Supporting Information

Silver nanostars with high SERS performance

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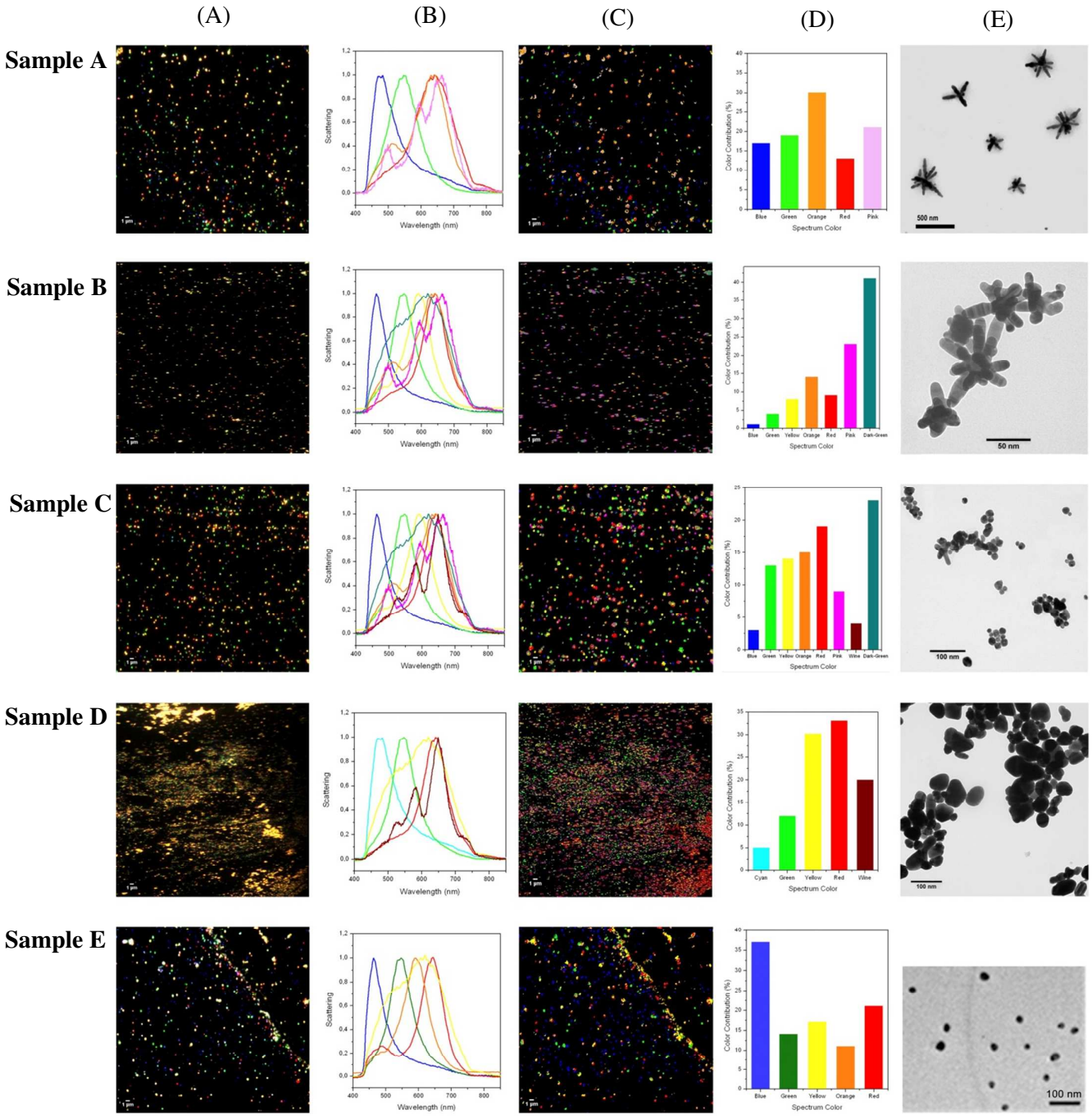

Figura S1

Dark field images obtained in 35µm x 35µm areas for all the prepared samples (A), most frequent scattering emission spectra measured on the analysis of the Dark field images (B), Maps of Dark-Field images obtained by mapping the most frequent scattering spectra on the analyzed area (C), distribution of the metal NPs giving rise to the most frequent scattering spectra (D) and TEM images (E) of different samples used in this work.

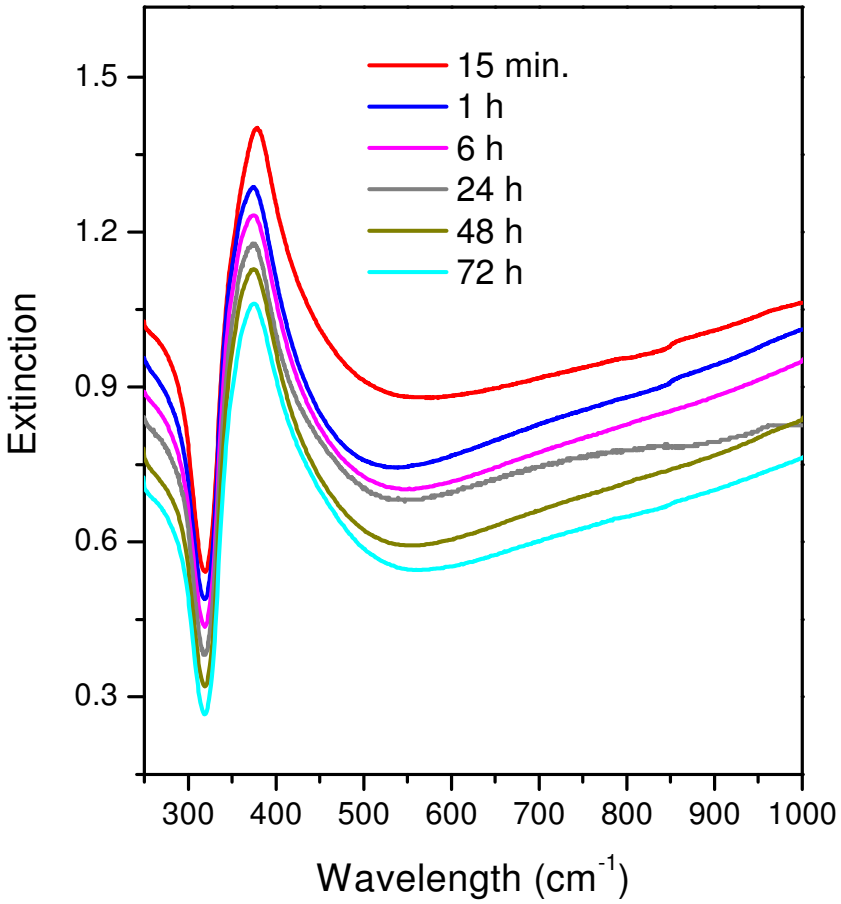

Figura S2

Variation in time of the extinction spectrum of sample A.

Experiment for the detection of Probenecid drug using AgNS of sample A

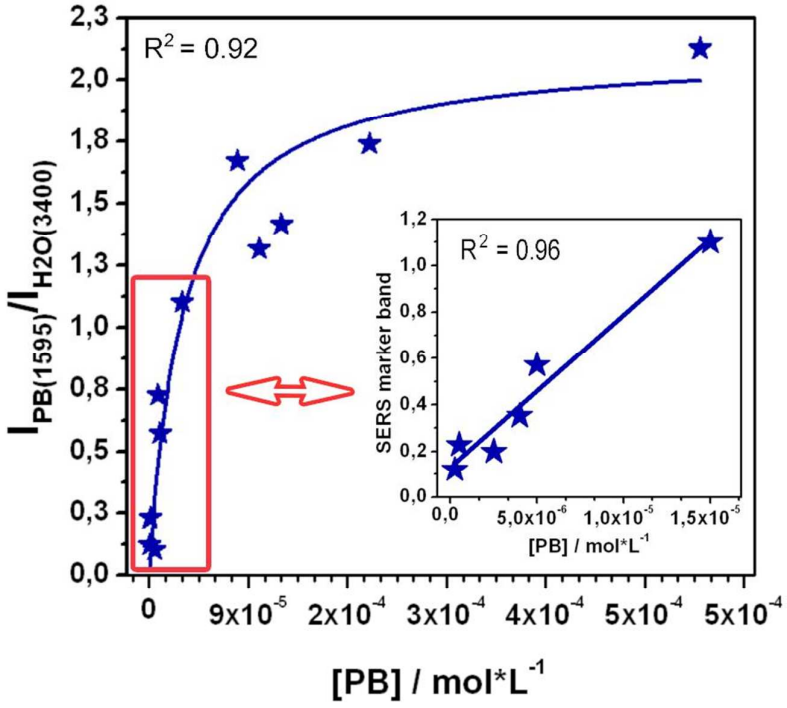

Figure S3. Adsorption isotherms obtained from the variation of the relative SERS intensity of PB band at 1595 cm^{-1} on AgNS at different drug concentrations. Excitation at 532 nm.

The isotherm adsorption of Figure S3 follows a simple adsorption-saturation Langmuir curve, thus indicating that there is no significant intermolecular interaction between PB molecules on the surface. The general expression of a Langmuir adsorption can be expressed by the following equation:

$$\phi / \phi_{\infty} = \frac{K_{ad}[PB]}{1 + K_{ad}[PB]} \qquad (1)$$

Where K_{ad} is the adsorption constant of Probenecid (PB) on the AgNS surface, ϕ is the amount of adsorbed molecules at a concentration [PB] and ϕ_{∞} is the maximum number

of molecules which can be adsorbed on the surface. Since the SERS intensity exclusively depends on the number of molecules adsorbed on a plasmonic surface, the ϕ/ϕ_∞ ratio can be approximated to the SERS intensity ratio I_s/I_{sm} (where I_s is the SERS intensity at concentration [*PB*] and I_{sm} is the SERS intensity in conditions of saturation, i.e. at maximum surface coverage. Therefore, to fit the SERS intensity versus the drug concentration in the sample, Equation (1) can be re-expressed into the following Langmuir-type expression:

$$I_S = \frac{K_{ad} I_{sm} [PB]}{1 + K_{ad} [PB]} \qquad (2)$$

The fitting of the adsorption isotherms to the Equation (2) leads to parameters shown in Table S1. At very low PB concentrations, i.e. when K_{ad} [PB]<<1, Equation (2) becomes linear: $I_S = K_{ad} I_{sm} [PB]$, and a calibration line can be then built (inset in Figure S3). The limit of detection (LOD) shown in the Table S1was calculated from the linear fitting as the concentration at which a signal-to-noise ratio of 3 can be measured.

Finally, the Enhanced Factor (E_F) was calculated from the following expression:

$$E_F = \frac{I_{SERS} [PB]_{ethanol}}{I_{ethanol} [PB]_{AgNS}} \qquad (3)$$

Where I_{SERS} is the SERS intensity of the PB 1595 cm^{-1} band, $[PB]_{ethanol}$ is the concentration of the drug in ethanol used as reference, $I_{ethanol}$ is the intensity of the PB band in ethanol and $[PB]_{AgNS}$ is the concentration of the drug in the SERS experiment. The E_F calculated when $[PB]_{ethanol} = 10^{-2}$ M, and $[PB]_{AgNS} = 5 \times 10^{-7}$ M, and at 532 nm was 1.72×10^5.

Table S1. Adsorption parameters deduced from the probenecid adsorption isotherms

Sample A	
Sensitivity (K_{ad}*I_{sm})	$(3.27\pm0.35)\times10^{4}$
LOD (ppb)	51.3
I_{sm}	1.93 ± 0.14
K_{ad} (mol^{-1}*L)	$(4.63\pm1.51)\times10^{4}$