

***Supplemental Information:***

**Plasmonic Based Raman sensor for Ultra-sensitive detection of  
Pharmaceutical waste**

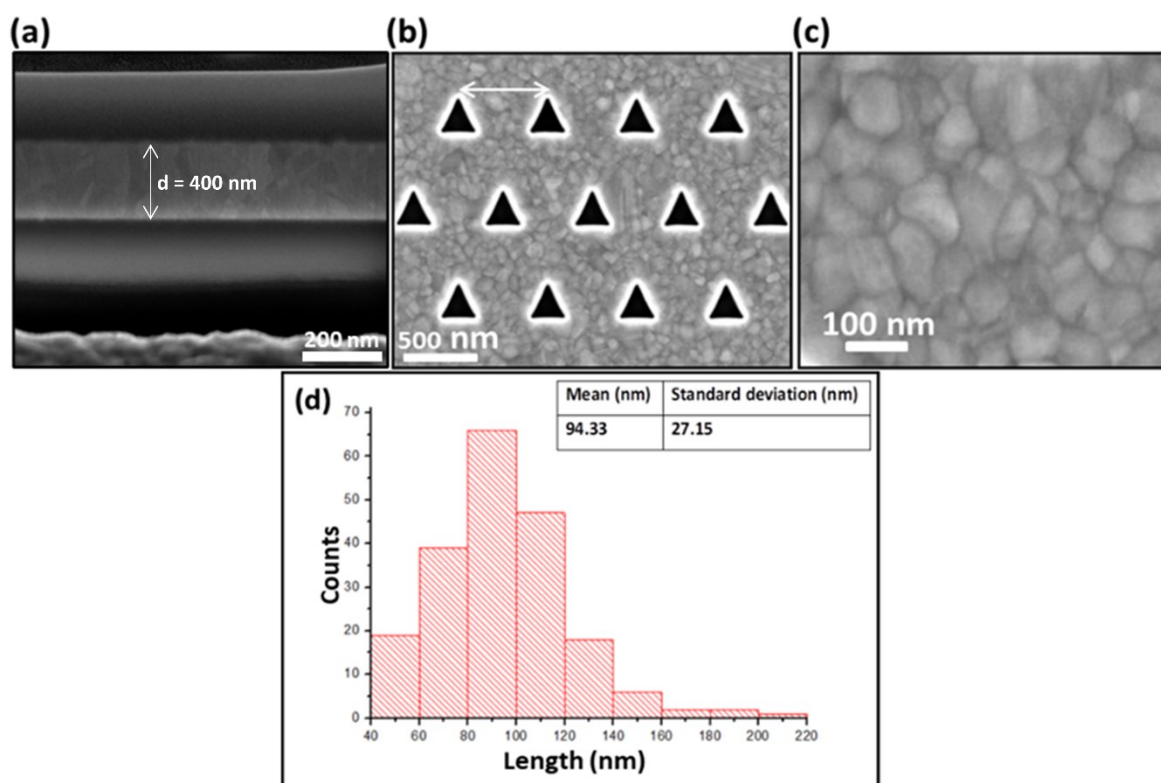
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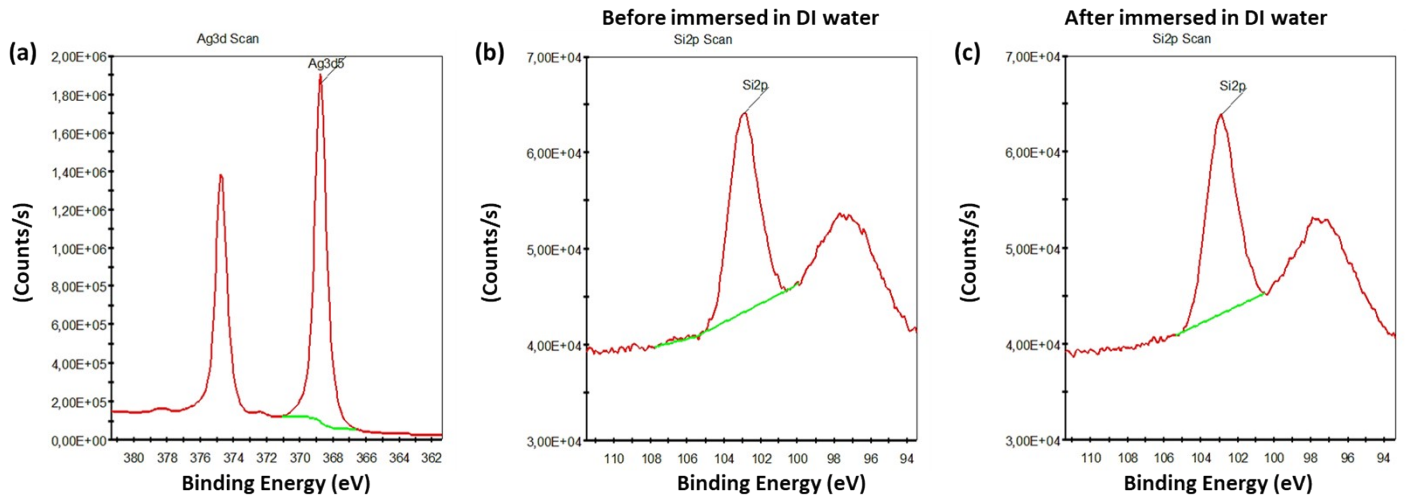
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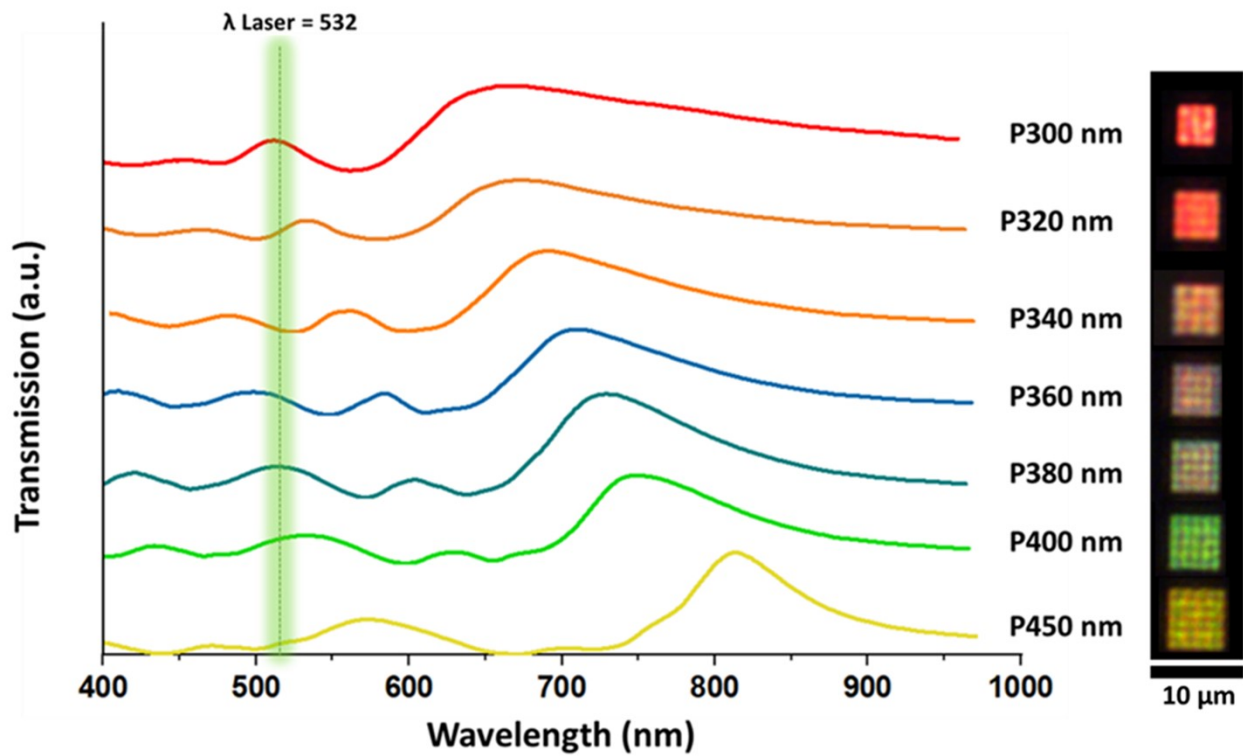
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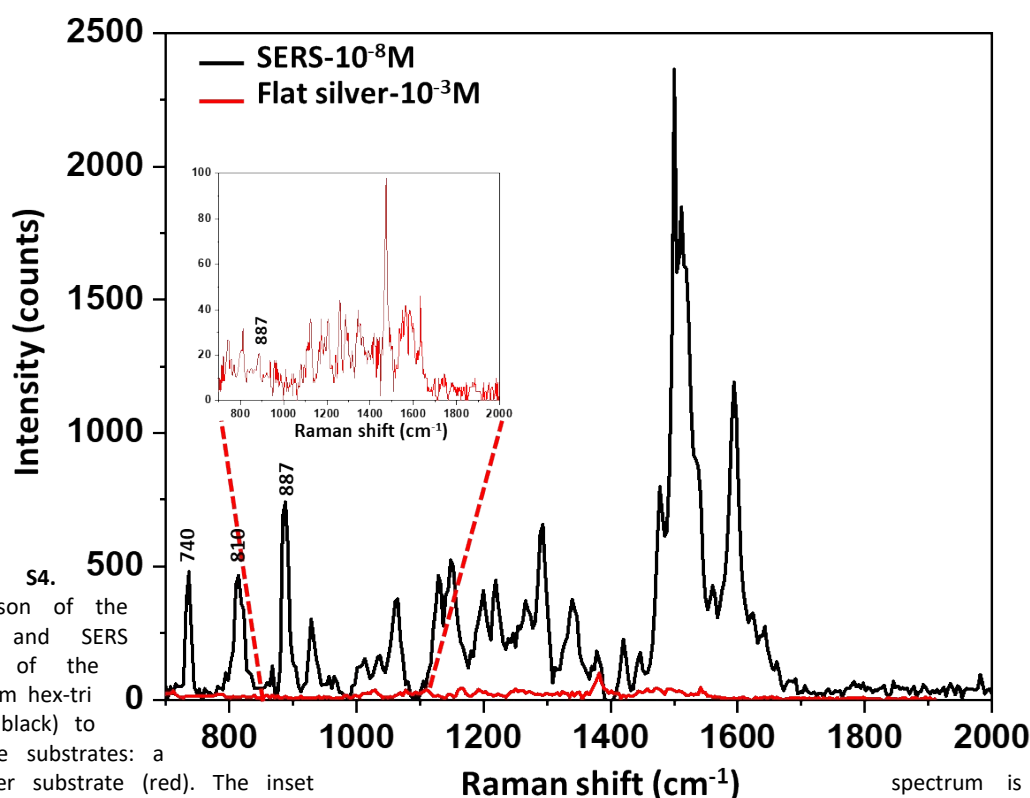
**Figure S1.** (a) HRSEM image of cross-sectional view ( $52^\circ$ ) with FIB. 200 nm thickness of Ag film on glass substrate. (b) HRSEM images: hexagonal hole-array of triangular nano-cavities with  $P=600 \text{ nm}$ . (c) a surface view ( $0^\circ$ ) typical Ag film, average grain size 94 nm (d) Histogram.



**Figure S2.** X-ray photoelectron spectroscopy (XPS) energy bands, Ag-Silica, ~5 nm layer of Silica. (a) Ag3d Scan. (b) Si2p Scan before immersed in DI water. (c) Si2p Scan After immersed in DI water.



**Figure S3.** Transmission spectra- hexagonal arrays of triangular holes of Ag200nm in different periodicity, X40 magnification, 0.6 NA, black-body illumination. Transmission images of this arrays Shown from the right side of the Figure, taken at X50 magnification with 0.7 NA, black-body illumination.



**Figure S4.** Comparison of the Raman and SERS spectra of the p=400 nm hex-tri sensor (black) to reference substrates: a flat silver substrate (red). The inset spectrum is zoom in of the red.

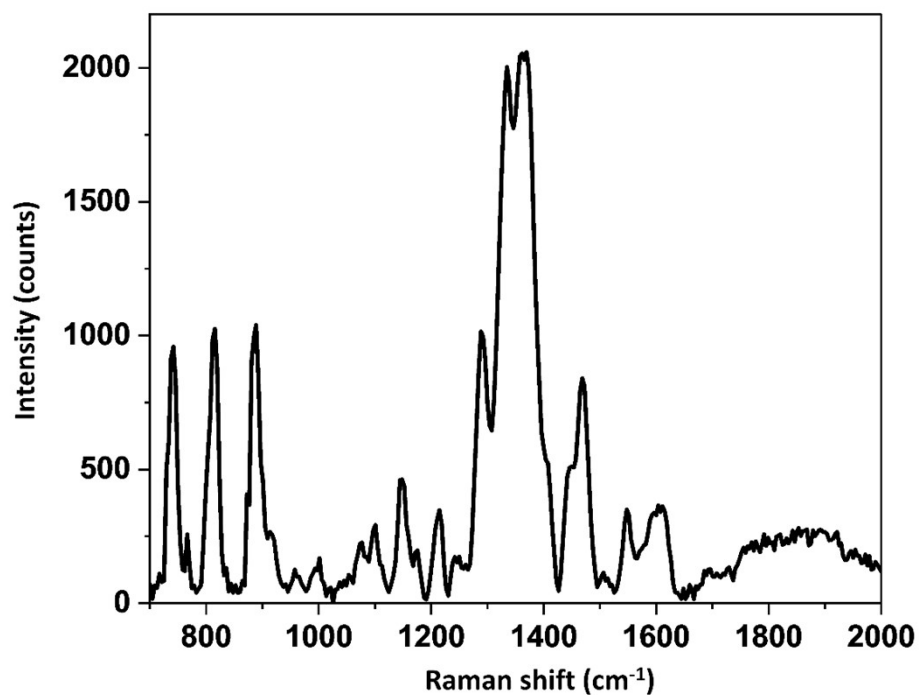
#### Calculations of enhancement factor (EF)

The enhancement factor (EF) of the SERS devices  $EF = 4 \times 10^6$  with respect to a silver substrate reference. Our calculations are based on the following equation:

$$EF = \frac{I(SERS) * C(Raman)}{I(Raman) * C(SERS)}$$

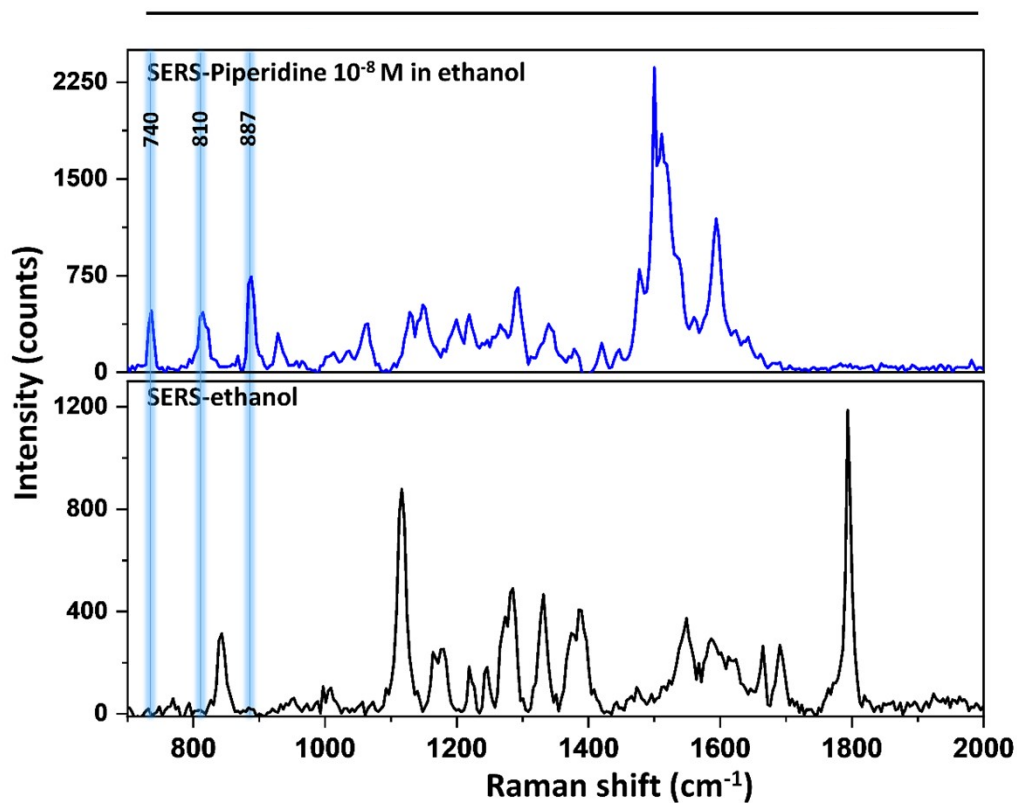
where  $I(SERS)$  and  $I(Raman)$  are the intensities of the SERS and reference signals, respectively, and  $C(SERS)$  and  $C(Raman)$  are the concentrations of the analyte in the SERS and reference measurements, respectively.

$$EF = \frac{I(SERS) * C(Raman)}{I(Raman) * C(SERS)} = \frac{800 * 10^{-3}M}{20 * 10^{-8}M} = 4 * 10^6$$

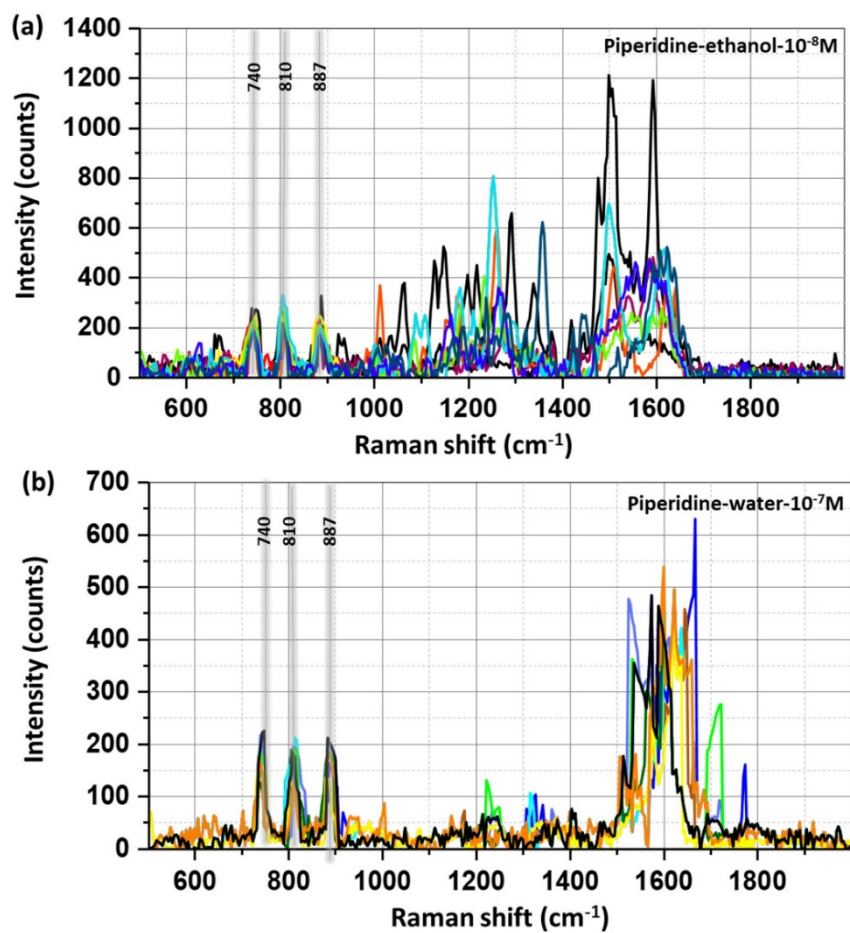


**FigureS5.** Raman spectra taken from our plasmonic devices (hexagonal triangular array with P400 nm) after being immersed in solution of piperidine in ethanol with concentration of 10<sup>-3</sup>M using N.A. of 0.6.

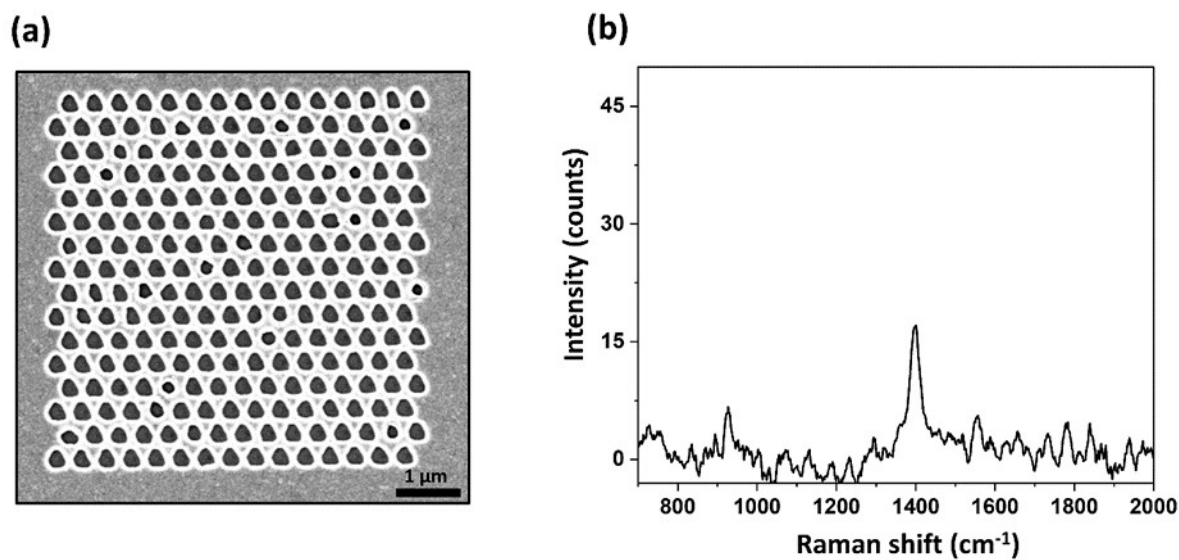
**Table S1.** Vibrational modes of the piperidine molecule.



**Figure S6.** Comparison between Raman spectra of the SERS device (p400 nm), once with immersion in ethanol(black), and once with immersion in piperidine dissolved in ethanol  $10^{-8}$ M (blue), which at the end are dried in nitrogen. The laser parameters:  $\lambda=532$  nm X50 magnification, N.A.=0.6, Power=0.55mW, acquisition tim



**Figure S7.** Repeatability of the SERS device (a) SERS spectra of  $10^{-8}$ M Piperidine dissolved in ethanol. (b) SERS spectra of  $10^{-7}$ M Piperidine dissolved in DI water. All the spectra taken from multiple selected spots on our device.



**Figure S8.** Non-well milled arrays of hexagonal hole of triangular nano-cavities with  $P=400$  nm. (a) HRSEM images of the arrays. (b) SERS measurements of Ag/SiO<sub>2</sub>/piperidine concentration  $10^{-7}$ M in ethanol.