

Supporting Information

Citrate-Regulated Surface Morphology of SiO₂@Au Particles to Control the Surface Plasmonic Properties

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Preparation of bare SiO₂ particles. Bare SiO₂ particles were prepared by Stöber method. Typically, 2.4 mL of ammonia solution (28 %) and 0.6 mL of ultrapure water were added to 30 mL of ethanol under stirring. After the temperature of the reaction medium reached 40 °C, 0.1 mL of TEOS was poured to the reaction medium. The resulting SiO₂ particles were collected with the aid of centrifugation at 8000 rpm for 10 min and re-dispersed in H₂O (30 mL) after 12 h. The centrifugation/re-disperison cycle was repeated three times to purify the resulting bare SiO₂ particles.

Synthesis of 4 nm Au nanoparticles. 0.1 mL of the aqueous solution of Na₃Cit (0.17 M) and 1 mL of the aqueous solution of NaBH₄ (0.01 M) were subsequently added into 20 mL of the aqueous solution of HAuCl₄ (0.25 mM and pH of 3.18) under vigorous stirring at 4°C. While the color of the reaction solution changed quickly to reddish brown, the Au nanoparticles with sizes of ca. 4 nm were produced.

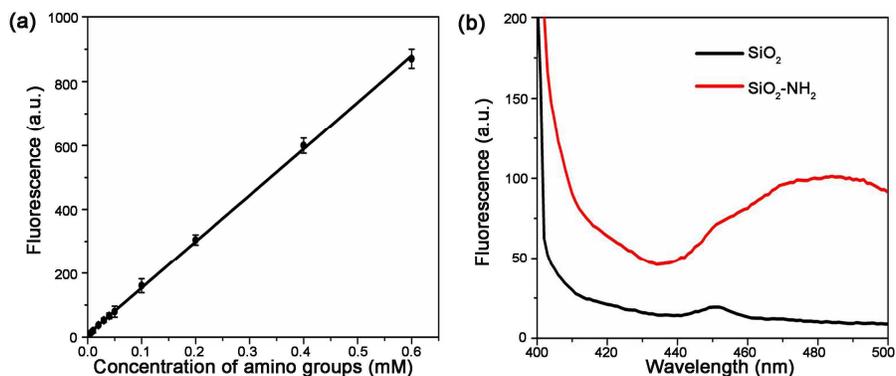


Figure S1. (a) Calibration curve of fluorescamine method obtained by plotting the fluorescence of the fluorescamine reagent versus the concentration of the aqueous solution of APTES. (b) The fluorescence emission spectra of the fluorescamine reagents in the aqueous dispersions of bare SiO₂ (black curve) and SiO₂-NH₂ particles (red curve).

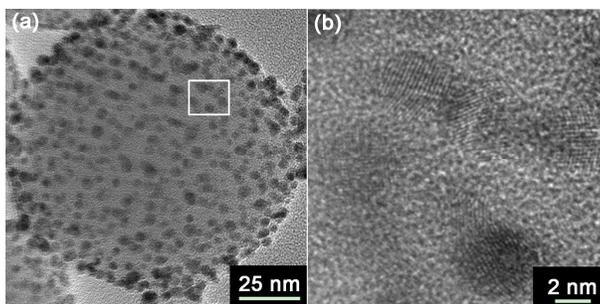


Figure S2. (a) TEM and (b) HRTEM images of SiO₂-NH₂ spheres, decorated with ca. 4 nm Au nanoparticles.

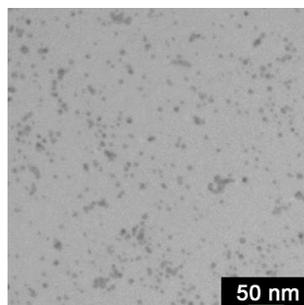


Figure S3. TEM image of Au nanoparticles prepared by NaBH_4 reduction of HAuCl_4 in the presence of Na_3Cit as the stabilizer.

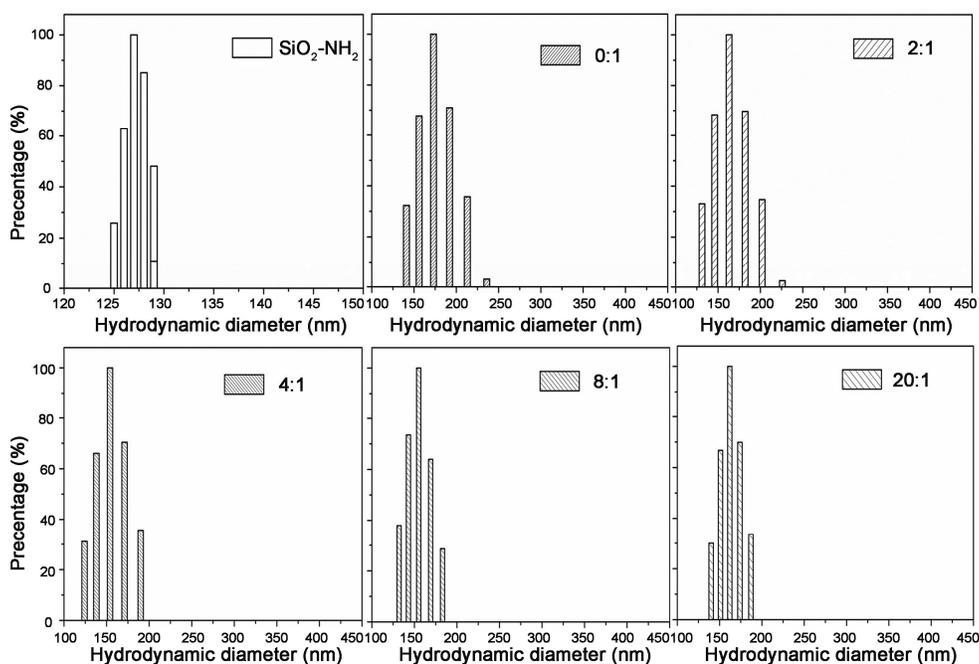


Figure S4. Profiles of the size distributions of the $\text{SiO}_2\text{-NH}_2$ and the $\text{SiO}_2\text{@Au}$ particles prepared at the Na_3Cit -to- HAuCl_4 molar ratio of 0:1, 2:1, 4:1, 8:1, and 20:1. The particle size distribution are determined by DLS analysis. No noticeable difference in size distribution between the $\text{SiO}_2\text{-NH}_2$ and the $\text{SiO}_2\text{@Au}$ particles derived thereof, highlighting little particle aggregation during the formation of $\text{SiO}_2\text{@Au}$ particles.

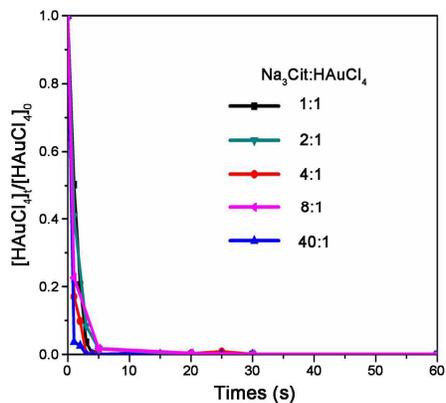


Figure S5. Temporal evolution of the Au (III) ions in the growth solutions at different Na_3Cit -to- HAuCl_4 molar ratios, 1:1, 2:1, 4:1, 8:1, and 40:1.

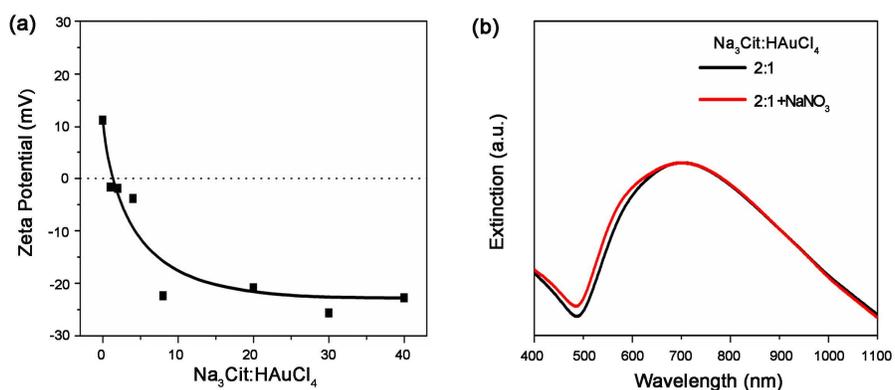


Figure S6. (a) Plot of the zeta potential value of the Au nanoparticle-decorated $\text{SiO}_2\text{-NH}_2$ spheres versus the Na_3Cit -to- HAuCl_4 molar ratio. The spheres are dispersed in the growth solution in the absence of hydroxylamine; the positive zeta-potential arises from the Au nanoparticle-free, NH_2 -functionalized surface regions on the SiO_2 spheres when only HAuCl_4 is present in the growth solution (at the Na_3Cit -to- HAuCl_4 molar ratio of 0:1). (b) Normalized UV-vis spectra of the $\text{SiO}_2\text{@Au}$ particles prepared at the Na_3Cit -to- HAuCl_4 molar ratio of 2:1 in the absence (black curve) and presence of NaNO_3 (red curve).

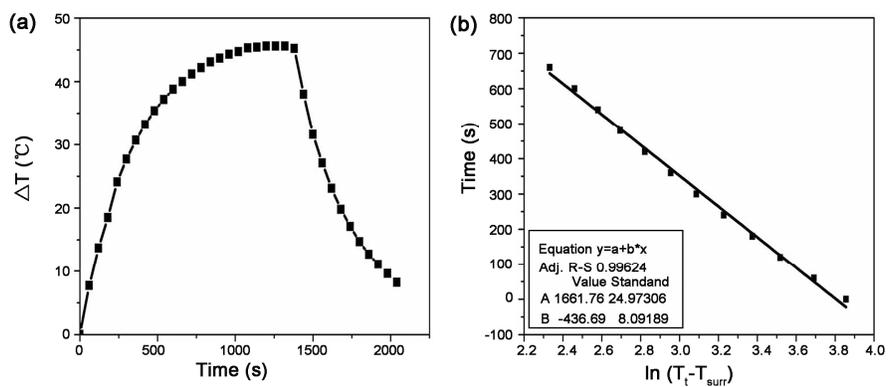


Figure S7 (a) Temporal evolution of the temperature of the aqueous dispersion of SiO₂@Au particles produced at the Na₃Cit-to-HAuCl₄ molar ratio of 8:1. (b) Plot of time versus $\ln(T_t - T_{surr})$ during the cooling period.