Surface- and step-edge functionalization by N-heterocyclic carbenes

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N-Heterocyclic carbenes (NHCs) are established ligands for the chemical and electronic functionalization of surfaces and nanoparticles, offering valuable opportunities for tuning their catalytic properties [1]. In this study, we employ non-contact atomic force microscopy (nc-AFM) with CuOx-tips [2] and scanning tunneling microscopy (STM), complemented by density functional theory (DFT) calculations, to investigate the adsorption behavior of various NHCs on single-crystalline metal surfaces.

An upright adsorption geometry (Fig. 1a) is identified as a characteristic feature of NHCs on metal surfaces [3]. Moreover, the functionalization of NHCs with hydroxyl side groups R-OH leads to the formation of extended two-dimensional networks on the flat terraces of the Ag(111) surface, suggesting that hydrogen bonding mediated by the hydroxyl groups significantly enhances intermolecular interactions (Fig. 1b,c). In addition to such networks on flat terraces, we examine the nucleation behavior of different NHCs at atomically defined step edges of the Au(788) surface (Fig 1d). Finally, electrochemical voltammetry experiments are conducted allowing to correlate the observed structures with their catalytic performance in the CO_2 reduction reaction [4].

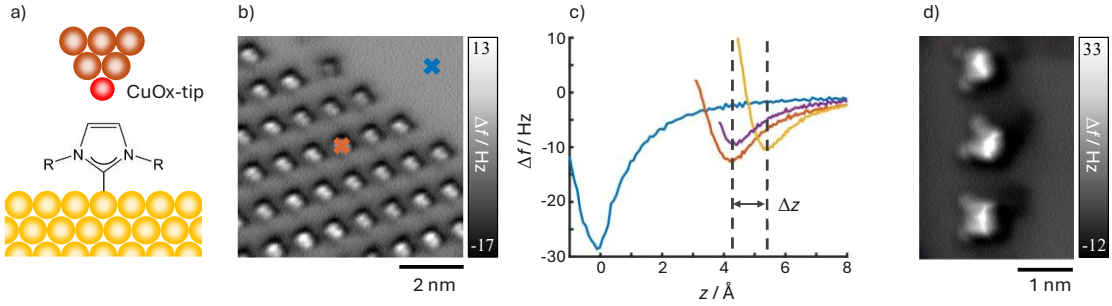

Figure 1. **(a)** Structual model of a NHC with side groups R adsorbed to a metal surface. **(b)** nc-AFM of hydroxyl functionalized NHCs on Ag(111). **(c)** Δf (z) curves for examining adsorbtion heights of the measurement in (b). **(d)** nc-AFM of NHCs at the step edge of Au(788).

Reference

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