Electronic Supplementary Information for:

Highly uniform SERS substrates formed by wrinkle-confined drying of gold colloids

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Materials and Methods:

Chemicals: Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$), ascorbic acid, cetyltrimethylammonium bromide (CTAB), trisodium citrate dihydrate, isopropanol and benzenethiol (BT) were supplied by Sigma-Aldrich. Polydimethylsiloxane (PDMS) Sylgard (184) silicon elastomer, curing agent and precursor were purchased from Dow Corning, USA. Mucasol was obtained from Merz. All reactants were used without further purification. Milli-Q water (18 MΩ cm^{-1}) was used in all aqueous solutions. The reaction vessels were washed with aqua regia prior to all the experiments. All chemicals were analytical grade or better.

Preparation of monodisperse gold nanoparticles: Spherical gold nanoparticles were prepared via a seed mediated approach following the method previously reported by Rodriguez-Fernandez et al..[1] Briefly, a seed solution of ~12 nm particles ([Au]=0.5 mM) was prepared by citrate reduction and then diluted to double the initial volume with a 0.03 M CTAB solution. Overgrowth of the seeds, was carried out by adding (at 35 °C) the seed solution to a growth solution containing $HAuCl_4$ ($2.5\ 10^{-4}$ M), CTAB (0.015 M), and ascorbic acid ($5\ 10^{-4}$ M). The mean diameter of the obtained gold particles was 66 nm (Figure S1). Prior to the stamping process, the particle concentration was increased as follows: 30 mL of the obtained gold dispersion was centrifuged (7000 rpm, 10 min) and redispersed in a total volume of 0.6 mL, with a final gold concentration of 3.75 mg/mL.

Fabrication of PDMS stamps:[2-3] The PDMS elastomer was prepared by mixing Sylgard 184 with a 10:1 ratio by mass of prepolymer to curing agent. The mixture was stirred and filled in a carefully cleaned, flat Petri dish. After 24 h at room temperature and baking at 60 °C for 2 h, the cross-linked PDMS was cut into 30 mm × 8 mm stripes. These were stretched uniaxially in a custom-made apparatus to a strain of 125% of their intial length.[4] The stretched substrates were oxidized during either 50 or 150 s in oxygen plasma at 0.2 mbar using a plasma etcher operating at 0.1 kW (flecto10, Plasma Technology, Germany).[5] After cooling, the samples were relaxed with a strain releasing rate of 240 µm/s. The hydrophilic stamps were used directly after plasma treatment.

Nanoparticle stamping: The glass slides used as substrates for the stamping process were previously cleaned with a strong surfactant (mucasol), milli-Q water, and isopropanol. The glass slides were then sonicated for 15 min in a mixture of milli-Q water (75%) and isopropanol (25%), followed by the well known Standard Clean 1 (SC-1 or RCA 1)[6], comprising the treatment with a mixture of H_2O, H_2O_2, NH_4OH (5:1:1) at 70 °C during 15 min and extensive washing with milli-Q water. The gold colloid (10µL, 3.75 mg/mL) was drop-cast onto a glass slide and allowed to spread. Thereafter, the wrinkled PDMS stamp was placed on the substrate and left undisturbed for 12 h.

Characterization: UV-VIS spectroscopy (PerkinElmer, Lambda 19), transmission and scanning electron microscopy (TEM, LEO 922 EFTEM operating at 200 kV and LEO 1530 FE-SEM, Zeiss, respectively), were applied to characterize the optical response, structure, and size of the nanoparticles and their arrays. AFM images were obtained using a commercial atomic force microscope (Dimension™ 3100M equiped with a Nanoscope IIIm controler, Veeco Instruments Inc., USA) operating in the tapping mode. Silicon cantilevers with a force constant of typically 35-47.2 N/m (OMCL-AC160TS, Olympus, Japan, typical frequency of 303 kHz) were utilized.

Dark-field imaging and spectroscopy on individual Au nanoparticle arrays were carried out on an inverted optical microscope (ZEISS Observer A1) equipped with an Acton SpectraPro 2150i monochromator and a Princeton Instruments Pixis 1024 charge-coupled device (CCD), which was thermoelectrically cooled to -50 ºC. Au nanoparticle arrays on glass slides were illuminated by white light from a 100 W tungsten lamp through a dark-field condenser (NA = 0.8). The scattered light was collected with a 40× objective (LD Plan-NEOFLUAR, NA = 0.6) and reflected to the entrance slit of the monochromator for imaging and spectroscopy. Scattering spectra from individual Au nanoparticle arrays were corrected by subtracting background spectra taken from the adjacent regions containing no Au nanoparticles.

Near field calculation: Localized surface plasmon scattering spectra and electric field enhancement at the Au nanoparticle arrays were calculated using the finite-difference time-domain (FDTD) method. In the calculation, the arrays were modelled as spherical Au nanoparticles linearly aligned on a glass substrate. Based on the SEM experimental measurements, the diameter of the nanoparticles was set at 66 nm. The dielectric function used for Au in the calculation was described by the free electron Drude model with parameters set to match the standard experimental values.[7] The refractive index of the surrounding media, air, and the glass substrate were taken to be 1.0 and 1.52, respectively. The incident light was parallel along the normal to the substrate. The mesh size used in the calculation was set to 1 nm for single-line arrays and 1.5 nm for double-line arrays, respectively. The gap distance between neighbouring nanoparticles within each array was 8 nm, corresponding to that determined from SEM images.

SERS characterization: Benzenethiol was adsorbed, from the gas phase, on the whole surface of the metallic samples by casting a drop of BT (0.1 M in ethanol) in a Petri dish where the substrate was also contained. SERS spectra were collected in backscattering geometry with a Renishaw Invia Reflex system equipped with 2D-CCD detector and a Leica confocal microscope. The spectrograph uses a high resolution grating (1800 g cm^{-1}) with additional bandpass filter optics. Excitation of the sample was carried out with a 633 nm He-Ne laser line, with acquisition times of 200 ms and power at the sample of about 1mW, using the Renishaw's StreamLine accesory. The laser was focused onto the sample with a 100× objective. For comparison, gold island films of 9 nm mass thickness were prepared in a Balzers BSV 080 glow discharge evaporation unit. The metal films were deposited on preheated (200 °C) glass slides (Corning). During film deposition, the background pressure was maintained at 10^{-6} Torr, and the deposition rate (0.5 Å s^{-1}) was monitored using an XTC Inficon quartz crystal oscillator.

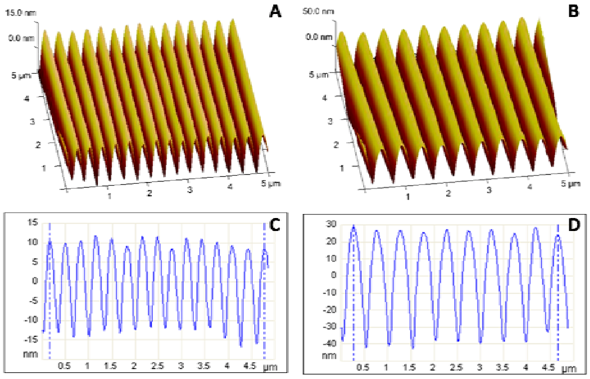

Figure S1. AFM 3D topographic maps from the height images (A,B) and height profiles (C,D) for wrinkled PDMS stamp after an exposure time of 50 and 150 s to the oxygen plasma.

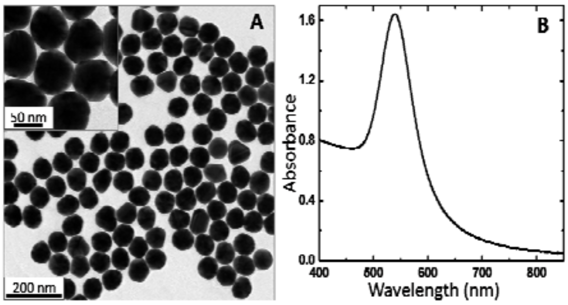

Figure S2. TEM micrograph (A) and UV-vis-NIR spectrum of the employed 66 nm gold nanoparticle colloid.

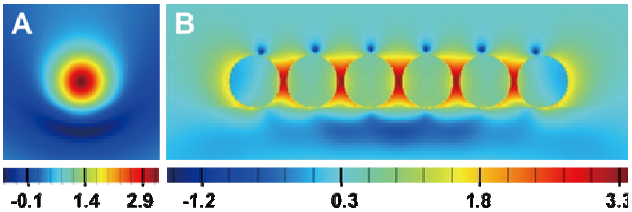

Figure S3. Electric field intensity enhancement contours at a logarithmic scale for a single-line Au nanoparticle array. The nanoparticle array consists of six nanoparticles which are linearly aligned in a row with a gap distance of 8 nm. The diameter of the nanoparticles is 66 nm. Projections are shown in the yz plane (A) and xz plane (B) of the Au nanoparticles array. The mesh size is 1 nm.

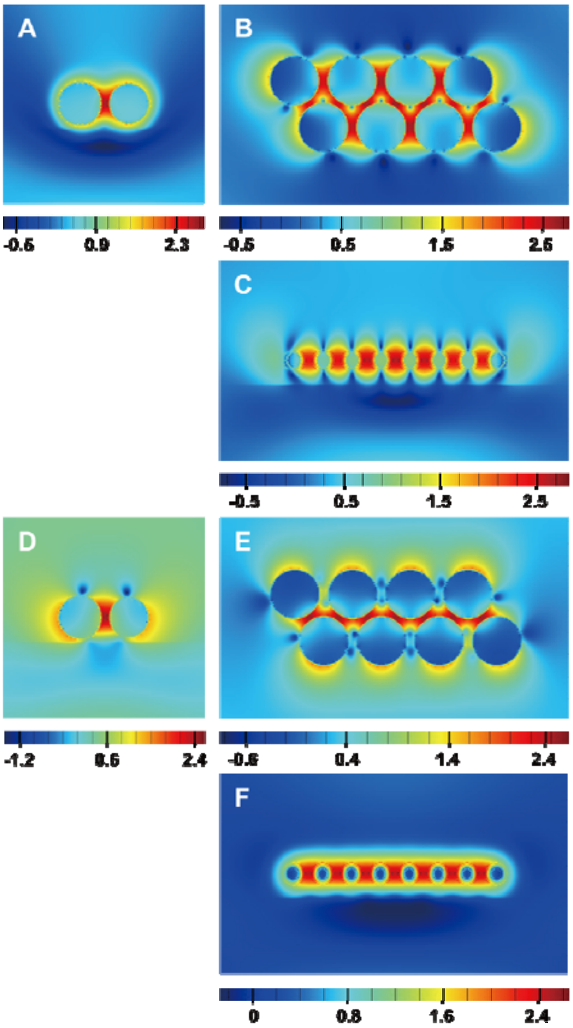

Figure S4. Electric field intensity enhancement contours at a logarithmic scale for a double-line Au nanoparticle array. The array consists of eight nanoparticles linearly aligned in two alternate rows with a closest gap distance of 8 nm. (A-C) yz, xy, and xz projections of E-field enhancement maps for the double-line array, with excitation polarization in the x direction. (D-F) yz, xy, and xz projections of E-field enhancement maps for excitation polarization in the y direction.

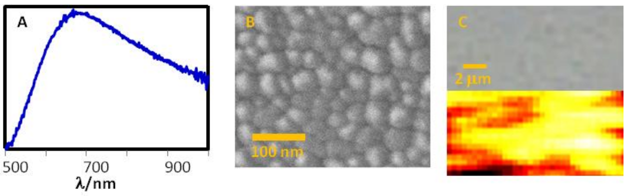

Figure S5. Vis-NIR spectrum (A), SEM image (B), and optical and SERS imaging of a 9 nm gold island film.

Notes and references

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