Supplementary Information for

Dimer-on-mirror SERS substrates with attogram sensitivity fabricated by colloidal lithography

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Materials and methods

Chemicals

Trans-1,2-bis(4-pyridyl)ethylene, 97% (BPE) was purchased from Sigma Aldrich (CAS Number 13362-78-2). Ultra-pure water for the dilutions came from a MilliQ system purified to a resistivity of >18.2 MΩ cm-1.

Dilution methodology. 10.3 mg BPE powder (equals 9.991 mg pure BPE) were weighted directly into a measurement flask (100 ± 0.5 ml) and filled up to the marking with MilliQ water giving a solution of 100 ppm (550 µM). Approximately a factor 8 from the theoretical solubility in water,50 sonication in 30 min was still used in precaution to avoid residue crystals. Followed was this dilution series:

20 µl 550×10-6 M → 1000 µl; 2 ppm, 11×10-6 M
10 µl → 1000 µl; 20 ppb, 110×10-9 M
5 µl → 1000 µl; 100 ppt, 5.5×10-10 M
1 µl → 100 µl; 1 ppt, 5.5×10-12 M
5 µl → 1000 µl; 5 ppq, 2.7×10-14 M
5 µl → 1000 µl; 0.025 ppq, 1.4×10-16 M

Using pipettes: Transferpette, 0.5 – 10 ± 0.2 µl (Pooled standard deviation over the interval), Transferpette, 100 - 1000 ± 5 µl (@ 1000 µl) and Biohit 10 – 100 ± 0.5 µl (@ 100 µl). Error analysis for the dilution series shows that the final amount of molecules for 0.5 µl of the lowest concentration can be determined to 42 ± 14.

Nanofabrication

Hole-mask colloidal lithography

The samples were prepared on cover slips glass substrates (Menzel-Gläser #2). First a 3 nm chromium layer (adhesion), a 100 nm gold layer, a 2 nm chromium layer (adhesion), and a 60 nm silica spacer were evaporated onto the substrates. A resist is then spin-coated (PMMA-A4) and baked on top of the sample surface. A surfactant is spread on the resist to allow charged PS beads to attach on the surface. The beads surface density can be controlled by changing the charges content in the PS colloidal solution beforehand. A 10 nm gold layer is evaporated, covering both beads and resist. The beads are removed by tape-stripping. Etching of the accessible PMMA is done by an oxygen plasma at 50W. The aim of this step is to obtain a hole whose diameter at the silica-resist interface is larger than at the gold-resist interface. A first layer of gold is evaporated at a relatively low angle with respect to the normal, the sample substrate is then rotated before achieving a second gold evaporation (in the case of dimers for example). As a last step the resist layer is removed by ultrasonication in successive baths of acetone, isopropanol, and distilled water.

Raman microscopy

For the Raman microscopy measurements a Horiba XploRA ONE™ microscope was used with an internal 638 nm laser diode (operating at a maximum of 2 mW, 10 % of full power) and a 10x/0.2NA objective. The CCD spectrometer was air-cooled to -60 ^{o}C. The confocal pinhole was set to 100 µm, slit was 300 µm and the 1200T grating was centred at 1150 cm^{-1}. The spectrometer integration time was 1 s and the step-size for XY matrixes was 10 µm. The confocal laser spot-size had a theoretical minimum size of 4 µm, and an experimentally determined value of 10 µm.

Portable Raman device measurements

The portable Raman instrumentation, First Defender RMX (Thermo Fisher Scientific Inc), named FD-RMX, was used with a fixed integration time of 10 s and with output power of 240 mW of the 785 nm laser beam focused on the SERS sample via optics with a working distance of 5 mm. The laser spot diameter on the SERS substrates was approximately 150 µm and the spectral resolution was about 10 cm^{-1} according to the manufacturer.

Simulations

The simulations were done by the finite difference time domain (FDTD) method with the software FDTD Solutions. The refractive indexes of gold (Au) and chromium (Cr) are taken from *Handbook of Optical Constants of Solids*.[72]

The refractive index of the surrounding matrix is 1.25. The mesh size around Au dimer structure is $1\times1\times1$ nm^3. Periodic boundary conditions are used for *x* and *y* direction boundaries. The periodic sizes along *x* and *y* directions are both 350 nm. Perfectly matched layer conditions are used for *z* direction boundaries. The source is plane wave which propagates along *z* direction.

Characterization (SEM)

The samples were imaged in a Quanta (FEI, Netherland) SEM in environmental mode for in-plane view. For the tilted view similar samples were also prepared on a Si substrate and characterized using a Leo ULTRA (Zeiss, Germany) SEM.

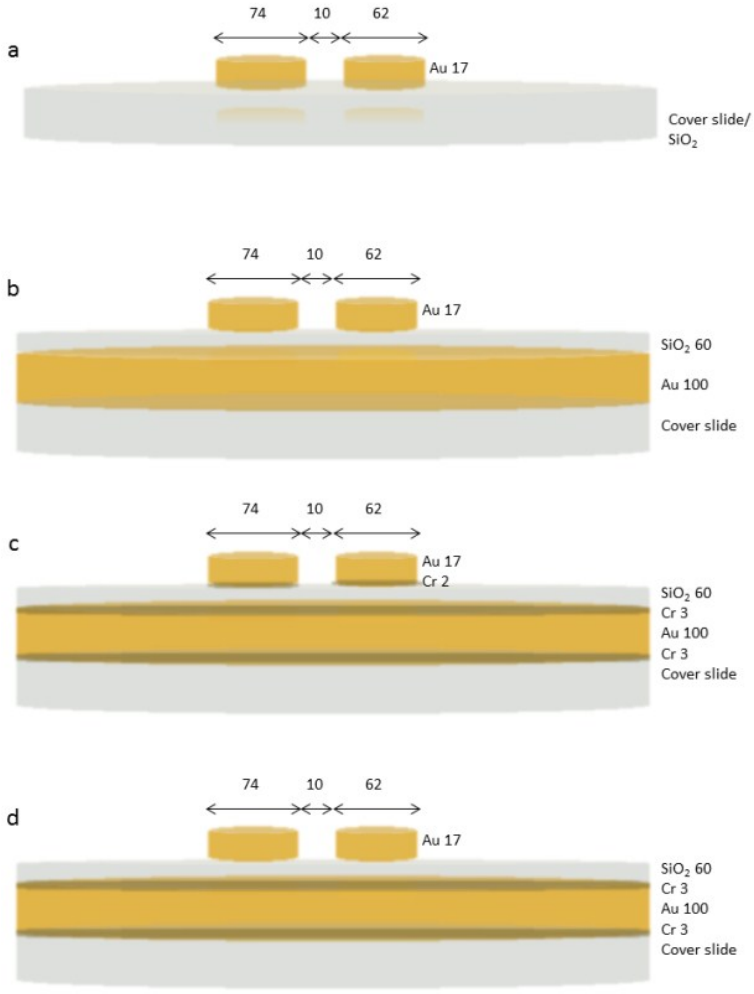

Fig. S1 Schematic illustration of the dimer on mirror configurations (also used for simulations) estimated from SEM images of the HCL fabricated substrates. Distances (numbers) are specified in nm.

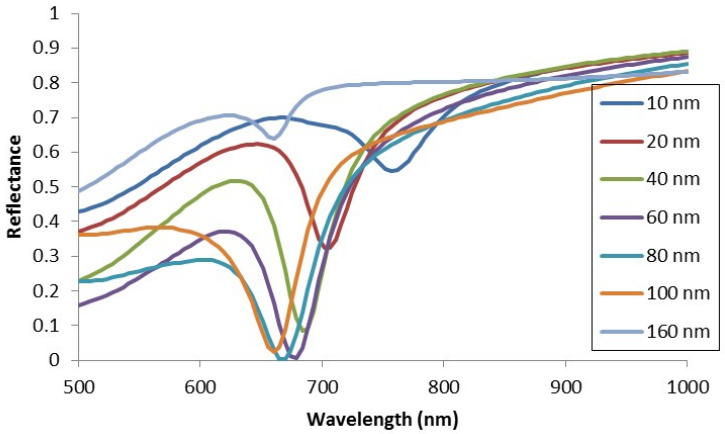

Fig. S2 Simulated reflectance spectrum for gold dimers on gold mirror at different SiO_2 spacer distance.

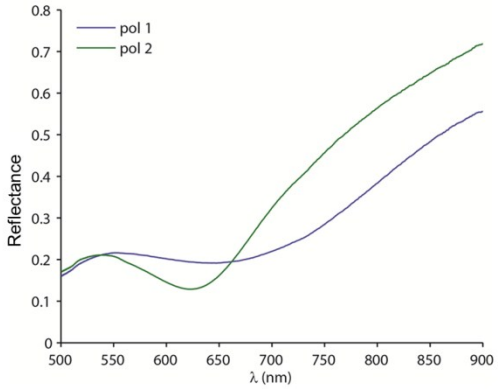

Fig. S3 Reflectance spectrum for the dimers on optimized mirror distance (60 nm). Pol 2 corresponds to the polarization in used in the simulations. Pol 1 is polarized parallel to the long dimer axis.