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Surface Enhanced Raman Spectroscopy of Organic Molecules Adsorbed on Silvered Porous Silicon Covered with Graphene

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We registered surface enhanced Raman scattering (SERS) spectra of human lactoferrin molecules adsorbed on a silvered porous silicon from 10^{-6}–10^{-18} M solutions. It was found that porous silicon template causes negative surface potential of silver particles and their chemical resistivity to oxidation. These properties allowed to attract positively charged lactoferrin molecules and prevent their interaction with metallic particles upon 473 nm laser excitation. The SERS spectra of lactoferrin adsorbed from 10^{-6} M solution were rather weak but decrease of the concentration down to 10^{-10} M led to enormous growth of the SERS signal. This effect took a place as tetramers of lactoferrin breaks down to monomeric units while its concentration is reduced. Tetramers are too large for uniform distribution of electromagnetic field from silver particles to provide an intensive SERS signal from the top part of the molecules in contrast to monomers that can be completely excited. The SERS-spectra at the 10^{-14} and 10^{-16} M concentrations were less intensive and started to change due to heating to the temperature of lactoferrin denaturation. To prevent overheating the analyte molecules on the silvered *por*-Si were protected with graphene, which allowed detecting lactoferrin adsorbed from the 10^{-18} M solution.