

Supplementary Information

Direct laser writing of random Au nanoparticles three-dimensional structures for highly reproducible micro-SERS measurements

1. SERS background of the Au woodpile structures

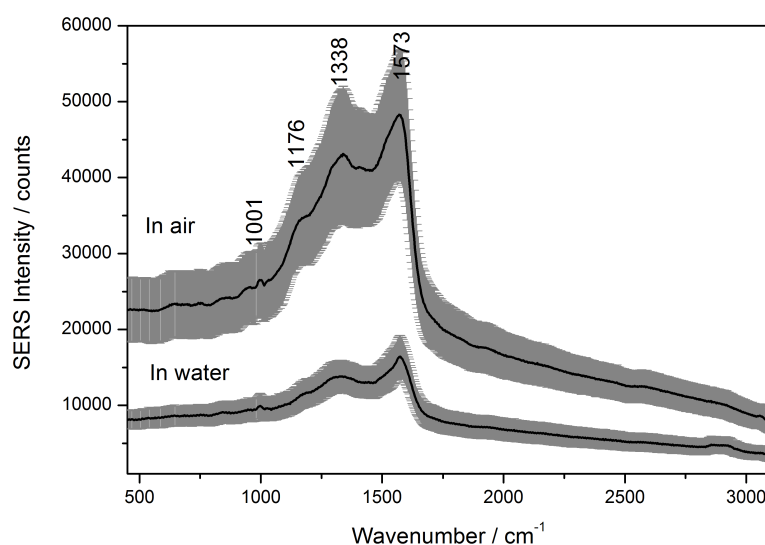


Figure S1. Averaged SERS spectra of as-prepared Au woodpiles of 3mm thickness, $\lambda_{\text{exc}} = 632.8$ nm.

The spectrum of the as-prepared substrates is dominated by the bands of amorphous carbon, peaking at 1573 and 1338 cm^{-1} . It is possible that the laser employed for the photoreduction has degraded part of the photoproducts, which remain on the surface. These byproducts are most probably from the oxidation of TPO, which is present in the reaction medium in a concentration of 44 mM. This hypothesis is coherent with the position of the weaker band at 1001 cm^{-1} , which could be a ring breathing vibration of non-degraded photoproduct. The weak shoulder at 1176 cm^{-1} may be assigned to the C-C stretching vibration of some aliphatic residues of isopropanol. Remnants of CTAB are less likely to be noticed as background, as this molecule has a weak Raman cross-section and is present in the reaction medium at a very low concentration (0.02 mM).

This spectral background is quenched to a great extent in the presence of water and even further when a new molecule is adsorbed on the Au surface. Its profile is constant and it can be subtracted from the raw data without introducing artifacts to the spectra.

2. Calculation of the limit of detection of BPE by SERS.

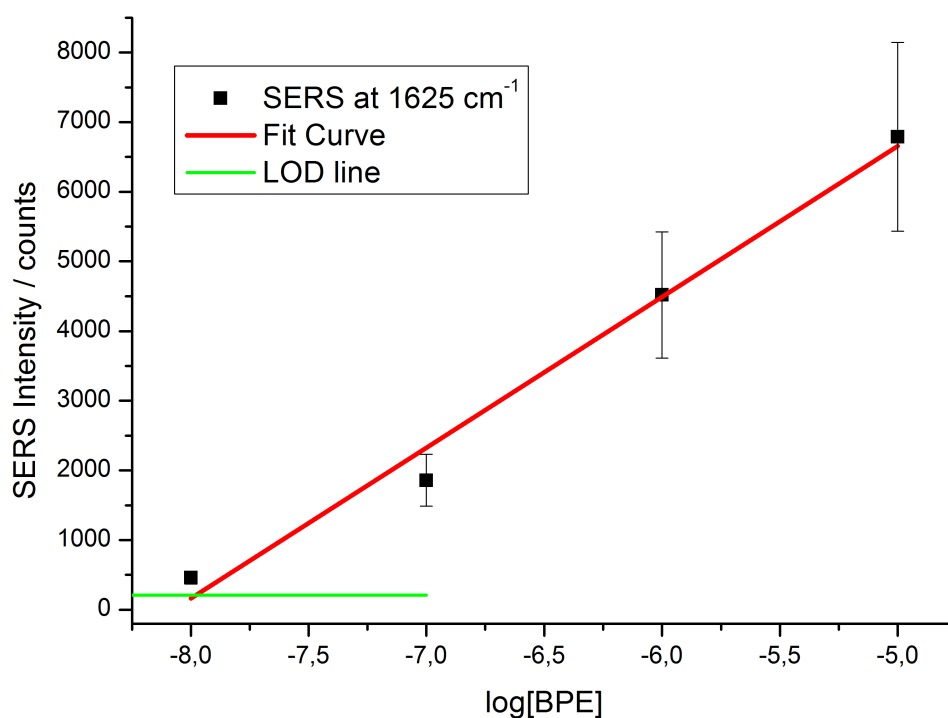


Figure S2. Variation of SERS intensity of BPE with its concentration and linear fit.

The linear fit equation reads as follows:

$$I_{\text{SERS}} = (1.74 \pm 0.3) \cdot 10^4 - (2.2 \pm 0.4) \cdot 10^3 \cdot \log[\text{BPE}]$$

The limit of detection value (LOD) of 10^{-8} M is calculated as the BPE concentration resulting from this equation giving $I_{\text{LOD}} = 3\sigma_{\text{B}}$, where $\sigma_{\text{B}}=69.97$ is the standard deviation of the SERS signal measured in a blank sample (water drop).

3. Study of the Raman spectrum of BPE in solution

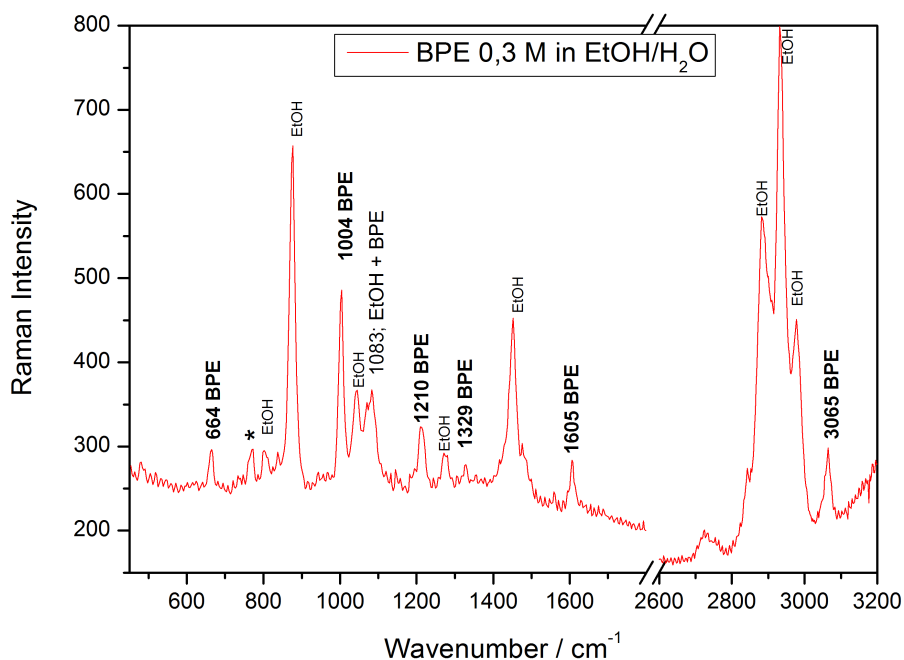


Figure S3. Conventional Raman spectrum of BPE 0.298 M dissolved in an ethanol/water 1:2 mixture. $\lambda_{\text{exc}} = 633 \text{ nm}$, acquisition time = 0.5 s, 40 accumulations. The band marked with an asterisk (*) comes from the plastic of the eppendorf tube in which it was contained.

Table S1. Frequency values and assignment of the main bands of BPE in the solid state¹, aqueous/ethanol solution and SERS on Au3D substrates.

Solid ¹	Solution	SERS Au	SERS Ag ¹	Assignment
670	664	661	655	Ring breathing
995	1004	1010	1012	Ring breathing
1108	1083	--	1073	$\nu(\text{C-C})_p$, $\delta(\text{C-C})$, $\delta(\text{C-H})_p$
1198	1210	1197	1201	$\nu(\text{Ring-C}_v)$, $\delta(\text{CH})_p$
1309	1329	1332	1329	$\delta(\text{CH})$, $\delta(\text{C=C})_v$
1595	1605	1605	1608	$\nu(\text{C-C})_p$
1635	--	1632	1641	$\nu(\text{C=C})_v$

p = pyridyl, v = vinyl

The bands which are visible in common Raman spectrum of the solution correspond mainly to the aromatic moiety. Frequency changes found in SERS are also found in the solution spectrum. Thus, the change in the chemical environment appears to have a similar effect whether if it is due to

¹ According to ref. 1, excitation at 633 nm.

chemisorption on the metal surface or formation of hydrogen bonds in a protic solvent. Also, the weaker shifts on the Au surface suggest a weaker interaction with this metal in comparison to Ag.

4. 3D fabrication control: Thickness on woodpile structures

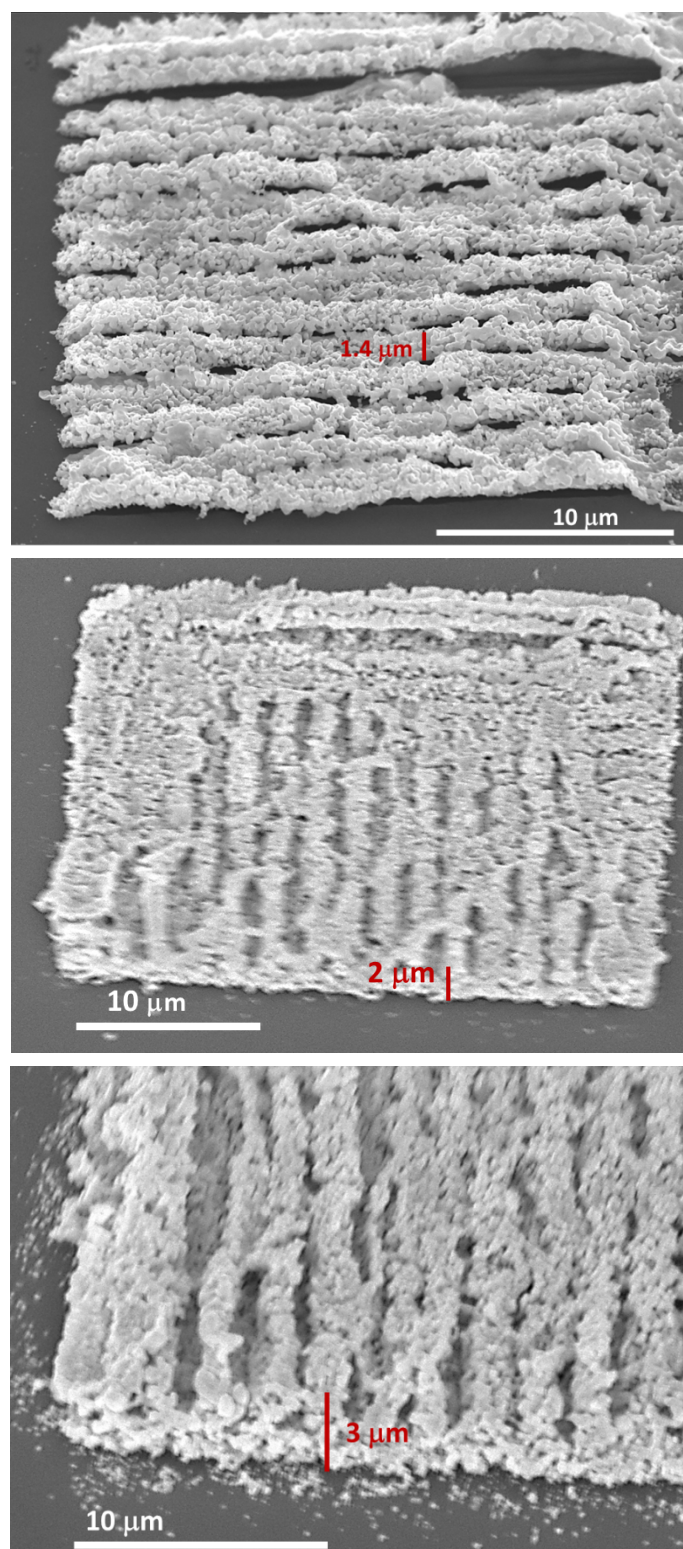


Figure S4. SEM images of woodpile structures of increasing thicknesses.

The average thicknesses of the woodpile structures as determined by SEM were: $1.4 \pm 0.1 \mu\text{m}$; $2.3 \pm 0.3 \mu\text{m}$ and $3.1 \pm 0.4 \mu\text{m}$.