Plasmonic response and SERS modulation in electrochemical applied potentials

We study the optical response of individual nm-wide plasmonic nanocavities using a nanoparticle-on-mirror design utilised as an electrode in an electrochemical cell. In this geometry Au nanoparticles are separated from a bulk Au film by an ultrathin molecular spacer, giving intense and stable Raman amplification of 100 molecules. Modulation of the plasmonic spectra and the SERS response is observed with applied voltage under a variety of electrolytes. Different scenarios are discussed to untangle the various mechanisms that can be involved in the electronic interaction between NPs and electrode surfaces.

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