SUPPORTING INFORMATION

Synthesis of Thiolate-Protected Au Nanoparticles Revisited: U-Shape Trend between the Size of Nanoparticles and Thiol-to-Au Ratio

Tiankai Chen[†], Zhentao Luo[†], Qiaofeng Yao, Andrea Xin Hui Yeo and Jianping Xie*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585

EXPERIMENTAL SECTION

Chemicals

Ultrapure Millipore water (18.2 M Ω) was used throughout the experiment. Hydrogen tetrachloroaurate (III) hydrate (HAuCl₄·3H₂O) from *Alfa Aesar*; sodium borohydride (NaBH₄) and 3-mercaptobenzoic acid (3-MBA), from *Sigma-Aldrich*; sodium hydroxide (NaOH) from *Merck* were used as received without further purification.

Synthesis of gold nanoparticles/nanoclusters using different thiol-to-gold ratios $(R_{SR/Au})$

In a typical synthesis using a thiol-to-Au ratio ($R_{SR/Au}$) of 1:8, aqueous solutions of 3-MBA (50 mM in 150 mM NaOH, 0.0125 mL) followed by HAuCl₄ (39.93 mM, 0.125 mL) were added to ultrapure water (~4.47 mL) under stirring (500 rpm) at 25 °C. The pH of the solution was increased to ~12.6 using 1 M NaOH solution and the reaction was allowed to stand for 30 minutes before the addition of NaBH₄ (100 mM in 100 mM NaOH, 0.100 mL). The total volume of the solution after the addition of all chemicals was 5 mL. The product was collected for further analysis after 72 h stirring (500 rpm) at room temperature. This procedure was repeated for other thiol-to-Au ratios by varying the amount of 3-MBA added.

Material characterization

UV-Vis absorption spectra were acquired on a Shimadzu UV-1800 spectrometer using standard quartz cuvette. Transmission electron microscopy (TEM) images of the assynthesized Au NPs/NCs were taken on a JEOL JEM 2010 microscope operating at 200 kV. The size of Au NPs/NCs was obtained automatically on the TEM images using Gatan Digital Micrograph software offline. Polyacrylamide gel-electrophoresis (PAGE) experiments were carried out using a vertical electrophoresis cell (Mini-PROTEAN Tetra Cell, Bio-Rad) that employs discontinuous gels with a size of $1.0 \times 83 \times 73$ mm. The resolving and stacking gel were prepared by 30 wt% and 3 wt% of acrylamide monomers [acrylamide/bis-(acrylamide) = 29:1], respectively. For analytical gels (10-well), sample solutions (12 µL of Au NPs/NCs with 2 µL of 60 vol% glycerol) were loaded into the wells of the stacking gel. The eluting buffer consists of 1.5 mM Tris-HCl (pH 8.8) (diluted to ten times). The electrophoresis was allowed to run for ~ 1.5 h at a fixed voltage of 150 V. Electrospray ionization mass spectroscopy (ESI-MS) was done on a Bruker microTOF-Q ESI time-of-flight system operating in negative ion mode. The samples were directly injected into the chamber at 20 µL·min⁻¹. The instrument parameters were set as: capillary voltage, 4 kV; nebulizer, 0.4 bars; dry gas, 4 L·min⁻¹ at 120 °C.



Fig. S1 TEM images and size histograms of Au NPs synthesized at $R_{SR/Au} = (a) 1:8$, (b) 1:3, (c) 1:1, (d) 2:1, (e) 3:1, (f) 5:1 and (g) 8:1. Scale bar = 20 nm.



Fig. S2 UV-Vis absorption spectra of 3-MBA with a characteristic peak at ~330 nm.



Fig. S3 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[H_4AuO_4]^-$. The red line is the corresponding simulated isotope distribution.



Fig. S4 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of [AuCl₂]⁻. The red line is the corresponding simulated isotope distribution.



Fig. S5 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of [H₃AuO₃Cl]⁻. The red line is the corresponding simulated isotope distribution.



Fig. S6 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[H_5AuO_4Cl - H^+ + Na^+]^-$. The red line is the corresponding simulated isotope distribution.



Fig. S7 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[H_4AuO_3Cl_2 - H^+ + Na^+]^-$. The red line is the corresponding simulated isotope distribution.



Fig. S8 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of [Au(SR)Cl]⁻ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S9 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[Au(SR)_2]^-$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S10 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[Au(SR)_3 - 3H^+ + 3Na^+]^{2-}$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S11 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[H_{15}Au_2O_9]^-$. The red line is the corresponding simulated isotope distribution.



Fig. S12 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[H_{14}Au_2O_8Cl]^-$. The red line is the corresponding simulated isotope distribution.



Fig. S13 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[H_{13}Au_2O_7Cl_2]^-$. The red line is the corresponding simulated isotope distribution.



Fig. S14 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[Au_2(SR)_2 - H^+]^-$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S15 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[Au_2(SR)_3]^-$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S16 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[Au_4(SR)_4 - H^+]^-$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S17 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[Au_5(SR)_5 - 2H^+]^{2-}$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S18 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[Au_6(SR)_6 - 2H^+]^{2-}$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S19 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[Au_{10}(SR)_{10} - 5H^+ + 2Na^+]^{3-}$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.



Fig. S20 Zoom in ESI-MS spectra (top panel) and isotope distribution (bottom panel) of $[RS-SR - H^+]^-$ (where SR denotes 3-MBA). The red line is the corresponding simulated isotope distribution.