Disentangling atomic contrast on bimodal atomic force microscopy and simultaneous scanning tunneling microscopy on the TiO_2(101) anatase surface

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Abstract

Titanium dioxide (TiO_2) is a highly strategic material with important applications in energy-related developments, including photocatalytic production of hydrogen and solar energy conversion schemes. Since most of the peculiar TiO_2 properties are surface-mediated, a deep understanding of the TiO_2 surface properties is presented as critical issue to develop high-performance applications. Probably, the most studied TiO_2 form is rutile because it was one of the first bulk single crystal displaying high quality surfaces at reasonable prices. Rutile surfaces has been extensively studied at atomic scale over several decades with both scanning tunneling microscopy (STM) [1,2] and atomic force microscopy (AFM) [3,4]. However, TiO_2 anatase has superior performance than rutile in several energy harvesting related issues. At variance with the rutile structure, very few experimental studies on large single crystals of anatase exist, and the structure [5,6], intrinsic defects [7], and phenomenology [8,9] of the TiO_2 anatase surfaces are still not very well understood.

Here, we present an atomic scale characterization of the TiO_2(101) anatase surface by means of bimodal AFM and simultaneous STM measurements (Fig.1). By using Pt-Ir covered cantilevers, we are able to detect the average tunneling current flowing between the cantilever and a conductive sample while performing atomic resolution dynamic AFM [10]. Simultaneously, it is also possible to operate AFM in bimodal mode [11]. In this work, we use the variation of the resonant frequency of the first eigenmode of a rectangular cantilever to acquire topographic images while simultaneously detecting the variation of the resonant frequency of the second eigenmode, which is driven at ultra-small oscillation amplitudes (typically between 8 to 40 pm), and therefore, it is very sensitive to the short-range tip-surface interaction force [12]. In this presentation we will show how the combination of the different channels of information provided by simultaneous bimodal AFM/STM operation allows us to clarify the contribution of the different atomic species of the TiO_2(101) anatase surface to the atomic resolution images. This is further corroborated by the study of the bonding structure of molecular water on the TiO_2(101) anatase surface. We will also show that the average tunneling current enables to pinpoint subsurface defects that are otherwise unrevealed in the topographic AFM images (Fig. 1).

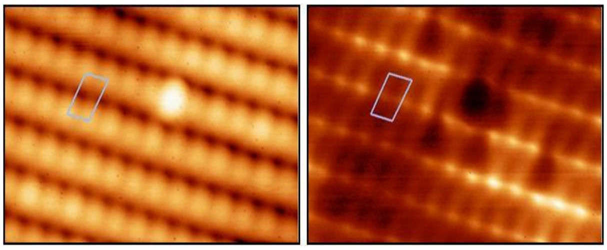

Figure 1. Atomic scale characterization of the titanium dioxide (101) anatase surface: (left) AFM topographic image and (right) corresponding average tunneling current image recorded simultaneously by bimodal AFM/STM. The rectangle in both images marks the same surface region for reference

References

[1] Wendt et al.,Science, **320**, (2008) 1755-1759
[2] Matthey et al., Science, **315**, (2007) 1692-1696
[3] Enevoldsen, et al.,Phys. Rev. B **78**, (2008) 045416.
[4] Bechstein, et al., Nanotechnology **20**, (2009) 505703.
[5] Hebenstreit et al., Physical Review B **62**, (2000) R16334.
[6] Gong et al., Nature Materials **5**, (2006) 665
[7] He et al., Physical Review Letters **102**, (2009) 106105
[8] He et al., Nature Materials **8**, (2009) 585
[9] Grinter et al., J. Phys. Chem. C **116**, (2012) 11643
[10] Sawada et al., Appl. Phys. Lett. **94**, (2009) 173117
[11] Kawai et al., Physical Review Letters **103**, (2009) 220801
[12] Giessibl, Reviews of Modern Physics **75**, (2003) 949