Supplementary Material (ESI) for Chemical Communications

Supporting information for

Correlated AFM and SERS imaging of the transition from nanotriangle to nanohole arrays

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Experimental section

Nanohole array fabrication

The fabrication of nanohole arrays from etched nanosphere lithography (NSL) masks was based on previous reports [1, 2]. Glass microscope slides (22 x 22 mm) were first cleaned in a piranha solution (75% v/v H_2SO_4: 25% H_2O_2) for 90 minutes at 80 ^oC. Then, the glass slides were thoroughly rinsed with MilliQ water and sonication. Thereafter, they are immersed in a 5:1:1 v/v solution of water/H_2O_2/NH_4OH and sonicated for 60 minutes. Once more, the glass slides were thoroughly rinsed with MilliQ water and sonication. The glass slides were stored in clean MilliQ water, which was replaced regularly.

The nanosphere lithography (NSL) masks were prepared by drop coating of a nanosphere solution (35 µL) on the clean glass slides. The nanosphere solution was prepared by mixing 37 µL of stock nanosphere solution (Thermo Scientific, 10% w/w) with 200 µL of water and 100 µL of ethanol. Keeping the substrates underneath a Petri dish slightly raised with the tip of a pipette tip evaporated the excess solvent slowly. Overnight drying allowed the formation of greater surface area of a single monolayer of the nanospheres.

The NSL masks were then etched by oxygen plasma. A plasma cleaner (Harrick Plasma Cleaner PDC-32G) was used at high power (18 W) from 0 to 10 minutes with a 20 minute vacuum step prior to etching. An oxygen flow of 15 mL/min in the plasma chamber was maintained throughout the entire process. Thereafter, a 1 nm chromium layer followed by a 125 nm silver layer were deposited onto the SERS surfaces. The chromium layer was necessary to insure the adhesion of the silver layer. Finally, removing the NSL mask by sonication of the substrates in a solution of ethanol for a few minutes exposed the nanoholes. For each etch time, four identically prepared samples were fabricated and tested. The size of the nanostructured SERS substrates were measured by AFM in contact mode on an Alpha SNOM (Witec) with 256 x 256 pixels resolution and a scanning rate of 1 Hz. Table S1 reports the diameter of the nanohole and the ratio of diameter/periodicity (D/P).

LSPR measurements

The nanohole arrays were first studied by LSPR in the reflectance mode, as previously reported [3]. A 6 around 1 reflectance probe was used and the spectral range covered was from 400 to 900 nm. The data were analyzed with MatLab to obtain the reflectance spectra considering flat silver as the reference [3].

Raman spectroscopy measurements

The nanohole arrays were immerged in 0.5 mM 4-nitrobenzene thiol (4-NBT) aqueous solution for at least 12 hrs. The samples were then thoroughly rinsed with water and air-dried prior to the Raman measurements. The Raman spectrum for each sample was measured using a Renishaw InVia Raman microscope with a 633 nm and a 785 nm laser excitation. The spectra were acquired for 10 seconds at 1% of the laser power corresponding to 35 µW for the 633 nm laser and to 0.35 mW for the 785 nm laser. The region covering 800 to 1800 cm^{-1} Raman shift was monitored for the characteristic Raman peaks of 4-NBT, which are at 1082, 1112, 1350, and 1575 cm^{-1}. The response is reported as a percentage of the response vs. nanotriangles, where the Raman response of nanotriangle arrays correspond to 100%.

Raman images

Raman analysis was carried out using WiTec alpha300 instrumentation, which facilitated the mapping of approximately 10 x 10 µm areas. The false colour Raman map of intensity were obtained using a 633 nm excitation laser selected to match one of the LSPR bands of the substrates. The parameters were set as following: λ_{ex}=633 nm, 0.01 s integration time, 100x objective, which result in approximately 200 nm spatial resolution. The intensity of the v(C-C) stretch of 4-NBT at 1574 cm^{-1} was mapped resulting in a false colour image of the Raman enhancement over the analysis area. Three maps were taken from three separate, identically prepared samples for each etch time. All maps from samples with the same etch time resembled one another to a high degree highlighting the reproducibility of the Raman response from the substrates.

Correlated AFM and Raman images

Close contact mode AFM images were performed on a NanoInk DPN5000 instrumentation. Images were 512 x 512 pixel resolution, with a 0.3 Hz scan rate. The scanned areas intentionally included crystallisation defects and/or scratches to act as points of reference between the AFM and Raman images.

Table S1. Physical properties of the nanotriangle and nanohole arrays.

Etch time (min)	Hole diameter (nm)	Diameter/Periodicity (D/P)
0	820 ± 25 *	1.00
1	629 ± 51	0.77
2	565 ± 41	0.69
4	468 ± 35	0.57
6	460 ± 35	0.56
8	422 ± 60	0.52
10	356 ± 30	0.43

*Value reported by the manufacturer (Thermo Scientific particle technology)

References

1. Murray-Methot, M. P.; Ratel, M.; Masson, J. F., *Journal of Physical Chemistry C* **2010,** *114*, 8268-8275.
2. Masson, J. F.; Murray-Methot, M. P.; Live, L. S., *Analyst* **2010,** *135*, 1483-1489.
3. Masson, J. F.; Gibson, K. F.; Provencher-Girard, A., *J. Phys. Chem. C* **2010**, Accepted for publication, jp-2010-06450y.

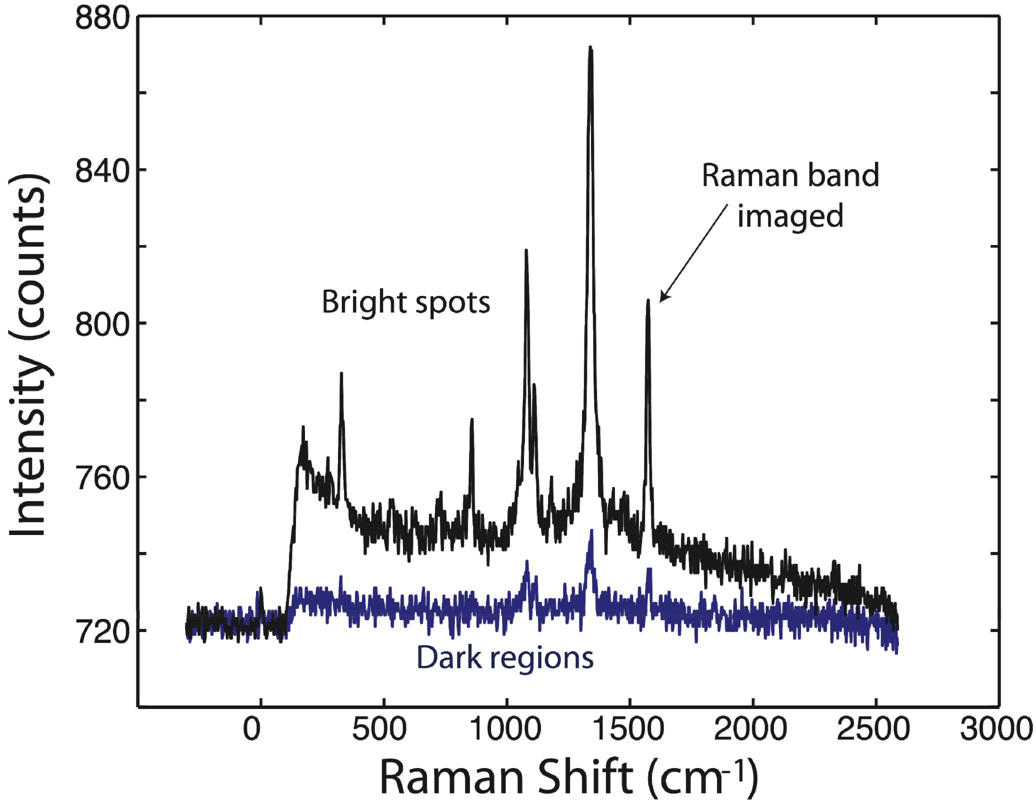

Figure S1. SERS spectra of 4-nitrobenzenethiol on the nanostructured surfaces. The spectrum in black corresponds to the bright regions of the Raman images, while the spectrum in blue corresponds to the dark regions of low SERS intensity. The 4-NBT band at a 1574 cm^{-1} was mapped in the Raman images.

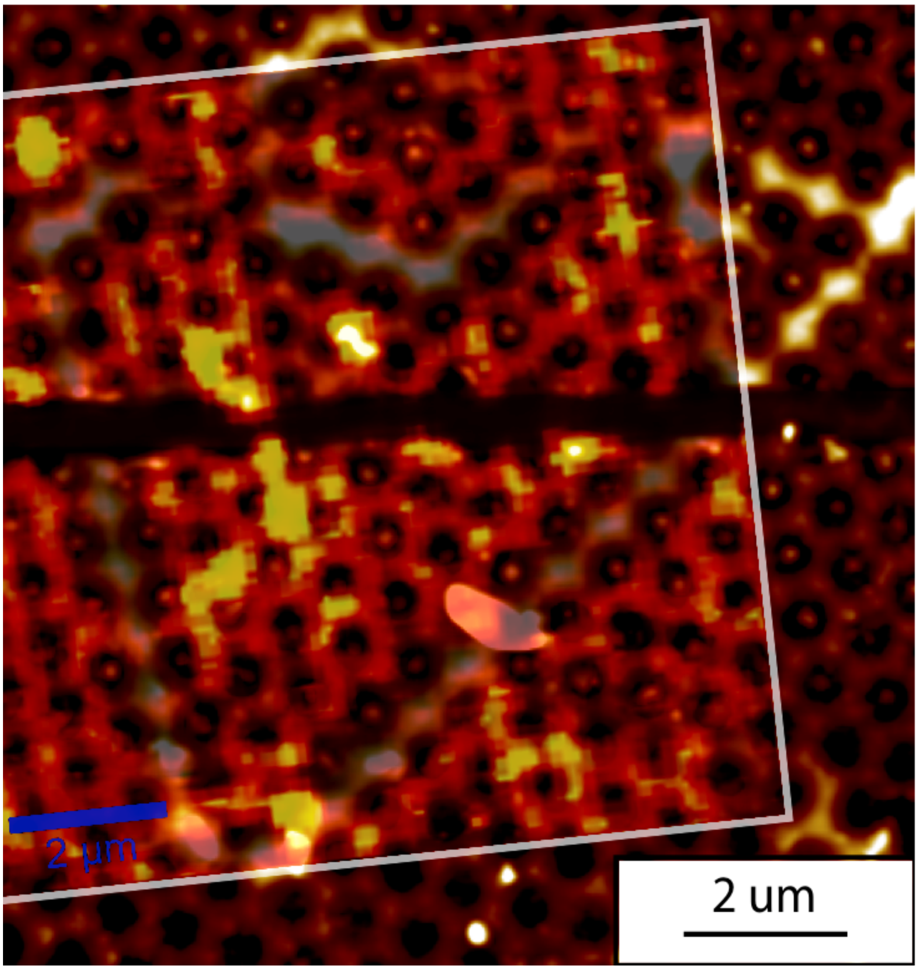

Figure S2. High resolution version of Figure 4 (right panel) demonstrating the correlation of the AFM and Raman images for D/P 0.69.

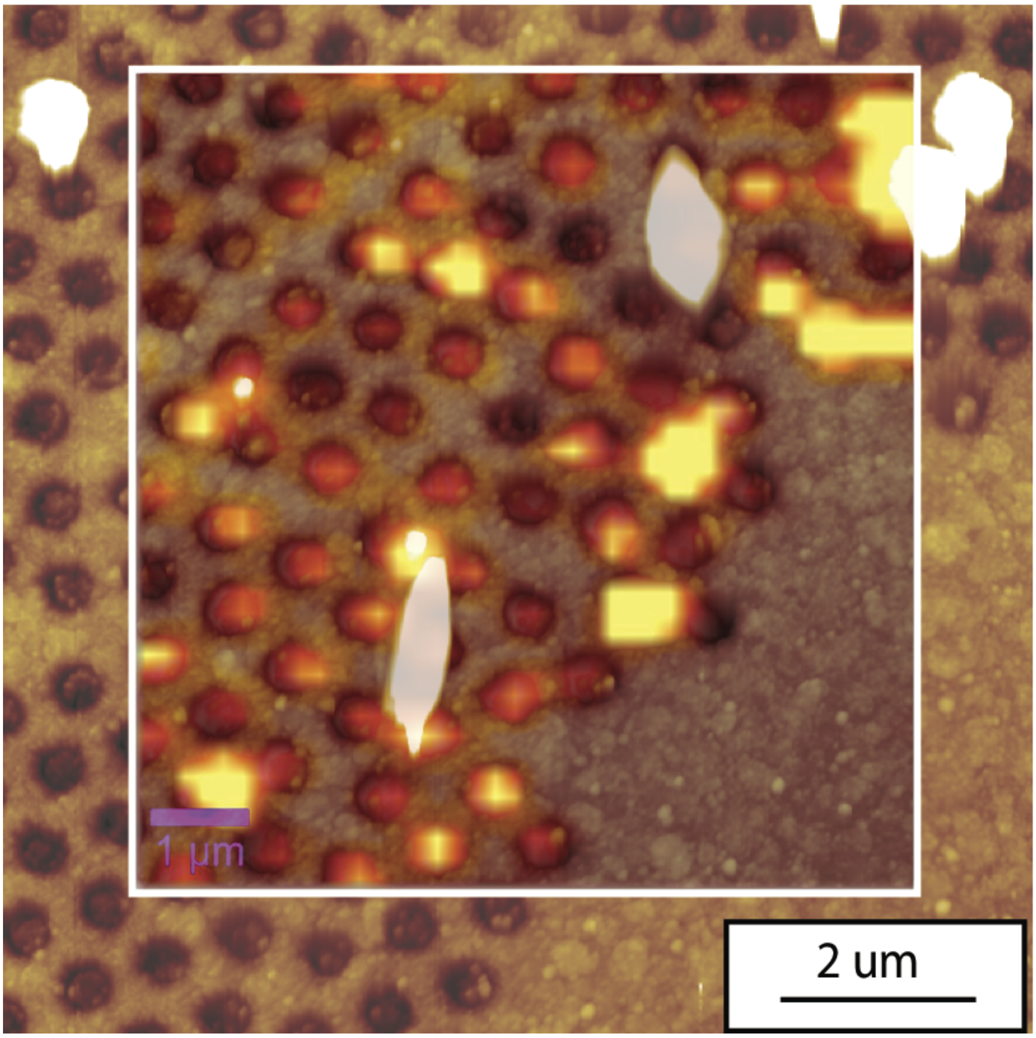

Figure S3. High resolution version of Figure 5 (right panel) demonstrating the correlation of the AFM and Raman images for D/P 0.43.

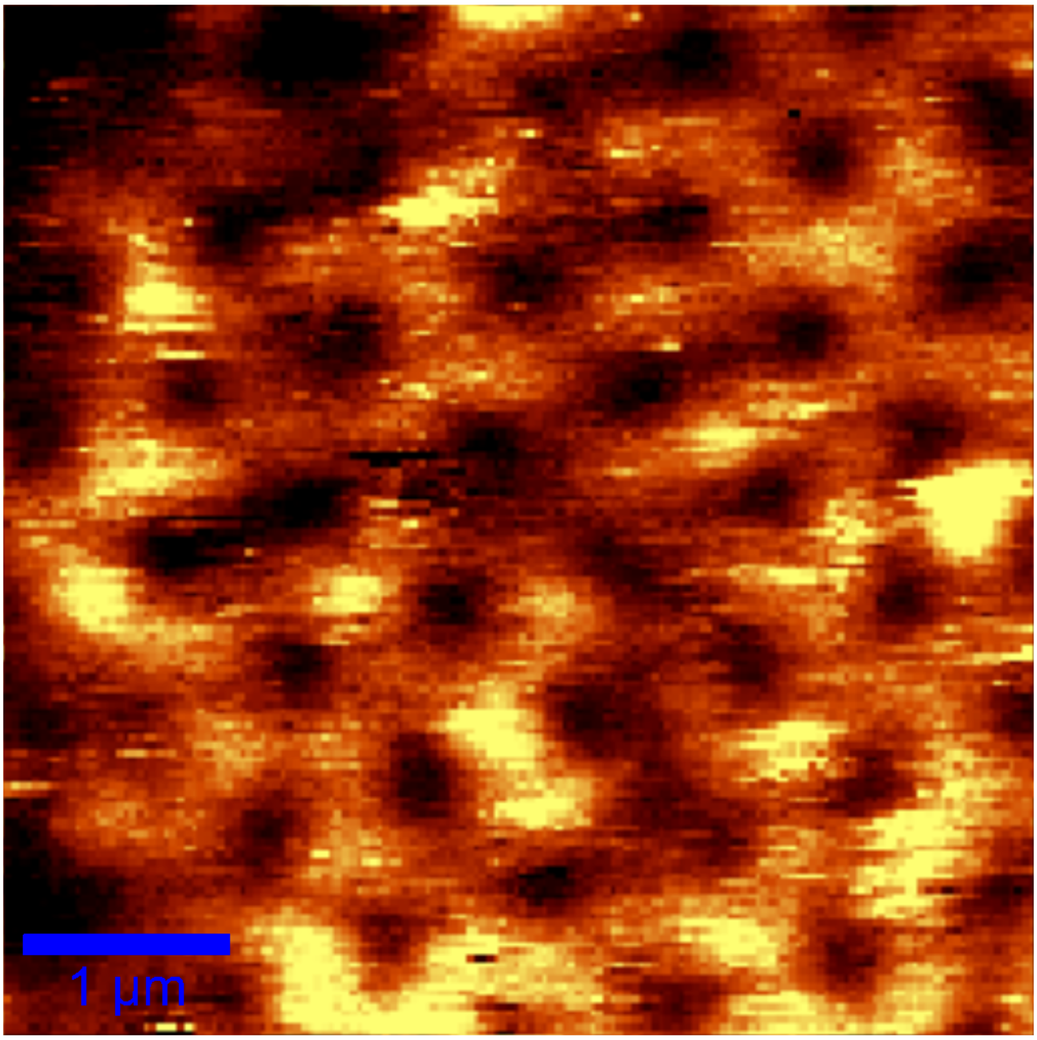

Figure S4. Raman image with high spatial resolution of D/P 0.69 with a scanning area of 5 x 5 µm

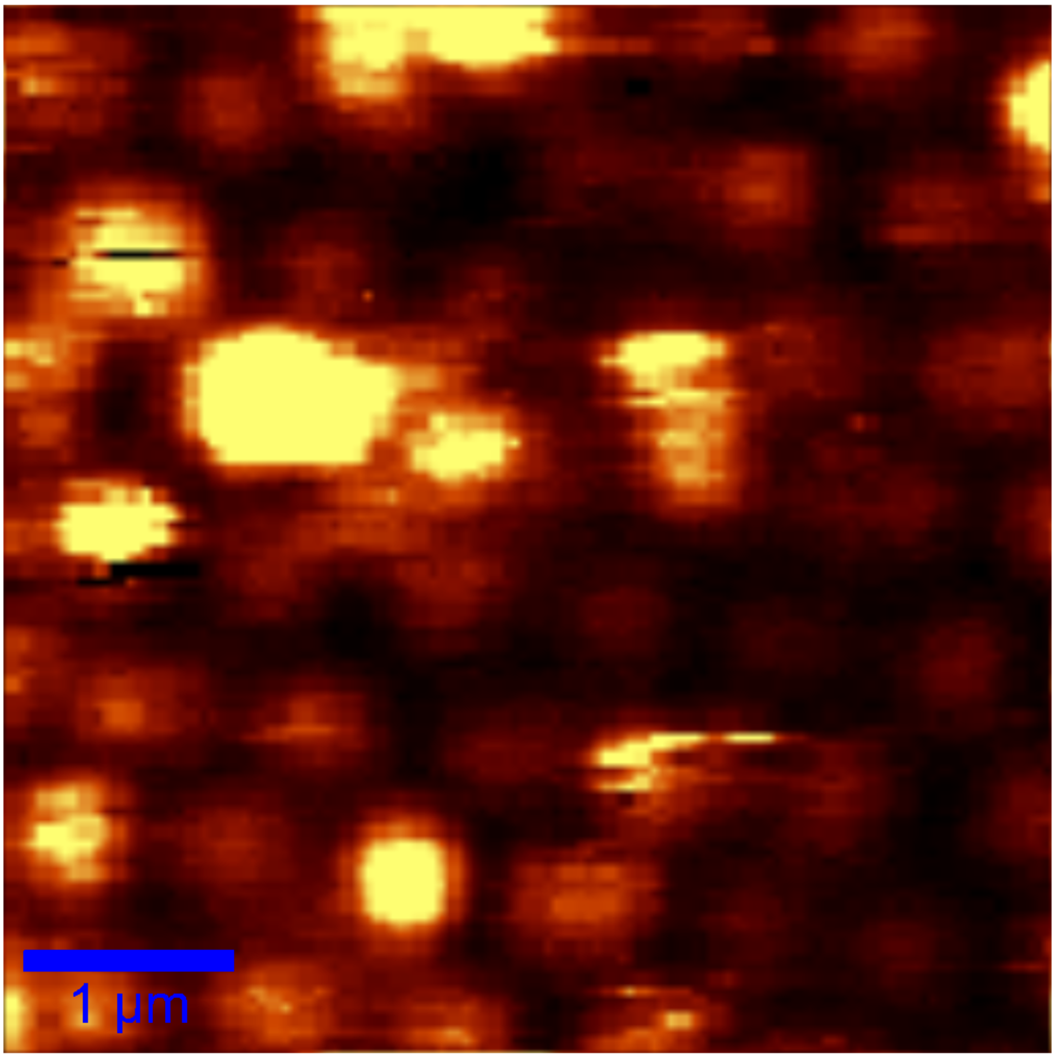

Figure S5. Raman image with high spatial resolution of D/P 0.43 with a scanning area of 5 x 5 µm