Highly effective SERS nanopattern substrate. The enhancement is demonstrated using thiophenol as a molecular probe

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The number of different types of Surface-enhanced Raman Scattering (SERS) substrates available for experimentation is increasing at high speed. New alternatives are introduced and explored every year in the literature including both novel nano-particles in solution as well as self-assembled or engineered structures with different levels of control over their optical properties. In this work silver nanopattern obtained by the nano-sphere lithography approach was prepared and characterized by AFM. This method basically exploits the regular patterns formed by self-assembly of dielectric (polystyrene, PS) nano-spheres on a surface upon drying. The evaporation of a silver film on top of the array can be followed by the lift-off of the nano-spheres themselves in which case an array of interstitial sites is left on the surface [1-2] (Fig. 1). We have observed in the AFM images that the shape of the nanopatterns is regular but the surface is rough and they are homogeneously distributed with dimensions in the subwavelength range.

Figure 1. AFM images of PS nano-spheres (1x1µm)(a) and silver nanopatterns (0.6x0.6µm) (b).



SERS properties of this substrate were examined by using thiophenol (TP) as molecular probe through the preparation of self-assembled monolayer (SAM) by dipping the substrates for 1h in 0.1mM solution of TP in CH_2CI_2 at the temperature of 25°C. Samples were subsequently rinsed with solutions solvents and dried before scanning.

The surface interaction of this molecule has been studied by several groups and the most significant Raman change after the adsorption is the disappearance of the S-H stretching mode at about 2566 cm⁻¹ in the SERS spectrum and indicating that an Ag-S bond has been formed [3]. The reproducibility on different areas of this substrate has been analyzed by using this molecular probe concluding that a fairly homogeneous distribution of the SERS intensity is observed (Fig. 2) which is a prerequisite for applications as ultrasensitive sensing assemblies. **Figure 2.** Raman mapping of TP on silver nanopatterns and related Raman spectra.



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