Supplementary Information (SI) for Nanoscale Advances.

Title: Development of two-photon polymerized (2PP) periodic nanostructures for label-free SERS biosensing

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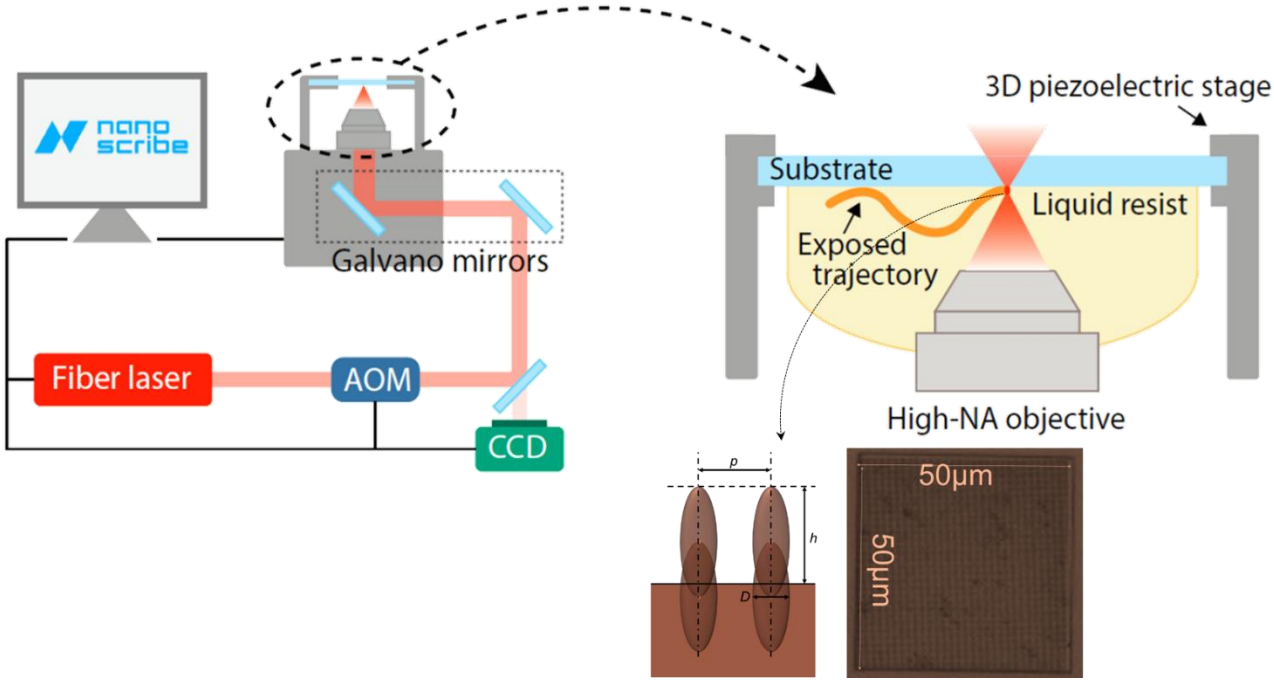

Fig. 1 Schematic demonstration of the 2PP fabrication process.

Designed Pitch	300		400		600	
Designed Height (H)	100	300	400	600	400	600
Measured Pitch in X	300±20	315±2	340±10	320±5	590±40	
Measured Pitch in Y	300±20	315±2	400±150	450±175	585±5	
Measured Height in X	75±30	65±15	150±20	160±20	610±5	Collapsed
Measured Height in Y	115±20	125±10	350±150	530±200	675±5	
Measured Diameter in X	250±15	235±5	350±5	335±15	420±20	
Measured Diameter in Y	235±5	235±5	330±20	335±15	355±5	

Table 1. Measured characteristics for single-voxel-based structures. X and Y represent horizontal and vertical cross-sections of 3D AFM measurements. All values are in *nm* units.

Designed Diameter	250			300			400		
Designed Pitch	300	350	380	300	350	380	300	350	380
Measured parameters for P=12 mW laser power									
Height	Not polymerized pillars						30±10	63±4	70±10
Diameter							210±5	210±5	280±10
Pitch							320±20	400±50	430±20
Measured parameters for P=14.25 mW laser power									
Height	55±5	55±2	60±5	175±15	225±10	190±10	320±10	390±5	390±10
Diameter	210±10	220±10	210±10	220±10	220±10	220±10	255±5	265±5	280±5
Pitch	285±25	340±5	380 ± 10	320±10	350± 10	360±15	390±15	425±10	485±15
							320±10	390±5	390±10
Measured parameters for P=15 mW laser power									
Height	165±15	215±15	190±10	**345±20**	**325±20**	**390±10**	300±100	465±5	485±10
Diameter	185±15	230±5	230±5	**260±5**	**250±10**	**265±10**	305±10	250±10	335±10
Pitch	260±10	330±30	390±15	**330±30**	**375±5**	**390±2**	375±5	430±20	455±15
							300±100	465±5	485±10
Measured parameters for P=16.5 mW laser power									
Height	220±80	250±100	350±10	270±100	450±50	445±5	400±150	450±150	550±100
Diameter	250±10	260±10	260±10	270±10	310±10	315±5	330±10	360±10	360±10
Pitch	270±50	310±30	350±30	350±150	385± 5	390±20	400±130	420±30	450±10

Table 2. Characteristics for nanostructures fabricated in the multilayer voxel mode. The most inhomogeneous substrates are underlined. In bold are the parameters used for the final fabrication. All values are in nm units.

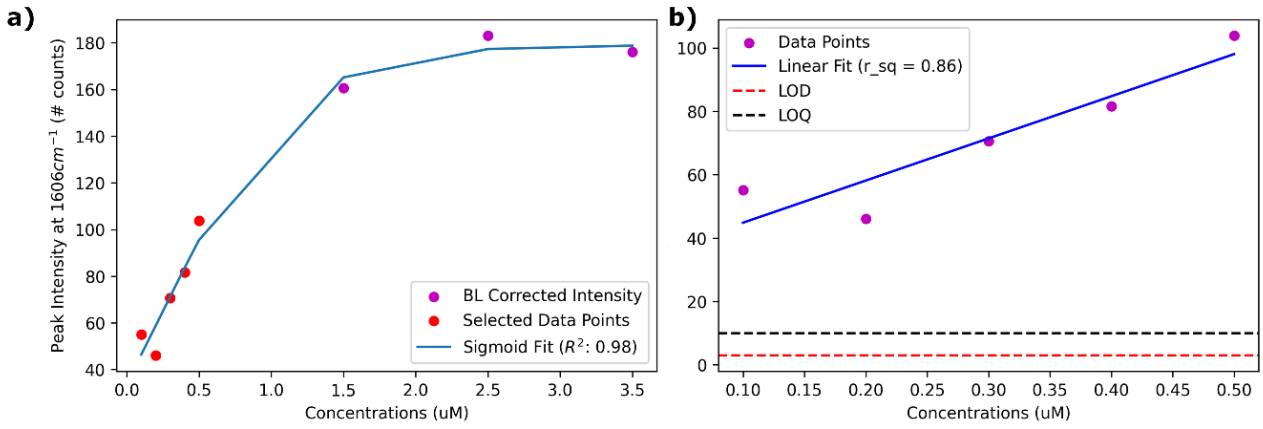

Fig. 2. The 1606 cm^{-1} peak intensity versus BPE concentration i.e. calibration plot for a Collapsed Single-Voxel (a). The "selected data points" refer to the points selected for the calculation of the limit of detection (b).

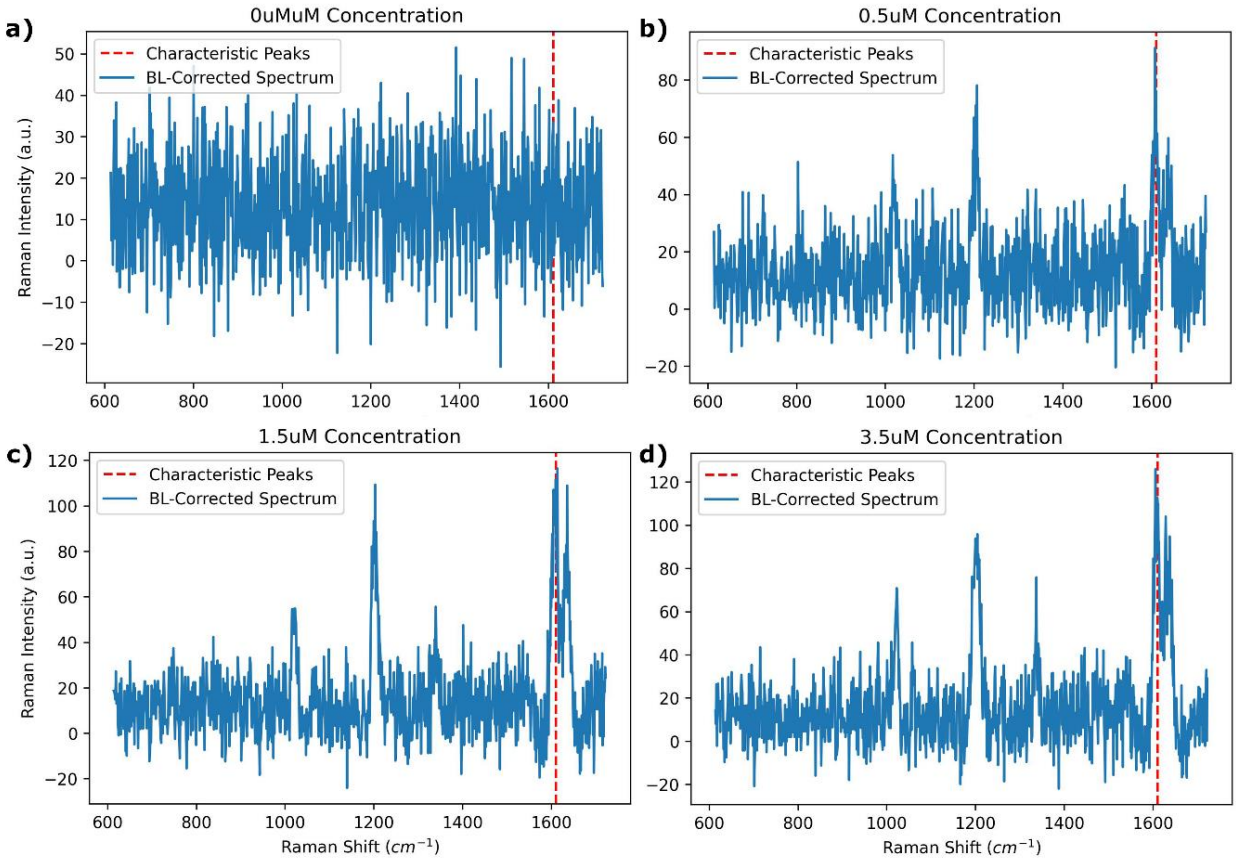

Fig. 3. The evolution of the BPE spectrum with increasing BPE concentration for a Collapsed Single-Voxel. The concentrations are 0 i.e. no analyte (a), 0.5 µM (b), 1.5 µM (c), and 3.5 µM (d).