

Electronic Supplementary Information

Sinapinic acid-directed synthesis of gold nanocluster and its application to quantitative matrix-assisted laser desorption/ionization mass spectrometry

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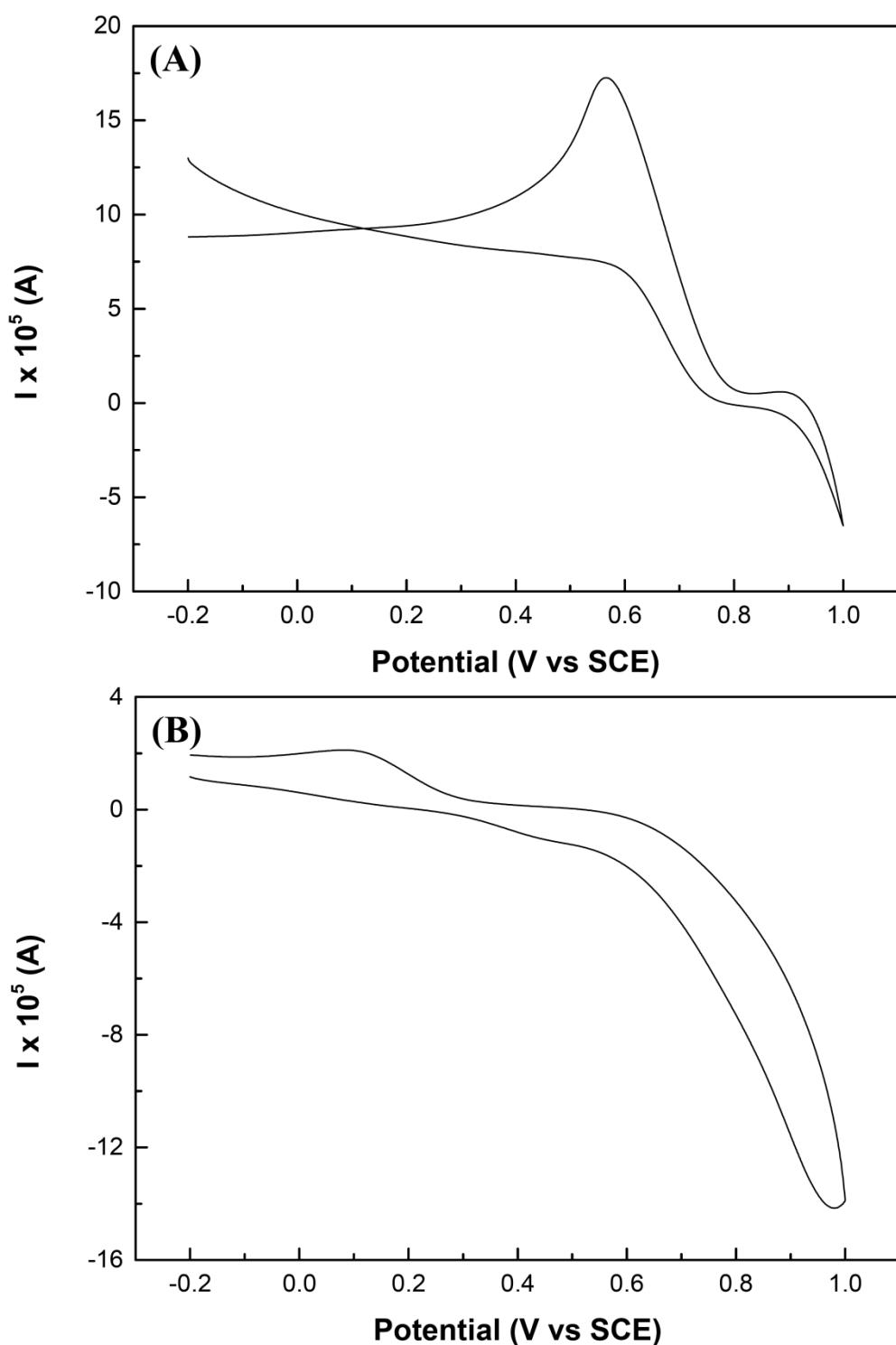


Figure S1. Cyclic voltammogram of (A) 2 mM HAuCl₄ and (B) 33 mg/mL SA in a solution containing 45% v/v acetonitrile, 55% v/v deionized water and 1 M KNO₃. The scan rate is 100 mV/s.

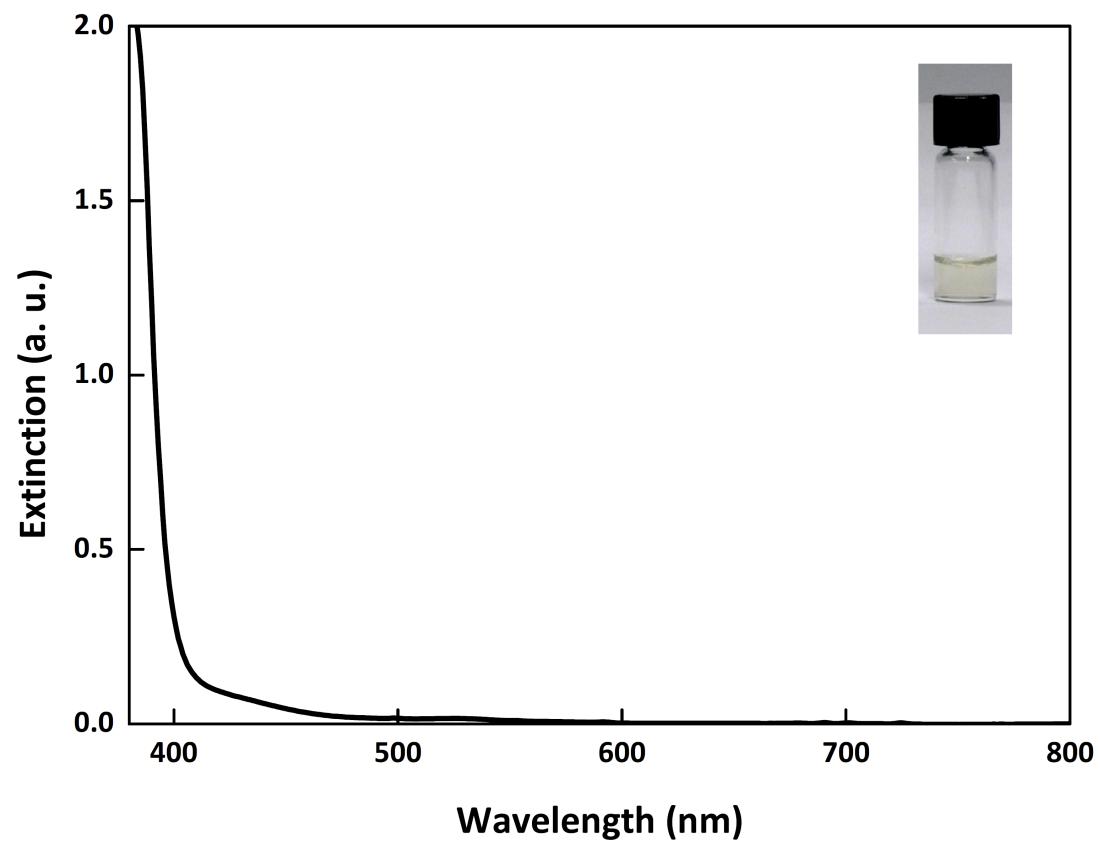


Figure S2. Absorption spectrum and photograph of the SA-AuNCs.

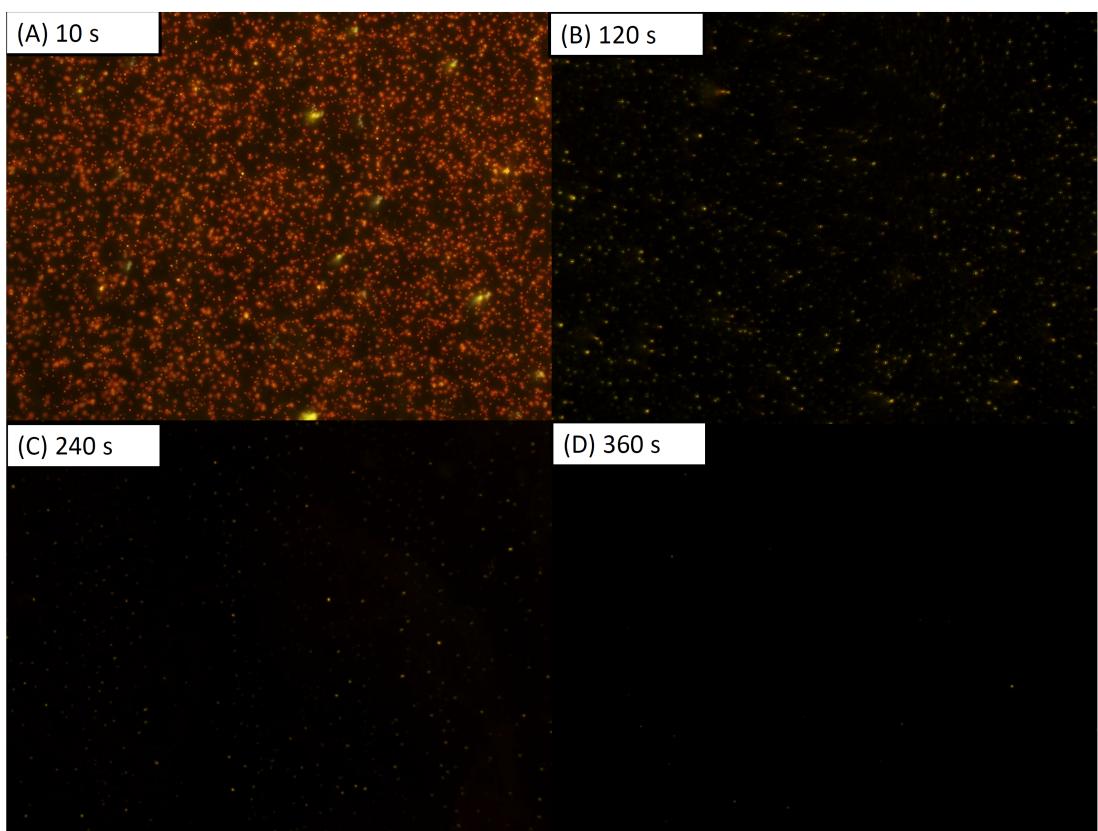


Figure S3. Scattering images of the products obtained from the incubation of 2 mM HAuCl₄ and 26 mg/mL SA in a mixture of 45% v/v acetonitrile and 55% v/v water at 10 s (A), 120 s (B), 240 s (C), and 360 s (D). Exposure times, 50 ms; scattering detection area using a 40× objective, 860 μm × 610 μm corresponding to 4080 (horizontal) × 3072 (vertical) pixels.

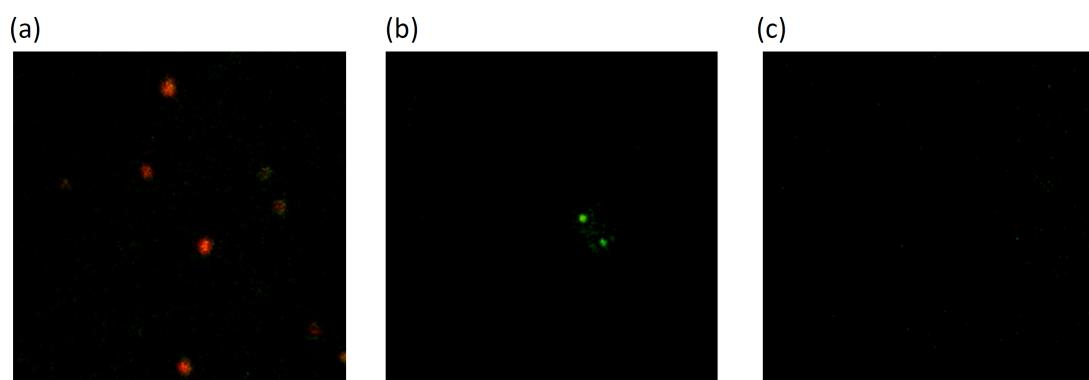


Figure S4. Scattering images of 150, 50, and 10 nm-diameter AuNPs. Exposure times, 50 ms; scattering detection area using a 100 \times objective.

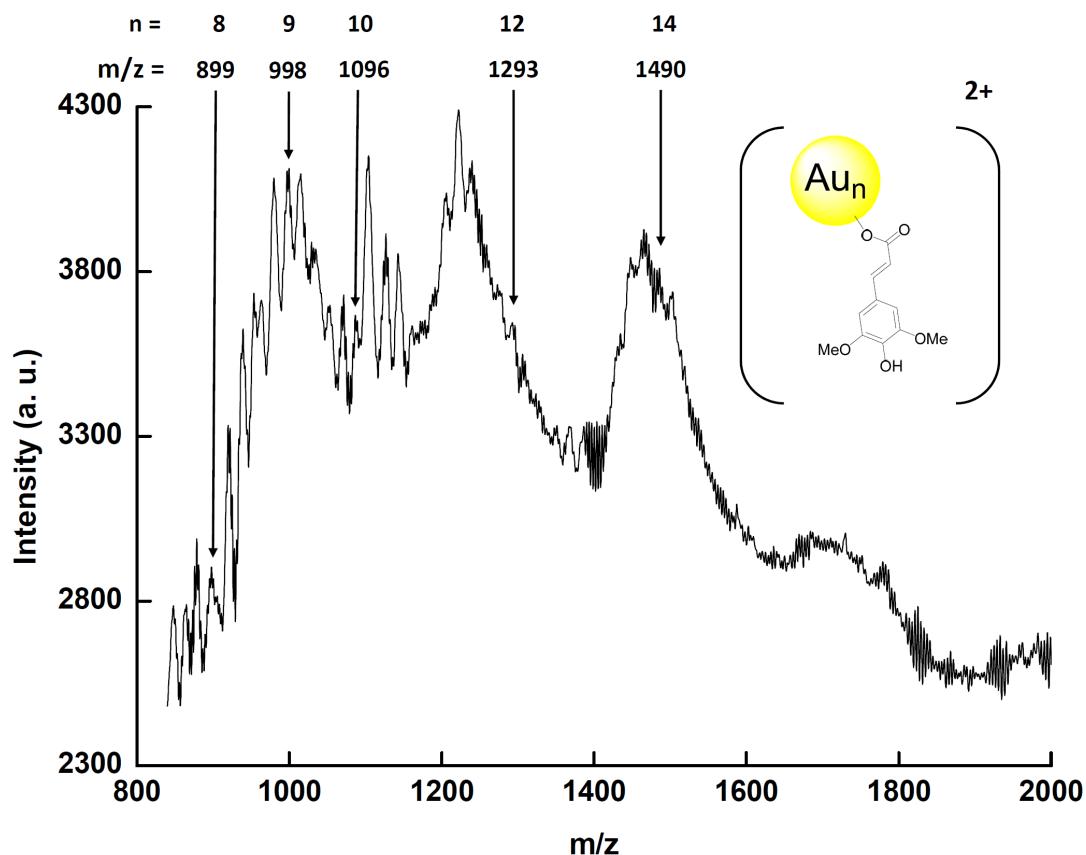


Figure S5. MALDI-TOF MS of the SA-AuNCs. The upper-right corner presents the schematic illustration of the possible structure of the SA-AuNCs. The peaks at m/z 899, 998, 1096, 1293, and 1490 are assigned for $[Au_8(SA)]^{2+}$, $[Au_9(SA)]^{2+}$, $[Au_{10}(SA)]^{2+}$, $[Au_{12}(SA)]^{2+}$, and $[Au_{14}(SA)]^{2+}$,

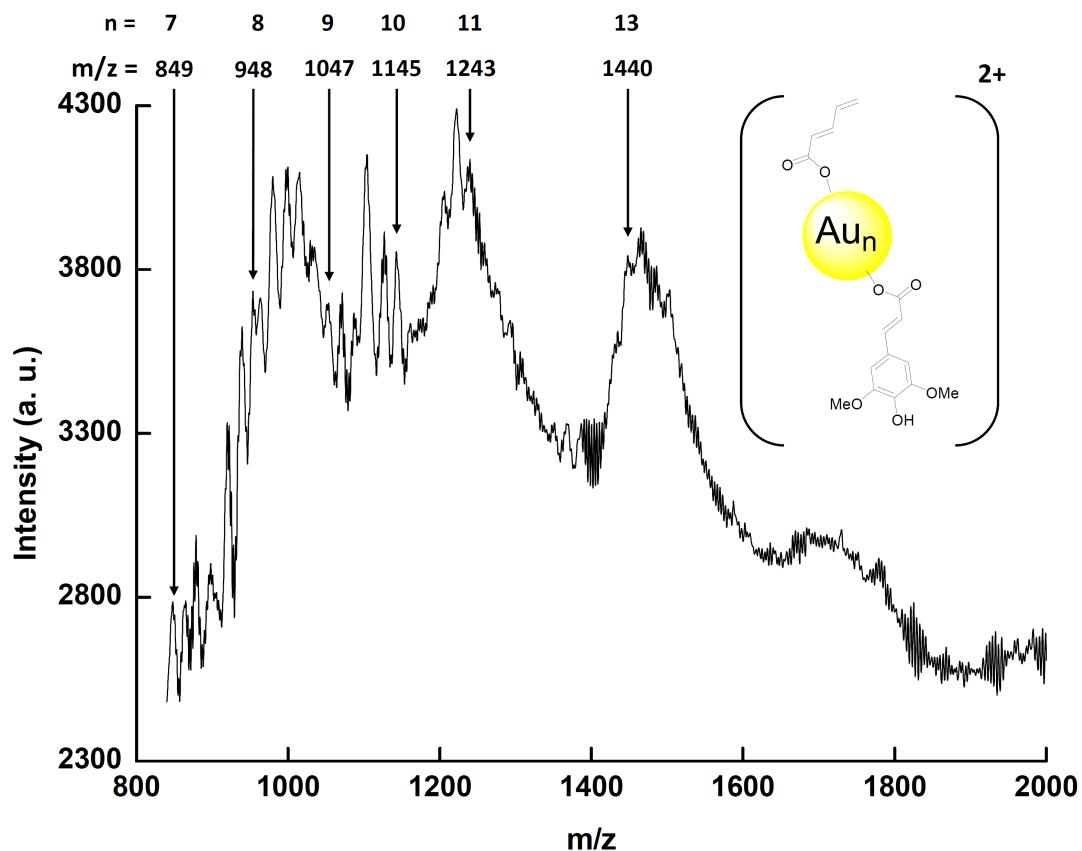


Figure S6. MALDI-TOF MS of the SA-AuNCs. The upper-right corner presents the schematic illustration of the possible structure of the SA-AuNCs. The peaks at m/z 849, 948, 1047, 1145, 1293, and 1440 are assigned for $[\text{Au}_7(\text{SA})(\text{SA fragment})]^{2+}$, $[\text{Au}_8(\text{SA})(\text{SA fragment})]^{2+}$, $[\text{Au}_9(\text{SA})(\text{SA fragment})]^{2+}$, $[\text{Au}_{10}(\text{SA})(\text{SA fragment})]^{2+}$, $[\text{Au}_{11}(\text{SA})(\text{SA fragment})]^{2+}$, and $[\text{Au}_{13}(\text{SA})(\text{SA fragment})]^{2+}$.

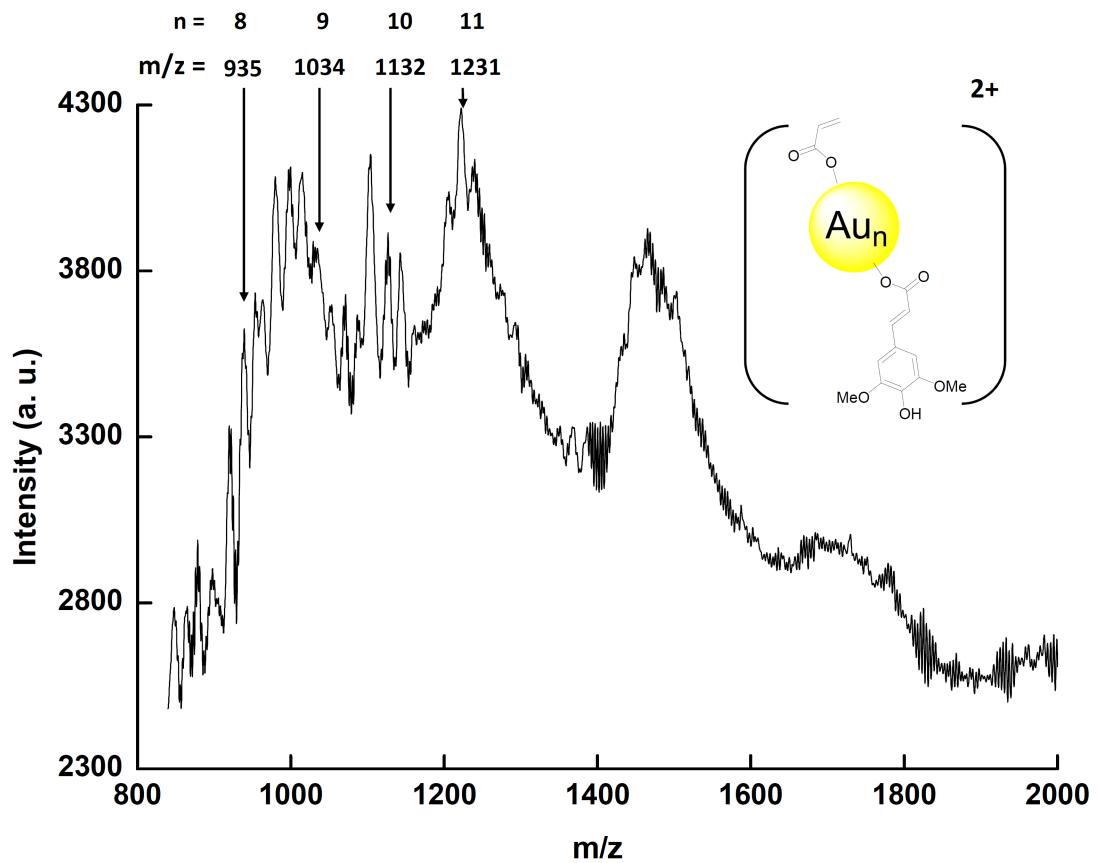


Figure S7. MALDI-TOF MS of the SA-AuNCs. The upper-right corner presents the schematic illustration of the possible structure of the SA-AuNCs. The peaks at m/z 935, 1034, 1132, and 1231 are assigned for $[\text{Au}_8(\text{SA})(\text{SA fragment})]^{2+}$, $[\text{Au}_9(\text{SA})(\text{SA fragment})]^{2+}$, $[\text{Au}_{10}(\text{SA})(\text{SA fragment})]^{2+}$, and $[\text{Au}_{11}(\text{SA})(\text{SA fragment})]^{2+}$.

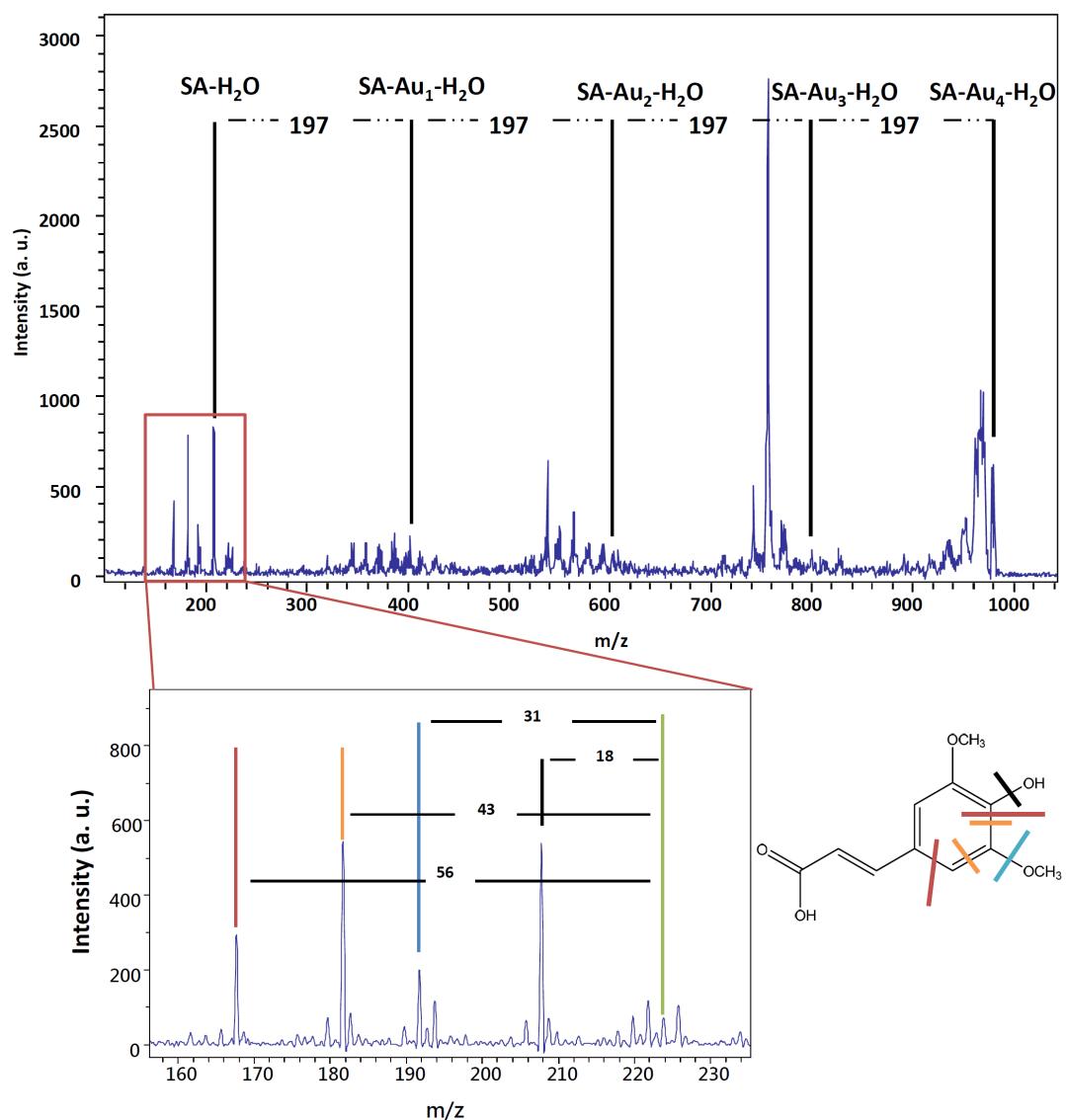


Figure S8. MALDI-TOF MS/MS spectrum of the SA-AuNCs.

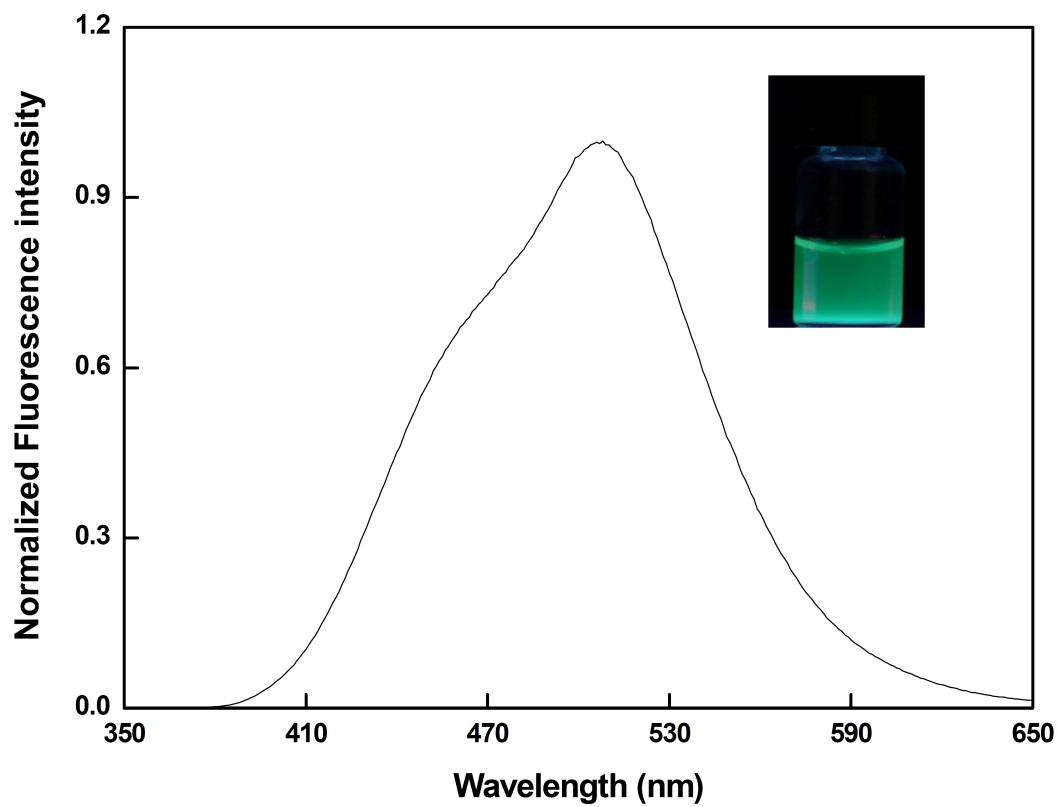


Figure S9. Fluorescence spectrum and photograph of lysozyme-modified AuNCs

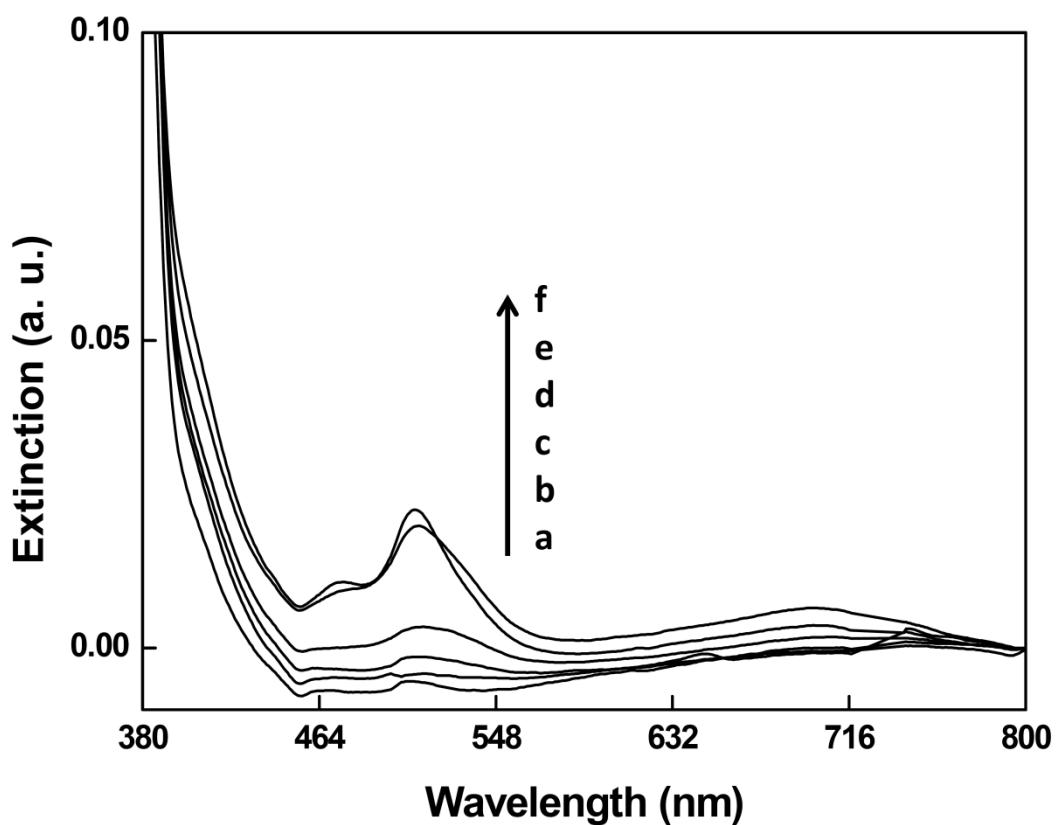


Figure S10. UV-vis spectra obtained from the incubation of 2 mM HAuCl₄ and 26 mg/mL SA in an aqueous solution containing (a) 45%, (b) 60%, (c), 68%, (d) 72%, (e) 76%, and (f) 80% v/v acetonitrile. The reaction proceeded at ambient temperature for 70 min. The small peak located at ~720 nm could be due to the background of the solvent.

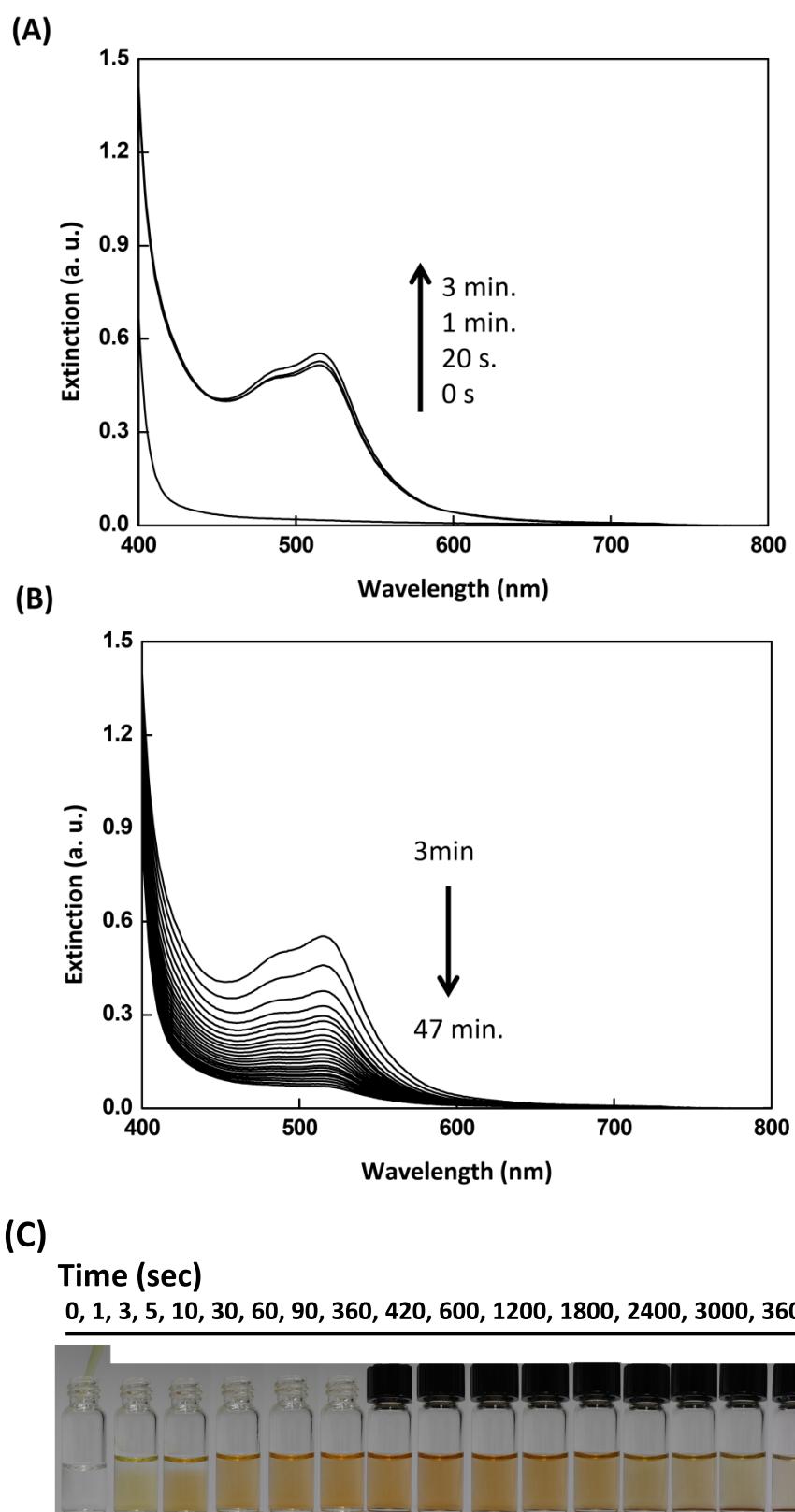


Figure S11. (A, B) UV-vis spectra and (C) photographs of the products obtained from the incubation of 2 mM HAuCl₄ and 26 mg/mL ferulic acid in a mixture of 45% v/v acetonitrile and 55% v/v water at different times.

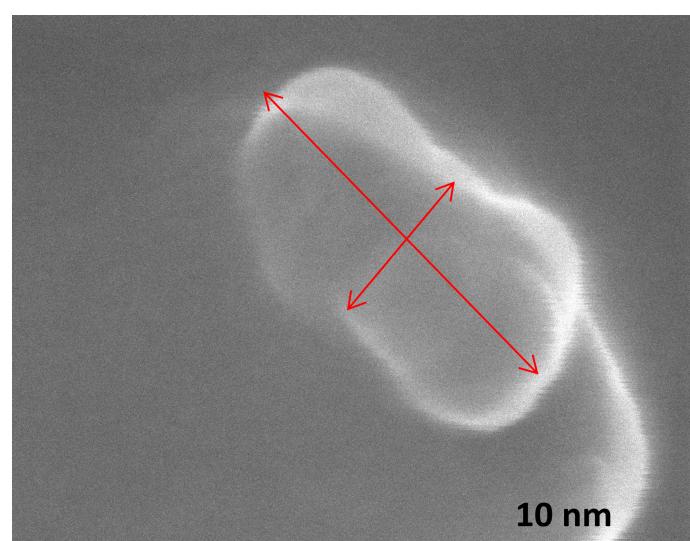


Figure S12. FESEM image of the SA-AuNCs after evaporation.



Figure S13. Steady-state crystal shape of the SA-AuNCs.

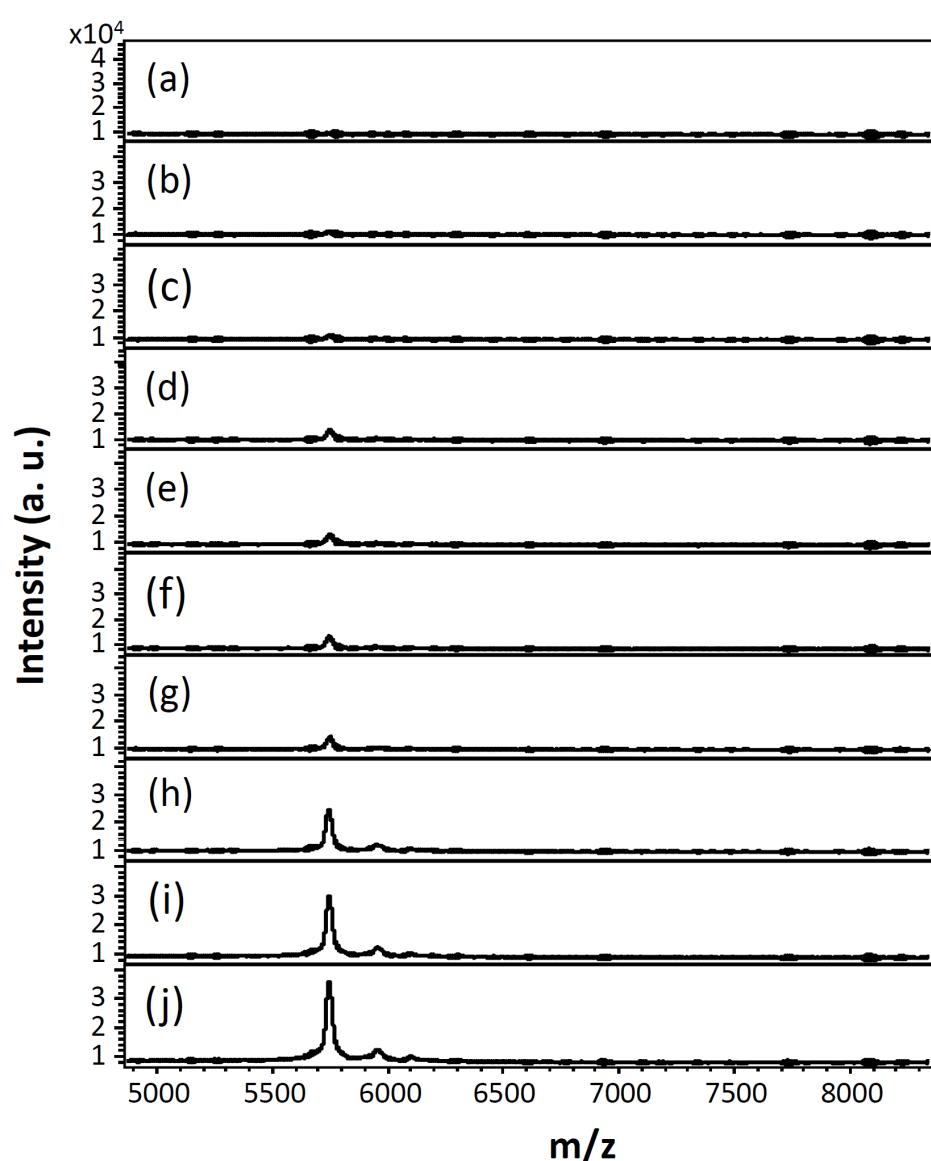


Figure S14. Mass spectra of insulin at concentrations of (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100, (g) 200, (h) 400, (i) 600, and (j) 800 nM.

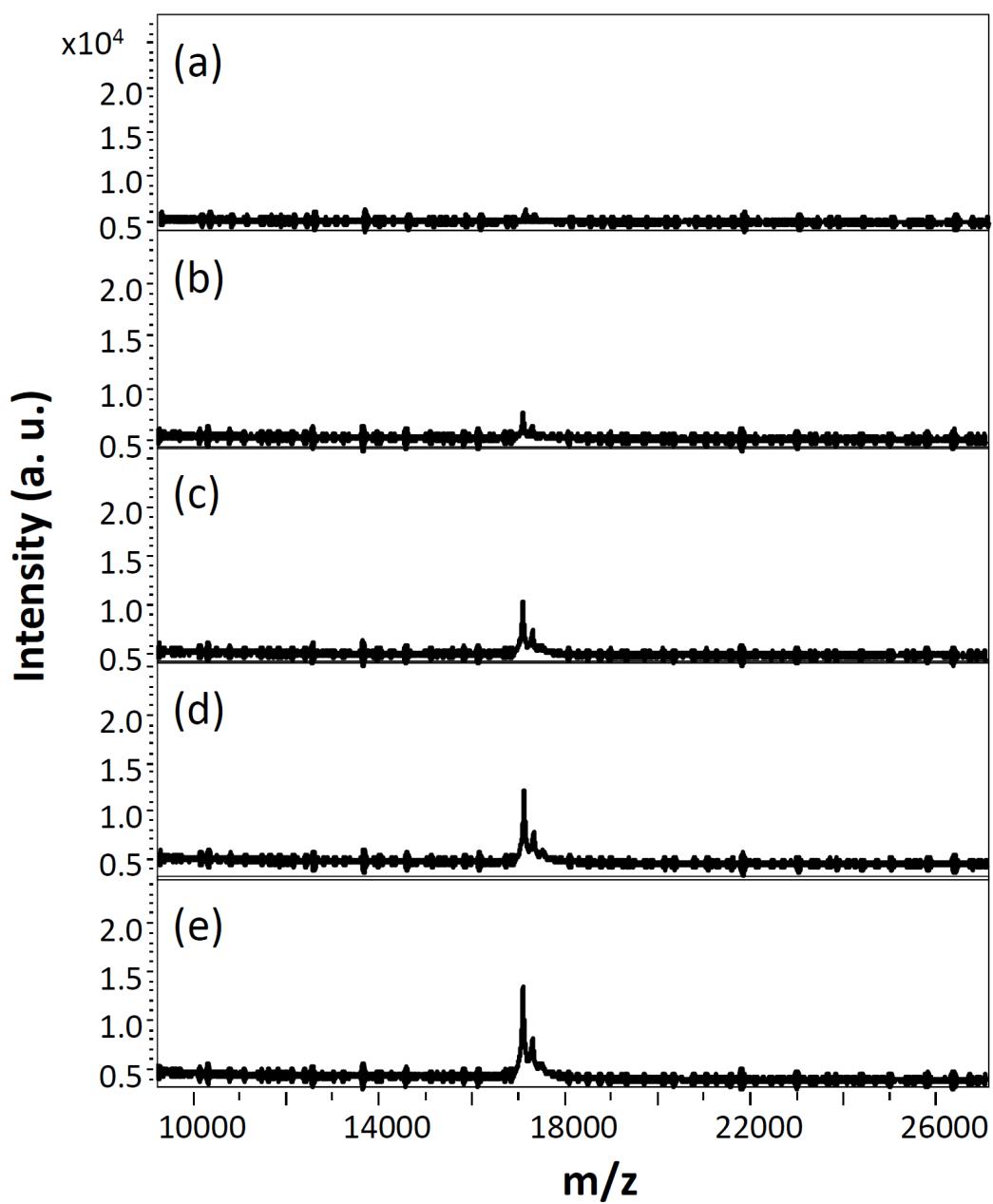


Figure S15. Mass spectra of myoglobin at concentrations of (a) 100, (b) 200, (c) 400, (d) 600, and (e) 800 nM.

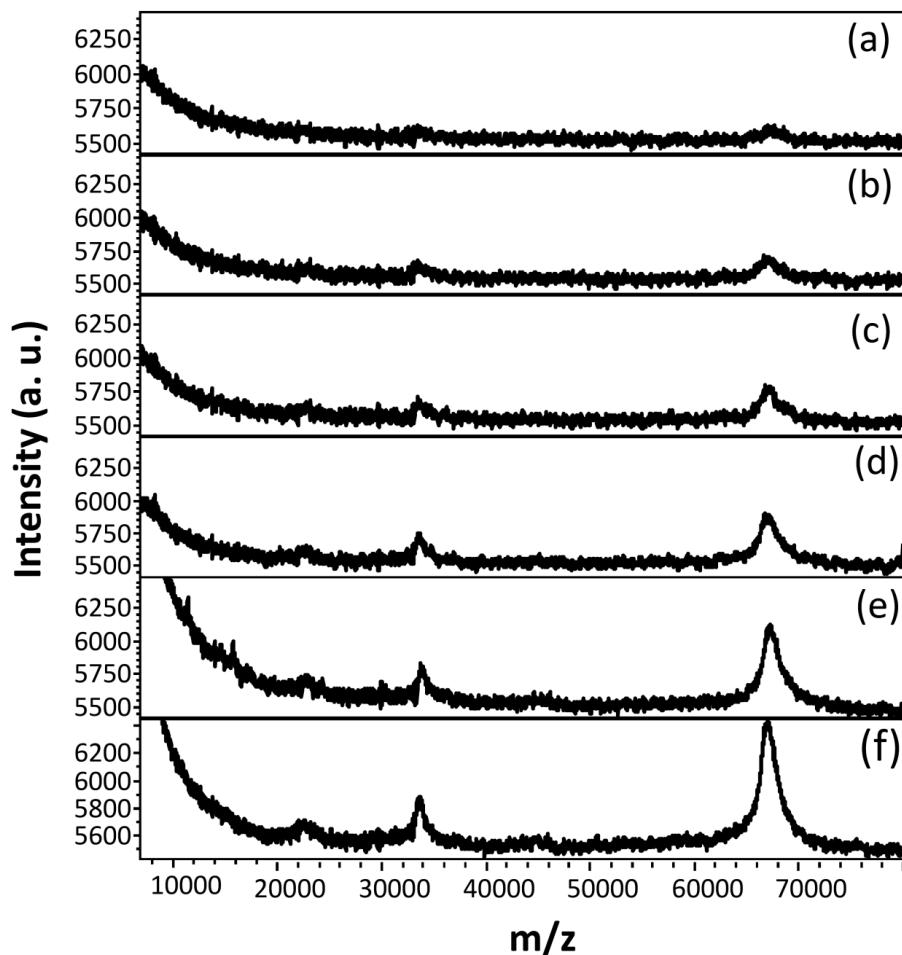


Figure S16. Mass spectra of insulin at concentrations of human serum albumin (a) 100, (b) 200, (c) 400, (d) 600, (e) 800, and (f) 1000 nM.

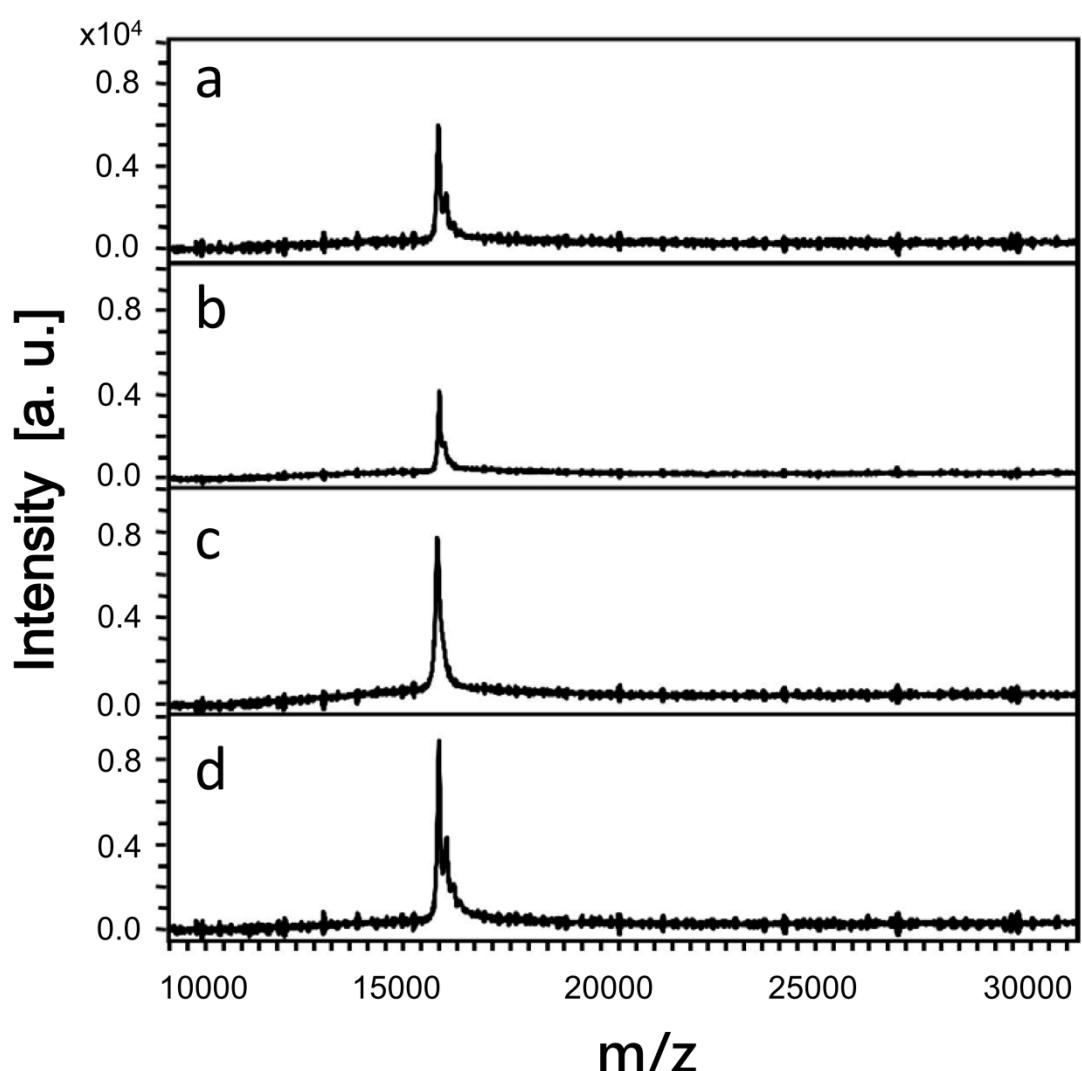


Figure S17. MALDI-TOF MS analysis of 1 μM myoglobin using (a) SA, (b) 2,5-dihydroxybenzoic acid, (c) α -cyano-4-hydroxycinnamic acid, and (d) SA-AuNCs as matrices.

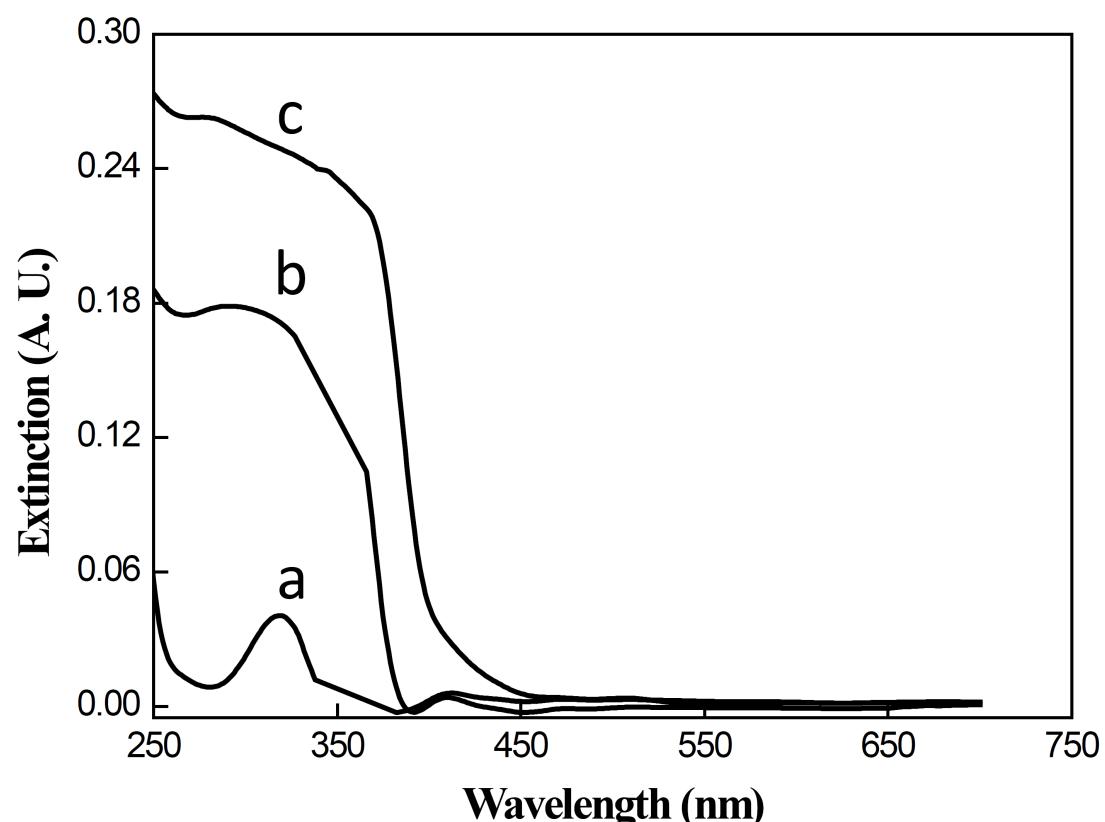


Figure S18. Absorption spectra of solutions of (a) 2 mM HAuCl₄, (b) 27 mg/ mL SA, and (c) 27 mg/mL SA-AuNCs