Single-Molecule Surface Enhanced Raman Scattering on Periodically Nanostructured Gold Films

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Surface enhanced Raman scattering (SERS) is a spectroscopic technique of great interest in chemistry, biochemistry, and biophysics because vibrational spectra provide characteristic fingerprints of molecular structure and can be used to specifically identify molecules [1]. Several reports have demonstrated the single molecule sensitivity of this technique [2], which opens a new doorway for the analysis of molecular dynamics. In order to achieve such sensitivity noble metal nanostructured surfaces are employed, which can be very effective in localization and enhancement of electromagnetic fields, when illuminated with laser radiation. Up to date most of the single molecule observations were performed by using randomly nanostructured gold or silver surfaces, like dimmers or large clusters of nanoparticles.

Here we report single molecule surface enhanced Raman scattering observations on a gold film patterned with periodic features. The employed SERS substrate consists of a gold film (100 nm thickness) evaporated on top of a regular array of polystyrene microspheres (450 nm diameter), which yields a two-dimensional array of metallic caps. The lateral dimensions of the metallic features exhibited by this type of substrate allow making correlation between topography and local SERS activity. We show by combining atomic force microscopy (AFM) and confocal Raman microscopy, that crevices between adjacent caps, which offer nanometric vicinity of metallic features, are the sites of super-enhanced Raman scattering. In figure 1 we show a typical SERS spectrum and a waterfall plot of SERS spectra recorded as a temporal series, which exhibit hallmarks of single molecule behavior, like fluctuations of the Raman intensity and Raman shift.

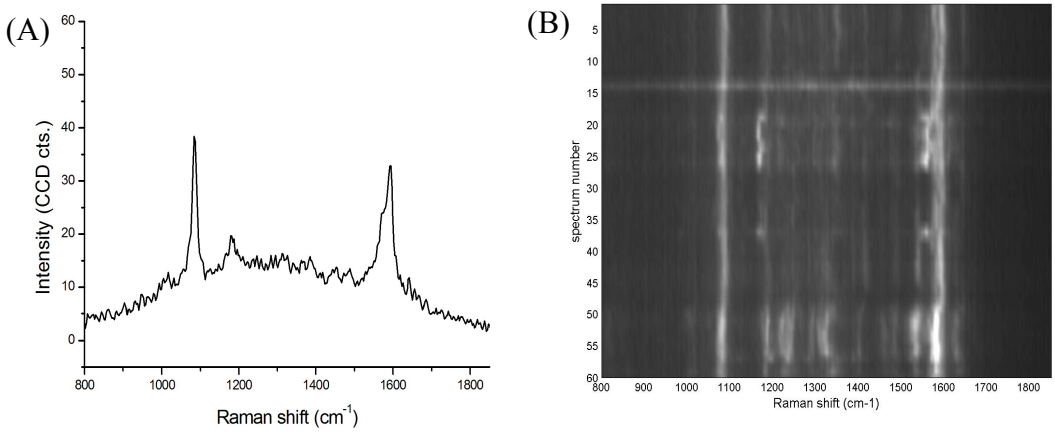

Fig.1: (A) Typical SERS spectrum and (B) Waterfall plot of SERS spectra (0.4 s integration time/spectrum) of p-atp molecules adsorbed on the gold substrate.

[1] T. V. Dinh, TrAC-Trends Anal. Chem. 17 (1998) 557-582.
[2] S. Nie, S. R. Emory, Science 275 (1997) 1102-1106.

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