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INVITED

Electrochemical TERS Elucidates Potential-Induced Molecular Reorientation and Chemical Conversion

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TERS provides chemical and topographic information of surfaces with high spatial resolution and submonolayer chemical sensitivity. To further the versatility of the TERS approach toward more complex systems such as biological membranes or energy conversion devices, adaptation of the technique to solid/liquid working conditions is essential. In my talk, I discuss our novel side-illumination EC-TERS setup design based on a commercial STM as a versatile, cost-efficient solution for TERS at (electrochemical) solid/liquid interfaces.[1,2] While the STM parameters are found to play a crucial role for solid/liquid TERS sensitivity,[3] the excitation beam aberrations due to the presence of the aqueous phase are small enough not to limit TER signal detection, leading to Raman enhancement factors in the order of 105 at μW laser power in the low-bias regime.

To demonstrate the versatility of our approach, we have studied the adsorption geometry and chemical reactivity of adenine/Au(111) as a function of the applied electrode potential.[4] Combining experimental EC-TERS and DFT simulation data, we conclude that protonated physisorbed adenine adopts a tilted orientation at low potentials, whereas it is vertically adsorbed around the potential of zero charge. Further potential increase induces adenine deprotonation and reorientation to a planar configuration. To conclude, by providing the unique possibility to access potential-controlled adsorbate (re)orientation and chemistry on the few-molecule level, EC-TERS holds unprecedented power to gather detailed insight into, for example, electrocatalytic conversion mechanisms or biophysical processes with extreme spatial and chemical resolution.

[1] N. Martín Sabanés, L. Driessen, K.F. Domke* Analytical Chemistry 2016, 88, 7108-7114.

[2] N. Martín Sabanés, K.F. Domke* ChemElectroChem 2017, DOI: 10.1 002/celc.201700293

[3] N. Martín Sabanés,* A. Elizabeth, J.H.K. Pfisterer, K.F. Domke* Faraday Discussions "Surface-enhanced Raman scattering" 2017, DOI: 10.1039/C7FD

[4] N. Martín Sabanés, T. Ohto, D. Andrienko, Y. Nagata, K.F. Domke* Angewandte Chemie International Edition 2017 (VIP paper), DOI: 10.1002/anie.201704460