Supporting Information

Aptamer-mediated SERS Intensity Amplification

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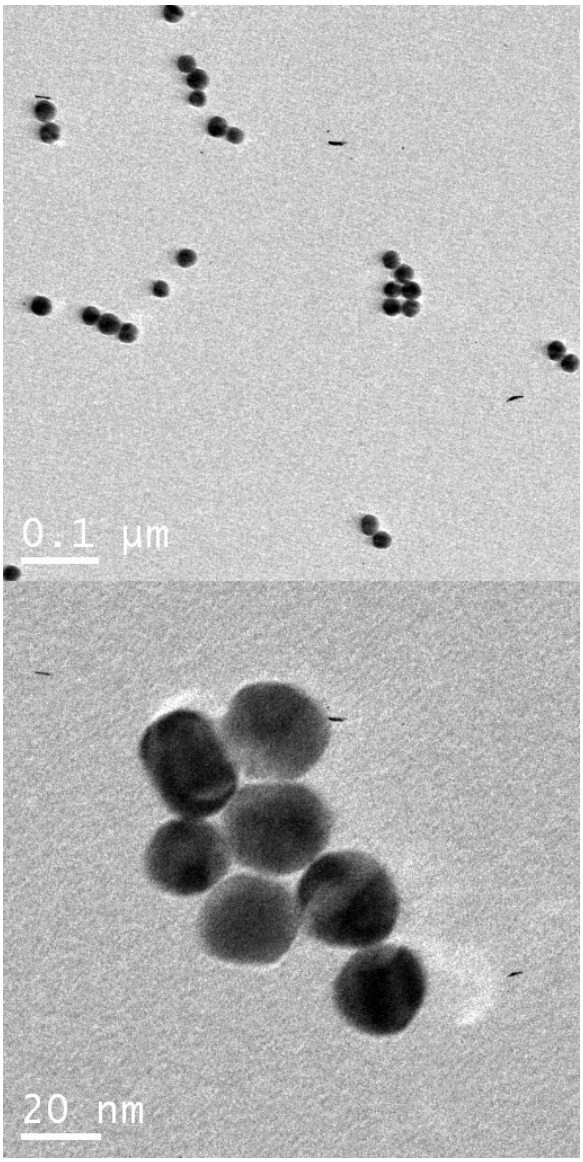
Materials: Au colloid (20 ± 3 nm), adenosine, uridine, cytidine, and guanosine were purchased from Sigma. 4-mercapto-1-butanol, 4-aminobenzenethiol (4-ABT), and Tris(2-carboxyethyl)phosphine hydrochloride (TCEP) were purchased from Aldrich. Oligonucleotides were purchased from Integrated DNA Technologies. Unless otherwise specified, chemicals and solvents were reagent grade. Triply distilled water of resistivity greater than 18 MΩcm was used throughout.

Preparation of samples: 0.1mL of 0.1 mM DNA1 (5'-TTT TTT ACT CAT CTG TGA AGA GAA CCT GGG GGA GTA TTG CGG AGG AAG GT -3') and DNA2 (5'- / BiotinTEG / CCC AGG TTC TCT TCA CAG ATG AGT AAA AAA A / C3-thiol / -3') in phosphate buffer solution were mixed in a test tube and incubated for 12 hours at 4 °C. Triethylene glycol (TEG) was use to connect the biotin molecules to the 5'-DNA strand. 1μl of 500 mM acetate buffer (pH 5.2) and 1.5 μl of 10 mM freshly prepared TCEP were added to the test tube to activate the thiol-modified DNA2. The sample was incubated at room temperature for 1 h. 300 nm thick Au films were deposited over a 15 nm thick titanium adhesion layer, in turn, deposited on a silicon wafer substrate (5 mm × 5 mm) using an E-beam evaporator. These Au substrates were dipped in the test tube at 4 °C for 12 hours to allow adsorption of DNA2 through its thiolate group onto the Au substrates and its hybridization with DNA1. Then the Au substrates were washed at least three times with buffer solution (NaCl 150 mM, Tris 5 mM), placed in 0.2 ml of buffer solution (NaCl 5 mM, Tris 5 mM), then passivated with 0.02 ml of 0.1 mM aqueous 4-mercapto-1-butanol solution to reduce nonspecific interactions between the Au substrate and DNA, avidin, and/or the Au nanoparticles . After 1 hour, the Au substrate was washed with buffer solution (NaCl 5 mM, Tris 5 mM), placed in PBS buffer solution and avidin was added. After approximately 5 min, the Au substrate which again was washed three times with PBS buffer was placed in 0.2 ml of buffer solution (NaCl 5 mM, Tris 5 mM), and 0.02 ml of Au colloid was added to the test tube. After 5 min, the Au substrate was washed with buffer (NaCl 150 mM, Tris 5 mM) then stored in a test tube containing 0.2 ml of buffer solution (NaCl 5 mM, Tris 5 mM) and 0.02 ml of 0.1 mM 4-ABT aqueous solution as added to the test tube. After 5 minutes, the Au substrate was washed with buffer solution and stored in buffer (NaCl 150 mM, Tris 5 mM) at 4 °C.

Characterization: Raman measurements were carried out on a LabRam system (Horiba Jobin Yvon) equipped with 1200 grooves/mm holographic gratings, and Peltier-cooled CCD camera detection. The 633 nm output of a high power Melles Griot He-Ne laser was used to excite the spectra which were collected in a back-scattering geometry using a confocal Raman microscope (high stability BX40) equipped with Olympus objectives (MPlan 10x). The spectral resolution was 1 cm^{-1}. All Raman measurements were carried out with the sample in the buffer solution (150 mM NaCl, 5 mM Tris) to which adenosine, cytosine, uridine, and guanine solution was added, as required, each dissolved in the same buffer. Atomic force microscope (Asylum Research MFD-3D AFM) topographic images were recorded in the tapping mode at a scan rate of 1 Hz, both in air and with the sample immersed in the same buffer as was used for the Raman measurements. A 125 μm-long Si_3N_4 cantilever coated with 70 nm Au with a nominal spring constant of 40 N/m at a frequency of 300 KHz (Ted Pella, Inc.). All AFM images are reported without any image processing.

Figure S1. TEM images of Au nanoparticles.



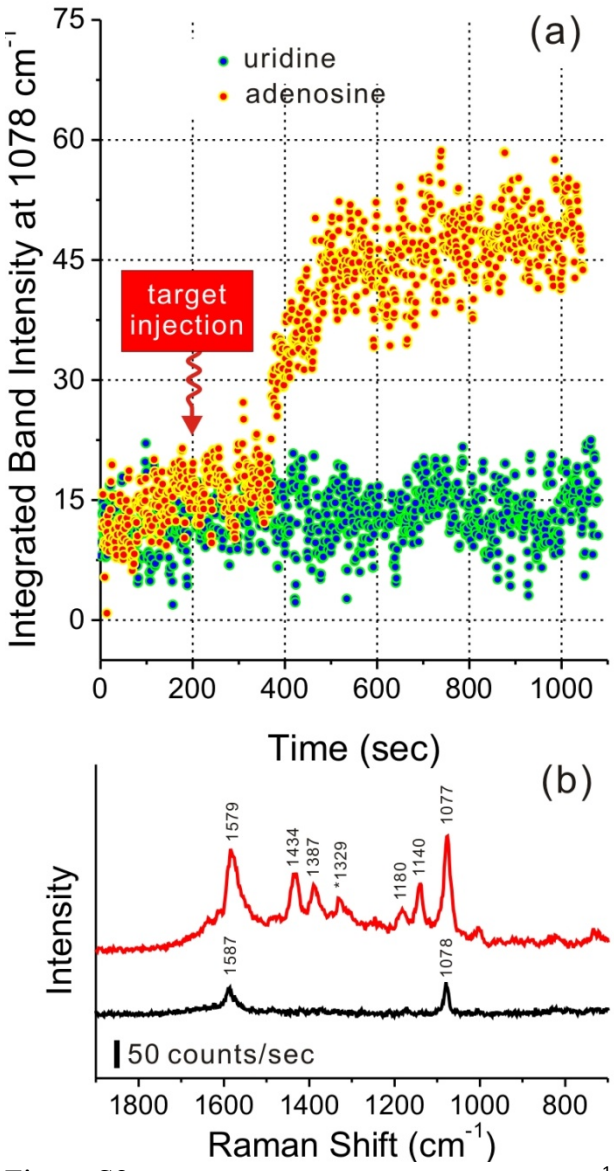


Figure S2. (a) The SERS intensity of the 1080 cm^{-1} band of 4-ABT adsorbed on Au the NPs monitored as a function of time, after adenosine (red dots) and uridine (blue dots) were injected into the buffer (at time=200 s). (b) SERS spectra of 4-ABT on Au NPs before (black) and after (red) adenosine injection. Spectra were obtained using 1.1 mW 633 nm laser excitation. Low incident power was used to prevent photothermal dehybridization.