# SERS from molecules bridging the gap of particle-in-cavity structures

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## Supplementary Information

### Experimental details:

The SSV substrates used were fabricated by nanosphere lithography as previously reported[1-4] using 600 nm spheres (Duke Scientific), and subsequent electrodeposition of gold to a film height of 0.75*d*. A typical SEM image is shown in figure 1. The NPs used in the study were synthesized using a citrate reduction method as described by Lee *et al.*[5], collected by centrifugation and re-suspended in 18 MΩ cm water. Prior to formation of the adsorbate monolayers the Au SSV substrates were electrochemically cleaned by cycling between -0.6 and 0.6 V vs SCE in 0.1 M KOH solution. The cleaned substrates were immersed in a 10 mM ethanolic solution of the adsorbate overnight, before rinsing with ethanol and drying with $N_2$. Subsequent NP adsorption was performed by immersing the adsorbate modified substrate in the NP suspension for 2 hrs, rinsing with water, and drying with $N_2$.

All spectra were recorded on a Renishaw 2000 spectrometer with a X50 objective providing a 5 μm spot size over 10 s and 633 nm HeNe laser with a power of 0.63 mW unless otherwise stated. Reflectance spectra were obtained on a home-made reflectance rig consisting of a computer controlled goniometer allowing complete control of angle of incidence and azimuthal angle of the sample. The illumination source was a supercontinuum white light laser, which allowed simultaneous measurement of visible and near IR light, using Ocean Optics USB2000 and NIR512 spectrometers respectively.

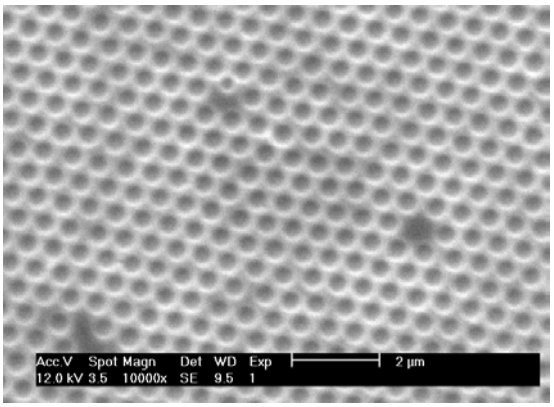


Figure 1. SEM micrograph of 600 nm 0.75d gold SSV substrate

## Notes and references

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