Harry Mönig

AFM with copper-oxide tips: Imaging atoms in real space with elemental selectivity

In scanning probe microscopy experiments, the identity of the tip-terminating atom and its bonding configuration at the apex can drastically affect the image contrast [1-3]. In particular, in the field of noncontact atomic force microscopy (nc-AFM), considerable progress has been made through the implementation of different tip functionalization approaches, which, in combination with the ultra-small oscillation amplitudes of qPlus-type force sensors, have led to a new era in surface chemistry [4, 5]. By far the most established probes used in nc-AFM experiments are CO-functionalized tips. They are prepared by first co-adsorbing a low density of CO molecules on the surface under study and then picking up a single molecule by a sharp metallic tip apex leading to a configuration where the O-atom points to the surface [1, 4, 5]. This significantly reduces chemical interactions within the tip-sample junction allowing for constant-height nc-AFM imaging in the repulsive force regime where organic nanostructures can be imaged with sub-molecular resolution [4, 5]. However, a major problem of using such probe particles for nc-AFM experiments is their lateral flexibility at the apex. It can lead to image distortions, a systematic overestimation of bond lengths, and even artificial contrast features [6-8]. The latter particularly concern surface sites with a strongly varying tip-sample potential where tip flexibility affects the contrast the most.

In the following, an alternative approach based on so called copper-oxide tips (CuOx-tips) is discussed. These tips consist of a Cu-apex terminated by a single O-atom, which is covalently bound in a tetrahedral configuration to its upper Cu-atoms (Fig. 1a). With this structure, CuOx-tips allow for stable constant-height imaging in the repulsive force regime and to resolve single bonds in organic nano-structures (Fig. 1b). At the same time, CuOx-tips are extremely rigid, which allows to largely neglect artefacts due to tip flexibility [3, 6, 7].

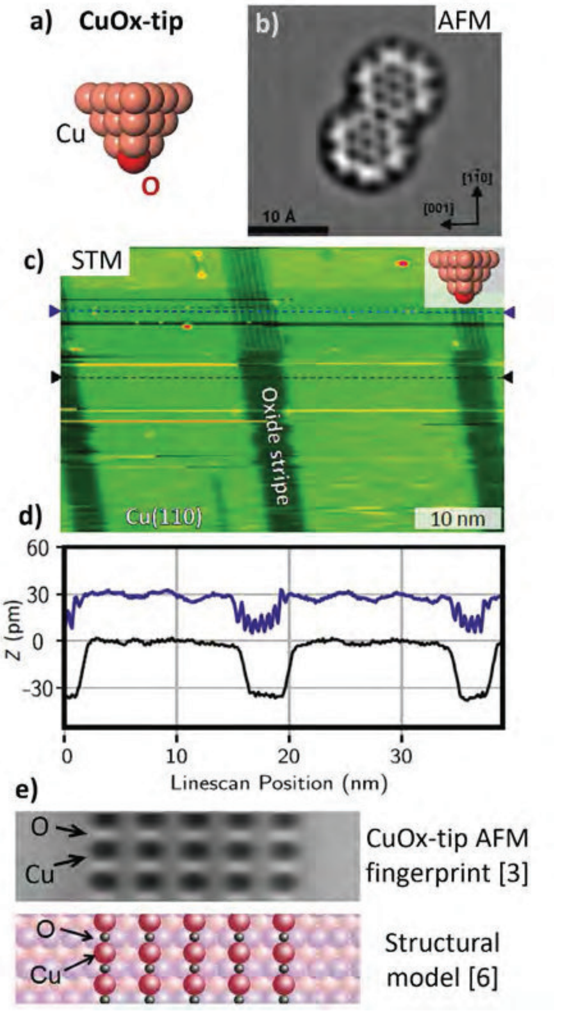

Fig. 1: a) DFT-optimized model of a CuOx-tip. b) Constant-height nc-AFM image of dicoronylene on Cu(110) recorded with a CuOx-tip (reprinted from ref. [6] with permission from Springer Nature). c) Constant-current STM image of a partially oxidized Cu(110) surface recorded during tip forming procedures [9]. d) Line profiles from c for a pure metallic apex (black) and after successful CuOx-tip functionalization (blue). e) Constant-height nc-AFM on an oxide stripe (adapted from ref. [3] with permission from Royal Society of Chemistry). Such a contrast serves as a fingerprint allowing to unambiguously verify a CuOx-tip. Structural model reprinted from ref. [6] with permission from Springer Nature.

CuOx-tips can be prepared by controlled tip indentations and voltage pulses on a slightly oxidized single crystalline Cu substrate. Figure 1c shows a scanning tunneling microscopy (STM) image of a partially oxidized Cu(110) surface showing the typical (2x1)O-reconstructed oxide stripes, which is acquired during such tip forming procedures [9]. While recording the lower part of the image, the tip is terminated in a pure metallic apex where frequent tip indentations and voltage pulses below the horizontal scan line result in instabilities. Due to the reduced density of states, the topographically elevated oxide stripes appear as deep trenches in the STM contrast at feedback settings of -0.1 V/50 pA (see also black line profile in Fig. 1d). Only when the tip picks up copper-oxide material from the sur-

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face leading to an O termination at the apex, the STM contrast changes significantly (upper part of Fig. 1d). This not only increases the resolution, but also reduces the apparent depth of the trenches (blue line profile in Fig. 1d). Yet, it is important to note that such a change in the STM contrast alone does not prove a CuOx-tip termination. In principle, any passivated tip could show such a contrast. To unambiguously verify a CuOx-tip termination, the recording of an nc-AFM image above one of the oxide stripes is required. As demonstrated by systematic DFT simulations, only a contrast as shown in Fig. 1e allows to confirm the formation of a CuOx-tip. In fact, a constant-height nc-AFM contrast as shown in Fig. 1e serves as fingerprint for a CuOx-tip [3, 6, 7]. Here, single Cu-atoms within the (2x1)O-reconstruction appear as dark ellipsoidal depressions, while the O-atoms are imaged as bright contrast features (dominated by repulsive forces) in between (Fig. 1d). As shown in the following, this remarkable chemical selectivity for metal- and oxygen atoms is a specific property of CuOx-tips, which can even be generalized for the whole class of metal-oxide surfaces.

As a first step for this generalization, the role of the tip termination was investigated by comparing the contrast of four commonly used probe tips. The upper panels in Fig. 2 show constant-height nc-AFM images of (2x1)O-reconstructed oxide stripes recorded with four atomically defined tip-terminations at tip-heights of maximum contrast [3]. It was found that the high reactivity of pure Cu-tips (Fig. 2a) leads to atomic relaxations within the tip-sample junction already in the attractive force regime. Therefore, imaging at even more reduced tip-sample distances leads to unstable imaging conditions and sudden tip changes. For the case of Xe- and CO-passivated tips, it is possible to enter the repulsive force regime (Fig. 2b, c). However, the observed contrast does not allow to clearly identify specific atomic surface sites, rather the images appear strongly distorted and show emphasized contrast signatures at inter-atomic sites (i.e. between the O-Cu-O rows). Mechanistic simulations allowed to explain these findings by dynamic tip bending effects, which are particularly emphasized due to the strongly varying tip-sample potential between Cu- and O-sites [3]. On the contrary, the data recorded with a CuOx-tip show a pronounced site-specific interaction and shape distinction for the Cu- and O atoms within the (2x1)O-reconstructed oxide stripes (Fig. 2d). Therefore, the identification of Cu- and O-sites is straight forward. As demonstrated by height-dependent imaging in combination with force-distance spectroscopy, the observed elemental selectivity is obtained over an extended range of tip-heights [3].

Force-distance *($F(Z)$)* simulations based on density functional theory (DFT) provide a more detailed view on the contrast mechanism. The lower panels in Fig. 2 show corresponding $F(Z)$ curves from O- and Cu-sites for all four tips, plotted on identical force scales to facilitate comparability. As the contrast is solely based on lateral differences in the chemical interaction, the simulated data are plotted without van der Waals contributions, which add only a background without any lateral variation for each tip. On both atomic sites, the Cu-tip shows pronounced minima at $Z < 3$ Å, which can be associated with a strong attraction and related high chemical reactivity, especially on the O-site. With the differing force interaction of the Cu- and O sites, such force curves indicate a strong contrast at $Z < 3$ Å, which in principle would allow to clearly distinguish the atoms within this force regime. However, the high chemical forces in combination

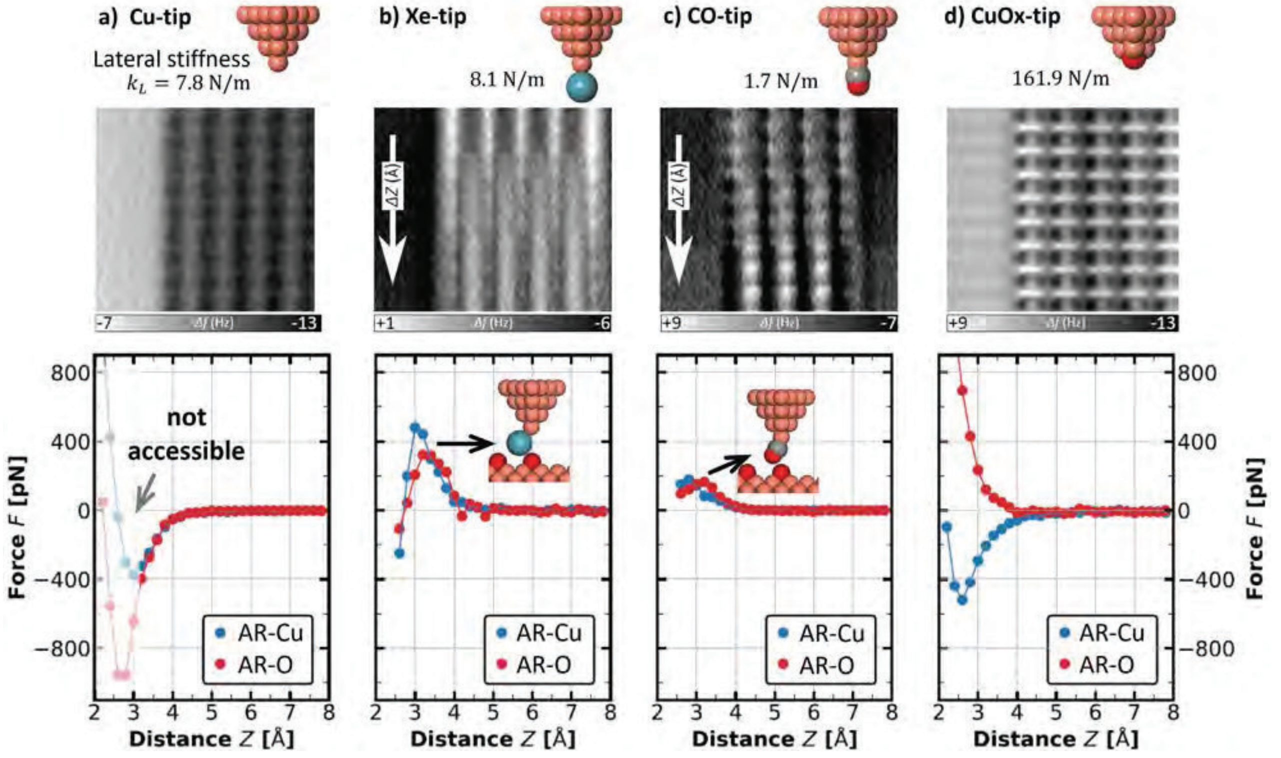

Fig. 2: (Upper panels) Comparison of nc-AFM images for various atomically defined tip terminations, recorded in constant-height mode above (2x1)O-reconstructed oxide stripes of a partially oxidized Cu(110) surface. The DFT-derived lateral spring constants given next to the tip models allow to quantify tip flexibility. (Lower panels) DFT-simulated *$F(Z)$* force-distance spectra where the vdW components have been subtracted to assess the chemical interactions for O- and Cu sites. Adapted from ref. [3] with permission from Royal Society of Chemistry.

with a weak stiffness of the Cu-tip leads to atomic relaxations within the tip-sample junction. Therefore, the tip-height regime in which a strong contrast could be expected is not accessible without the metallic tip reacting with surface oxygen [3, 7]. On the contrary, the Xe- and CO-tip both hardly show any attraction, which confirms the chemical passivation of these two tips. At the same time, the force-distance curves show nearly no separation, which explains the experimentally observed weak contrast between the O- and Cu-sites. In addition, both show kink-like maxima around Z = 3 Å, which are typical for lateral bending effects of the Xe- and CO probe particles [3, 8]. In comparison, the curves for the CuOx-tip show a largely inert interaction on the O-site and a moderate attraction (i.e. reactivity) on the Cu-site. This leads to a distinct separation of the F(z) curves at Z < 4 Å (Fig. 2d), which is in agreement with the experimentally observed strong contrast. Furthermore, due to the high stiffness of the CuOx-tips, artefacts due to tip bending effects are absent. The differences in tip flexibility are demonstrated by a quantitative comparison of the DFT-derived lateral spring constants, given in the top row of Fig. 2 [3].

Up to this point, elemental selectivity was observed only for the (2x1)O-reconstructed Cu(110) surface. Consequently, the next steps in this research addressed the question if this finding applies to other reconstructions and other metal oxide surfaces as well. For a systematic investigation of this issue, CuOx-tip nc-AFM imaging was applied to various O-induced reconstructions, namely Cu(110) (6x2)O, Cu(100) (2√2x√2)R45°O, and Ag(111) p(4x4)O. Even for these surfaces where metal and oxygen atoms occupy sites with a variety of different relative heights, the distinct elemental selectivity of the contrast allowed to directly identify atomic sites and defect structures [10].

To further understand the origin of this contrast, theoretical simulations based on DFT were employed. In Fig. 3a, b, experimental CuOx-tip images of the Cu(100) (2√2x√2)R45°O surface and an OH defect on (magnetite) Fe$_3$O$_4$(001) are compared to corresponding maps of the local electrostatic potential E^{el}_{pot}. These simulated potential maps were derived from DFT-optimized structures of these well-known surfaces and do not consider any tip interaction. Therefore, the remarkable agreement of the experimental data and the E^{el}_{pot}-maps reveals that the elemental selectivity of CuOx-tips is mainly based on electrostatic interactions [10]. In this simple picture, the tip-terminating O atom of the CuOx-tip can be regarded as a single point charge e$^-$, which is scanned above the strongly varying charge density between metal- and oxygen sites (Fig. 3c). In fact, considering the charge density accumulation at the apex of a CuOx-tip by Bader charge analysis, leads to a partial charge similar to CO-tips of roughly 1 e$^-$ [6].

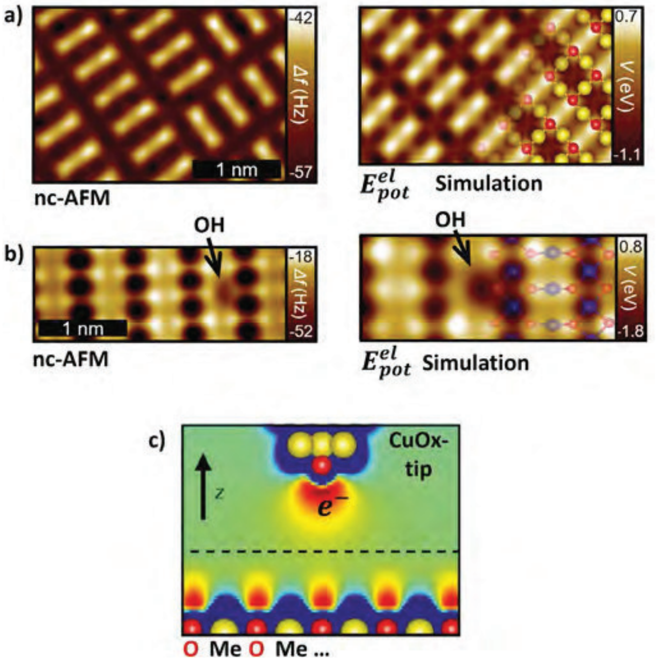

Fig. 3: a) and b) Comparison of experimental CuOx-tip nc-AFM data from the Cu(100) (2√2x√2)R45°O- and Fe$_3$O$_4$(001) surfaces (left) with electrostatic potential maps (right) derived from DFT optimized surface models. c) Cross section of the electrostatic potential of the CuOx-tip and a metal oxide surface. The O-termination of the tip leads to an increased electron density at the apex dominating the interaction with the surface. Reprinted with permission from ref. [10]. Copyright 2014 American Chemical Society.

By extending this methodology to surfaces with highly complex, a priori unknown surface structures, and to surfaces of bulk metal-oxide materials, demonstrates the powerful capability of this approach [10, 12]. Figure 4a shows data of a titanium oxide (TiO$_x$) thin film grown on a Pt(111) substrate where the arrangement of 4-fold and 3-fold coordinated titanium atoms leads to a surface structure with a high degree of complexity [10]. Similarly, Figure 4b shows CuOx-tip measurements of an Al$_2$O$_3$(0001) surface which forms a (√31x√31)R±9° reconstruction exhibiting a stochiometric composition and emphasizing the applicability also to insulating surfaces [12]. In these experiments, the distinct contrast obtained with the CuOx-tip provided immediate access to the metal- and oxygen sublattices. Beyond that, imaging with such an elemental selectivity provides access to a direct structural characterization of atomic-scale point defects (Fig. 3b) [10, 12], which play an important role

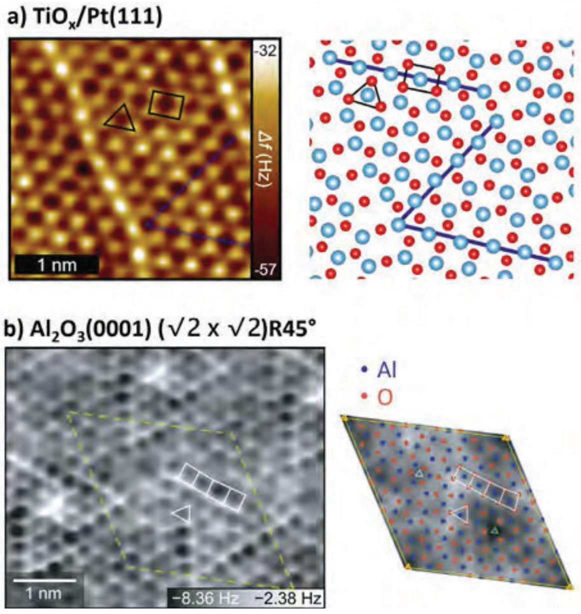

Fig. 4: a) nc-AFM data of a titanium oxide thin film grown on Pt(111). The elemental selectivity of the CuOx-tip allows to directly obtain the surface structure (shown on the right). b) CuOx-tip nc-AFM image recorded on the bulk insulator Al$_2$O$_3$ (left). The surface structure can be directly derived from the experiment (right). Reprinted from ref. [12], with permission from AAAS.

in the fundamental understanding of the catalytic, optical, and electronic properties of metal-oxide materials [10, 11, 13].

With their universal elemental selectivity on metal-oxide surfaces, CuOx-tip functionalization constitutes a powerful methodology for the atomic-scale characterization of this technologically relevant class of materials. The successful application to even highly complex surfaces and defects where conclusive structural models had been missing so far, must be set in context to the longstanding dream for scanning probe microscopy to directly determine the elemental identity of single atoms [14-16]. Our approach allows to drastically reduce the theoretical efforts and related indirect structural considerations and assumptions (e.g. for tip terminations and atomic positions) for the development of structural surface models. Moreover, CuOx-tips allow neglecting imaging artefacts due to tip-flexibility [6, 7] and can be routinely used at liquid nitrogen temperatures (e.g. nc-AFM data in Fig. 3a, b and Fig. 4a) [10, 17]. These highly desired properties make these probes unique for standardized scanning probe microscopy experiments.

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PD Dr. Harry Mönig

Harry Mönig, leader of the Nanoscale Interface Analytics group at the University of Münster, received his diploma in physics from the University of Kassel in 2005. After that, he continued his research with a doctorate on synchrotron-based interface analytics of chalcopyrite thin film solar cells at the Helmholtz Zentrum Berlin / BESSY. After completing his PhD in 2009, Harry Mönig worked as a postdoc at Yale University on simultaneous STM/nc-AFM measurements and force spectroscopy on metal oxide surfaces, before starting his current role in 2012. In 2019, he was appointed Privatdozent after finishing his habilitation thesis on correlating macroscopic and nanoscale phenomena in interface science.

Harry Mönig's current research focuses on nanoscale chemistry, single atom catalysis, electrocatalysis and interface analytics for solar cells. He made important contributions to the field of high-resolution nc-AFM by developing a new technique to image surfaces with copper-oxide terminated AFM/STM tips. Due to the rigidity of the copper-oxide tip, this technique is especially suited to study oxide and insulator surfaces.