

Supporting Information

A SERS and Electrical Sensor from Gas-Phase Generated Ag Nanoparticles Self-Assembled on Planar Substrates

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Schematics of Magnetron Sputtering Nanoparticle Generator

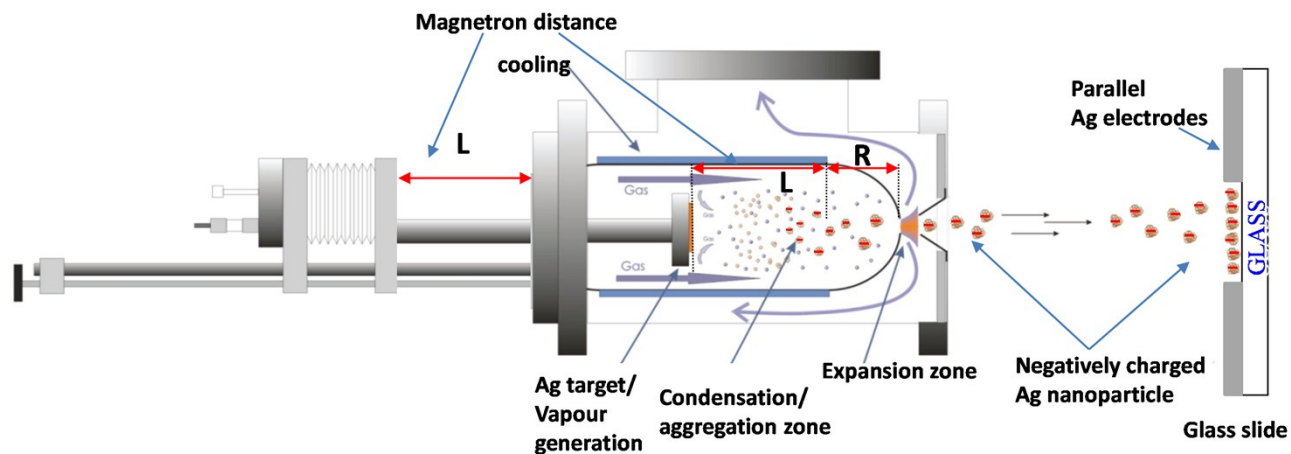


Figure S1. Magnetron sputtering nanoparticle generation source (Nanogen 50, Mantis) used to generate the gas-phase silver nanoparticles. The magnetron distance (L) and total aggregation length ($R + L$) are indicated in the figure.

Height of gas-phase generated Ag NP film

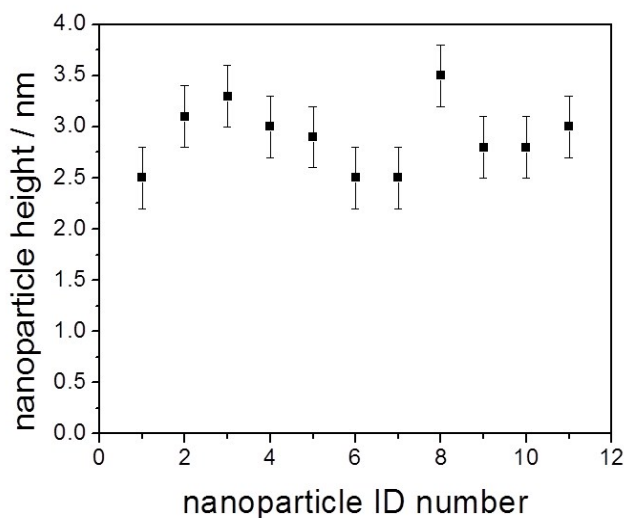


Figure S2. Ag Nanoparticle heights measured along a line in an AFM image. The x-axis identifies 11 of the randomly numbered Ag NPs in an AFM line scan.

AFM measurement of the close-packed nanoparticle monolayer substrate (Fig. 2b) shows a slightly larger NP dimension compared to the SEM measurements of the same sample. This is

not surprising as the lateral dimension a nanostructure becomes comparable to the tip dimension of the AFM probe.² In fact, the only accurate and traceable dimension that can be precisely determined by AFM is the height. It is also known that the lateral dimension of nanostructure as measured by AFM can be larger than its actual value due to the physical size of the AFM tip. The typical lateral size measured in the AFM topography image in Fig. 2c is about 15 nm. AFM measurement on the height of the Ag nanoparticles, on the other hand, is accurate. Assuming the nanoparticle is near-spherical, the mean diameter of the Ag nanoparticles obtained from the height measurements is 2.9 ± 0.3 nm (see Fig. S2). This is consistent with both the mass spectrometry measurement (inset of Fig. 1c) and our previous STM results.¹

Comparison of the performance between the DRDC substrate and commercial substrates

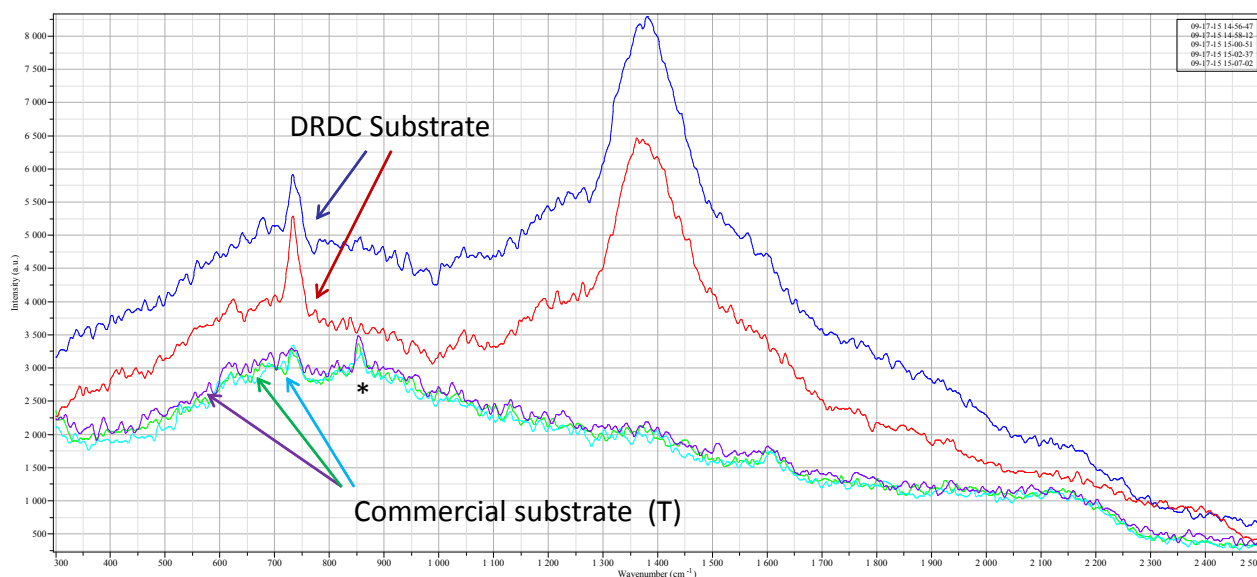


Figure S3 Comparison of the performance between the DRDC substrate and a commercial (T) substrate using a handheld Raman (785 nm, ReporteR, SciAps). Both substrates were immersed in 1 mM adenine aqueous solution for 20 secs. The DRDC substrate shows signature band of adenine at 720 cm⁻¹ while the commercial (T) substrate shows no fingerprint peak of adenine.

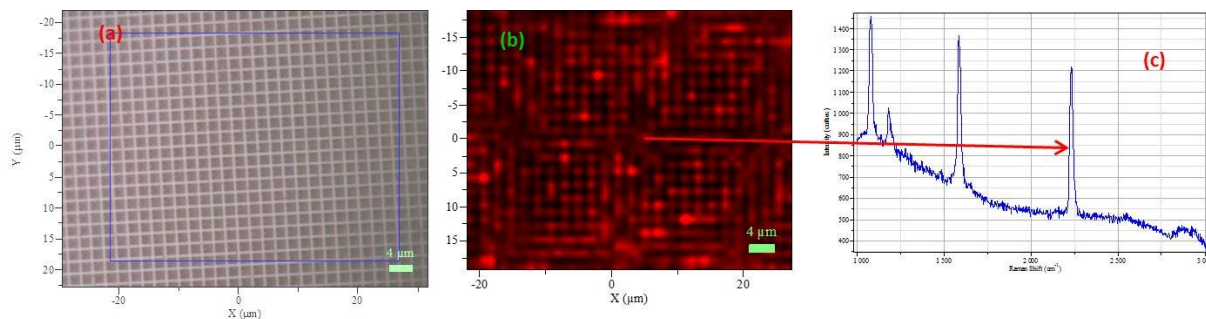


Figure S4 SERS Intensity map of the Commercial (K) substrate which was immersed in a 0.2 mM 4-mercaptobenzonitrile (4-MBN) solution for 45 minutes. The wavelength of the excitation laser is 633 nm. (a) Optical image of the substrate. Blue box outline the area mapped out with a tightly focused laser beam. (b) SERS intensity map of 2220 cm^{-1} vibrational band. The data acquisition time for each pixel is 3 seconds. (c) A sample spectrum taken at the pixel indicated by the red arrow. The intensity variation is over one order of magnitude. The standard deviation is $\pm 80\%$.

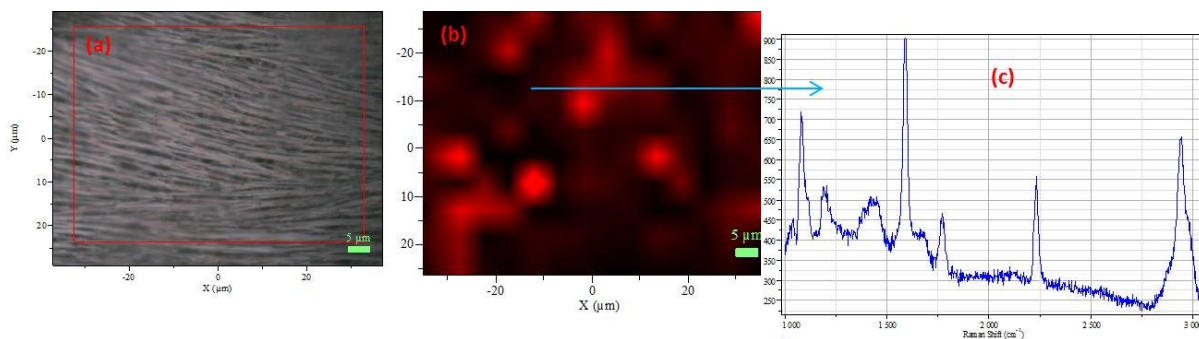


Figure S5 SERS Intensity map of the Commercial (A) substrate which was immersed in a 0.2 mM 4-mercaptobenzonitrile (4-MBN) solution for 45 minutes. The wavelength of the excitation laser is 633 nm. (a) Optical image of the substrate. Red box outline the area mapped out with a tightly focused laser beam. (b) SERS intensity map of 2220 cm^{-1} vibrational band. The data acquisition time for each pixel is 3 seconds. (c) A sample spectrum taken at the pixel indicated by the blue arrow. The intensity variation is over one order of magnitude. The standard deviation is $\pm 102\%$.

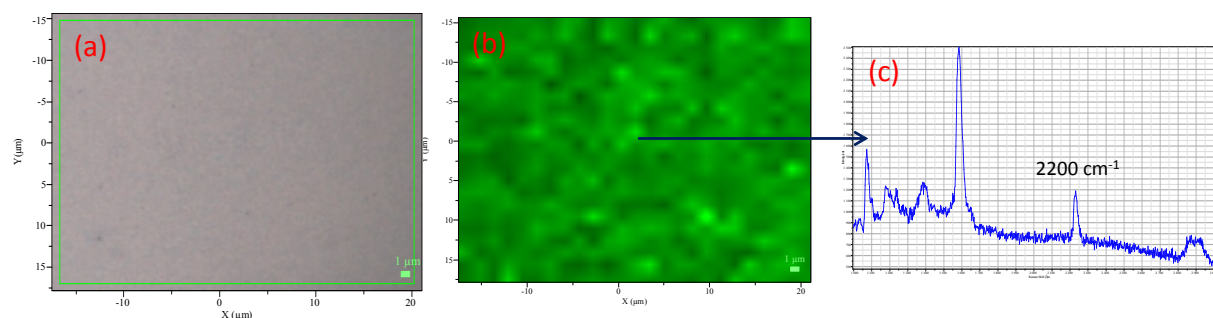


Figure S6 SERS Intensity map of the DRDC (D) substrate which was immersed in a 0.2 mM 4-mercaptobenzonitrile (4-MBN) solution for 45 minutes. The wavelength of the excitation laser is 632.8 nm. (a) Optical image of the substrate. Green box outline the area mapped out with a tightly focused laser beam. (b) SERS intensity map of 2200 cm⁻¹ vibrational band. The data acquisition time for each pixel is 1 second. (c) A sample spectrum taken at the pixel indicated by the blue arrow. The standard deviation is $\pm 22\%$.

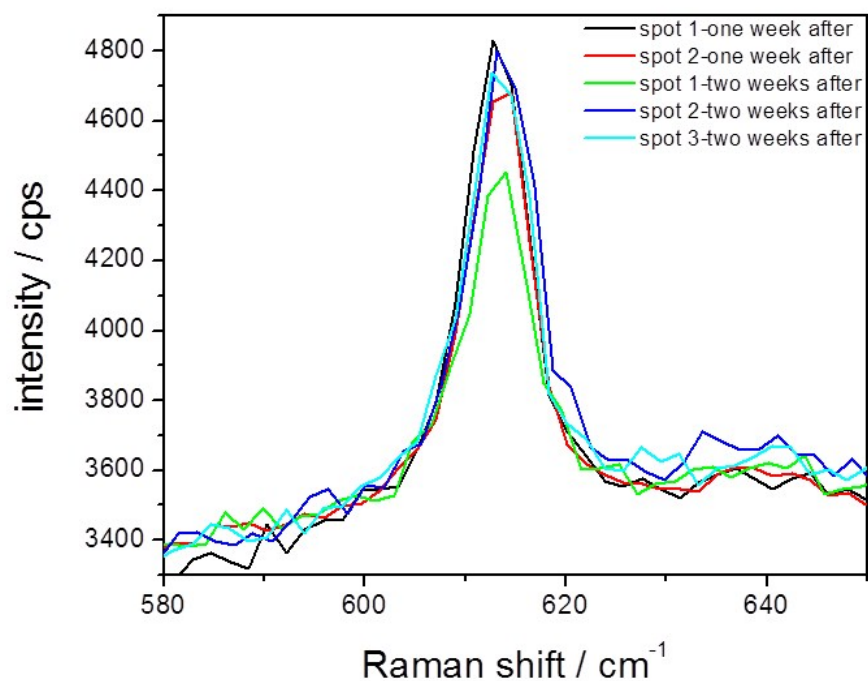


Figure S7 SERS Spectra recorded one week and two weeks after the exposure of the DRDC SERS substrate to R6G 70 μM aqueous solution for 30 seconds. All spots were randomly selected on the 1 cm-sized substrate. The standard deviation is $\pm 12\%$ measured across the substrate two weeks after the exposure.

1. Pedersen, D. B.; Wang, S., Remarkably strong interparticle coupling in two-dimensional ensembles of naked silver quantum dots: The effect on optical and conduction characteristics. *J. Phys. Chem. C* **2009**, *113* (12), 4797-4803.
2. Grobelny, J.; DelRio, F. W.; Pradeep, N.; Kim, D-I.; Hackley, V. A.; and Cook, R. F. NIST - NCL Joint Assay Protocol, PCC-6: "Size Measurement of Nanoparticles Using Atomic Force Microscopy"