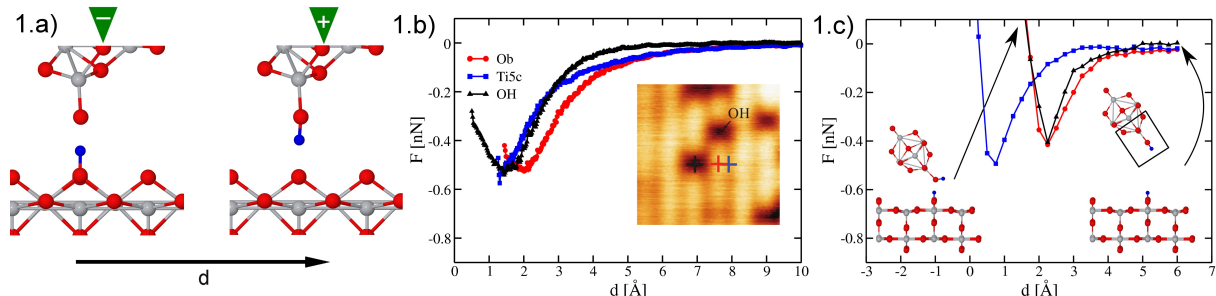


Understanding image contrast in TiO₂ with force spectroscopy and theoretical simulations

Delia Fernández-Torre¹, Ayhan Yurtsever², César González³, Pavel Jelínek⁴, Pablo Pou¹, Yoshiaki Sugimoto², Masayuki Abe², Seizo Morita², and Rubén Pérez¹

¹Depto de Física Teórica de la Materia Condensada, UAM, Madrid, E-28049, Spain; ²Graduate School of Engineering, Osaka University, Osaka, 565-0871, Japan; ³ICMM, CSIC, Madrid, E-28049, Spain; ⁴IoP, Academy of Sciences, Prague, 162 00, Czech Republic
E-mail: delia.fernandez@uam.es

Titanium dioxide (TiO₂) is important for a wide range of technological applications [1]. To optimize these processes or find new ones, it is essential to understand its surface properties and chemistry in detail. Atomically-resolved scanning probe microscopies, like non-contact atomic force microscopy (nc-AFM), combined with theoretical simulations, play a key role in this respect. In fact, the most stable facet of titania, rutile TiO₂(110), has been extensively studied with nc-AFM in the last few years [2-4]. These experiments have demonstrated that a variety of different contrasts can be obtained, depending on the tip termination. The two most common contrasts are the protrusion and the hole mode imaging modes, and correspond, respectively, to imaging bright the positive or the negative surface ions. Theoretical simulations based on single nc-AFM images or combined STM and nc-AFM images have shown that tip models terminated with a negative or a positive ion picked up from the surface can account for these observations [2,3]. However, establishing an unambiguous theoretical interpretation is difficult, since sometimes the same nc-AFM image can be explained by different models, and even different underlying tip-sample interactions [3,4]. Our goal in this work is to overcome this difficulty by combining force spectroscopy (FS) measurements and first-principles simulations [5]. To explain the FS experiments, we performed simulations for a broad range of tip model candidates. We found 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 (fig. 1a). We discarded previously proposed Ti-terminated tips due to their large reactivity with the surface, not observed in the experimental forces (fig. 1b). Interestingly, all measured forces turned out to be attractive over all surface sites, and we can explain this through different atomic relaxations happening at the tip apex upon approach to the surface sites (fig. 1c). Our models also let us explain observed contrast reversals by means of H transfer to/from the tip. We have also applied these same models to study metal atoms (K,Pt) adsorbed on TiO₂. As tip contamination by surface material is common in other oxides, we expect that these or similar tips and mechanisms will be also valid to study them.



References

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