Probing the Stability of Trisodium Citrate Dihydrate Adsorption on NaCl in Ethanol

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Understanding the interactions of additives with crystal surfaces is crucial for controlling crystal growth in various applications. Numerous investigations have focused on additive adsorption on crystal surfaces,[1-2] yet the process of desorption remains relatively underexplored. We have previously observed the in situ adsorption of trisodium citrate dihydrate on a NaCl(100) surface. These findings suggest that trisodium citrate dihydrate adsorbs preferentially along the step edge rather than on the terrace and can be mobile as the number of water molecules increases. However, the strength of the adsorption has not been evaluated. In this study, the adsorption strength was investigated using a frequency modulation atomic force microscope (FM-AFM (SPM-8000FM prototype, Shimadzu)) through observations involving ethanol.

First, a NaCl crystal freshly cleaved into the (100) plane was dripped with 2 microliters of trisodium citrate dihydrate solution (0.04 M in pure water) under relative humidity (RH) < 40%. FM-AFM imaging revealed that trisodium citrate dihydrate formed clusters preferentially along step edges and some parts on the terrace (Fig. 1 (a)). Subsequently, ethanol was dripped onto the surface coated with additives in an attempt to dissolve and remove the adsorbed clusters. At an RH of 32%, the treated surface appeared smooth and flat, resembling bare NaCl (Fig. 1 (b)). However, upon reducing the humidity, the trisodium citrate dihydrate clusters became visible (Fig. 1 (c)). Fig. 2 (a) shows another additive-coated sample. Next, we rinsed the additive-coated surface in ethanol solution. FM-AFM image taken in air revealed that trisodium citrate dihydrate clusters remained on the surface after rinsing in ethanol (Fig. 2 (b)). Since most regions still showed clusters on the step edges and terraces, the adsorption is considered to be strong. In the presentation, we will discuss the adsorption dynamics of trisodium citrate dihydrate on NaCl surface after removal attempt by ethanol.

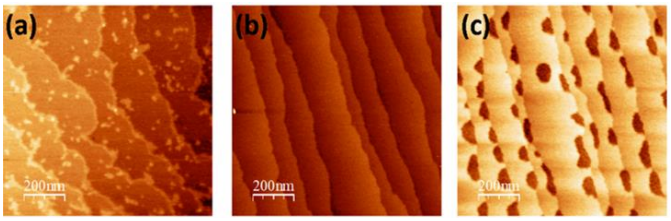

Fig. 1. FM-AFM images taken in air: (a) additives adsorbed on NaCl (RH 27%), (b) the surface resembling bare NaCl surface after dripping with ethanol (RH 32%), and (c) further drying led to the appearance of additive clusters (RH 29%).

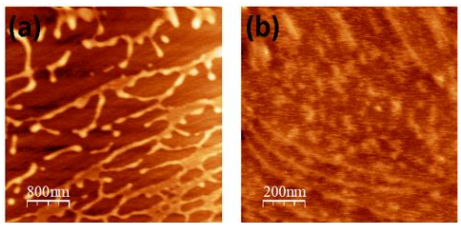

Fig. 2. FM-AFM images taken in air: (a) additives adsorbed on NaCl (RH 25%), (b) additive clusters remained on the surface after rinsing in ethanol (RH 23%).

References

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[2] J. Chi, W. Zhang, L. Wang, and C. V. Putnis, Nat. Commun. 14, 7741 (2023).