

Supporting information for:

Surface Modification of Gold Nanorods through a Place Exchange Reaction inside an Ionic Exchange Resin

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Experimental Section

Chemicals and Materials: Hydrogen tetrachloroaurate(III) hydrate (HAuCl_4) was purchased from Strem Chemicals (Newburyport, MA). Cetyltrimethylammonium bromide (CTAB) and Amberlite IRA-67 ion exchange resin were purchased from Aldrich (Milwaukee, WI). Mercaptosuccinic acid and 11-mercaptoundecanoic acid were purchased from Aldrich (Milwaukee, WI). All solvents and chemicals were used without any further purification. Ultrapure water (resistivity 18.3 $\text{M}\Omega$ cm) was used throughout the work.

Instrumentation: UV-Vis absorption Spectra were recorded using a Cary 300 spectrometer. High resolution transmission electron microscopy (HRTEM) was conducted on a FEI TECNAI F30 at 300 KeV. Samples were prepared by placing 5 μL of sample in appropriate solvents onto a 400 mesh carbon/formvar coated copper grid and immediately wicked off using filter paper. $^1\text{H-NMR}$ spectrum was obtained from a Varian 300 MHz instrument. XPS spectrum was recorded on a VG ESCALAB 220i XPS system, which is equipped with a monochromated Al K_α source ($h\nu = 1486.6$ Ev) and semi-spherical energy analyzer.

Synthesis of CTAB-protected Gold Nanorods: Gold nanorods (GNRs) with an aspect ratio of 4:1 were synthesized using a seed-mediated growth method in the presence of a shape-directing

surfactant, cetyltrimethylammonium bromide (CTAB). Gold nanoparticle seeds were first prepared by adding 250 μL of 4 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ to 9 mL of 0.1 M cetyltrimethylammonium bromide (CTAB), 600 μL of ice-cold 0.01 M NaBH_4 was then added with vigorous stirring for 2 hours at room temperature. For the preparation of GNRs, 5 mL of 4 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 400 μL of 8 mM AgNO_3 were added to the 35 mL of 0.1 M CTAB solution at 25°C. To this solution 280 μL of 0.0788 M ascorbic acid was then added, which changed the solution color from dark yellow to colorless. To initiate the growth of GNRs, 100 μL of the seed solution was added to the growth solution, and the reaction was stirred at 28°C for 12 hours. The resulting solution of GNRs was centrifuged twice at 8500 rpm for 30 minutes to remove excessive CTAB surfactants. The GNRs were then re-dispersed in ultrapure water with the concentration of ~ 1 mg/mL.

Thiol Place Exchange Reaction of GNRs in Solution: 200 μL of 15 mM mercaptosuccinic acid aqueous solution was added dropwise into a 1 mL of CTAB-capped GNR aqueous solution. The reaction mixture allowed to shake at room temperature for 1 h, and the solution color change to blue gradually.

Surface Modifications of Gold Nanorods using Ion Exchange Resin: To 1.1 gram dry ionic exchange polymer beads (Imberlite IR-67) suspended in 2 mL of ultrapure water, 2 mL of 1 mg/mL GNRs aqueous solution was added. The suspension was gently shaken at room temperature for 3 hours. The effective loading of GNRs inside the pore of ionic exchange polymer beads was visually observed from the darkening of the polymer beads and the clearance of the aqueous solution color. After washing with water to remove the unloaded GNRs, and drying with methanol, the GNR-loaded ionic exchange polymer beads were suspended in 5 mL of 11-mercaptopundecanoic acid (MUA) chloroform solution (1 mg/mL). The place exchange reaction between the 11-mercaptopundecanoic acid (MUA) and the GNRs were allowed to

proceed for 2 hour with gentle shaking at room temperature. During this time, the chloroform solution turned into dark red gradually, which indicated the diffusion of GNRs out of polymer beads and into the chloroform solution. At the end of the reaction, the chloroform solution was collected. The crude product was washed with methanol and chloroform 4~5 times with occasional sonication followed by centrifugation. The GNRs were then redissolved in chloroform. The yield of the purified gold nanorods product is around 0.8 mg per gram resin.

Figure S1. XPS spectrum of CTAB-GNRs

