Supporting information

EXPERIMENTAL SECTION

Materials

Thiolated DNA oligonucleotides, purified by high performance liquid chromatography (HPLC), were purchased from Shanghai Sangon Biological Engineering Technology & Services Co., Ltd (Shanghai, P.R. China). All other chemicals used in this study were purchased from Sigma–Aldrich, unless stated otherwise. DI water obtained using a Milli-Q device (18.2 M Ω, Millipore, Molsheim, France) was used in all experiments. All glassware was soaked in aqua regia for 24 h, then rinsed at least three times with deionized water and dried in an oven.

Instrument

UV-Vis spectra were acquired on a UNICO 2100 PC UV-Vis spectrophotometer and processed with Origin Lab software. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 operating at an acceleration voltage of 200 kV. For the TEM examination, 10 μL of each sample was dried in air and dispersed onto a 20 copper grid coated with a carbon film. Raman spectra were measured using a LabRam-HR800 Micro-Raman spectrometer with Lab-spec 5.0 software attached to a liquid cell.

Synthesis of Au NRs

Au NRs with an aspect ratio of 2.5 were synthesized using a well-known seed-mediated growth method with some modifications. Initially, 0.125 mL of a 10 mM $HAuCl_4$ solution was added to 2.5 mL of 0.20 M CTAB solution, which was kept at a constant temperature of 28°C. Immediately, a deep orange colored solution was obtained. Then 0.3 mL of freshly prepared 10 mM $NaBH_4$ solution was quickly added to one portion and mixed by inversion. The solution was rapidly stirred for 2 min, and the solution turned pale brown in color. To prepare the Au NRs, 0.5

mL of 10 mM $HAuCl_4$ was added to 5 mL of 0.2 M CTAB solution and then 4.5 mL of water was added. After that, 55 μL of 0.1 M ascorbic acid solution and 0.12 mL of 4 mM $AgNO_3$ solution were added to the reaction media followed by mixing for approximately 2 min. The solution then became colorless. Finally, 0.05 mL of seed solution was added and gently mixed by inversion for about 20 s. The Au NRs were used after 4 h.

Synthesis of Ag NPs

Ag NPs with a diameter of 10±1.3 nm were synthesized following the usual method with some modifications. Briefly, 0.6 mL of 0.1 M freshly prepared $NaBH_4$ (dissolved using ice-cold water) and 5 mL of 1% poly-vinylpyrrolidone (PVP) were added to 20 mL of distilled water in an iced water bath. The solution was kept in the iced water bath with high-speed stirring. Next, 5 mL of 10 mM $AgNO_3$ and 5 mL of 1% PVP were added to the mixture by simultaneous injection through two constant-flow pumps at the rate of 30 mL/h. The reaction solution was kept at 80°C for 2 h to remove unreacted $NaBH_4$, the prepared sample was yellow in color. The prepared Ag NPs solution was stored at 4°C. Before use, the Ag NPs solution was centrifuged and resuspended in 5 mM Tris-HNO_3 buffer, the concentration of Ag NPs was estimated to be 10 nM based on a previous method.

Preparation of single-stranded DNA modified-Au NRs and Ag NPs

For the preparation of Au NRs-DNA conjugates, first the Au NRs were concentrated ten times and resuspended in an appropriate volume of Buffer (5 mM CTAB: 5 mM Tris = 1:1 solution) at a final concentration of 10 nM. Thereafter, the Au NRs were functionalized with Mucin-1 complementary at a coupling ratio of 500 to 1. After the mixture was allowed to react at room temperature for 2 h with gentle shaking, 0.5 M $NaNO_3$ was added to bring the final salt concentration to 100 mM and then the mixture was incubated for 12 h with shaking. The excess DNA was removed by centrifugation at 3500 g for 10 min and the sediment was then resuspended in 0.5 mM Tris-HNO_3 buffer, this process was repeated three times.

Ag NPs were concentrated twice and then resuspended in 1 mM Tris–HNO_3 buffer at a final concentration of 50 nM. 4-aminothiophenol with a sulfhydryl group was assembled onto the Ag NPs surface through Ag-S band with final concentration of 10 μM and the mixture was incubated for 12 h. Then thiol-modified Mucin-1 aptamers dissolved in TE buffer were added to the Ag NPs solutions at a coupling ratio of 5 to 1. The mixture was left to stand for 12 h to complete the functionalization process. The functionalized particles were centrifuged (16,200 g, 15 min) and resuspended in 1 mM Tris-HNO_3 buffer.

Self-Assembly of Au NRs and Ag NPs

In order to form the satellite assemblies, 80 μL of Ag NPs-aptamers were mixed with 50 μL of Au NRs-complementary in 130 μL of 1 mM Tris-HNO_3 buffer (25 mM $MgCl_2$, pH 7.2) with gentle shaking for several minutes. The mixture was then incubated for 12 h at room temperature.

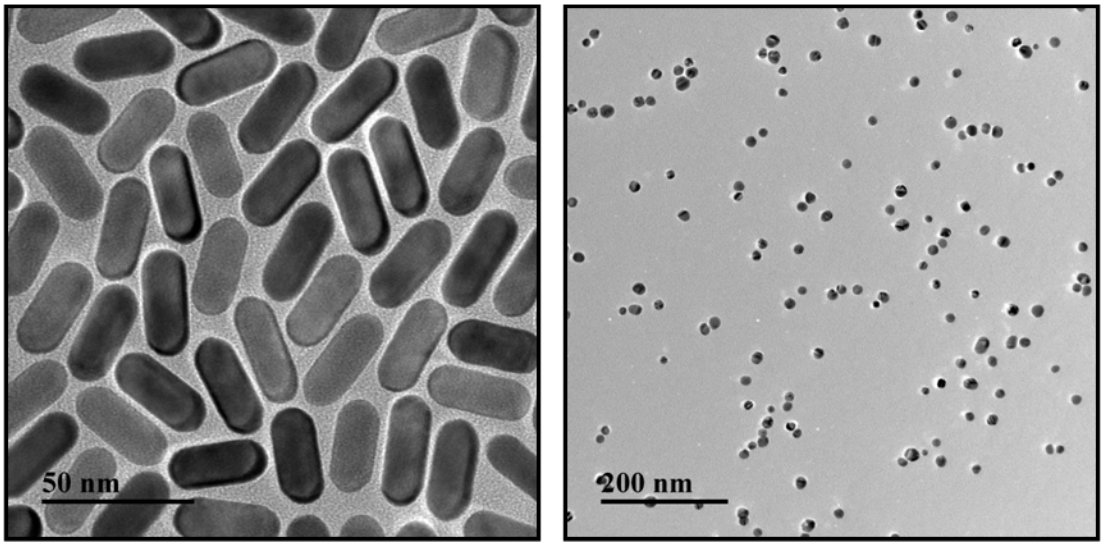

Fig. S1. Representative TEM images of (A) Au nanoroads and (B) silver nanoparticles.

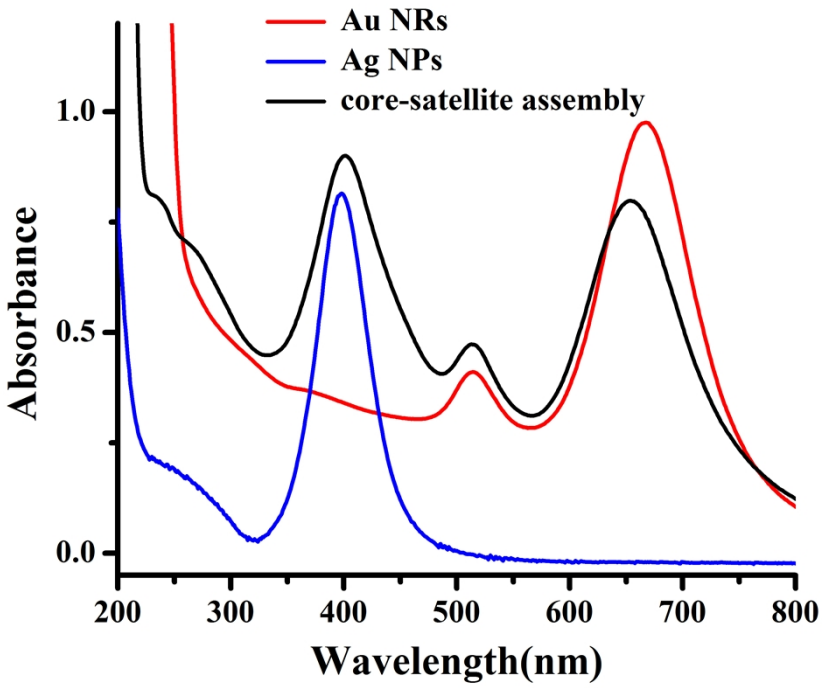

Fig. S2. The corresponding UV-vis of Au NRs, Ag NPs, and the Au NRs-Ag NPs core-satellite assemblies.

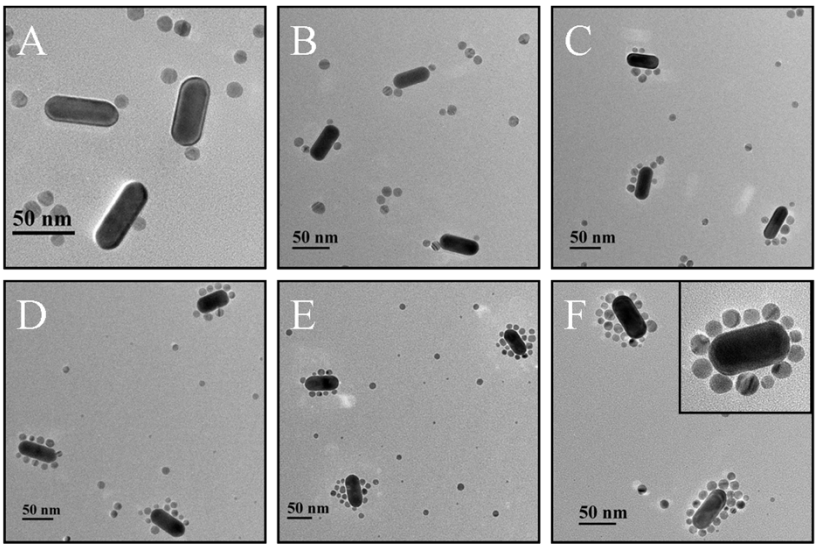

Fig. S3. Representative TEM images of Au NRs-Ag NPs core-satellite assemblies for different hybridization times, (a) 5 and (b) 30 min and (c) 1, (d) 3, (e) 6, and (f) 12 h.

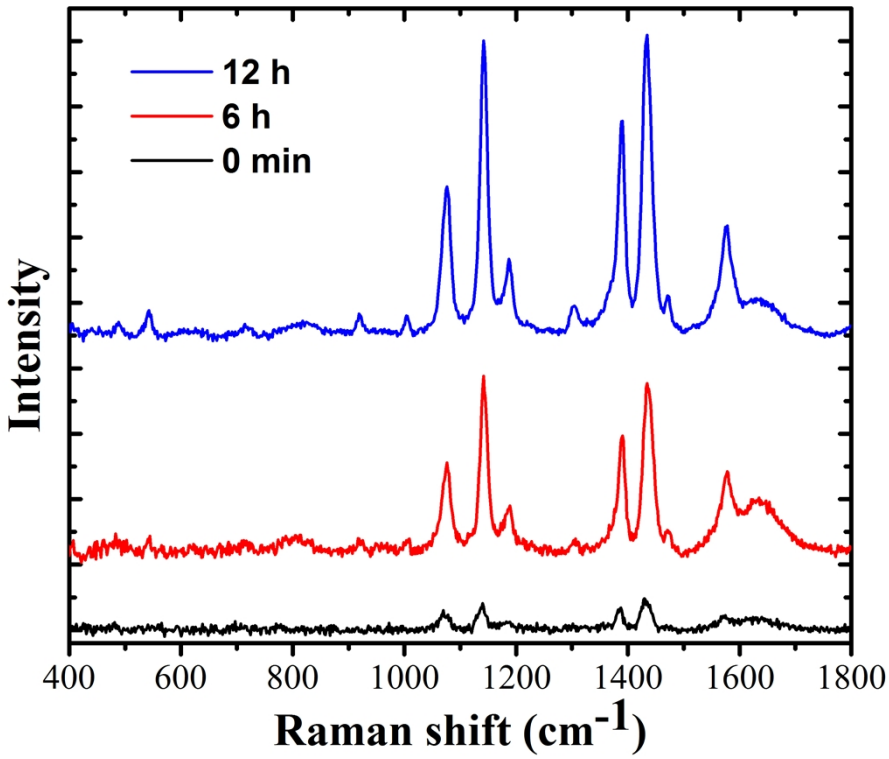

Fig. S4. Representative SERS spectra of Au NRs-Ag NPs core-satellite assemblies for different hybridization times. (a) 0, (b) 6 h, (c) 12 h.

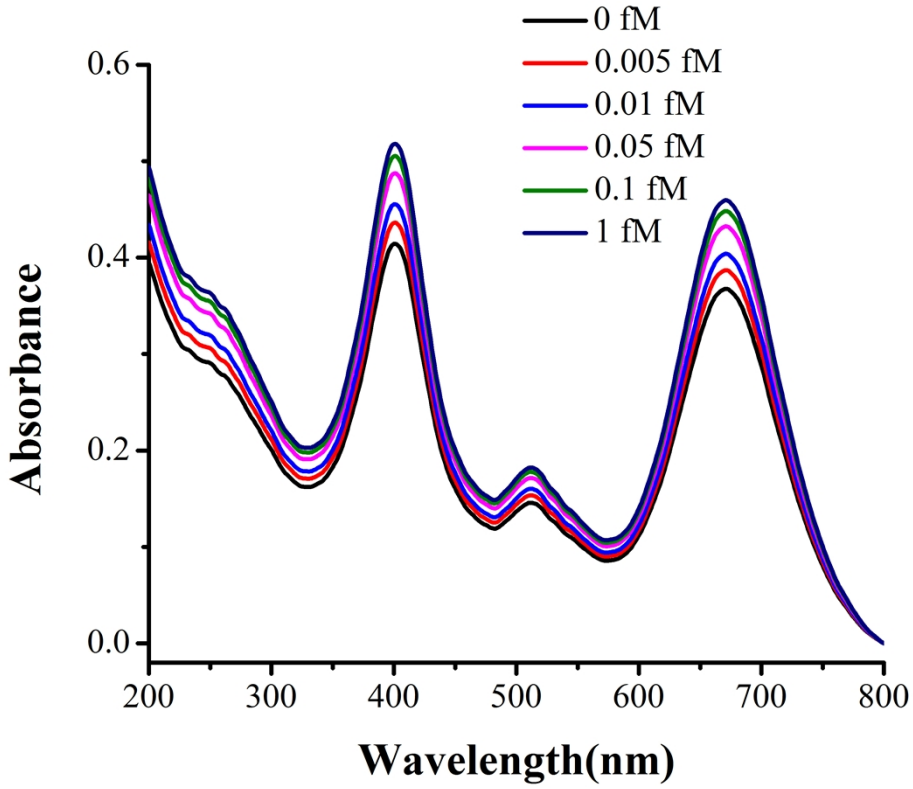

Fig. S5. UV-Vis spectra for Mucin-1 detection with various concentrations.

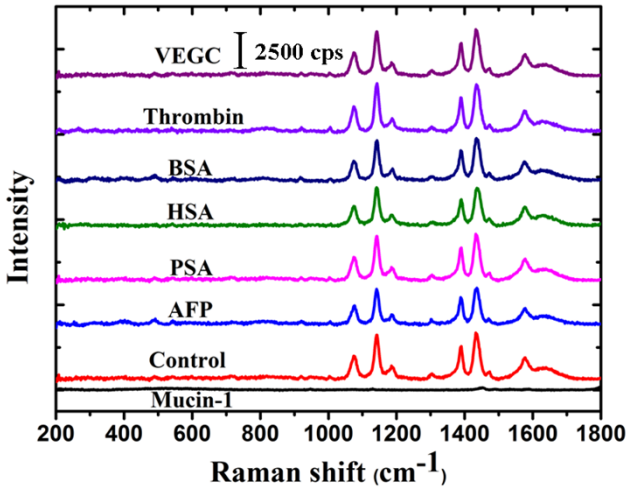

Fig. S6. SERS spectra of different targets. The concentration of different targets: Mucin-1 (0.5 fM), AFP (50 fM), PSA (50 fM), HAS (50 fM), BSA (50 fM), Thrombin (50 fM), VEGC (50 fM).