Statistical analysis of SERS substrate: silver nanoparticle Langmuir-Blodgett film as an example

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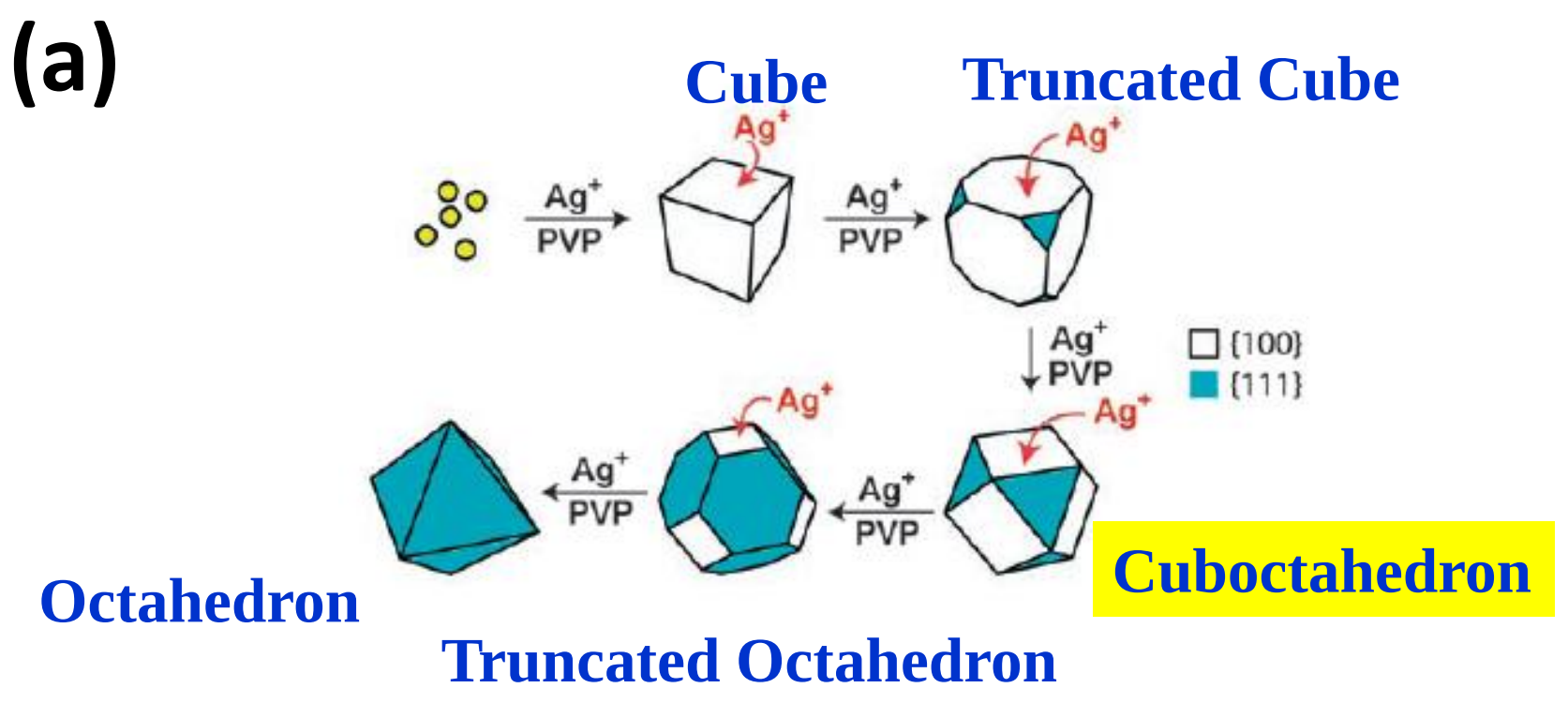
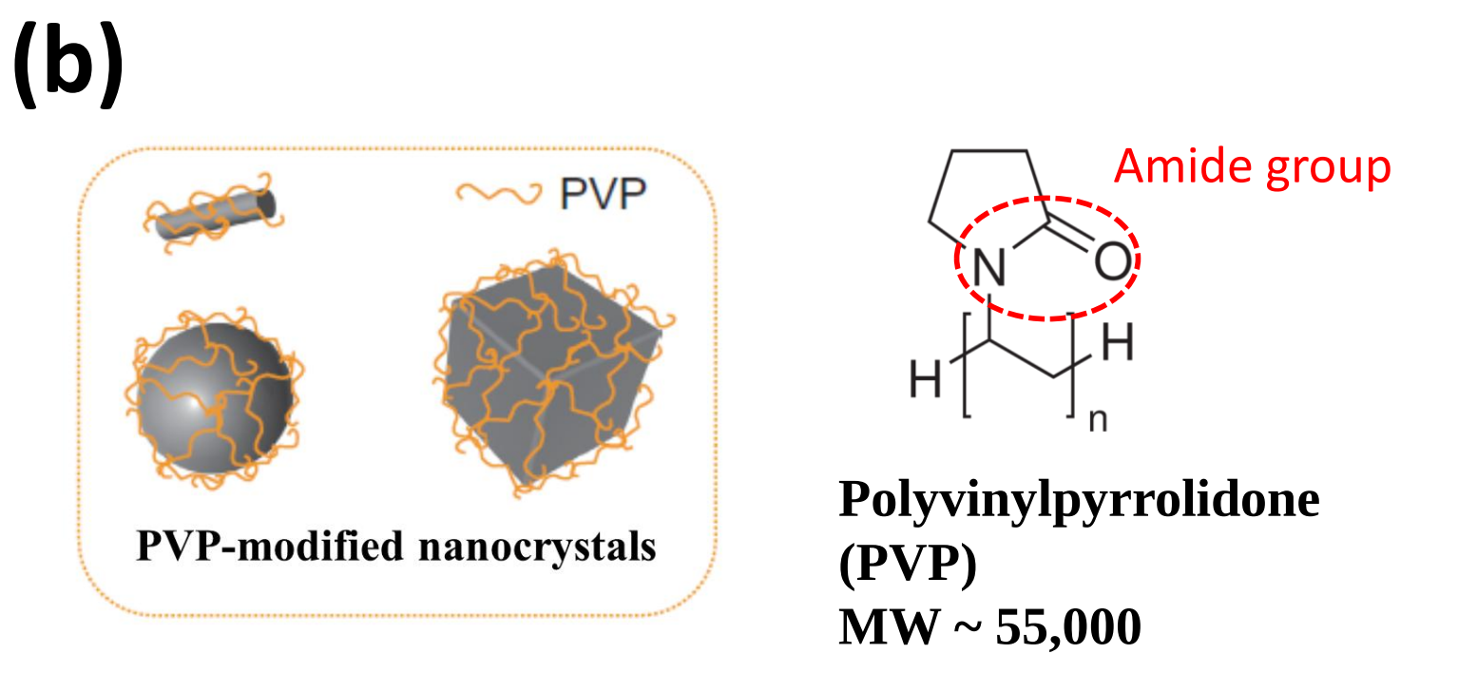
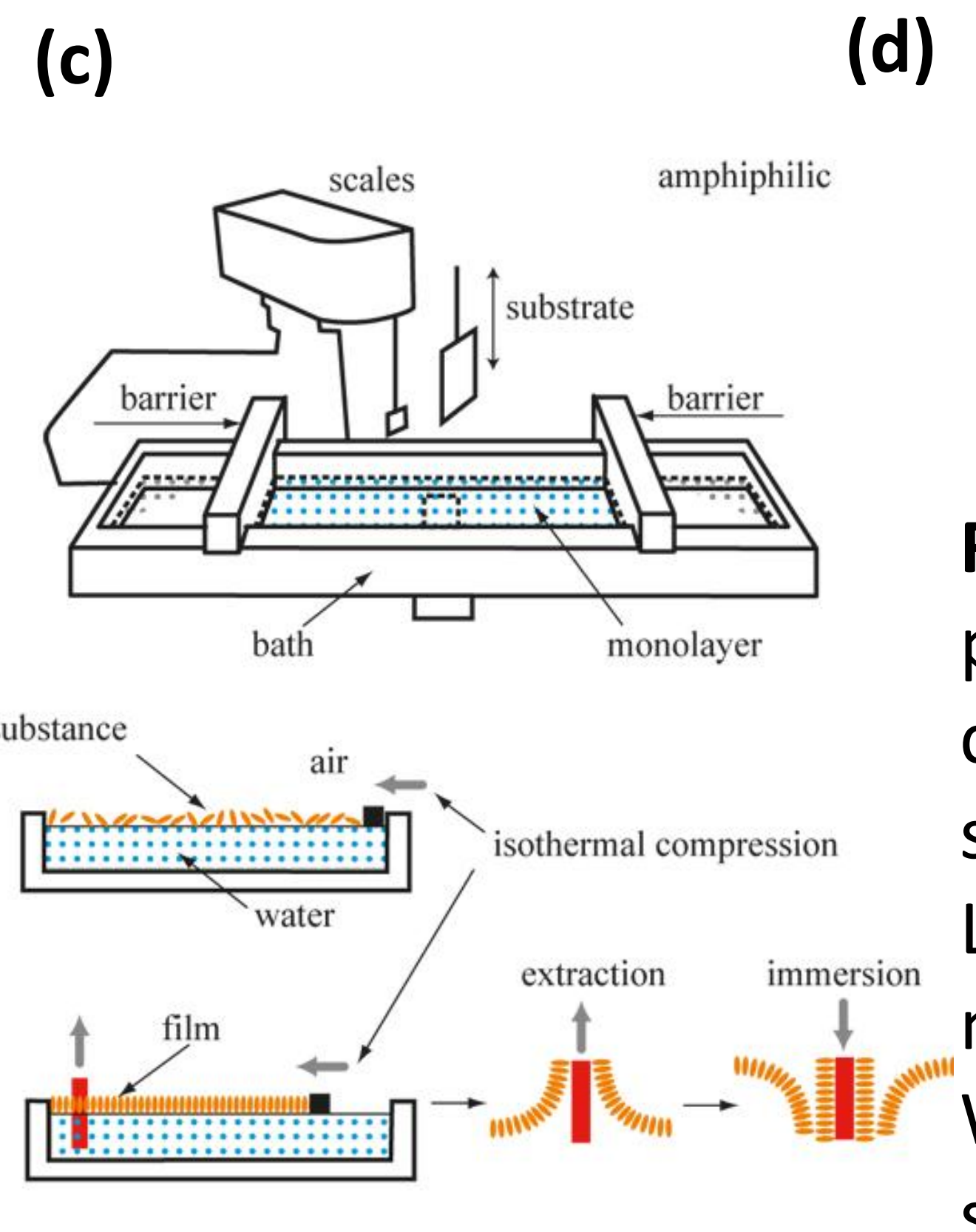
Abstract

In this study, we performed statistical analysis to quantify the distribution and time variation of hot spots in a SERS substrate. The studied substrate consists of a monolayer of silver nanoparticle (AgNP) made with Langmuir-Blodgett (LB) technique. The synthesis of the AgNPs involves the use of polyvinylpyrrolidone (PVP) as a shape controlling agent which remains on the surface of the nanoparticle. Using PVP as analyte, we investigate the temporal and spatial variation of SERS from the hot spots of AgNP LB film by performing time-lapsed Raman mapping of AgNP LB film, then use the total Raman signal intensity as estimate of the SERS enhancement factor. By analyzing the enhancement probability distribution, it allows us to quantitatively characterize the performance of SERS substrates and to realize the possible mechanism causing the large enhancement variation in SERS substrates..

Sample Description







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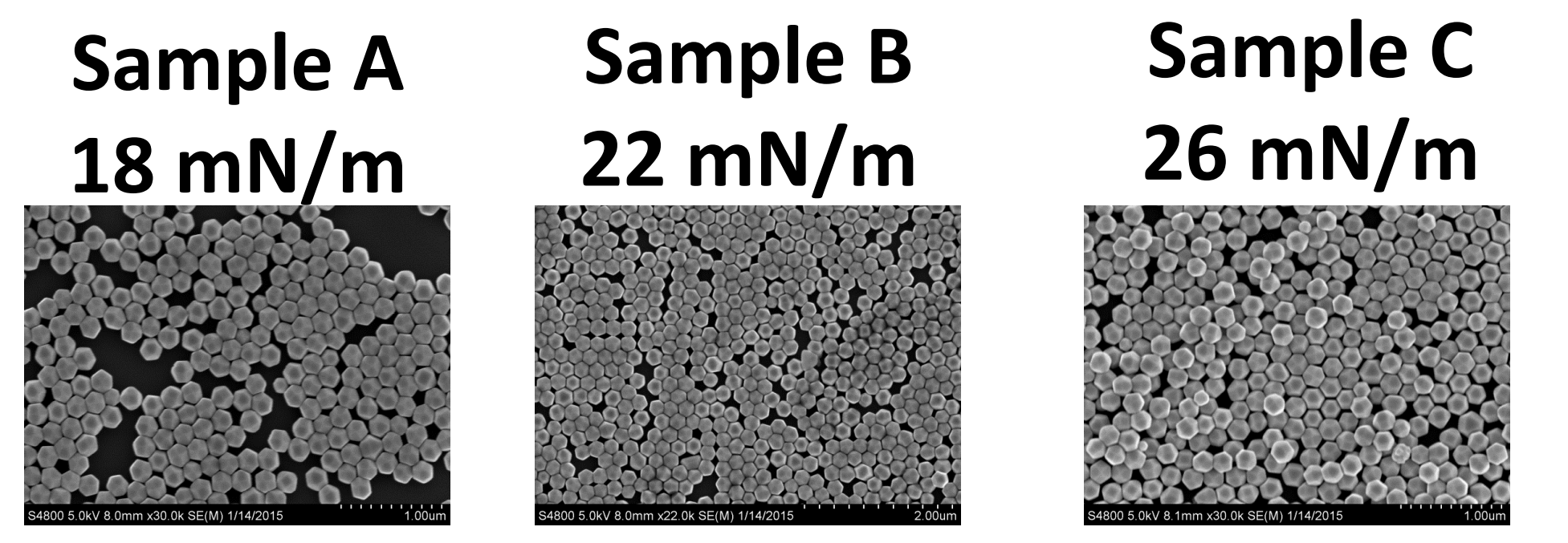


Fig. 1 (a) Synthesis of Ag nanoparticle with polyvinylpyrrolidone (PVP) as shape controlling agent (b) PVP remains on the surface of Ag nanoparticle after synthesis (c) Langmuir-Blodgett method for producing monolayer of Ag nanoparticle on a substrate. We prepared three LB film Ag nanoparticle samples with surface tension of 18, 22, and 26 mN/m. (d) The SEM images of the three samples shows variations in the AgNP packing.

Optical Measurement Setup

Optical measurements were performed on a home-built laser scanning confocal microscope using 532nm excitation. For focusing, we used a 100x NA0.9 objective, and on-sample power range from 4μW to 32 μW. The entrance of the optical fiber is used as the confocal pinhole, and the collected signal is sent to a photomultiplier tube or a spectrometer.

LB film enhanced PVP Raman Spectra

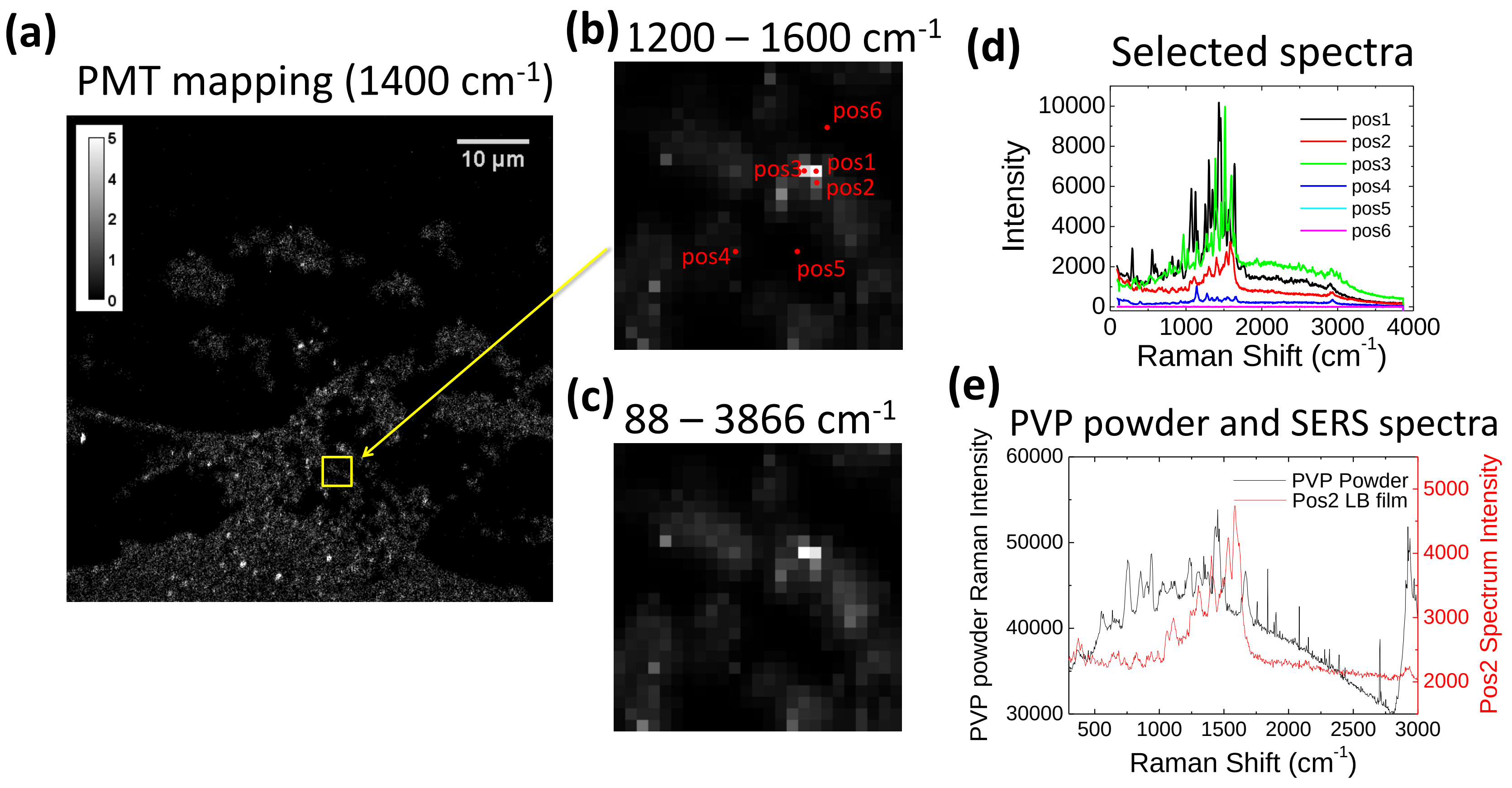
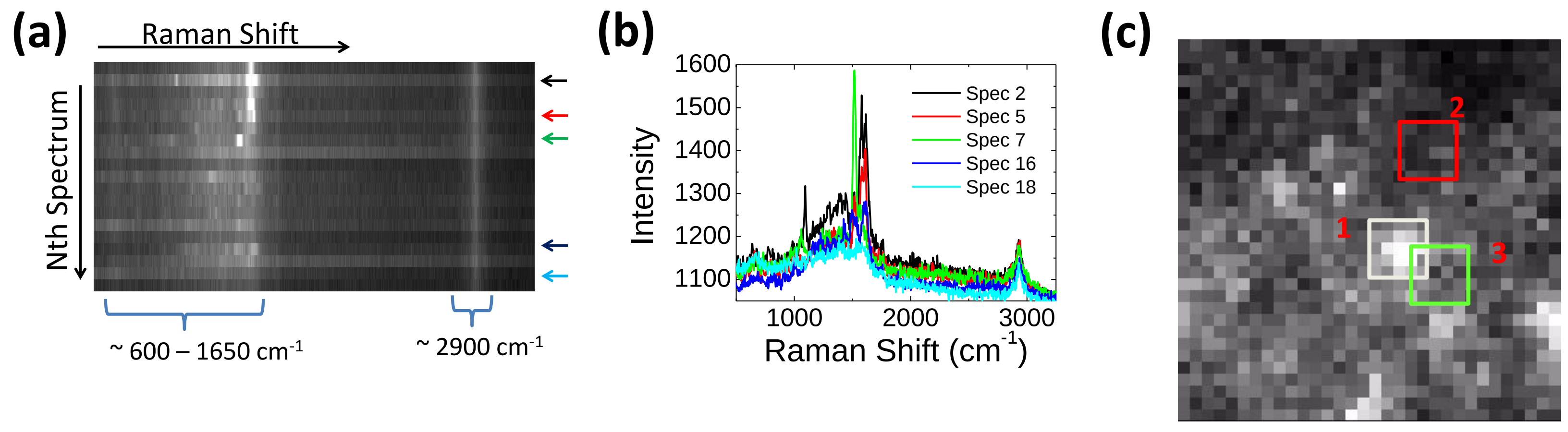


Fig. 2 (a) PMT mapping of LB film border area with 1400 cm^{-1} band selected with a monochrometer. Spectral mapping of region shown in (a) with intensity integrated over the band from (b) 1200 – 1600 cm^{-1} and (c) 88 – 3866 cm^{-1} (full range of the acquired spectrum). The similarity of (b) and (c) lead us to use the PMT intensity as SERS enhancement estimate. (d) Selected spectra from position indicated in (b). (e) comparison of SERS spectra with Raman spectra of PVP powder. Note that most of the enhancement occurs between 1100 – 1650 cm-1, corresponds to the Raman from amide group (Fig. 1b).

Time Lapsed PVP Raman Spectra



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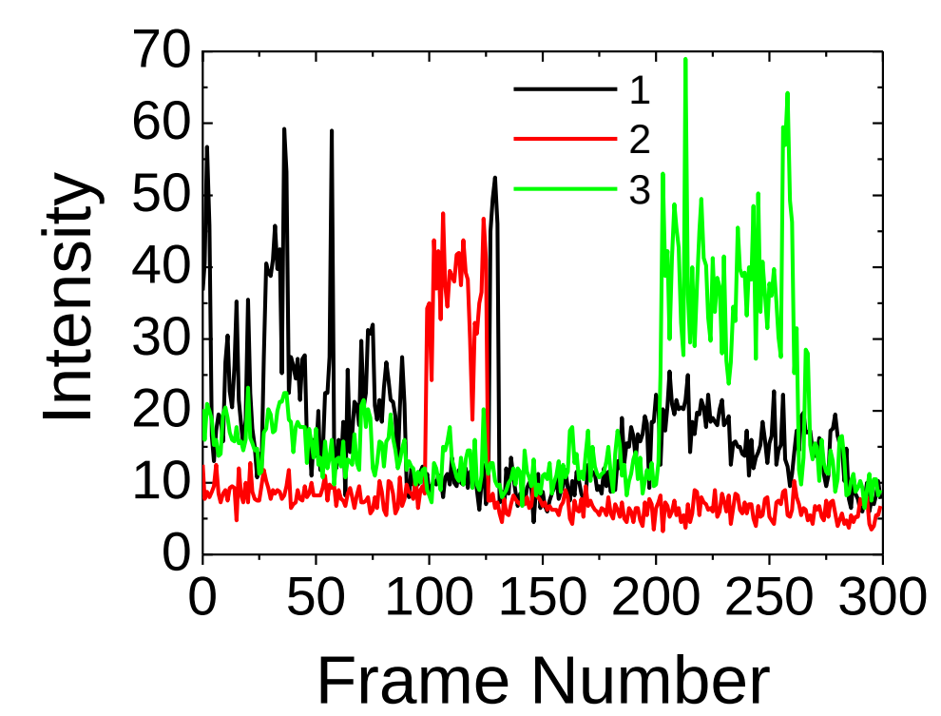


Fig. 3 (a) Time lapsed spectral acquisition of a single point on the LB film, with the spectra displayed as a 2D mapping. (b) Selected spectra from the time lapsed data. (c) Single scanned image from a 300 frame time-lapsed image of LB film. Image size: 4 μm x 4 μm. (d) Time variation of intensity of three marked areas shown in (c).

SERS Enhancement Statistics

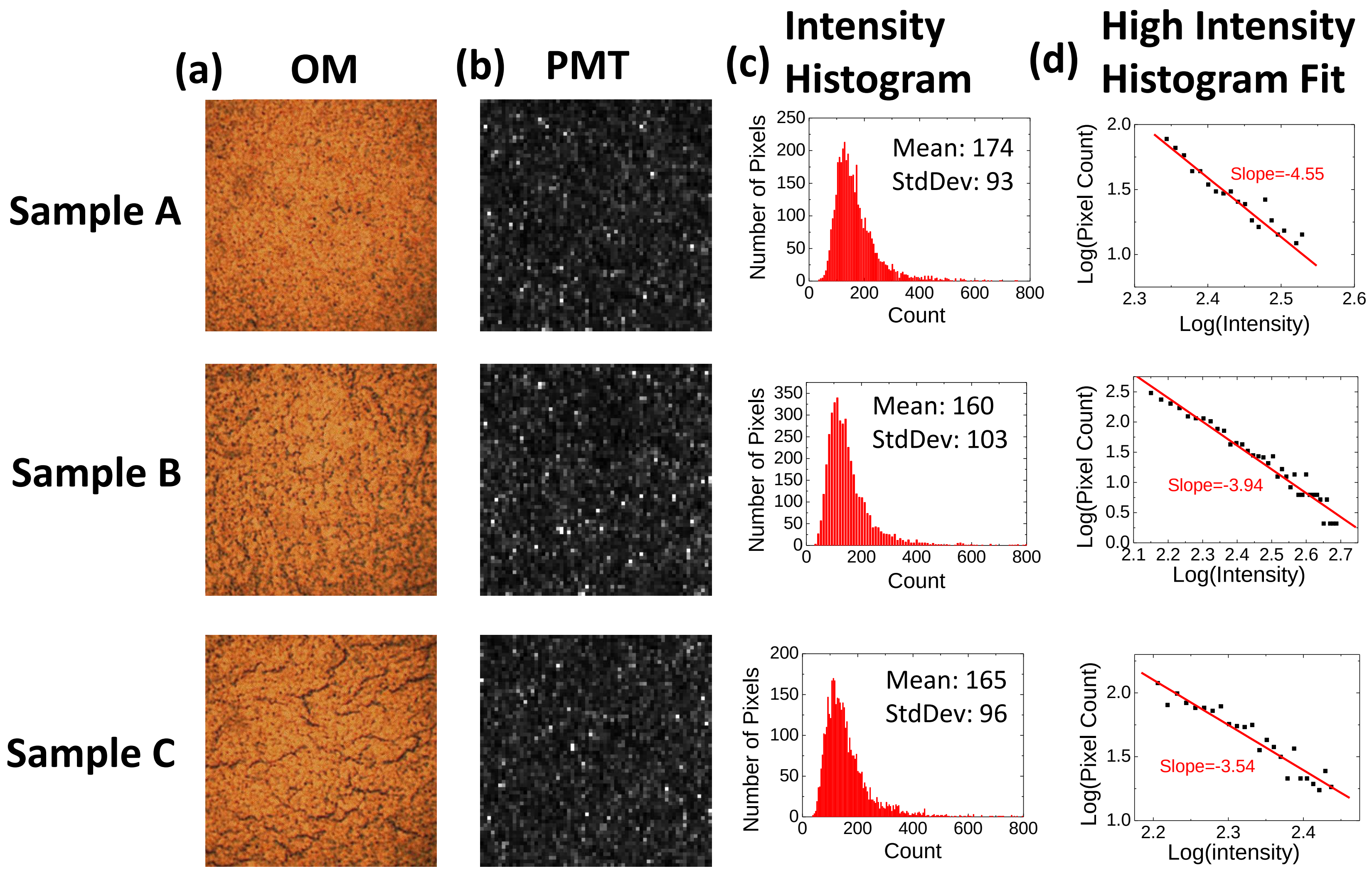
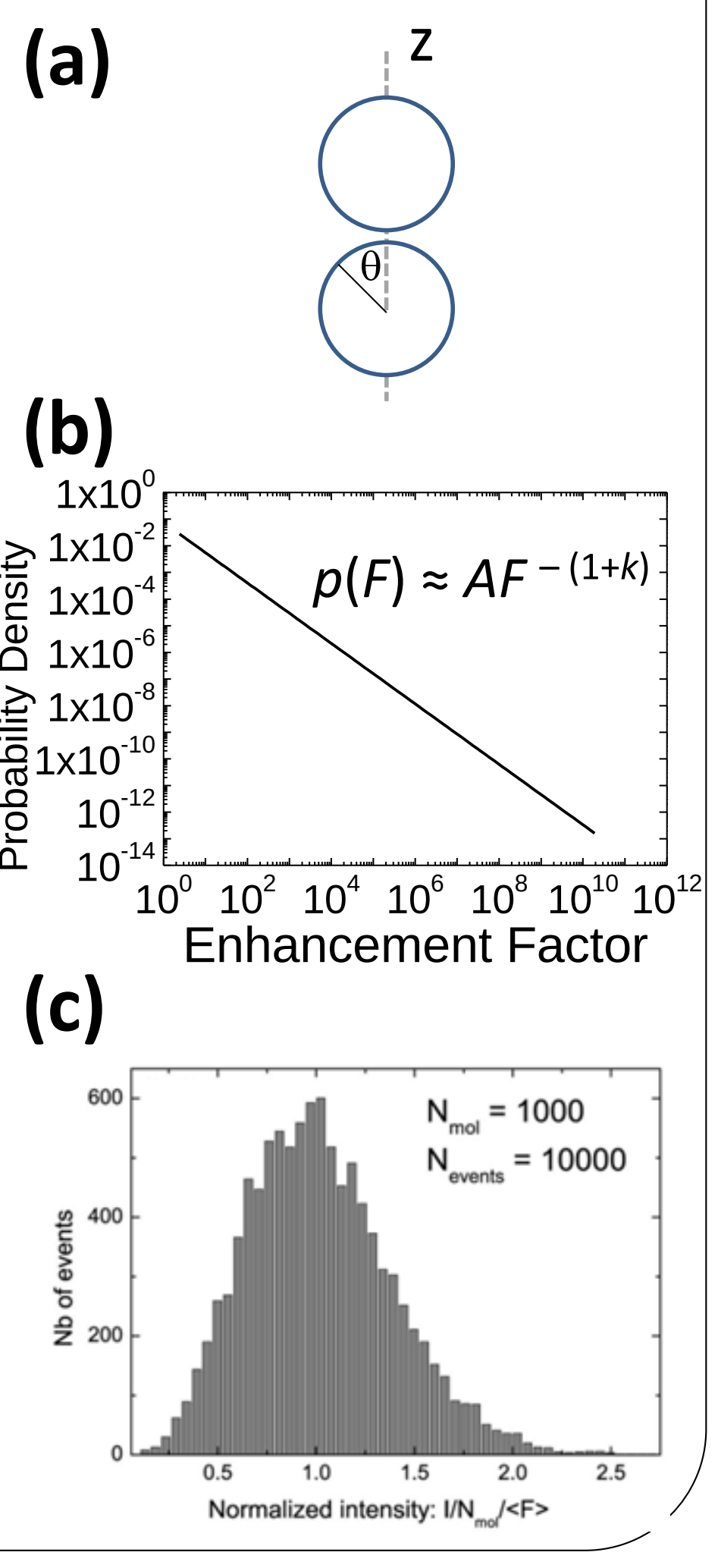


Fig. 4 (a) Optical microscope (OM) and (b) laser confocal scan image of three Ag nanoparticle LB film sample produced with different compression surface tension. (c) Histogram of the scanned image intensity distribution. (d) Linear fit to log-log plot of high intensity tail of the histogram.

Sample	Slope fit to high intensity distribution
A	-4.55
B	-3.94
C	-3.54

Enhancement Distribution Model

Fig. 5, Le Ru et al.[1] modeled the enhancement distribution of SERS substrate based on nanoparticle dimers (a) as the source of enhancement. By calculating the enhancement of the dimer as a function of angle θ, they showed that the enhancement probability distribution (b) has a power law dependence. This is effectively the intensity histogram when there is an average of one analyte molecule per dimer. For very large number of analyte per dimer, the intensity histogram becomes a normal distribution. But due to the large contribution from the most highly enhanced particles, the intensity distribution has a long tail deviation from a normal distribution even for an average of 1000 analytes per dimer (c). In our three samples, we find that the tail can be fitted by line of different slope in log-log plot.



Conclusion

We obtained intensity distribution representative of SERS enhancement for Ag nanoparticle LB film made with three different compression surface tension. The intensity histogram distribution can be interpreted using a model based on nanoparticle dimer. Although the three samples show similar average enhancement, the large intensity end of the distribution has a power law dependence consistent with the model, and showed a trend variation in relation to the sample compression surface tension.

Acknowledgement

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Reference

[1] E. C. Le Ru, et al. “Enhancement factor distribution around a single surface-enhanced Raman scattering hot spot and its relation to single molecule detection,“ J. Chem Phys., **125**, 204701 (2006).