Water and metal adsorbates on reducible oxide surfaces: Can theory help to understand the AFM and KPFM contrast?.

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Metal oxides play a key role in a wide range of technological applications. To optimize their performance, it is essential to understand their surface properties and chemistry in detail. Noncontact atomic force microscopy (nc-AFM) provides a natural tool for atomic-scale imaging of these insulating materials. Some of these materials, including ceria (CeO_2), and particularly titania (TiO_2), have been extensively studied with nc-AFM in the last few years. Experiments on the rutile $TiO_2(110)$ surface show, at variance with STM, that a variety of different contrasts can be obtained, and frequent changes among different imaging modes are observed during scanning. The two most common contrasts are the "protrusion" and the "hole" mode imaging modes, that correspond, to imaging bright the positive or the negative surface ions respectively, but other contrasts like the "neutral" mode and the "all-inclusive" mode –where all the different chemical species and defects are imaged simultaneously—have been also identified.

Understanding the image contrast mechanisms and characterizing the associated tip structures is crucial to extract quantitative information from nc-AFM measurements and to identify the nature of the observed defects. While in many cases the same nc-AFM image can be explained by different models, and even different underlying tip-sample interactions, we show here that the combination of force spectroscopy (FS) measurements and first-principles simulations can provide an unambiguous identification of the tip structure and the image contrast mechanism [1]. In particular, we show that the best tips to explain the protrusion and hole mode forces are TiO_x-based clusters differing in just one H atom at the tip apex, discarding previously proposed Ti-terminated tips that would lead to forces much larger than the ones observed in the experiments. The less frequent neutral and all-inclusive images are associated to Si tips where contamination is limited to just an O atom or OH group at the apex. These models provide a natural explanation to the observed contrast reversals by means of H transfer to/from the tip, an event that we indeed observe in our simulations. As tip contamination by surface material is common while imaging oxides, we expect these tips and imaging mechanisms to be valid for other oxides. Our results for the imaging of water on CeO_2 [2], defects on the CuO surface oxide [3] and of metal adsorbates on TiO_2 support this conclusion.

[1] A. Yurtsever et al., Phys. Rev. B **85**, 125416 (2012).
[2] D. Fernández-Torre et al., J. Phys. Chem. C 116, 13584 (2012).
[3] M. Z. Baykara et al., submitted (2013).