

Keysight Technologies

Humidity-dependent Surface Chemistry Studied by Keysight 7500 Atomic Force Microscopy

Application Note

Introduction

One of the key advantages of atomic force microscopy (AFM) over other members within the microscopy family is its capability of being operated under different environments. Particularly, a complete control of the relative humidity (RH) in air surrounding the localized tip/sample region is highly desired for an AFM as it will render users a valuable means to address a lot of humidity-dependent issues. The Keysight Technologies, Inc. 7500 AFM system is comprised of a sealed environmental chamber with eight accessible ports and a build-in humidity sensor, thus allowing the *in situ* monitoring and control of the RH during AFM measurements. In this application brief, investigations of the influence of humidity on selected surface reactions using Keysight 7500 AFM will be presented.

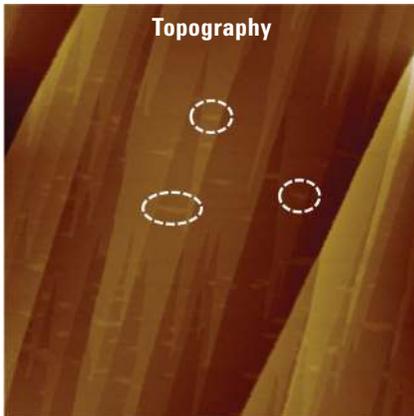


Figure 1. AFM detection of calcite surface reactions under controlled humidity conditions. AFM topography of the resulting calcite surface after hydroxylation reactions. Scan size: $1.2\mu\text{m} \times 1.2\mu\text{m}$.

AFM Detection of Calcite Surface Reactions Under Controlled Humidity Conditions

It is proposed that calcite (CaCO_3) could undergo hydroxylation with atmospheric water under ambient conditions through a surface reaction that can be expressed as $\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})(\text{CO}_3\text{H})$ to yield surface species identified as S- CO_3H and S- CaOH , where S-

represents the calcite surface. In order to demonstrate that the hydroxylation reaction of calcite surfaces can be captured from an AFM point of view, a freshly cleaved CaCO_3 sample was placed into the AFM chamber for a certain period of time while the relative humidity inside was maintained at a preferable level. Then it was checked by an AFM. Showing in Figure 1 is AFM topography of the resulting surface. In addition to those surface features such as the smooth domains and straight step edges that are intrinsic to the calcite material, some newly formed protrusion islands are clearly resolved. Three selected examples are highlighted using the dotted white circles. Such surface morphologies are not observed on those calcite samples when they were imaged immediately after transferring into the AFM chamber or the relative humidity is very low. Therefore, AFM enables the direct visualization and recognition of calcite surface changes.

AFM-based Material Sensing Related to Calcite Hydroxylation Reactions

Further proof of identifying the hydroxylation process of calcite requires additional evidence in term of its chemical nature. In principle, hydroxylation-associated reactions will result into the formation of new surface species terminated with either

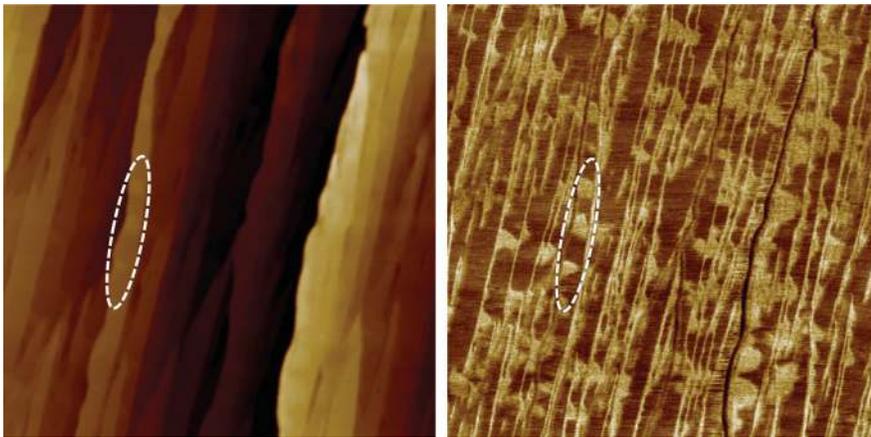


Figure 2. Differentiation of distinctive chemical identities associated with calcite hydroxylation reactions. AFM topography (left) and corresponding friction image (right) of the resulting calcite surface after hydroxylation reactions. Scan size: 800 nm × 800 nm.

hydroxyl (-OH) or carboxylic acid (-CO₃H) functionalities. Those changes in interfacial chemistry can be examined by contact mode AFM imaging whose friction (or lateral force) responses are very sensitive to the tip/sample adhesion that is also dependent on their chemical properties. As can be seen in Figure 2, at those locations in topography images (left) where surface reaction-induced protrusion features are present, they exhibit very different contrasts with respect to the surrounding calcite regions in the corresponding friction image (right), and thus providing us some valuable evidence on the formation of distinctive chemical identities.

In situ AFM Studies on the Kinetics and Reaction Pathways of Calcite Hydroxylation Process

The evolution and the dynamics of the calcite surfaces under ambient conditions can be monitored using *in situ* AFM imaging. Showing in Figure 3 are three selected time-dependent topographic images of the same region. The surface coverage of hydroxylated areas keeps growing over time. In addition, they provide the direct and unambiguous proof that calcite hydroxylation actually grow through two

pathways: an increase in the number of nuclei, and the growth of each nucleus. Both cases are exemplified at those location marked with a red circle and a green circle, respectively.

Summary

Using investigations of the reaction chemistry and changes of carbonate surfaces under ambient conditions as an example, it is demonstrated that AFM measurements under controlled humidity conditions can be achieved and will open up new horizons for their applications in a wide variety of scientific fields.

AFM Instrumentation from Keysight

Keysight offers high-precision, modular AFM solutions for research, industry, and education. Exceptional worldwide support is provided by experienced application scientists and technical service personnel. Keysight's leading-edge R&D laboratories are dedicated to the timely introduction and optimization of innovative and easy-to-use AFM technologies.

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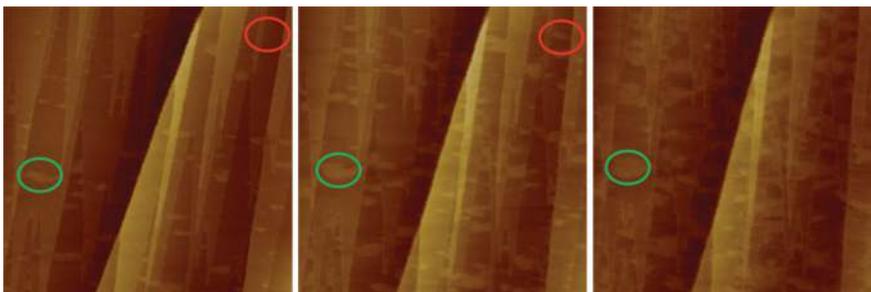


Figure 3. AFM studies of the kinetics and reaction pathways of calcite hydroxylation reactions. In situ and time-dependent AFM topographic images of a selected location during the hydroxylation process. Scan size: 1 μm × 1 μm.