

INVITED

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:

- [1] N. Jiang, N. Chiang, L. R. Madison, E. A. Pozzi, M. R. Wasielewski, T. Seideman, M. A. Ratner, M. C. Hersam, G. C. Schatz, and R. P. Van Duyne, "Nanoscale Chemical Imaging of a Dynamic Molecular Phase Boundary with Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy," *Nano Letters*, **16**, 3898-3904 (2016).
- [2] N. Chiang, D. Chulhai, G. Goubert, X. Chen, E. Pozzi, N. Jiang, M. Hersam, T. Seideman, L. Jensen, and R. P. Van Duyne, "Conformational Contrast of Surface-Mediated Molecular Switches Yields Angstrom-Scale Spatial Resolution in Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy," *Nano Letters*, **16**, 7774-7778 (2016).
- [3] D. Kurouski, M. Mattei, and R. P. Van Duyne, "Probing Redox Reactions at the Nanoscale with Electrochemical Tip-Enhanced Raman Spectroscopy," *Nano Letters*, **15**, 7956-7962 (2015).
- [4] M. Mattei, G. Kang, G. Goubert, D. Chulhai, L. Jensen, G. C. Schatz, and R. P. Van Duyne, "Tip-Enhanced Raman Voltammetry: Coverage Dependence and Quantitative Modeling," *Nano Letters*, **17**, 590-596 (2017).