

A Robust Procedure for the Functionalization of Gold Nanorods and Noble Metal Nanoparticles

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S1 Materials.

Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium borohydride (NaBH_4), silver nitrate, ascorbic acid, cetyltrimethylammonium bromide (CTAB; Cat. number H9151), 11-mercaptoundecaonic acid (MUA), 3-amino-5-mercapto-1,2,4-triazole (AMTAZ) and dodecanethiol were obtained from Sigma-Aldrich and used as received. Polyethyleneglycol thiol (PEG-SH, Fw 5000) was obtained from Rapp polymer. Water used in the experiments was purified with a Millipore water treatment system (organic content less than 5 ppb).

S2 Gold Nanorods and Nanoparticles Synthesis.

Gold nanorods were prepared using the seed-mediated method in presence of the cationic surfactant cetyltrimethylammonium bromide (CTAB). To prepare the gold seeds, an aqueous CTAB solution (0.2 M, 5.0 mL) was mixed with 0.5 mM NaAuCl_4 (5.0 mL) prior to the addition of ice-cold 0.01 M NaBH_4 (0.6 mL). The brownish-yellow seed solution was then added (12 μL) under strong agitation to a growth solution prepared as follow. CTAB (0.2 M, 10.0 mL) was mixed with 1.0 mM NaAuCl_4 (10.0 mL) and

various amounts of AgNO_3 (0.1 M). 78.8 mM ascorbic acid (1.4 mL) was then added as a mild reducing agent which resulted into disappearance of the colour of the growth solution. The reaction was left to proceed for 24 h at 28 °C and the rods solutions were purified by centrifugation at 7000 rpm for 10 min and resuspended in milliQ water. Gold Nanoparticles were synthesized using a standard method based on the citrate reduction of gold chloride. A 1% trisodium citrate solution in water was added to a 0.01% solution of NaAuCl_4 under reflux and kept under strong agitation. The colour change indicated the successful synthesis of the gold nanoparticles.

S3. Characterization.

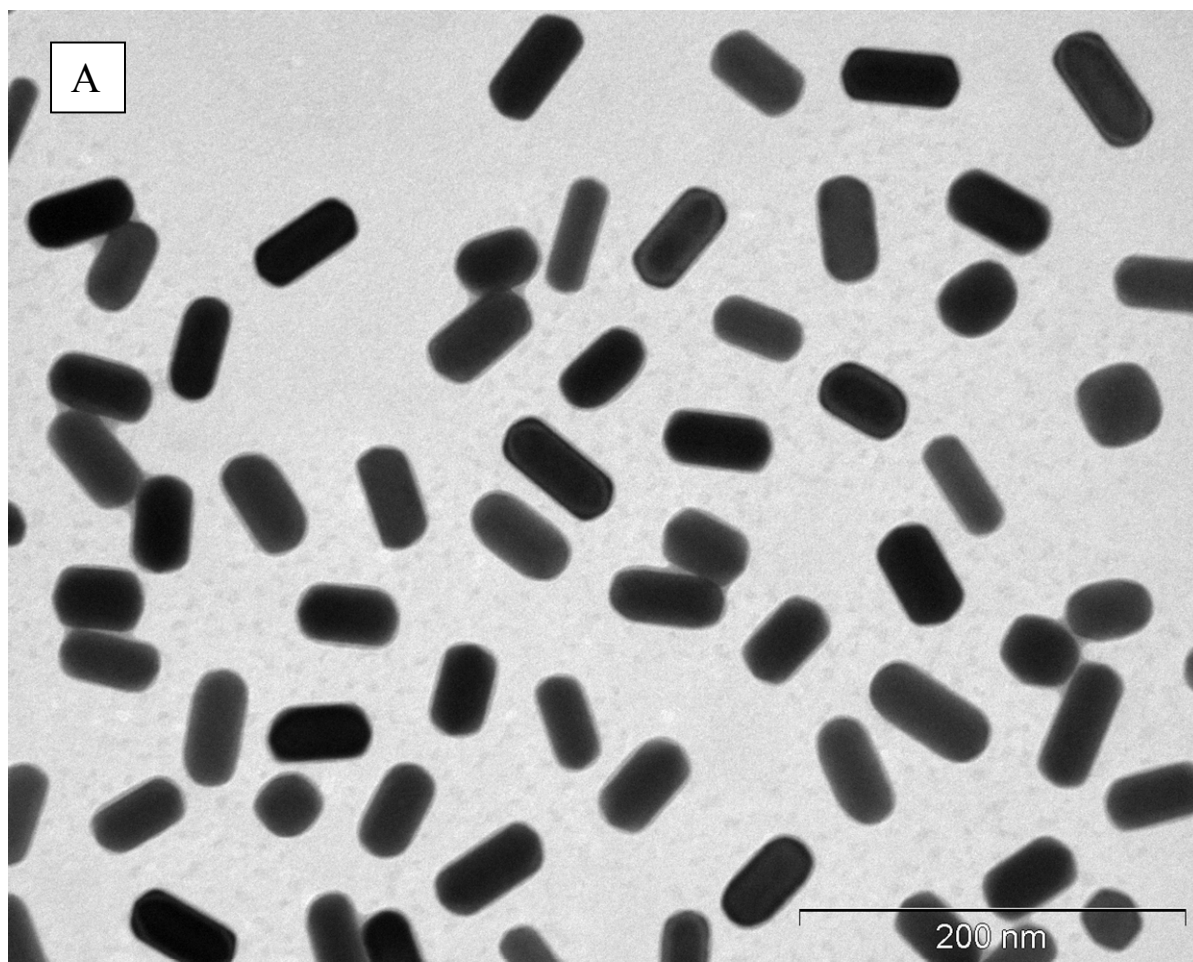
UVvisible absorption measurements were carried out with a Varian Cary 5 UV-vis-NIR spectrophotometer at room temperature. The sample grids for TEM measurements were prepared by dropping gold nanorods dispersion onto the copper grids. Grids were imaged using a JEOL 2010F scanning transmission electron microscope (TEM) equipped with a field emission gun electron source operated at 200 kV (JEOL, Japan). Elemental analyses were conducted using XPS. The nanoparticles were washed at least 4 times using centrifugation/resuspension in appropriate buffer/solvent. A concentrated nanoparticle solution was then drop-cast onto gold-coated silicon wafers. XPS analyses were conducted using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer with a monochromatic Al $K\alpha$ X-ray source and a hemispherical analyzer. The pass energy was 20 eV with a resolution of 0.3 eV for high-resolution spectra. Spectra were collected at a photoelectron takeoff angle of 90°. Binding energies were referenced to the C1s hydrocarbon carbon peak at 285.0 eV to compensate for surface charging effects. Component fitting of the high resolution spectra was performed using CasaXPS version 2.3.12 software. Shirley-type backgrounds were used and constrained to a full width at half-maximum between 0.9 and 1.5 eV. The peak fits used 70% Gaussian/30% Lorentzian peak shapes.

S4. Ligand Exchange Procedures

The first step of the ligand exchange procedure relies on the introduction of a polyethyleneglycol layer to provide steric stabilization to the gold nanorods. Under vigorous stirring, equi-volumic solutions of gold nanorods in H₂O (x 1 wash) and polyethyleneglycol-thiol solution (1 mg/mL in H₂O) were mixed, sonicated for 30 sec and left to react for 2 h. Excess PEG molecules were removed by centrifugation at 7000 rpm for 10 min and the PEGylated rods were resuspended in H₂O (functionalization) or tetrahydrofuran (THF) (hydrophobization).

The second step of the process involves the displacement of residual CTAB molecules and exchange of the PEG-SH layer introduced during the first step. To functionalize the gold nanorods with carboxylic and amine groups, MUA and AMTAZ were used respectively. 250 μ L of a 10 mM solution of MUA prepared in ethanol/water was mixed with 500 μ L of the PEGylated gold nanorods solution dispersed in H₂O. The mixture was placed in a sonic bath and the temperature of the bath was increased to 55 °C and the gold nanorods solution was sonicated for another 60 min. The mixture was kept at room temperature overnight after which sedimentation of the rods could be observed. The nanorods were redispersed for in a sonic bath and then the excess MUA was removed using centrifugation at 7000 rpm for 10 min. The MUA-coated gold nanorods could be readily redispersed into H₂O (pH 9 obtained with 0.1 M NaOH). A similar procedure was used with slight modifications for AMTAZ; a 2 mM solution (pH4) was used and the AMTAZ coated gold nanorods were redispersed at pH4.

To hydrophobize the gold nanorods, alkanethiols such as dodecanethiol were selected. In a typical experiment, PEGylated gold nanorods resuspended in THF were mixed with an ethanolic solution of dodecanethiol (5 mg/mL). As for the functionalization process, the mixture was sonicated for 30 min and then 60 min at 50 °C and then left to react overnight at RT. After purification using 2 rounds of centrifugation (7000 rpm, 10 min), the nanorods could be readily resuspended in THF or CHCl₃ and yielded clear colored solutions. A similar methodology was used to hydrophobize the citrate-gold nanoparticles.



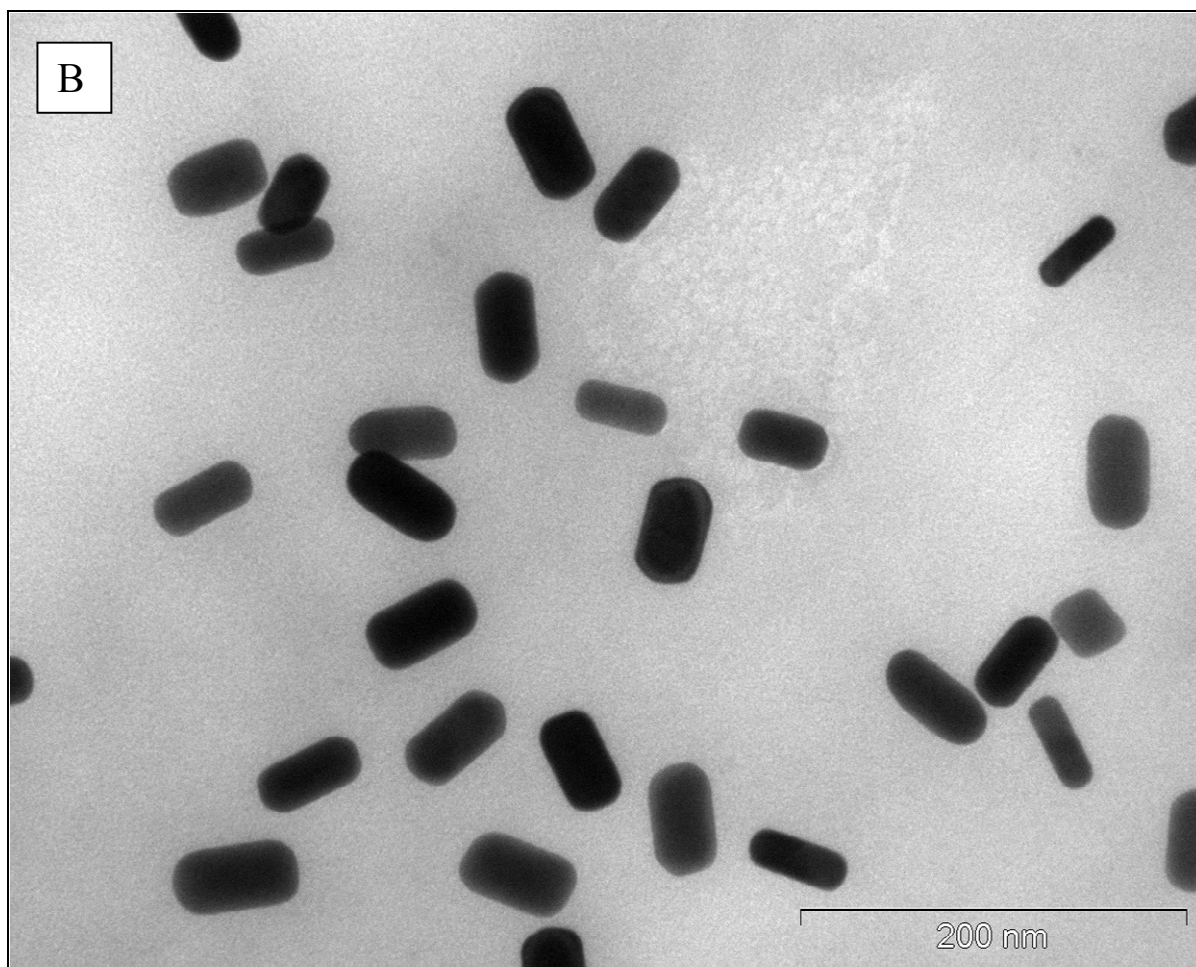


Figure S1. TEM of gold nanorods (A) before (H_2O) and (B) after (THF) the two-steps ligand exchange procedure with dodecanethiol.

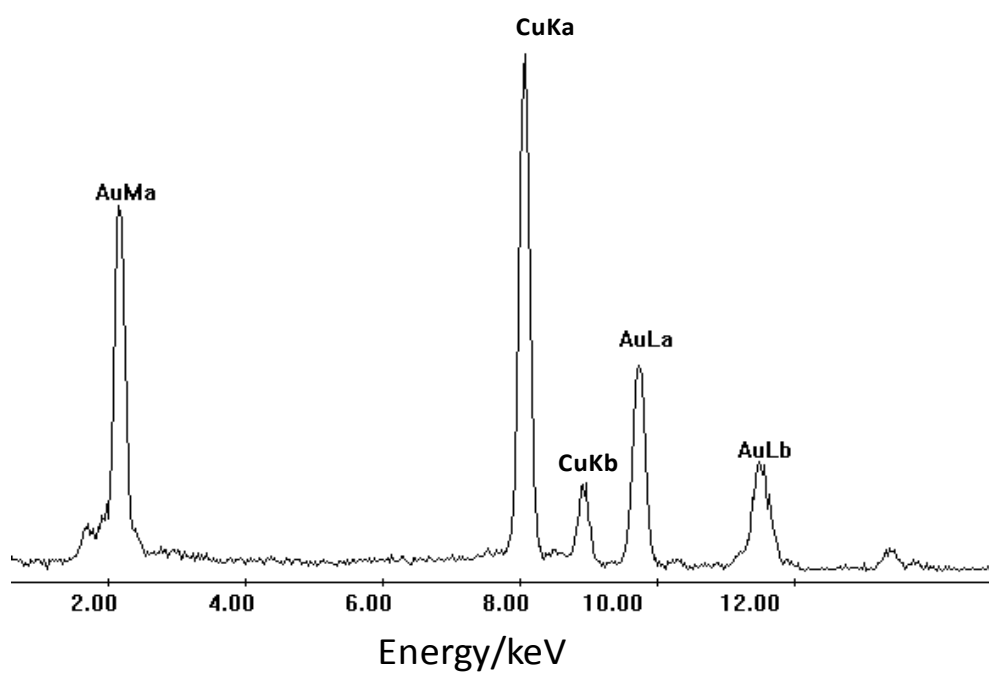


Figure S2. EDX spectrum of hydrophobized gold nanorods.

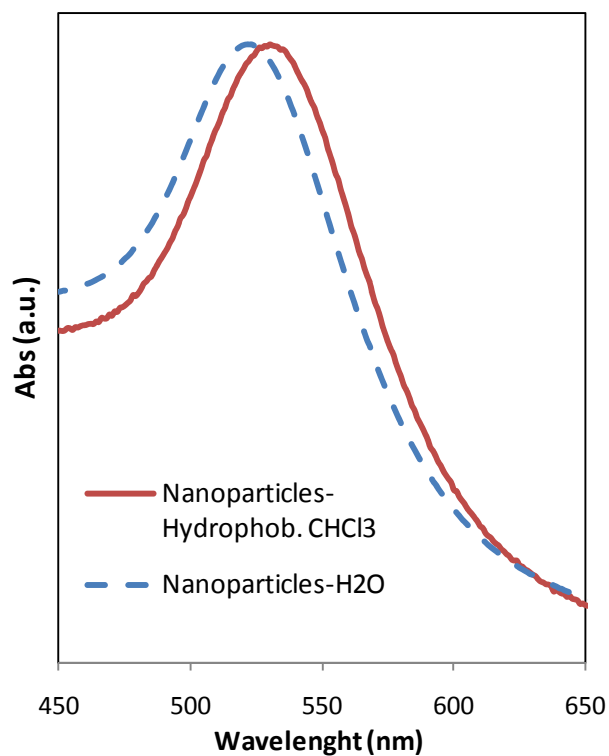


Figure S3. UV-Vis absorption spectra of the as synthesized citrate gold nanoparticles in H₂O (dash line) and the hydrophobized dodecanethiol coated gold nanoparticles in THF (solid line). The spectra have been normalized.

Table S1. XPS elemental ratios recorded on coated gold nanorods.

Samples	% XPS elemental composition					
	C	Au	N	S	O	Br
CTAB	56.3	23.4	2.5	-	6.5	7.2
PEG	48.7	22.1	0	2.2	23.2	0.8
MUA	56	22.1	0	2	17.1	0
AMTAZ	32.7	32.5	12.1	3.5	14.9	0
Hydrophobized	55.1	26.1	0	2.1	11	0