Application Note

Applying *Power*SERS for ppb-Level Detection of Organic Molecules

Introduction

The *Power*SERS substrate by Silver Factory Technology is unique in the SERS market. We use silver nanocubes as building blocks. These are single crystal nanoparticles with well-defined edges and corners, exhibiting very strong electromagnetic field. [1] Moreover, we use bottom-up assembly method to form closely packed silver nanocube monolayer to give rise to additional hotspots via interparticle plasmonic coupling. As a result, our *Power*SERS substrate exhibits the following properties:

1) **100 million times SERS enhancement factor** as compared to normal Raman signals of molecules,
2) Limit of detection at **part-per-billion levels**, which enables trace liquid or gaseous analyte(s) detection through their unique molecular vibrational fingerprints,
3) Excellent signal reproducibility with **< 3% in signal variation** across a large measuring area.

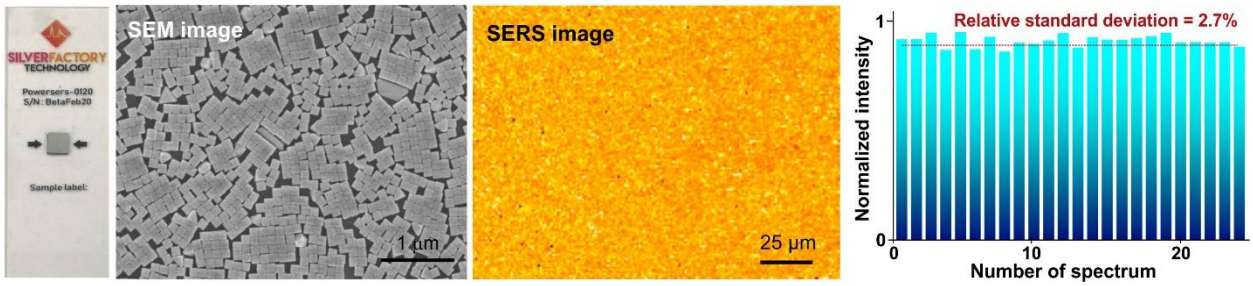

Figure 1. A digital photograph, SEM image and SERS image of *Power*SERS. The SERS signal variation is <3% across a large area.

We evaluated the performance of our *Power*SERS substrates using Technospex's uRaman series. Three common laser wavelengths, i.e. 532 nm, 633 nm and 785 nm, were used in this test. Methylene blue (MB) was used as the probe molecule and its concentrations were varied from 1 part-per-million (ppm) to 100 part-per-trillion (ppt). A droplet of MB solution of 2 µL was drop-casted on the PowerSERS substrate and dried over time. Typical analyte volumes for *Power*SERS are 1 – 10 µL. Experimental details for the measurements were tabulated in Table 1. The data collected is presented without any post-processing (e.g. background removal or smoothing).

Table 1. Parameters used in the performance evaluation of *Power*SERS substrates.

Raman system	uRaman-532	uRaman-633	uRaman-785
Microscopy objectives	20× Nikon Plan Apo λ, NA = 0.75	4× Nikon Plan Apo λ, NA = 0.2	20× Nikon Plan Apo λ, NA = 0.75
Laser power setting	5 mW	3.5 mW	25 mW
Acquisition time	0.5 s (one time measurement, no post-processing treatment)		
Analyte	Methylene blue (MB)		
Analyte concentration	1 ppm, 100 ppb, 10 ppb, 1 ppb, 0.1 ppb.		

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Results

Our *Power*SERS is a highly sensitive SERS sensor capable of achieving a low limit of detection **(LOD) at ppb levels** when using MB as probe molecule at different laser wavelengths (532, 633, 785 nm; Figure 2)**.** The detection is quantitative across 4-5 orders of concentration magnitude, from ppm to ppb levels. *Power*SERS also demonstrates strong Raman enhancements across a broad range of laser excitation wavelength. This broadband enhancement effect spans from visible to near-IR regions.

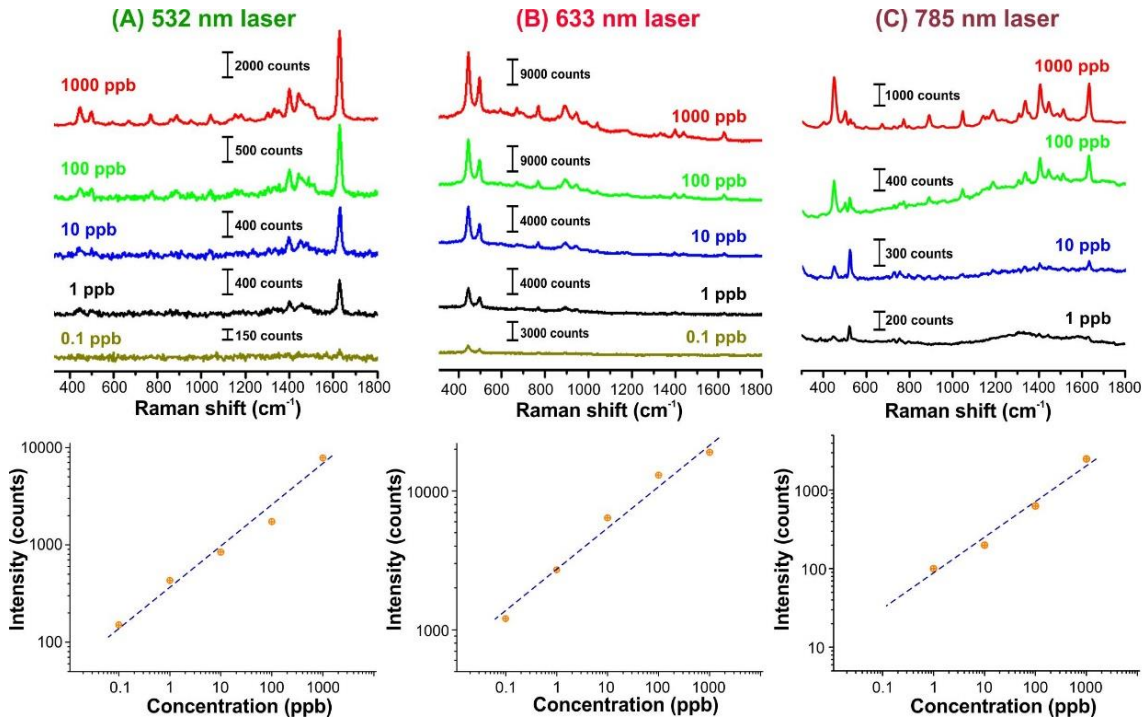

Figure 2. (A – C) SERS spectra of methylene blue (MB) at various concentrations measured using 532, 633 and 785 nm excitation laser wavelengths, respectively. *Power*SERS substrate allows the detection of MB probe molecule down to part-per-billion levels (0.1 – 1 ppb detection limit) using different laser wavelengths.

We note that the vibrational fingerprint of the same molecule obtained using SERS **can vary under different laser excitation wavelengths.** This is due to the differences in molecular vibrational responses when exposed to different photon energy. When using 633 nm laser (Figure 3), SERS peaks at 448 cm^{-1} and 501 cm^{-1} are much stronger than the C-C ring stretching mode at 1628cm^{-1}.[2] This is because the excitation wavelength coincides with the fluorescence emission of the MB (from λ = 600 -700 nm and λ_{max} = 650 nm), thereby resulting in additional resonance SERS effect. Nevertheless, it is clear that MB vibrational signature are enhanced at all excitation wavelengths tested, indicating that analyte molecules

experience strong electromagnetic enhancement arising from the localized surface plasmon resonance of Ag nanocubes in our *PowerSERS* substrate (see all dash lines in Figure 3).

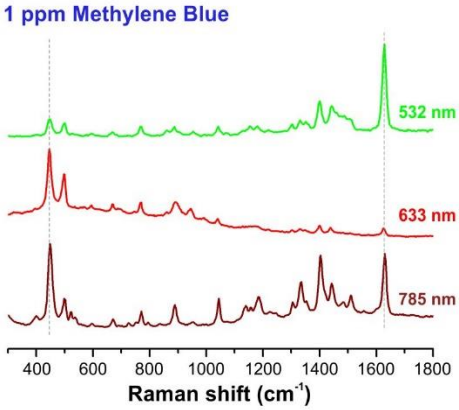

Figure 3. The SERS intensities of the same molecule can differ when excited by different laser wavelength. C-C ring stretching mode (1628 cm^{-1}) is dominant using 532 nm laser excitation, whereas C-N-C skeletal deformation (449 cm^{-1}) is strongest using 633 nm laser excitation. Both 449 cm^{-1} and 1628 cm^{-1} are distinct using 785 nm laser.

Finally, as a comparison, **our *Power*SERS can detect 10,000 lower concentration** than another commercial SERS product (Product-X) under the same measurement conditions (**Figure 4**). Our *Power*SERS substrate obtains a peak intensity of ~400 counts at 1 ppb, whereas Product-X obtains the same intensity counts only when using 10,000 higher concentration of MB (at 10000 ppb, or 10 ppm). More importantly, *Power*SERS exhibits **negligible background interference** necessary for trace analyte detection. In contrast, Product-X demonstrates high background interference that could impede molecular detection (Figure 4).

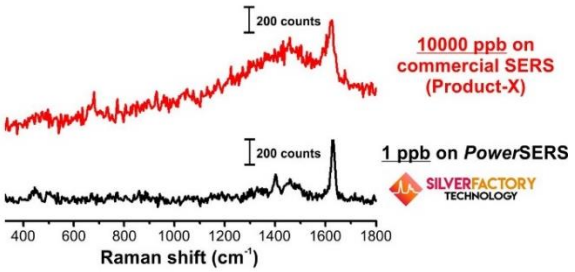

Figure 4. SERS responses from *Power*SERS and another SERS product (Product-X) measured at 532 nm laser. Under the same measurement conditions, our *Power*SERS can detect 10,000 times lower concentration than Product-X.

In summary, *Power*SERS is an ultimate broadband, ultra-sensitive and quantitative SERS substrate that affords a superior part-per-billion detection limit with minimal background interference.

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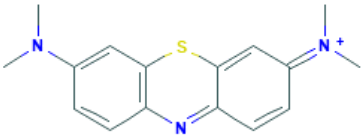
Reference

1. PowerSERS brochure. https://silverfactorytechnology.com/resources
2. Li, C., et al., *Food control* **2016**, *65*, 99-105. https://doi.org/10.1016/j.foodcont.2016.01.017

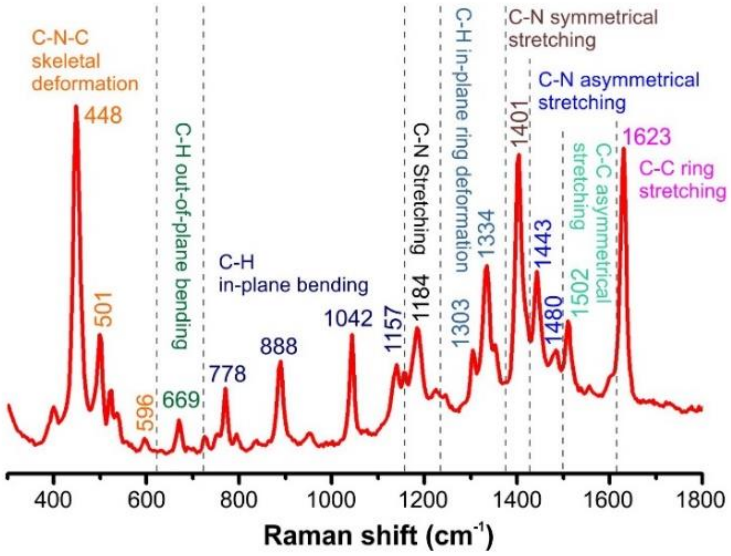
Supporting information

Structure of Methylene blue

PubChem https://pubchem.ncbi.nlm.nih.gov/compound/Methylene-blue#section=2D-Structure



Raman band assignment of Methylene Blue.[2]



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