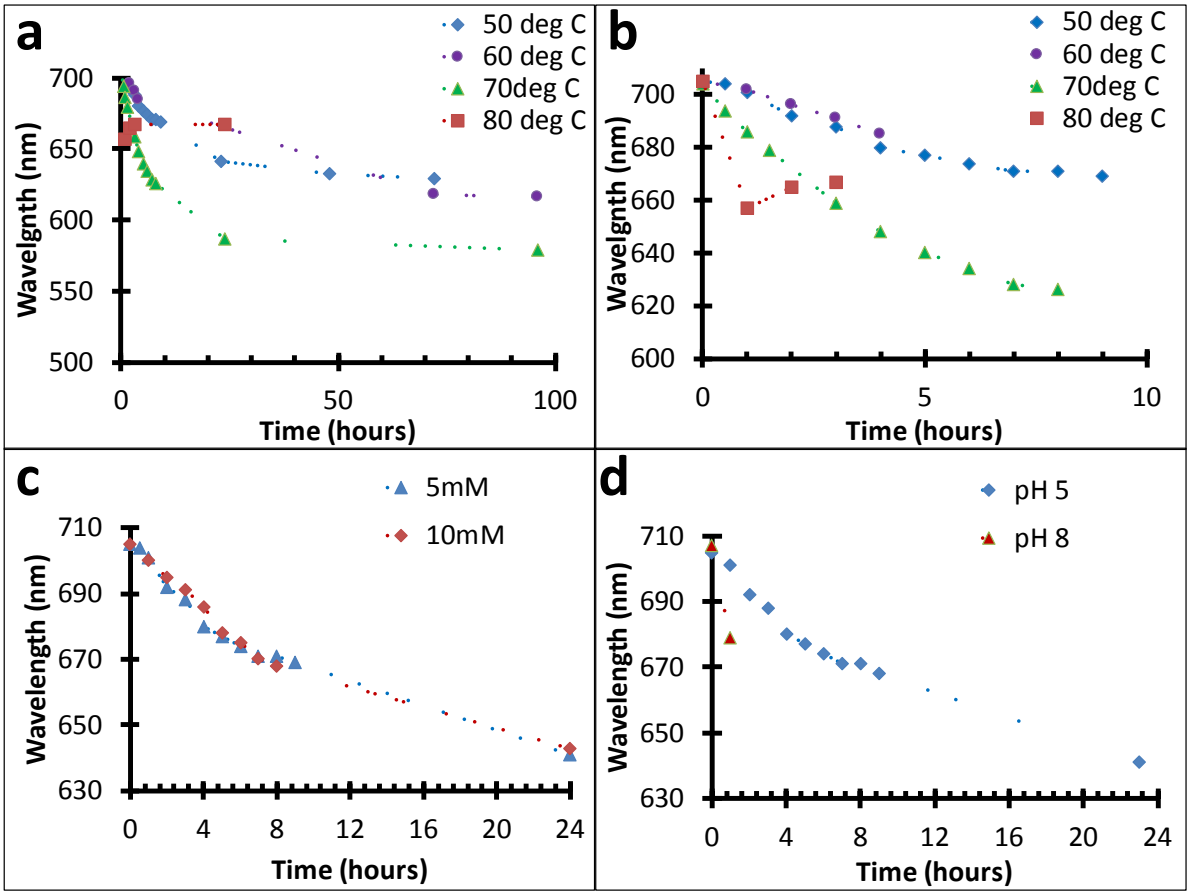

Figure S1. Influence of various parameters on rate of etching by cysteamine. **(a)** Effect of temperature over 24 h., **(b)** Effect of temperature extended over 4 days, **(c)** Effect of cysteamine concentration, **(d)** Effect of pH.

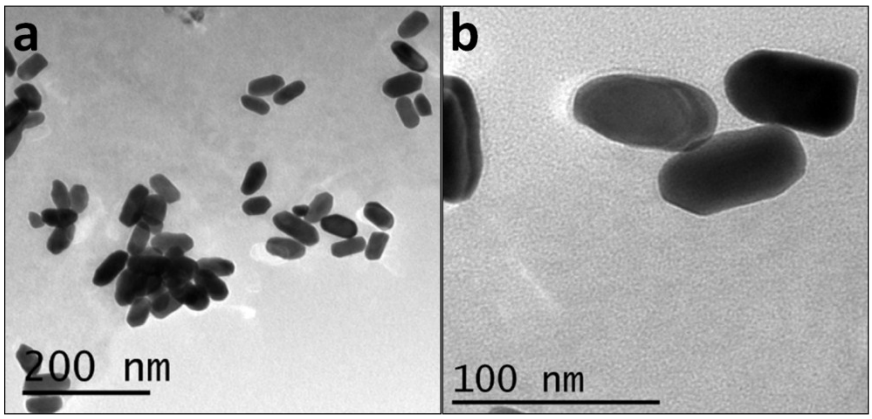

Figure S2. CTAB-stabilized AuNRs after etching with 5 mM cysteamine at 60^{0}C for 72 hours. After over 24 hours, AuNRs do not get shorter but instead begin to become more irregularly shaped.

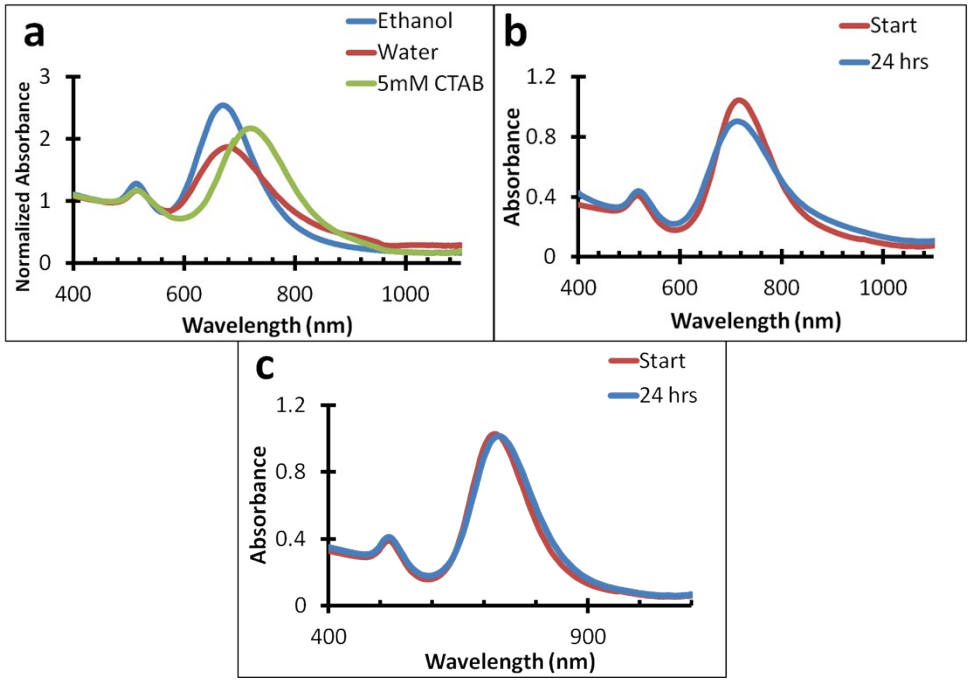

Figure S3. UV-vis spectra for control tests of AuNR etching using silica end-coated AuNRs. **(a)** Spectra 24 hours after cysteamine addition using different solvents. We see the same shift in water and ethanol, indicating the same degree of etching; however, the longitudinal plasmon peak in the aqueous sample is broader, indicating some aggregation. Ethanol was used for the majority of tests due to the better solubility of the AuNRs. Using 5 mM CTAB, no etching was observed after 24 hours. **(b)** Spectra before and after heating at 60^{0}C for 24 hours. We see no change in the longitudinal peak position, indicating that etching is occurring due to cysteamine and not simply from heating. **(c)** Spectra before and after addition of 5 mM mercaptopropionic acid, indicating that not all other thiols will behave the same way as cysteamine.

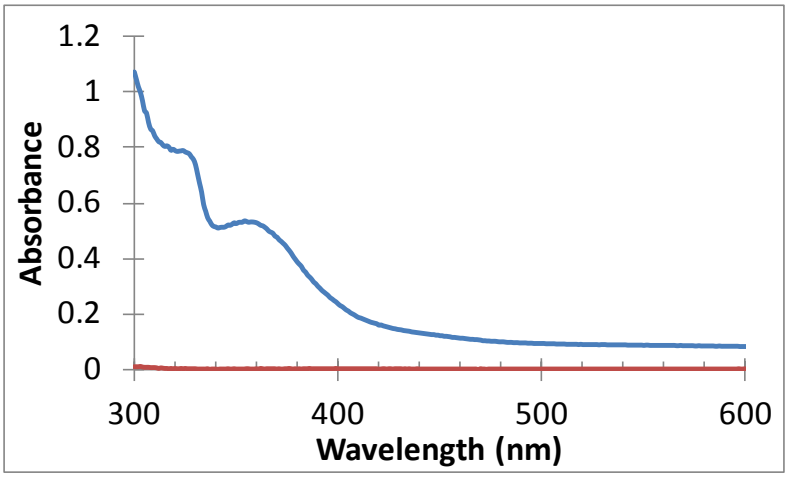

Figure S4. Assessment of H_2O_2 formation. Blue curve: Absorption spectrum obtained after performing iodometric assay for H_2O_2 on a 5 mM cysteamine sample heated to 60°C for 6 hours. The blank was performed on the assay solution (methanol, glacial acetic acid, KI and EDTA) before adding the cysteamine solution. The formation of H_2O_2 is indicated by the emergence of the peak at 360 nm. Red curve: Absorption spectrum of cysteamine (65 mM) at room temperature in water, as a control, showing no absorbance in this range.

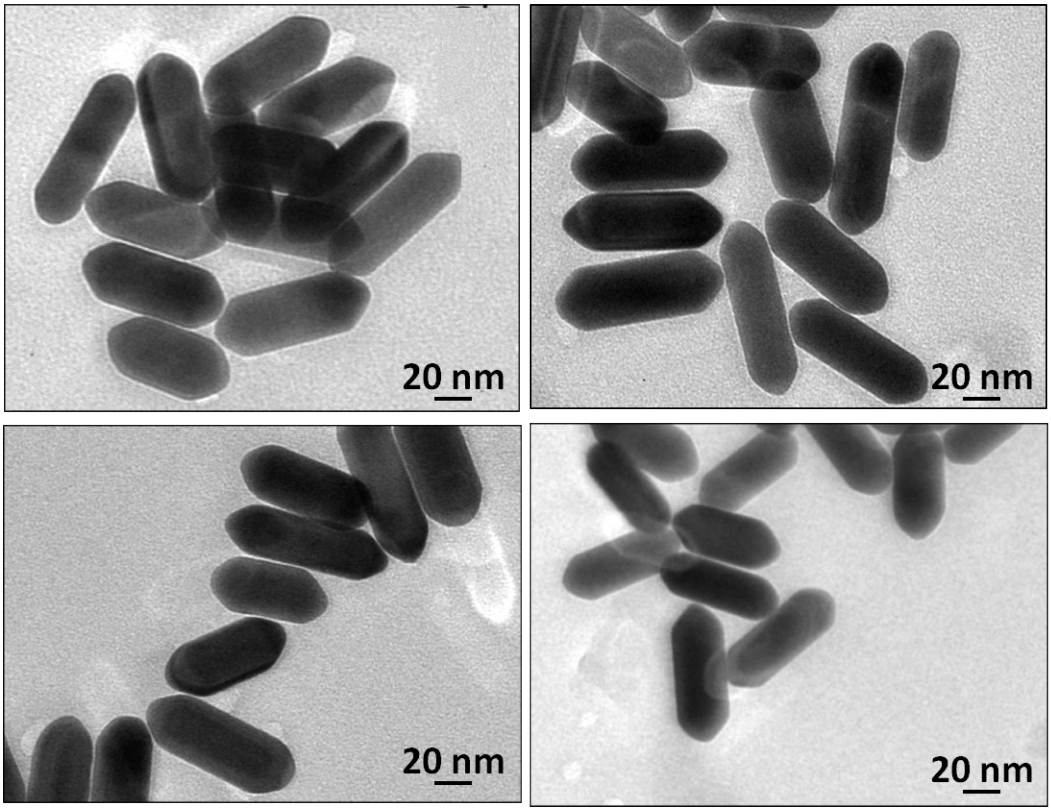

Figure S5. Additional lower-magnification TEM images of AuNRs after etching with cysteamine. AuNRs were end-coated with silica, then etched for 24 hours using 53 mM cysteamine.

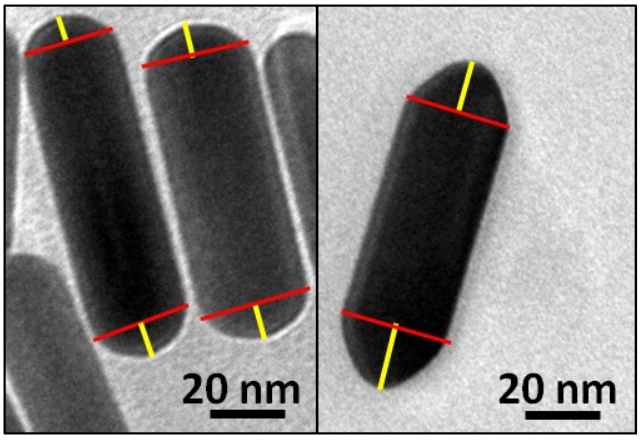

Figure S6. TEM pictures of unetched (left) and etched (right) AuNRs, with lines depicting how tip length is measured. Red lines represent the ends of the cylindrical part of the AuNRs. Yellow lines, representing the tip length, are drawn perpendicularly to the red lines from the red line to the tip of the AuNR.

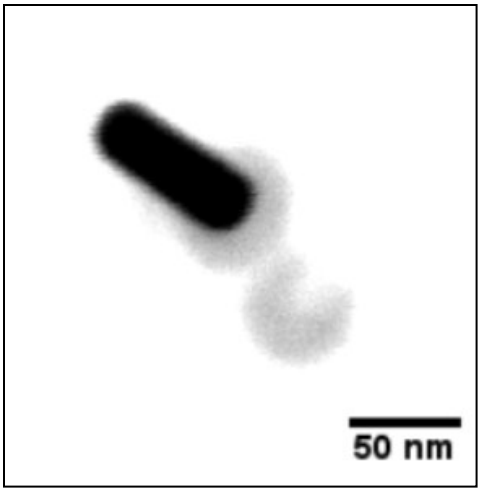

Figure S7. STEM image showing a silica end-coated AuNR. One end remains coated with silica. It appears the silica has been dislodged from the other end. A silica cap is also shown located below the AuNR.

References:

1. Ye, X.; Zheng, C.; Chen, J.; Gao, Y.; Murray, C. B., Using Binary Surfactant Mixtures To Simultaneously Improve the Dimensional Tunability and Monodispersity in the Seeded Growth of Gold Nanorods. *Nano Letters* **2013,** *13* (2), 765-771.
2. Hinman, J. G.; Eller, J. R.; Lin, W.; Li, J.; Li, J.; Murphy, C. J., Oxidation State of Capping Agent Affects Spatial Reactivity on Gold Nanorods. *Journal of the American Chemical Society* **2017,** *139* (29), 9851-9854.
3. Wang, F.; Cheng, S.; Bao, Z.; Wang, J., Anisotropic Overgrowth of Metal Heterostructures Induced by a Site-Selective Silica Coating. *Angewandte Chemie International Edition* **2013,** *52* (39), 10344-10348.
4. DeLong, J. M.; Prange, R. K.; Hodges, D. M.; Forney, C. F.; Bishop, M. C.; Quilliam, M., Using a Modified Ferrous Oxidation−Xylenol Orange (FOX) Assay for Detection of Lipid Hydroperoxides in Plant Tissue. *Journal of Agricultural and Food Chemistry* **2002,** *50* (2), 248-254.
5. Olmon, R. L.; Slovick, B.; Johnson, T. W.; Shelton, D.; Oh, S.-H.; Boreman, G. D.; Raschke, M. B., Optical dielectric function of gold. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012,** *86* (23), 235147/1-235147/9.