Controlling the Charge State of Organic Molecules on Ultrathin Oxide Films

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Charge transfer processes through ultrathin, metal-supported oxide films have received increasing attention in recent years because of the possibility to control the charge state of adsorbates or the direction of catalytic reactions. In this regard, Ag(001)-supported MgO(001) thin films have attracted specific attention. Since the first prediction and observation of charged gold atoms on the surface of MgO(001) ultrathin films, several investigations have shown that dielectric thin films on metal substrates can promote charge transfer and are, thus, more than just a decoupling layer for adsorbates. In most cases described in the literature, for adsorption of atoms or molecules on ultrathin dielectrics but also on weakly interacting metal surfaces, single integer charge transfer into the molecular adsorbate has been reported, which is due to a favorable combination of a substrate with a sufficiently low work function and an adsorbate with a high electron affinity.

By contrast, atomic scale investigations into double negative charging of molecular adsorbates or charge transfer from the adsorbate into the substrate, which requires substrates with very high work function, are rarely found. In this talk, I will present the results, obtained with scanning tunnelling microscopy and spectroscopy, photoemission spectroscopy and supported by DFT, of our latest studies that deal with these aspects. After presenting new insights about charge transfer into Au islands on MgO(001) thin films and how the morphology (2D vs 3D) can be controlled by specific sample treatments, I will switch to organic molecules, specifically PTCDA (Perylene tetracarboxylic-dianhydride) as adsorbates, to show how the transition from single to double integer charging of the PTCDA molecules is achieved by controlling the work function of the MgO(001)/Ag(001) substrate.

To study charge transfer in the reverse direction, from adsorbate into the substrate, a high work function substrate has to be selected. Here, MoO_3 monolayer films on Pd(100) turned out to be a good choice. Adsorption of phthalocyanine (2H-Pc) molecules resulted indeed in the formation of 2H-Pc^+. However, the presence of antiphase domain boundaries in the MoO_3 film as preferred adsorption sites and the weak interaction between the MoO_3 film, which is oxygen terminated, and the 2H-Pc molecules, which leads to a transition of a flat-lying to a standing molecular orientation with increasing coverage, pose some problems. Therefore, I will finally present a synthetic procedure that allows us to study with STM flat lying 2H-Pc molecules on the MoO_3 exclusively.