GDCh-Kolloquium am Institut für Chemie neuer Materialien der Universität Osnabrück

24. Oktober 2017 um 17.15 h, Raum 32 / 107

Elucidating molecular electrochemistry with nearfield Raman spectroscopy

Katrin Domke

Max Planck Institute for Polymer Research, Mainz

Abstract

One crucial parameter that determines surface reactivity or device functionality in a large variety of applications, such as heterogeneous catalysis, electrochemical energy conversion schemes, biotechnology or molecular electronics, is the adsorption geometry of the (re)active molecules. Accessing adsorbate orientation in relation to specific surface sites in situ or in operando is a first crucial step toward controlling interfacial geometries for improved device architecture. However, suitable in-situ techniques to study molecular orientation at well- defined adsorption sites are still scarce. In my talk, I will present a novel electrochemical nearfield Raman spectroscopy (EC-TERS) tool that enables to access the vibrational fingerprint of less than 100 small, non-resonant molecules adsorbed at a potential-controlled Au surface. From the spectral changes observed as a function of potential, the conformational and chemical changes of showcase DNA base adenine in terms of adsorption and reorientation following molecular (de)protonation can be deduced by combining experimental and theoretical simulation data.

Furthermore, we plan to unravel the nucleation and growth mechanism of electrochemical metal-organic framework (MOF) synthesis. For the showcase CuBTC MOF, we find that the electrosynthesis proceeds from metallic Cu through a necessary Cu(I) intermediate, cuprite, and nucleation occurs at the electrode as opposed to solvothermal in-solution growth. Our findings allow us to suggest a simple, yet efficient new route toward MOF surface patterning. In a next step, we want to apply EC-TERS to study the MOF nucleation process, i.e. the very first bond formation of a CuBTC unit cell in situ.

In summary, EC-TERS is a unique addition to nanoscale spectroscopy of electrified solid/liquid interfaces that holds great potential to access molecular-scale chemistry in situ, for example to unravel electrocatalytic conversion mechanisms or biophysical processes on the single-protein level.