NC-AFM IMAGING OF DEFECT REACTIONS AT METAL OXIDE SURFACES: THEORETICAL PREDICTIONS

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The practice of NC-AFM (Non-contact Atomic Force Microscopy) imaging with atomic resolution has been achieved on several metal oxide surfaces, such as TiO_2 [1] and CeO_2 [2]. With this comes the opportunity to use AFM as a tool to examine surface chemistry in a direct manner. This is especially needed on wide-gap insulating materials, where STM methods are not applicable. However, the interpretation of AFM images is a complex task [3] and the advantages of the method cannot be exploited without cross-pollination between theory and experiment. Here we present the results of theoretical modeling, which demonstrate that NC-AFM imaging can be used for identifying the chemical nature of surface defects and observation and manipulation of photo-induced surface processes.

One material where atomic resolution can be achieved is Ceria, CeO_2 [2]. Ceria has major applications within the catalytic industry as a catalyst support e.g. in automobile three-way catalytic converters [4]. The usefulness of Ceria in this context stems from the ability of cerium ions to accommodate multiple charge states, allowing strong non-stoichiometry, CeO_{2-x}. Consequently, the system can act as an oxygen buffer stabilising the catalytic redox system. Unusually for an insulating material, study of Ceria surfaces with AFMs revealed a wealth of defects stable over a timespan of minutes [2], the nature of which was poorly, if at all, understood. In order to interpret experimental AFM data we need to understand the properties of the pure surface and defects at an atomistic level and be able to model the surface-tip interaction. Using complementary *ab initio* and empirical force field methods we examined a variety of proposed surface defects – oxygen vacancies and interstitials, alkaline-earth metals as well as a variety of absorbates, including molecular hydrogen. Potential defects were screened by calculating adsorption energies and surface diffusion barriers, which enabled us to determine which defects may have a sufficient site-occupancy time to be imaged by AFM and, hence, are candidates for the experimentally observed defects: These parameters are also fundamental in regards to the important ionic conduction properties and variable oxidation state of ceria in catalytic systems. Model images were constructed for the most likely defects and a comparison with available experimental data is made, allowing us to examine some of the models proposed for surface activity on the CeO_2 (111) surface.

Exciting as the opportunity to observe surface chemistry directly is, the possibility also exists to manipulate it using NC-AFM in combination with selective photo-excitation of low-coordinated surface sites. Our understanding of the surface physics of MgO allows us to present a proof of principle of the use of AFM in this way. Recent experiments [5] demonstrate that atomic resolution can be achieved with NC-AFM on the MgO (100) surface prepared by sputtering-annealing cycles. The images contain point defects, which can be attributed to Ca ions segregating at the surface as the result of high-temperature anneal. This provides a distinct possibility for tip calibration: The observation of Ca ions as bright spots in images identifies the tip as having negative polarity. Step edges and corners can also be observed in these images. Previously, we have demonstrated [6] that step edges and corners can be selectively excited and ionized using 5.4 eV and 4.6 eV photons, respectively. Ionization of oxygen corners at the MgO surface is accompanied by formation of localized O^- species clearly detectable using EPR [6]. Our theoretical calculations demonstrate that the ionization energy of oxygen corners can be strongly affected by the proximity of an AFM oxide tip: In particular, a negative polarity tip at 4 Å from the corner can reduce the corner

ionization energy by as much as 1 eV. This finding opens an opportunity for selectively ionizing only those step corners which are affected by interaction with the tip. Since O$^-$ species are stable at corners, this photo-induced reaction should be directly observed as a change in the NC-AFM image. Our calculations predict the change in contrast at the oxygen corner due to formation of O$^-$ species, which can be used for their identification. O$^-$ species are chemically very active and it should be possible to image their reactions with other species directly using NC-AFM. In particular, the homolytic dissociation of H$_2$ molecules at O$^-$ corners has been demonstrated experimentally. Our calculations predict the change in image contrast due to formation of OH$^-$ species at the corner. These results demonstrate that specific sites on the crystal surface can be identified and their chemical environment changed with NC-AFM, allowing their manipulation at an atomic level.

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