Surface-enhanced Raman spectroscopy of propranolol on different SERS substrates - a step towards dual SERS-electrochemical sensors for pharmaceutical pollution monitoring

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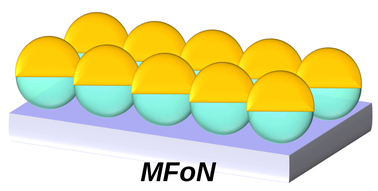
ABSTRACT

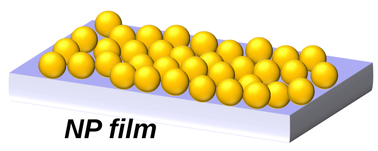
Abstract. Pollution of water by pharmaceuticals is a general environmental problem that requires routine monitoring of pollutants. Conventional methods used to quantify pharmaceuticals are relatively expensive and generally require long analysis time associated with the difficulties to perform field analyses. In this context we focus on developing a highly accessible analytical platform for fast, selective and ultrasensitive detection of these dangerous pollutants by combining SERS and electrochemistry. Here we present our recent efforts in obtaining and analyzing SERS spectra of β-blocker propranolol on different SERS substrates including self-assembled nanoparticle films and metal-coated microsphere arrays.

Experimental

Metal films over microspheres (MFoM): ordered arrays of SiO_2 microspheres (500 nm) are obtained on glass substrates by convective self-assembly (CSA); these are then coated by metal films (Au or Ag) deposited by sputtering [1,2].

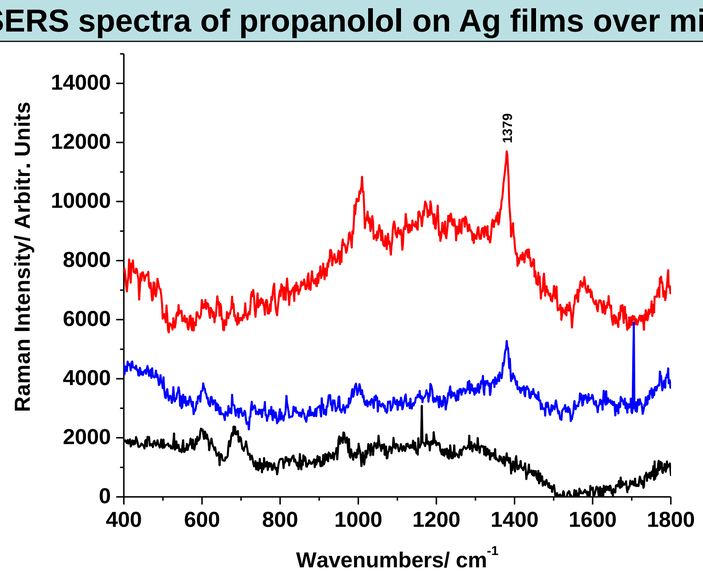
Colloidal nanoparticle films: colloidal Ag nanoparticles (NPs) are obtained by the Lee-Meisel chemical synthesis method; Au nanoparticles are prepared by the Turkevich-Frens method, adapted to yield ~50nm particles; then, these colloidal nanoparticles are deposited into films on solid support, by CSA [3].

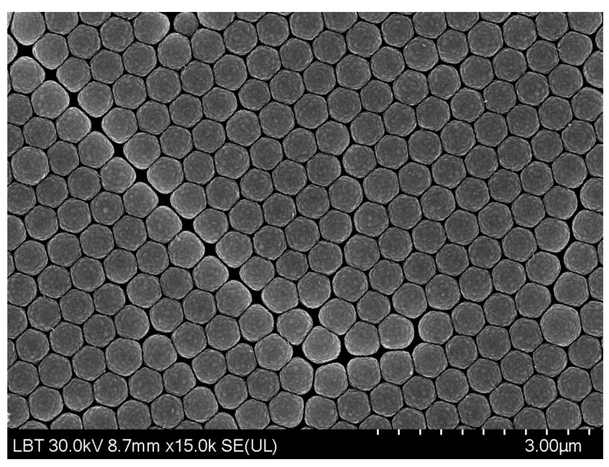




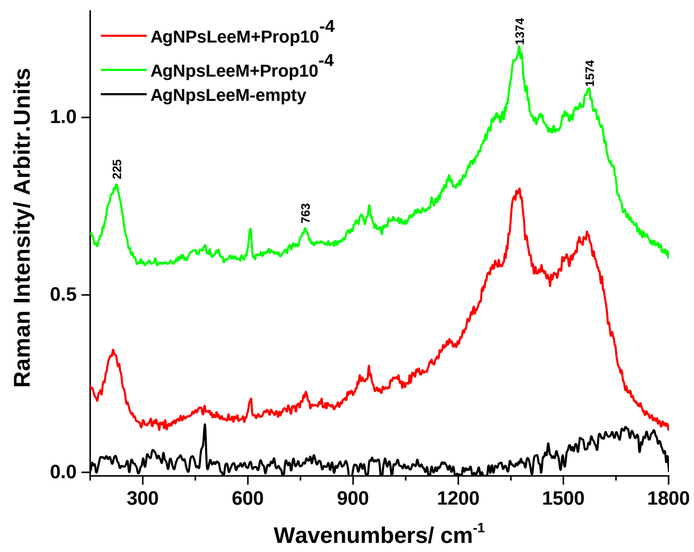
SERS analysis: 3µl drops of propranolol in alcohol solutions (10^{-4}M) are deposited on the samples and allowed to dry, prior to Raman measurements.

SERS spectra of propanolol on Ag films over microspheres

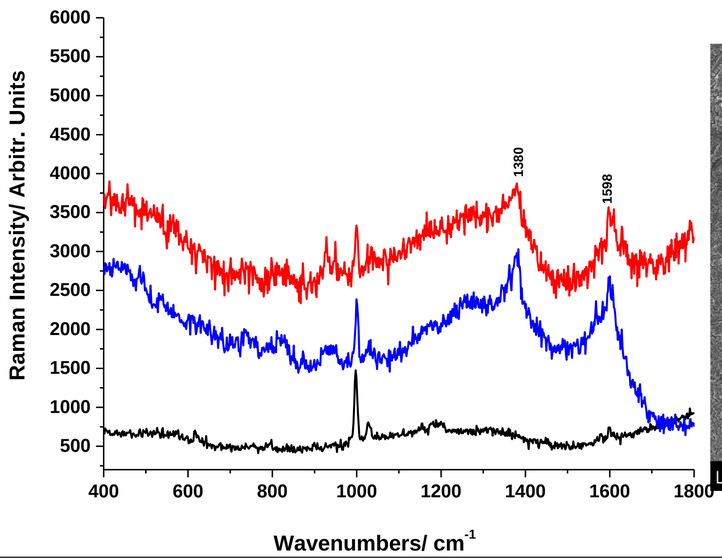


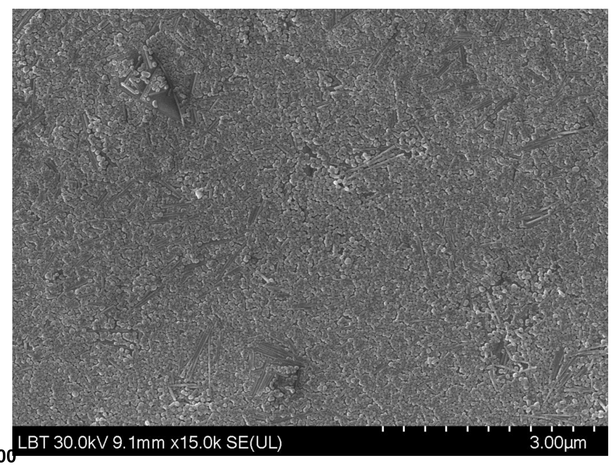


SERS spectra of propanolol on Ag NPs colloidal suspension

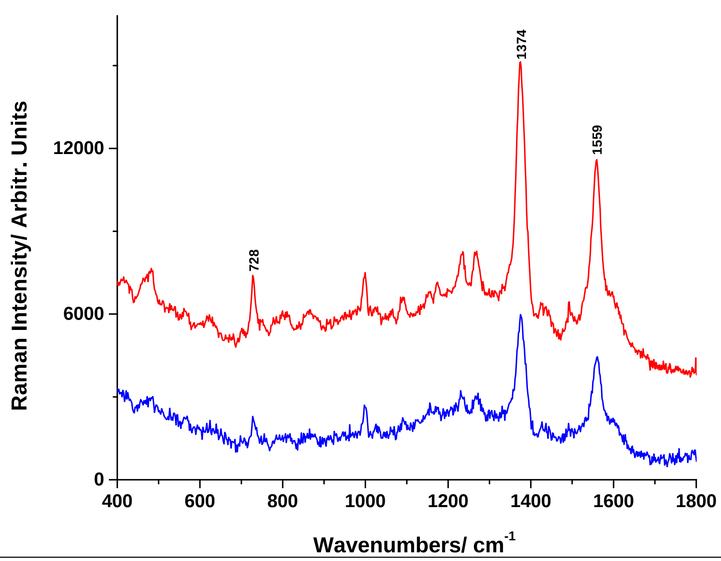


SERS spectra of propanolol on Ag NPs films

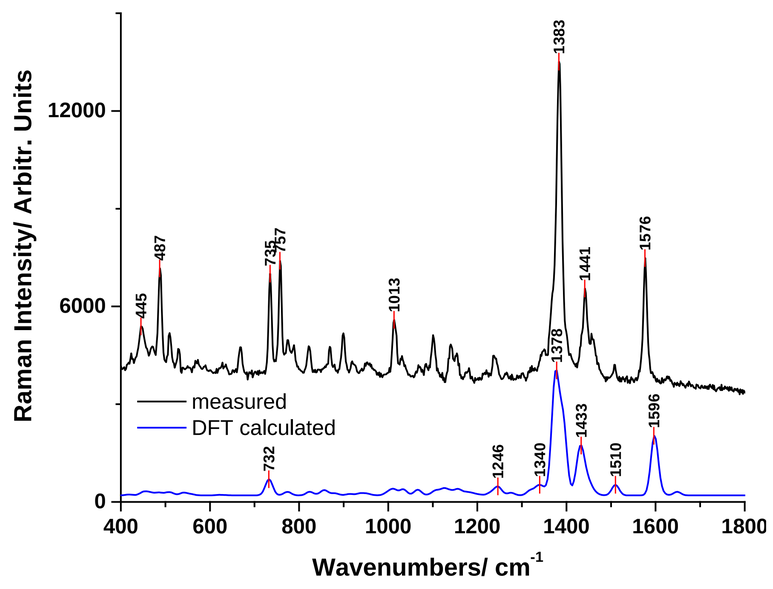




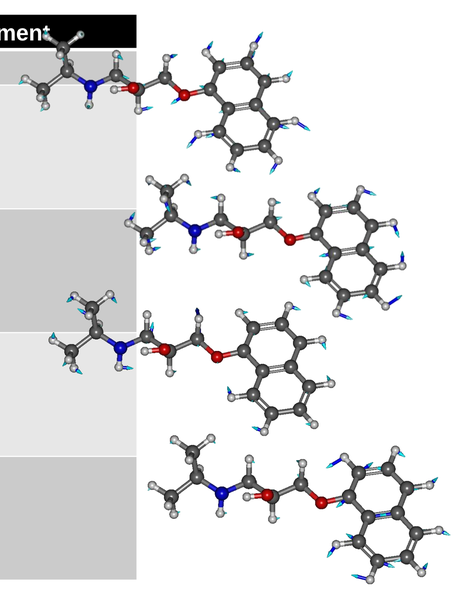
SERS spectra of propanolol on Au NPs films



DFT CALCULATIONS



Wavenumber (cm^{-1})		Vibrational assignment
Theoretical	**Experimental**	
732 (m)	735 (s)	Ring breathing, sym
1378 (vs) 1392 sh	1383 (vs)	Ring deformation, asym
1430 (s)	1441 (s)	CH_2 bend, C-N-H bend
1596 (s)	1576 (s)	Ring deformation, sym.



CONCLUSIONS

► Ag and Au colloidal nanoparticles were assembled into highdensity films;
► Ag films over microspheres SERS substrate were fabricated and characterized;
► SERS of propranolol on the different fabricated plasmonic platforms was explored;
► AuNP films seem to be the most promising among the tested SERS substrates;
► DFT calculations help in identifying and attributing the most prominent SERS bands.

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