Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Detection of Human Serum Albumin through Surface-Enhanced Raman Scattering Using Gold "Pearl Necklace" Nanomaterials as Substrates

Zong-Hong Lin, I-Cheng Chen and Huan-Tsung Chang*

Department of Chemistry, National Taiwan University, Taipei, Taiwan

*To whom correspondence should be addressed: changht@ntu.edu.tw

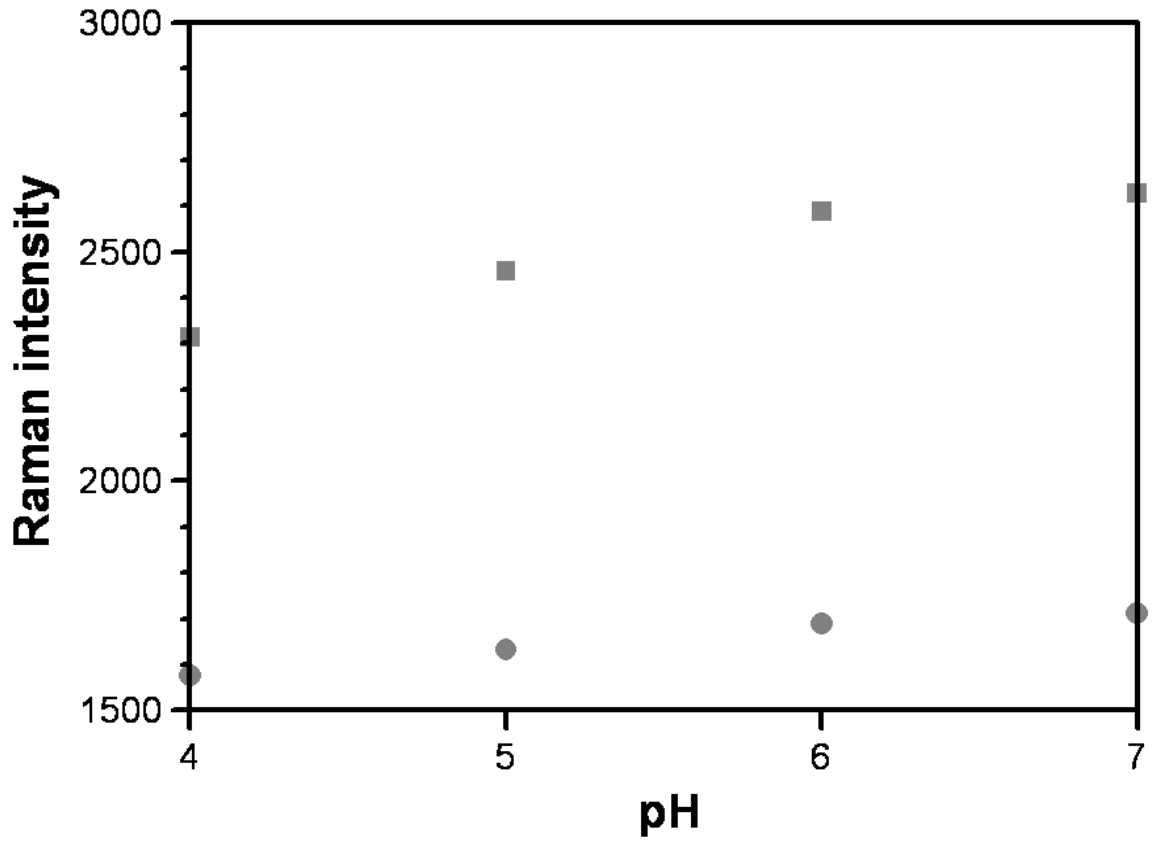

Fig. S1 SERS intensities of AB580 at 1327 cm^{-1} in different buffers (■: phosphate; ●: citrate). [AB580] = 0.1 μM; [HSA] = 1 nM; [Au PNNs] = 1X; [citrate] or [phosphate] = 10 mM.

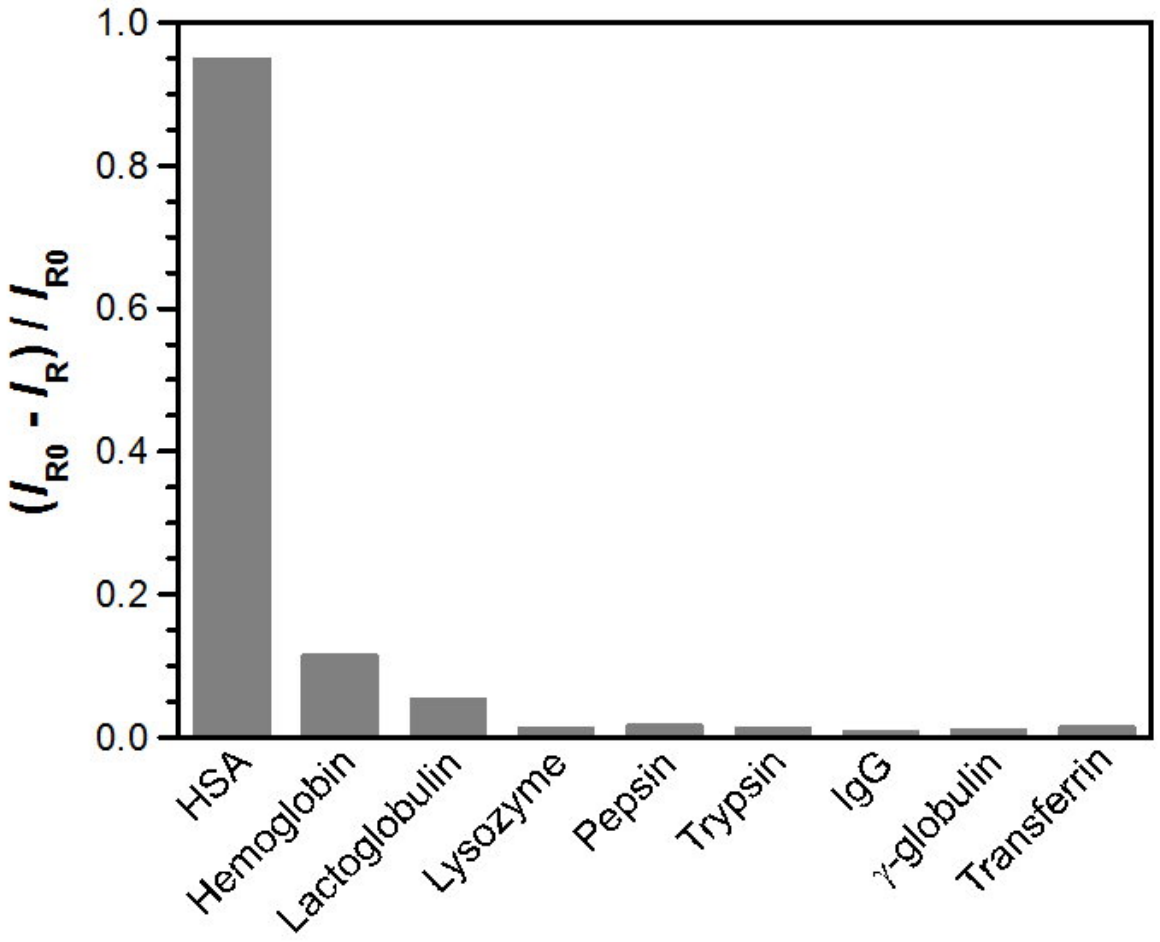

Fig. S2 Plot of the SERS ratios $[(I_{R0} - I_R)/I_{R0}]$ of AB 580 at 1327 cm^{-1} against different proteins (1 μM), where I_{R0} and I_R are the SERS intensities for AB 580 in the absence and presence of proteins and Au NPs, respectively. SERS signals were obtained using a constant content of Au PNNs (1X). The concentration of AB 580 was 1 μM.

EXPERIMENTAL SECTION

Materials. Sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB) were obtained from Acros (Geel, Belgium). Sodium tetrachloroaurate dihydrate and trisodium citrate dihydrate were obtained from Aldrich (Milwaukee, WI). Pepsin, lactoglobulin, hemoglobin, IgG, γ-globulin, trypsin, and HSA were purchased from Sigma (St. Louis, MO). Transferrin and lysozyme were purchased from MP Biomedicals LLC (Santa Ana, CA). AB 580 was purchased from Molecular Probes (Eugene, OR). Tellurium dioxide and hydrazine monohydrate were purchased from SHOWA (Tokyo, Japan). Sodium phosphate dibasic anhydrous and sodium phosphate monobasic monohydrate were purchased from JT Baker (Phillipsburg, NJ). Deionized water was obtained using a Milli-Q ultrapure (18.2 MΩ-cm) system.

56-nm Au NPs.[1] A $NaAuCl_4$ solution (50 mL, 0.01%) was brought to a vigorous boil with stirring in a round-bottom flask fitted with a reflux condenser; trisodium citrate (0.3 mL, 1%) was then added rapidly to the solution. The solution was heated under reflux for another 8 min, during which time its color changed from pale yellow to pale red. The solution was cooled to room temperature while stirring continuously. The average size (56 nm) of the synthesized Au NPs was verified through TEM analysis.

Te NWs.[2] Hydrazine (10 mL) was added slowly to a beaker containing tellurium dioxide (0.016 g) at room temperature under constant magnetic stirring. The solution changed color from colorless to blue after 120 min, indicating the formation of Te NWs (average length: 879 nm; average diameter: 19 nm). To terminate the reaction and stabilize the Te NWs, the mixture was diluted 10-fold with SDS (10 mM).

Au PNNs. The Te NWs were subjected to a centrifugation/wash cycle to remove most of the matrix, including SDS and hydrazine. The flocculate was re-dispersed in CTAB solution (10 mM). After 10 min, aqueous $NaAuCl_4$ (final concentration: 1 mM) was added to the aqueous solution containing the Te NWs. The Au PNNs were formed during a reaction time of 60 min. For simplicity, the concentration of these as-prepared Au PNNs is denoted as 1X. Prior to SERS analysis, the Au PNNs were centrifuged and then re-dispersed in deionized water.

Characterization. JEOL-1200EX II and FEI Tecnai-G2-F20 transmission electron microscopes were used to measure the sizes and shapes of the Te NWs, Au NPs, and Au PNN SERS substrates. UV–Vis absorption spectra of the NMs were recorded using a double-beam UV–Vis spectrophotometer (Cintra 10e, GBC, Victoria, Australia). Raman spectra were recorded using a Nicolet Almega dispersive Raman spectrometer (Waltham, MA, USA) equipped with a 50× objective, a visible Raman microscope, and a

charge-coupled detector; the excitation wavelength was 785 nm and the spectral aperture was 50 μm; the signal collection time for each sample was 30 s.

SERS Samples. For HSA assays, aliquots (1 mL) of standard solutions of sodium phosphate (10 mM, pH 7.0) containing HSA (from 10 pM to 1 μM) and 56-nm Au NPs (30 pM) were maintained at room temperature for 30 min. A fixed amount of AB 580 (final concentration: 1 μM) was then added to each of the solutions. After 30 min, the solutions were subjected to centrifugation to remove the free and HSA-bound Au NPs. The SERS-active Au PNN substrates were added to the supernatants. After 1 h, the samples were subjected to centrifugation (6000 rpm, 5 min) and then the pellets were re-dispersed in ultrapure water (10 μL). Finally, drops of the solutions were added separately onto silicon wafers and dried at room temperature. Three urine specimens were collected (without preservatives), centrifuged (3000*g*, 10 min), and stored at –4 °C. When required for use, the samples were thawed at room temperature. Different amounts of HSA (10 μL, 1–100 nM) were then spiked into the solutions (100 μL). The spiked urine samples were further diluted with deionized water (to 0.5 mL). The diluted urine samples were analyzed in the same manner as the standard HSA solutions. Triplicate measurements were conducted for each sample.

References

1. (a) G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20. (b) K. C. Grabar, R. G. Freeman, M. B. Hommer, M. J. Natan, *Anal. Chem.*, 1995, **67**, 735. (c) R. C. Mucic, J. J. Storhoff, C. A. Mirkin, R. L. Letsinger, *J. Am. Chem. Soc.*, 1998, **120**, 12674–12675.
2 Z.-H. Lin, Z. Yang, H.-T. Chang, *Cryst. Growth Des.*, 2008, 8, 351–357.