Nanoscale Chemical Imaging with UHV and EC-TERS

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Abstract

I will focus in on two recent projects in ultrahigh vacuum (UHV) and electrochemical (EC) TERS which illustrate the power of this emerging technique. First, new insights into the nature of a dynamic phase boundary involved in the room temperature (RT), UHV-TERS of the Ag tip/ N,N'-bis(2,6-diisopropylphenyl)-1,7-(4'-t-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (PPDI)/Ag(100) system will be described.[1] We have unraveled the orientation of PPDI molecules at the dynamic molecular domain boundary with ~4 nm spatial resolution by UHV-TERS mapping. TERS provides access to molecular adsorption geometries when STM provides no topographical information. Next, Angstrom-scale spatial resolution in TERS has been achieved.[2] At room temperature, the strong adsorbate-substrate interaction between the meso-tetrakis(3,5-di-tertiarybutylphenyl)-porphyrin (H₂TBPP) and the underlying Cu(111) substrate leads to the formation of the bowl up/down conformations. Through simultaneous UHV-TERS and STM analysis on the neighboring conformational isomers, we have observed ~15 cm⁻¹ spectral shift in one of the porphyrin-ring Raman modes and analyzed the origin of this shift using DFT calculations. Finally, I will discuss EC-TERS highlighting single molecule electrochemistry and the imaging of electrochemical reactions on the nanometer length scale.[3,4]

References: