Dataset demonstrating the working-principles of surface-exposed nanoparticle sheet enhanced Raman spectroscopy (SENSERS) for solvent-free SERS

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Here, we present surface-enhanced Raman data for the calculation of signal uniformity and enhancement factor in SENSERS (surface-exposed nanoparticle sheet enhanced Raman spectroscopy). SEM was used to characterize the microstructure of the solid sample. The interaction between the solid sample and surface-exposed nanoparticle sheet was characterized using SERS and SEM. Based on these data a “skin” versus “sheet” type calculation method was used to calculate the magnitude of Raman signal enhancement within SENSERS. The data presented in this article is related to the research article entitled “Pressing Solids Directly Into Sheets of Plasmonic Nanojunctions Enables Solvent-Free Surface-Enhanced Raman Spectroscopy” (Xu et al., 2018).

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The data presented in this article demonstrates the working principle of SENSERS for direct analysis of solid samples. Fig. 1 presents SERS evidence of the signal uniformity across the enhancing substrate. Figs. 2–7 show SEM characterizations and SERS mapping data along with theoretical calculations which demonstrate the working-principle of SENSERS. Fig. 8 presents SERS data and the theoretical calculations using a "skin” versus “sheet” type model to accurately calculate the signal enhancement factor for SENSERS. Fig. 9 presents SERS data which show that the signal enhancement achieved using SENSERS is comparable to that achieved via traditional solvent-based sampling methods in SERS.

2. Experimental design, materials and methods

2.1. Probing the signal enhancement uniformity of SENS

To probe the signal uniformity between different spots on one SENS as well as the signal reproducibility between different batches of SENS, we exposed two pieces of SENS to the vapor of TP solution to create a self-assembled monolayer of TP on the surface of particles. The intensity of the characteristic band for TP at 1573 cm⁻¹ corresponding to ring vibration for 10 random spots on two 1.5 × 1.5 cm² pieces of SENS are shown in A. The spectra are compared in B. The mean intensity of the 1573 cm⁻¹ peak for TP in SENS 1 and SENS 2 are 5217 and 5749 counts, respectively. The relative standard deviation for SENS 1 and SENS 2 are 11% and 5%, respectively.

2.2. Characterization of the solid sample coffee ring

To acquire proof-of-principle data for SENSERS, solid samples were fabricated by drying a 10 µL droplet of analyte solution on commercial aluminium tape. Fig. 2 show SEM images of a typical coffee ring sample formed from 10 µL of 10⁻³ M CV solution. Low magnification image A revealed that the...
The coffee ring consisted of an outer area with bulk solid CV deposits ca. 20 μm wide and an inner area scattered with numerous smaller crystals ca. 30 μm wide. The extended area of smaller crystals can be seen more clearly when viewed tilted under the SEM, as shown in C. The bulk solid deposit in the outer area was measured to be several hundred nm high while the scattered crystals in the inner area were estimated to be several tens of nm high.

The lowest concentration of detection is at $5 \times 10^{-7}$ M, 10 μL.

Thus the total weight of analyte present $m_{\text{total}}$ is:

$$V \times C \times M_{\text{CV}} = 5 \times 10^{-7} \times 10 \times 10^{-6} \times 408 \approx 2 \times 10^{-9} (\text{g}) = 2 (\text{ng})$$

where $V$ is the total volume of the sample, $C$ is the concentration of the analyte, $M_{\text{CV}}$ is the molecular weight of CV. As shown in Fig. 3, we assume that the radius of the dried droplet is 0.5 cm, the width of the coffee ring is 50 μm and that all the analytes are in the coffee ring area and evenly distributed. Therefore,

$$R = 5 \times 10^3 (\mu\text{m}); r = 5 \times 10^3 - 50 (\mu\text{m}).$$
Thus the total amount of sample area $S$ is:

$$\pi R^2 - \pi r^2 = \pi \left[ \left( 5 \times 10^3 \right)^2 - \left( 5 \times 10^3 - 50 \right)^2 \right] \approx 2493168 \ (\mu m^2)$$

**Fig. 2.** SEM characterization of CV (crystal violet) coffee ring ($10 \mu L \ 10^{-5} \text{ M}$) dried on aluminium tape. Low magnification image of the CV coffee ring (A). High magnification image of the CV coffee ring (B). Tilted image of the CV coffee ring (C).

**Fig. 3.** Schematic representation of the coffee ring sample and calculations for the detection limit of CV.
The diameter of the laser spot is 60 μm.
Thus the effective amount of analyte probed within the laser spot is:

\[
\left( \frac{m_{\text{total}}}{S} \right) \times \pi \left( \frac{60}{2} \right)^2 \approx 2 \times 10^{-3} \text{ng} = 2 \text{ pg}
\]

2.3. Probing the working-principle of SENSERS

For the typical non-adsorbing analytes tested, SERS signals could only be obtained after applying pressure. This was also the case for CV which adsorbs ionically to the NPs in solution. As a solid, CV acts as a non-adsorbing analyte. However, for covalently adsorbing analytes such as 4-MBA, intense SERS signals was observed immediately after the SENS was brought gently into contact with the analyte crystals. Moreover, the signals showed only a slight increase (ca. 2 fold) after the additional pressure was applied (Fig. 4).

As shown in Fig. 5, the mapping was performed with SENSERS stamped on a coffee ring sample dried from 10 μL of 10⁻⁴ M adenine solution. The dark line horizontally across the microscope image clearly shows the crater created through contact with the coffee ring crystals. A total of ten points, one
every 8 μm were taken along a line starting from point 1 which is within the dried droplet area and ca. 40 μm away from the coffee ring to point 10 which is the first point outside the dried droplet area. As expected a clear-cut difference in signal intensity was observed between point 9 and 10, due to the fact that there is no analyte present beyond the coffee ring. In contrast, as the probe spot moves from 9 to 1 the signal intensity first maintains at a strong level then decreases gradually which corresponds to the expected analyte distribution of a dried coffee ring sample. The signal intensity showed no decrease till point 4 which can be seen from the image to be ca. 20 μm away from the area that was initially in direct contact with the coffee ring.

Fig. 6 shows SEM data of the surface of SENS after being pressed on and then peeled off from an adenine coffee ring sample. As shown in A, the circular impression formed on the SENS after pressing the coffee ring sample can be clearly observed under the SEM and is ca. 4 mm in diameter. Focusing on a part of the crater revealed microcrystalline deposits (ca. 50 μm in length) as well as smaller debris (ca. 3 μm in length) scattered around the area (B). Higher magnification images of individual micro-crystals show that larger crystals have deformed under pressure (C). The smaller debris is nearly transparent, which indicates that they are extremely thin. The particle array beneath the crystals can be seen to be intact and undamaged (D). Tilted view revealed that the height of the smaller debris can range from hundreds of nm down to less than 50 nm at which point they become nearly transparent (E). Imaging the same spot with the backscattering detector confirmed that the NP array beneath the crystal debris (circled) is intact and undamaged (F).

As shown in Fig. 7, after drying 10 μL of 10^{-4} M adenine to create a coffee ring structure, a 100 μm^2 area (A) roughly estimated to be at the middle of the dried droplet was mapped with SENSERS moving 1 μm per spectrum. The corresponding heat signature map of the “adenine peak” at 736 cm^{-1} is shown in B.

To locate the SENSERS mapped area under the SEM the laser power of the HORIBA LabRam HR Raman microscope was switched to 100% to burn reference lines showing the outline of the mapped area, as highlighted with blue guidelines in A. The SENS was then peeled off the sample and the same area of the SENS that was in contact with the analyte area corresponding to the Raman map was characterized with SEM. Three areas of interest (1–3) are highlighted in A and B and the corresponding high magnification images of the three areas are shown in C, D, E, respectively. In area 1, a thin crystal island ca. 1 × 1 μm^2 in size can be observed under the SEM. Correspondingly, the signal intensity observed in SENSERS mapping at the area is high. However, it is worth noting that this high signal intensity is retained in a much larger area (ca. 10 × 10 μm^2) surrounding this crystal island, which
indicates that only a very thin amount of analyte crystals is required to give intense SENSERS signals. This effect is even more obvious in area 2, where SEM data only showed a field of particles with no identifiable crystal islands on top but SENSERS mapping data revealed that the bottom half of the area was covered in adenine. In area 3, which is shown to be an extremely “hot” area under SENSERS mapping, SEM data revealed that the particle array has been damaged during the pressing process and that 3-dimensional particle aggregates were formed. As a result intense SENSERS signal was observed.

Fig. 6. SEM data of SENS after being pressed onto an adenine coffee ring and then peeled off. Low magnification SEM image of the SENS area which contacted the coffee ring sample (A). High magnification SEM image showing microcrystalline deposits on the surface of SENS (B). High magnification SEM image of individual crystals on the surface of SENS (C) and (D). Tilted SEM image of microcrystalline deposits on the surface of SENS imaged using the secondary electron detector (E) and the backscattering detector (F).
As shown in Fig. 8, the purple and red spectra correspond to Raman data of pure TP and SERS data of adsorbed TP monolayer on SENS, respectively. We compare the intensity of the peak corresponding to ring stretching in TP (1587 cm$^{-1}$ in Raman and 1573 cm$^{-1}$ in SERS, which matches with literature) [2].

As mentioned in our research article [1], we adopt a “skin” versus “sheet” type analyte coverage model for calculating SERS enhancement factors (EF) of NP films from the literature [3,4].
\[ EF = \frac{\left[ \frac{I_{SERS}}{P_{SERS}} t_{SERS} \right]}{n_{SERS}} \frac{I_{Raman}}{P_{Raman} t_{Raman}} \frac{1}{n_{Raman}} \]

\( I \) corresponds to relative signal intensity; \( P \) corresponds to laser power; \( t \) corresponds to accumulation time; \( n \) corresponds to the number of effective molecules.

Since the laser power (\( P \)) and the accumulation time (\( t \)) used was the same for both Raman and SERS, the equation can be simplified to the following

\[ EF = \frac{I_{SERS}}{I_{Raman}} \frac{n_{SERS}}{n_{Raman}} \]

For SERS experiments of an adsorbed thiol monolayer, we assume that: the analytes have a “skin” type coverage i.e. the SERS effective molecules are a complete monolayer on the gold surface; the surface area of each TP molecule (\( A_{\text{thiol}} \)) is 1 nm² [3]. The area of the laser (\( A_{\text{laser}} \)) is a circle of 30 μm in radius (\( r_{\text{laser}} \)); the NPs in SENS are spherical with a radius (\( r_{\text{NP}} \)) of 25 nm; the full surface of the NPs are accessible to the analytes; the gaps between NPs are neglected.

Therefore, \( A_{\text{laser}} \) can be expressed as

\[ A_{\text{laser}} = \pi r_{\text{laser}}^2 = 9 \times 10^8 \pi \left( \text{nm}^2 \right) \]

The number of NPs (\( n_{\text{NPs}} \)) in the area of the laser can be expressed as

\[ n_{\text{NPs}} = \frac{A_{\text{laser}}}{A_{\text{NP cross section}}} = 1.44 \times 10^6 \]

The surface area for each NP (\( A_{\text{NP}} \)) can be expressed as

\[ A_{\text{NP}} = 4\pi r_{\text{NP}}^2 = 2500\pi \left( \text{nm}^2 \right) \]
The total surface area of NPs in the laser \((A_{\text{plasmonic}})\) can be expressed as

\[
A_{\text{plasmonic}} = n_{\text{NPs}} A_{\text{NP}} = 3.6 \times 10^9 \pi (nm^2)
\]

\(n_{\text{SERS}}\) can be expressed as

\[
n_{\text{SERS}} = \frac{A_{\text{plasmonic}}}{A_{\text{thiol}}} = 3.6 \times 10^9 \pi
\]

For Raman experiments, the density \((d_{\text{thiol}})\) of TP is 1.073 g/mL. The molecular weight \((M_{\text{thiol}})\) of TP is 110.18 g/mol.

The laser penetration depth is measured to be ca. 2 mm. Thus, effective volume of TP \((V_{\text{thiol}})\) in the laser beam can be expressed as

\[
V_{\text{thiol}} = \pi r_{\text{laser}}^2 h = 1.8 \times 10^{15} \pi (nm^3)
\]

The moles \((n_{\text{thiol}})\) of TP corresponding to this volume can be expressed as

\[
n_{\text{thiol}} = V_{\text{thiol}} d_{\text{thiol}}/M_{\text{thiol}} = 1.8 \times 10^{-8} (mol)
\]

\(n_{\text{Raman}}\) can be expressed as

\[
n_{\text{Raman}} = N_A n_{\text{thiol}} = 1.1 \pi \times 10^{16}
\]

The relative intensity of the two peaks \(I_{\text{SERS}}\) and \(I_{\text{Raman}}\) is 5749 and 1300 respectively. Thus the final EF for “skin” type coverage is

\[
EF = \frac{I_{\text{SERS}}/n_{\text{SERS}}}{I_{\text{Raman}}/n_{\text{Raman}}} = 1.3 \times 10^7
\]

For SENSERS, we assume “sheet” type analyte coverage, which is estimated to have an EF ca. 3 times lower than “skin” type. Thus, the EF for SENSERS is estimated to be \(4.5 \times 10^6\).

As shown in Fig. 9, spectrum 1 was averaged from 10 spectra taken randomly on the coffee ring of 10 \(\mu\)L of \(10^{-4}\) M adenine dried directly onto SENS. Spectrum 2 was averaged from 10 spectra taken randomly on the coffee ring of 10 \(\mu\)L of \(10^{-4}\) M adenine dried on aluminium backing with SENS pressed on top. While the EF of SENSERS was predicted to be ca. three times lower than conventional SERS, here the intensity of SENSERS is actually ca. two times stronger. This is because in this case, the surface hydrophobicity of SENS and the aluminium backing was different, which led to a smaller and more concentrated coffee ring on the aluminium backing.

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Transparency document

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