Electronic Supporting Information (ESI)

Facile Synthesis of Anisotropic Au@SiO$_2$ Core-Shell Nanostructures

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CONTENTS PAGE

1. Experimental Methods:

Synthesis of spherical Au nanoparticles: Our approach is based on a seeded growth method reported previously,[1] with slight modification. The difference in our method involves the type of surfactant used for stabilization of the spherical Au nanoparticles. Instead of using 80 mM CTABr, we chose to use 10 mM CTABr since this allows for suitable stabilization of the nanoparticles without requiring separation of excess CTABr by centrifugation. However, we found that this method yields low aspect ratio Au nanorods as a byproduct if the nanoparticles are grown above 20 nm in diameter. Since it is well known that CTABr surfactant favors the growth of anisotropic Au nanorods, we switched to CTACl (Br is replaced by Cl) instead. We found that by using 10 mM CTACl we were able to avoid the growth of anisotropic Au nanorods, while growing the Au nanospheres from 5-50 nm in diameter by simply adding more $HAuCl_4$ precursor.

Synthesis of anisotropic Au nanostructures: To obtain anisotropic Au nanostructures, spherical Au nanoparticles are used as “seeds” for the secondary growth of anisotropic Au nanorods or nanoprisms. The detailed synthesis of each Au architecture is given separately below.

Synthesis of Au Seeds: 1 mL of 10 mM sodium citrate solution and 1 mL of 10 mM $HAuCl_4$ solution was added to 37 mL Nanopure H_2O (18.2 MΩ cm) in a 50 mL beaker, while stirring. Meanwhile, a solution of 100 mM sodium borohydride ($NaBH_4$) was prepared and placed in an ice-bath for 10 minutes. Once cold, 1 mL of the 100 mM $NaBH_4$ solution was added to the sodium citrate-$HAuCl_4$ solution. The resulting solution immediately turned reddish-brown in color, which indicated the formation of Au nanoparticles approximately 5-7 nm in diameter. The Au seeds were left undisturbed at room temperature (22°C) for 2-3 hours to allow for hydrolysis of any remaining $NaBH_4$ before further use.

Synthesis of Au Nanorods: A single 100 mL growth solution consisting of 0.25 mM $HAuCl_4$ in 100 mM CTABr, maintained at 25°C (to prevent the crystallization of CTABr) was used for both nanorods and nanoprisms. Then, 550 µL of 100 mM ascorbic acid was added, at which time the solution turned colorless, indicating the reduction of $Au^{(III)}$ to $Au^{(I)}$. Next, 550 µL of 100 mM NaOH was added, raising the final pH of the solution to pH = 4. To initiate growth, 100 µL of Au seed solution was added, briefly stirred, and allowed to sit overnight (~10 hrs) in a water bath maintained at 25°C.

Synthesis of Au Nanoprisms: The synthesis conditions were identical to the Au nanorod synthesis, except that 50 mM CTABr was used (instead of 100 mM CTABr) and 10 µL of 100 mM NaI was added prior to Au seed addition in order to achieve a final concentration of 10 µM NaI.

Separation of Nanostructures: Under these synthesis conditions, the nanoprisms or nanorods were precipitated out of solution by allowing the products to sit overnight (~10 hours) in a water bath maintained at 25°C. The next morning the growth solution was poured out, while the precipitate was redispersed in 10 mL of 10 mM CTABr solution with brief sonication to afford high-purity solutions of nanorods or nanoprisms.

Synthesis of SiO_2 shell: Prior to synthesis of the silica shell, the as-prepared nanoparticle dispersions were centrifuged to remove any excess CTABr from solution. The anisotropic nanorods and nanoprisms were washed once by centrifugation at 4,000 rpm for 5 minutes and redispersed in 4 mL Nanopure H_2O (18 MΩ cm). The isotropic Au nanospheres were washed once at 14,000 rpm for 30 minutes and redispersed in 4 mL Nanopure H_2O (18 MΩ cm). The base-catalyzed condensation of SiO_2 shells onto the Au nanoparticle surface was accomplished by addition of 50 μL of 100 mM NaOH to the 4 mL Au nanostructure dispersion to achieve a final solution pH = 10. Silica shell formation was initiated by addition of various amounts of tetraehtylorthosilicate (TEOS) (5-10 μL TEOS) to the nanoparticle dispersion under vigorous stirring. The colloidal dispersion is allowed to react for 30 minutes while stirring, followed by another addition of TEOS. This can be repeated numerous times to achieve a final SiO_2 shell of the desired thickness. For example, synthesis of Au@SiO_2 nanorods with a 20 nm thick SiO_2 shell required three additions of 10 μL TEOS, with each addition separated by 30 minutes. After the final TEOS addition, the solution is allowed to react overnight while stirring. The next morning the Au@SiO_2 nanostructures are collected by centrifugation at 4,000 rpm for 5 minutes and redispersed in Nanopure H_2O (18 MΩ cm).

2. Additional Data and Transmission Electron Microscopy (TEM) images:

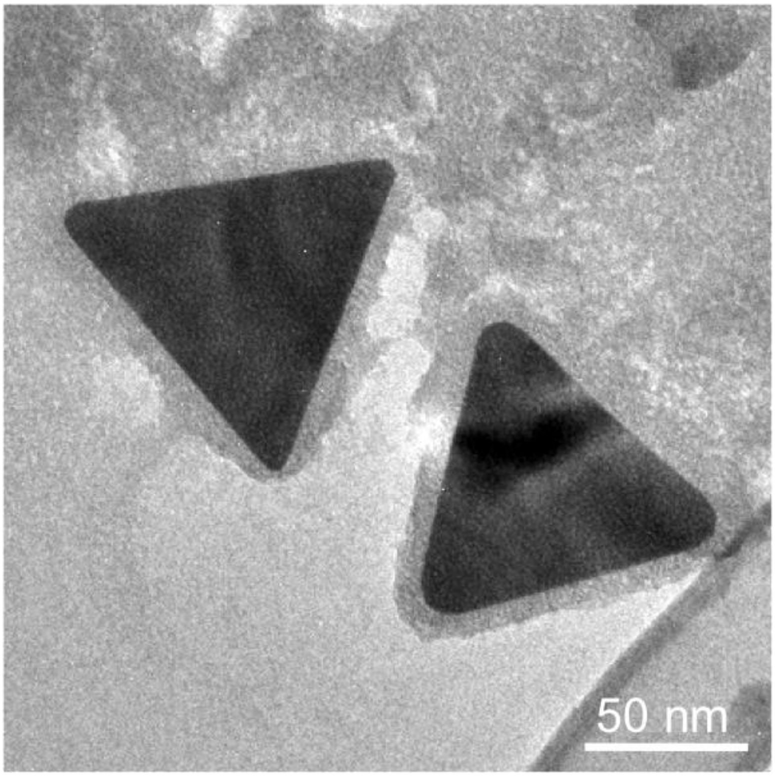

Figure S1: TEM image of SiO_2 coated Au nanoprisms synthesized from the as prepared CTABr-stabilized Au nanoprisms. The image shows a large amount of free silica formed as a by-product of the silica condensation reaction.

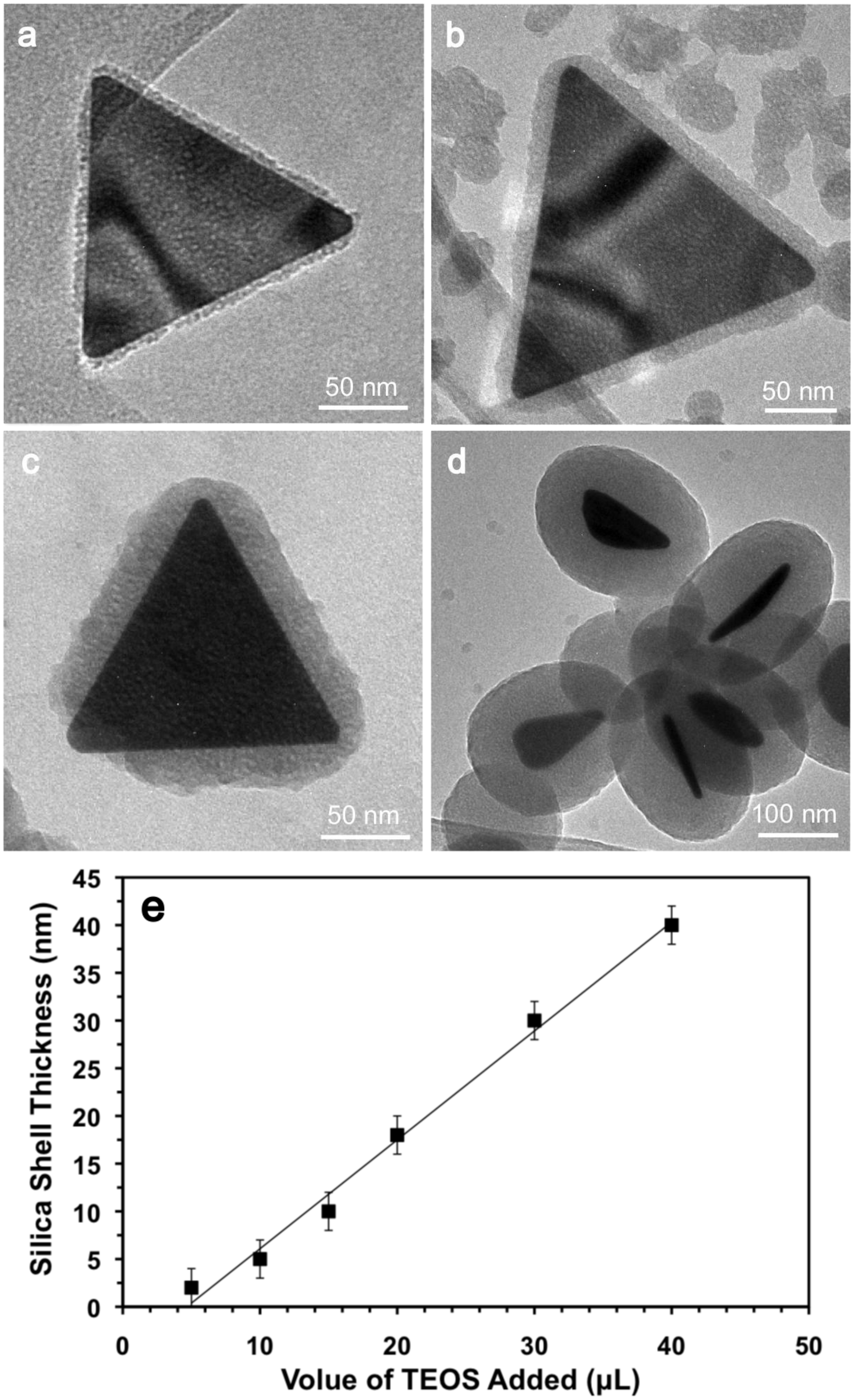

Figure S2: (a-d) TEM images of SiO$_2$ coated nanoprisms synthesized with increasing addition of silica precursor: (a) 10 μL, (b) 15 μL, (c) 20 μL, and (d) 40 μL TEOS. (e) Plot of silica shell thickness, showing the nearly linear relationship between amount of TEOS added and the thickness of the silica shell obtained.

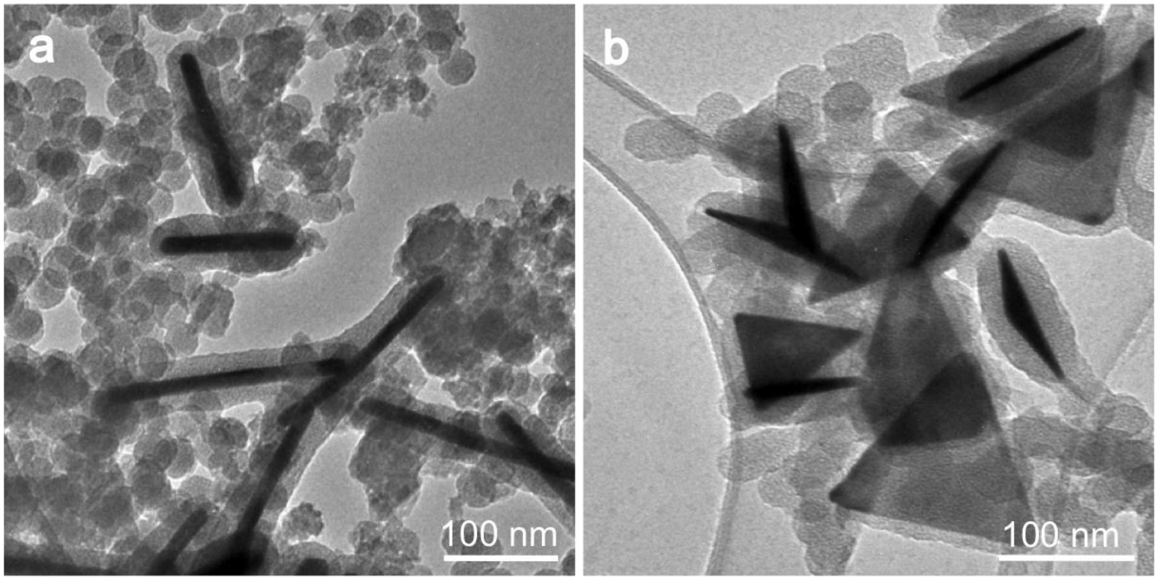

Figure S3: TEM images of SiO_2 coated nanorods (a) and nanoprisms (b) synthesized with 30 µL TEOS for both. This amount of silica precursor usually results in free silica nanoparticles forming in addition to the desired Au@SiO_2 core-shell morphology.

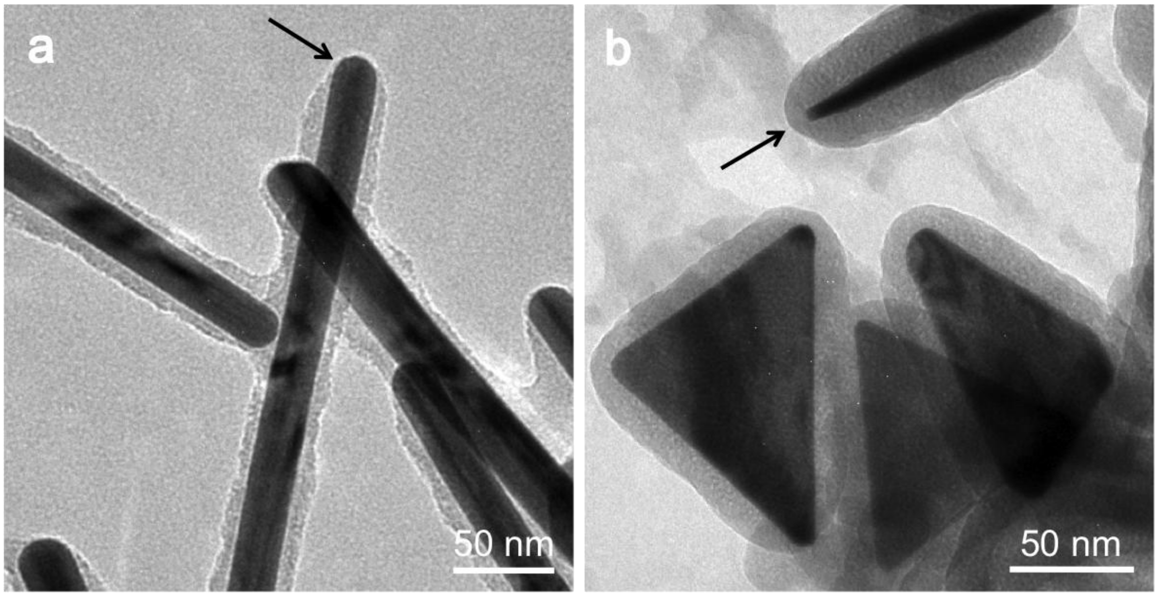

Figure S4: TEM images of SiO_2 coated Au nanorods (a) and nanoprisms (b), showing anisotropic growth of SiO_2 shell around the Au nanostructure. The tips of the Au nanorods and the vertices of the Au nanoprisms have much thinner SiO_2 shells (indicated by arrows) than the long axis of the nanorods and flat facets of the nanoprisms.

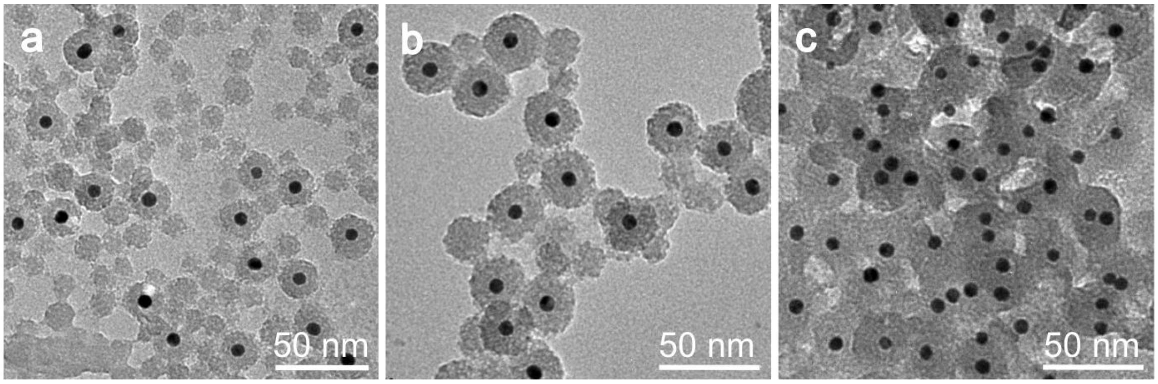

Figure S5: TEM images of SiO_2 coated Au nanoparticles synthesized with different Au nanoparticle number densities: (a) regular number density obtained after initial Au nanoparticle synthesis, (b) twice that of (a), and (c) three times that of (a).

3. Supporting Information References for Methods:

N. R. Jana, L. Gearheart, C. J. Murphy. *Langmuir, 2001,* ***17****, 6782-6786.*