

Supporting Information For
Quantitative Determination of Ligand Densities on Nanomaterials by X-Ray
Photoelectron Spectroscopy

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I. Synthesis of Functionalized Nanoparticles

All materials were used as received, unless otherwise noted. Gold tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), and sodium borohydride (NaBH_4) were obtained from Sigma-Aldrich. ω -(1-Mercaptoundec-11-yl)hexa(ethylene glycol) carboxylic acid ($\text{HS}-(\text{CH}_2)_{11}(\text{EG})_6\text{-COOH}$) was obtained from Prochimia. ω -(1-Mercaptoundec-11-yl)hexa(ethylene glycol) ($\text{HS}-(\text{CH}_2)_{11}(\text{EG})_6\text{-OH}$) was synthesized.¹ All water used is deionized using a Barnstead Nanopure water filtration system to a resistivity of 18.2 M Ω . Pall Minimate tangential flow filtration capsules (50 kD pore size) were used for purification of gold nanoparticles by diafiltration.

To determine how variation of core particle diameter affects the observed ligand signal for comparable ligand functionalization, gold particles of varying sizes were synthesized with either $\text{HS}-(\text{CH}_2)_{11}(\text{EG})_6\text{-COOH}$ or $\text{HS}-(\text{CH}_2)_{11}(\text{EG})_6\text{-OH}$ following previously published methods.²

1.3, 2.1, 4.1, and 6.1 nm diameter particles: To make smaller nanoparticles with nominal diameters of an *aqua regia*-cleaned 500 mL round bottom flask, 400 mL of nanopure deionized water, 1.5 mL of HAuCl_4 (0.1 M), and 1.5 mL 0.1 M $\text{HS}-(\text{CH}_2)_{11}(\text{EG})_6\text{-OH/COOH}$ (the capping ligand) were added sequentially. The resulting clear, colorless solution was stirred for 10 minutes. Afterward, 5.0 mL of a 0.1 M sodium borohydride was added to the solution. At this time, the solution rapidly turned red-orange. Following sodium borohydride addition, the AuNP solution was stirred for three hours. The crude AuNP solution was then purified by diafiltration.^{2b} The size of the nanoparticles was modified by altering the ratio of the capping ligand to Au. In each case, the capping ligand is present in excess. To ensure that as much excess ligand was removed from the AuNP samples as possible, the smaller AuNP samples (1.3 nm, 2.1 nm, 4.1 nm) were centrifuged (14.5 kxG, minimum 60 min) to pellet the Au particles.

The supernatant was removed and the particles were resuspended and sonicated in minimal water.

18 nm particles: 18 nm particles were made by a 2-step procedure where citrate-capped nanoparticles were made, followed by a ligand exchange.^{2a} Small-diameter citrate precursor AuNPs were first synthesized by flowing together in a millifluidic synthesis reactor a solution of 4.0 L of aqueous gold tetrachloroaurate (HAuCl₄, 10 mM) with 10.0 mM sodium citrate (aq) and 4.0 L of sodium borohydride (5.0 mM, aq). After exiting the reactor, the reddish-brown particles were stirred 3.0 hours and concentrated via diafiltration (5.0 volume equivalents).^{2b} These particles were then drop-cast onto a substrate. Citrate was removed via UV-Ozone and then samples were functionalized by immersion in a 10 mM ethanolic solution of HS-(CH₂)₁₁(EG)₆-OH overnight. Prior to analysis, the particle film was again rinsed with isopropyl alcohol and water.

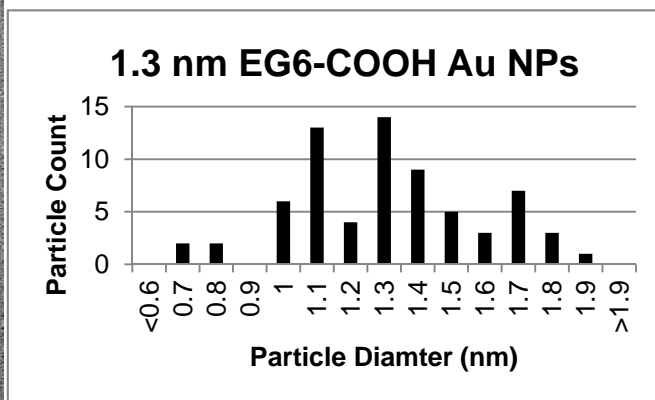
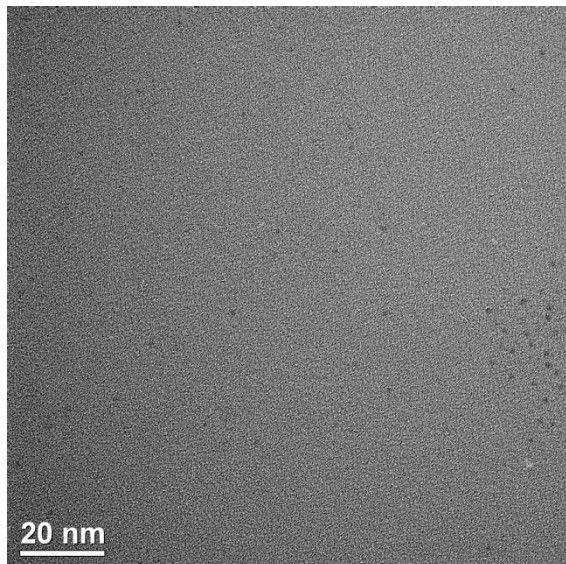
Planar Gold Samples: Gold was evaporated onto silicon with a Ti adhesion layer using an electron-beam evaporator, and the surface was functionalized and cleaned in the same manner as the particles.

In some cases, we made duplicate samples and exposed some of the samples to illumination to ultraviolet light from a low-pressure mercury lamp (nominally 254 nm, with some intensity at 185 nm). These exposure conditions remove organic material without otherwise altering the morphology of the films. XPS measurements on these “clean” films, when compared with the functionalized samples, allow direct determination of the attenuation of gold by the organic films. All samples were gently rinsed in water prior to analysis to remove potentially remaining unbound ligand.

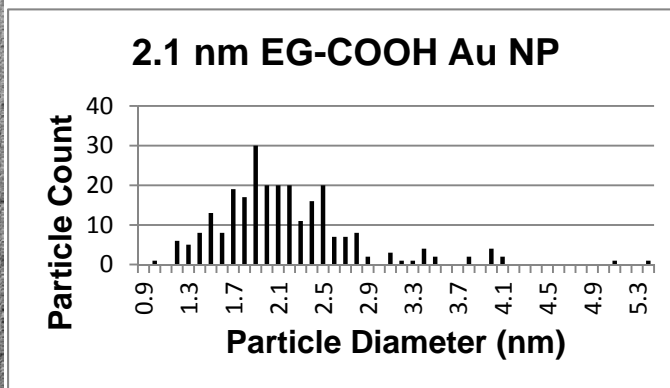
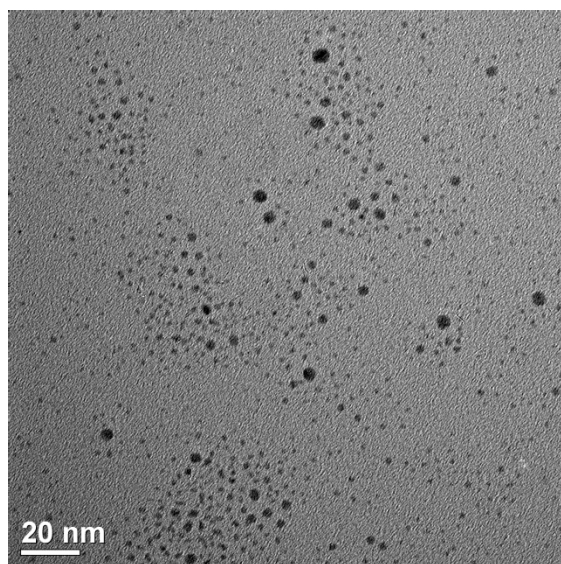
II. TEM Characterization

Nanoparticles were analyzed by transmission electron microscopy (TEM). Particles were diluted 10-fold in ethanol, dried onto a 300 mesh pure carbon grid (Ted Pella), and viewed with a Philips FEG CM200 Ultra Twin TEM at 200 kV accelerating voltage.

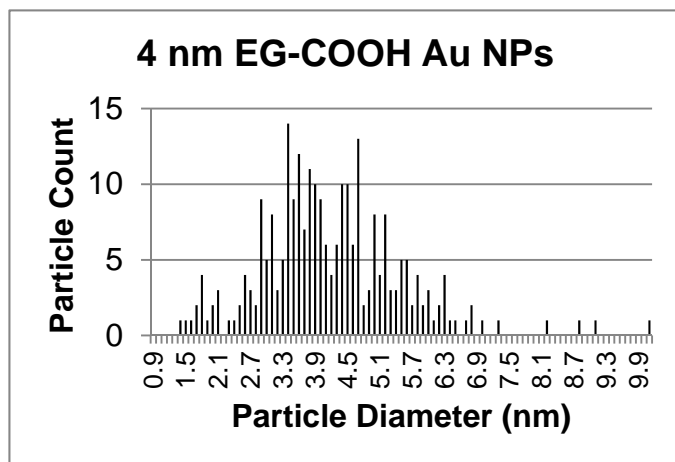
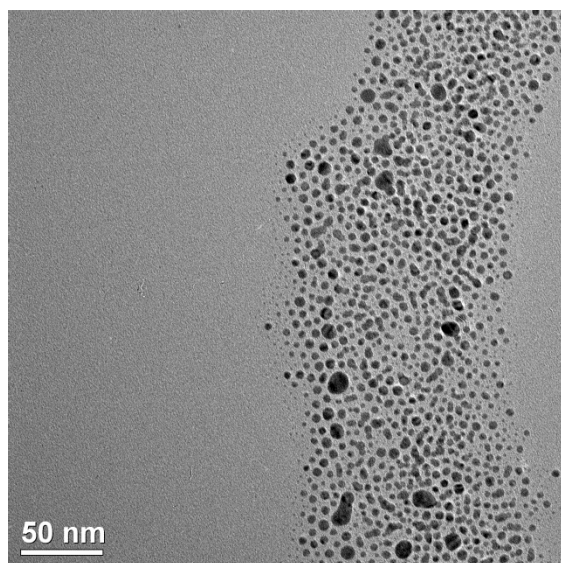
EG₆ -COOH Particles



Average particle diameter determined to be 1.3 ± 0.3 nm (n=69).

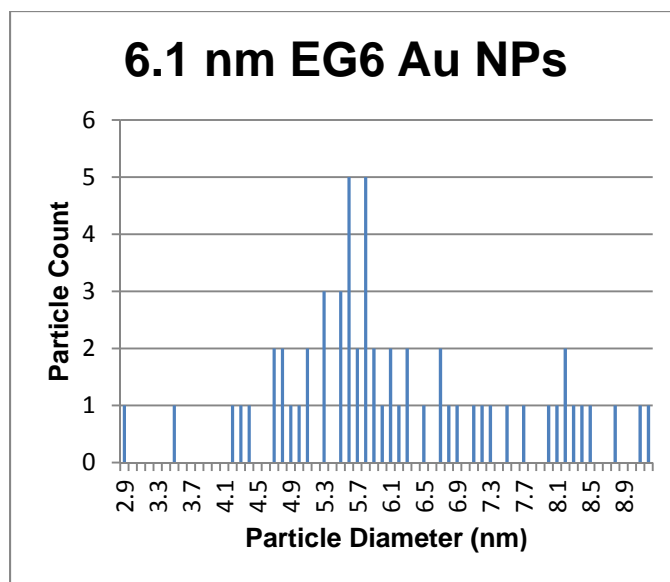
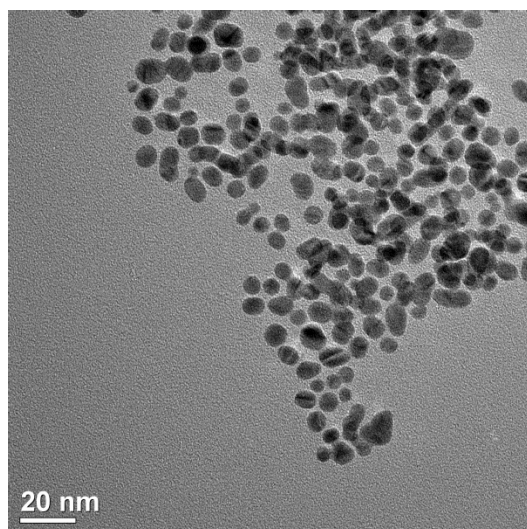


Average particle diameter determined to be 2.1 ± 0.6 nm (n=249).

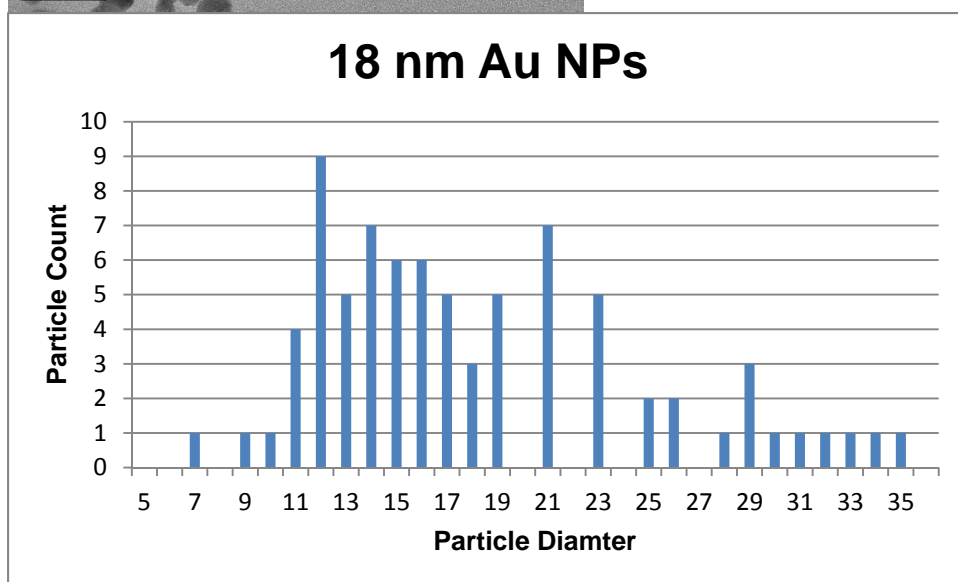
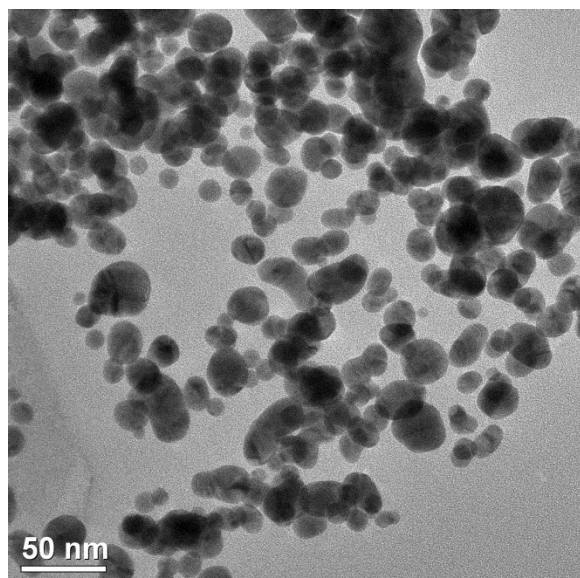


Average particle diameter determined to be 4 ± 1 (n=255).

EG-OH Particles



Average particle diameter determined to be 6.1 ± 1.5 nm (n=59).



Average particle diameter determined to be 18 ± 6 nm (n=79).

Citations

- (1) Putans, R. A., Torelli, Marco D., Jackson, K. Mensch, Arielle C., Meyer, Madeleine M., Pedersen, Joel A., Hamers, Robert J., Synthesis of modular ligands for functionalization of diamond surfaces with positive, negative, and neutral charge control. *In Preparation* **2014**.
- (2) (a) Jana, N. R.; Gearheart, L.; Murphy, C. J., Seeding Growth for Size Control of 5–40 nm Diameter Gold Nanoparticles. *Langmuir* **2001**, *17*, 6782-6786; (b) Sweeney, S. F.; Woehrle, G. H.; Hutchison, J. E., Rapid Purification and Size Separation of Gold Nanoparticles via Diafiltration. *J. Am. Chem. Soc.* **2006**, *128*, 3190-3197.