Ion-selective Imaging by Atomic Force Microscopy with a Crown-ether-modified Tip

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Ion-selective surface imaging was successfully attained by atomic force microscopy with a probe tip functionalized with a 15-crown-5 derivative. The frictional force images for nanopatterned substrates revealed enhanced contrasts attributable to the cation-binding interaction between the 15-crown-5 on the tip and potassium ions on the substrate.

Atomic force microscopy (AFM) can be used for in situ imaging of various materials, especially insulating samples such as biomaterials under desired conditions. However, conventional AFM lacks chemical imaging ability. In order to overcome this poor chemical sensitivity, chemical modification of AFM tips was proposed for providing specific chemical functionality. As has been demonstrated in pioneering work by Lieber's group,[1] AFM using chemically modified tips with self-assembled monolayers (SAMs) of alkanethiols can detect chemically patterned SAMs fabricated on substrates. The image of the chemical pattern can be obtained by frictional force microscopy (FFM) based on the chemical interactions between the terminal groups of the SAMs. This surface chemical imaging technique has been referred to as chemical force microscopy (CFM). As has been reviewed,[2] various chemical modifications have been reported for CFM tips. Recently, bioimaging based on AFM detection of the specific recognition force of biomolecules has been reported.[3] Moreover, high-resolution glucose imaging was attained by an AFM-tip-integrated biosensor.[4]

It has been already demonstrated that a variety of specific intermolecular forces ranging from biological and artificial molecules are successfully measured by AFM.[5–7] AFM measurements of specific host–guest interactions have been reported for some host molecules (cyclodextrin,[8] crown ether,[9] and calixarene[10]). Previously, we have reported that AFM tips functionalized with a crown-ether-SAM can be used to observe the cation-binding force at a molecular level.[9a] The previous work suggests strongly that the crown-ether-modified tip would have a potential ability to be applicable to CFM probes for surface ion mapping with high spatial resolution. Here, we report an ion-recognition imaging of alkali metal ions at a submicrometer scale by molecularly functionalized probe tips with a thiol bearing a terminal 15-crown-5 moiety (Figure 1). To the best of our knowledge, this is the first example of high-resolution ion-selective imaging based on AFM detection of cation binding force of an artificial host molecule bound to a tip.

We have designed and fabricated the well-defined nanopattern covered with the two different guest ions on Au substrates, as illustrated schematically in Figure 1, according to a literature method[11] (Supporting Information).[17] The patterned substrates with K^+ and Na^+ regions were used as samples for demonstrating the ion-selective imaging by the 15-crown-5-tip. This substrate is patterned with different sulfonate-terminated SAMs, thus possessing concave and convex domains (Figure S1).[17]

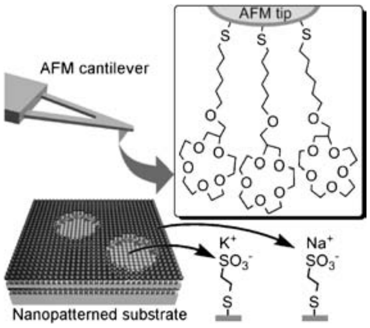

Figure 1. Schematic drawing of a 15-crown-5-modified AFM tip and Au substrate with nanopatterns of K^+ and Na^+ regions.

The concave domains have K^+ as counter ions of the sulfonate monolayer on the surface, while the convex ones possess Na^+.

Figure 2 shows typical images of the patterned substrate taken by a 15-crown-5-modified tip in ethanol, which was used as a solvent for measuring cation-binding interactions in previous studies.[9,10] These topographic and frictional force images were obtained simultaneously for an identical scan area. Figure 2a indicates that two circular holes were clearly observed. Several topographic images obtained at different positions showed that these holes are randomly distributed on the substrate surface. The size of the holes in diameter is in good agreement with that of the silica nanoparticle used as the mask. Furthermore, the depth of the holes was also consistent with the conditions for fabricating this nanopattern. Therefore, this AFM observation confirms clearly that nanopatterned SAMs on substrates were obtained just as we intended.

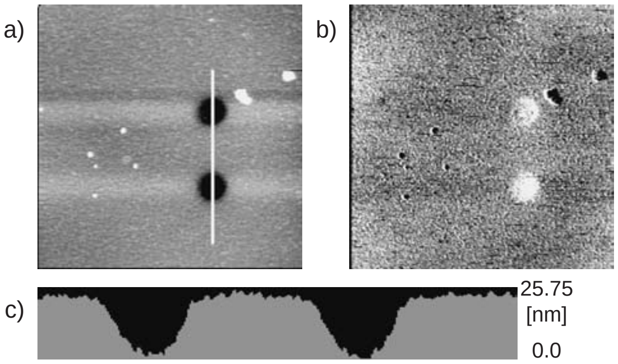

Figure 2. a) Topographic and b) frictional force images ($3 \times 3\,\mu m^2$) of $-SO_3K/-SO_3Na$ substrate recorded by a 15-crown-5-modified tip in ethanol. c) Cross section along a solid line drawn in a). In a), the darker regions correspond to lower heights. In b), the brighter parts indicate higher frictional force.

On the other hand, in the FFM image (Figure 2b), two circular patterns were observed. In this image, the brighter parts indicate the higher friction force regions. The observed circular patterns in Figure 2b are in excellent agreement to those in Figure 2a. Namely, the higher friction force was observed on the lower-height parts (i.e., holes). Since the lower parts are K^+ patterns of the patterned surface, these results indicate that the higher friction force signal was attained on K^+ regions than on Na^+ region. Thus, these images undoubtedly demonstrate that the chemical mapping of surface K^+ at submicrometer scale was successfully achieved. There are some microscopic techniques such as photoelectron spectromicroscopy[12] for surface chemical imaging. Surface imaging using these techniques must be conducted under vacuum and cannot provide images with submicrometer resolution at all. It should be noted that Figure 2b shows K^+ imaging with much higher resolution than these techniques.

Such ion-selective contrast of the frictional force (Figure 2b) would be attributable to the difference in the binding interaction of 15-crown-5 moieties on the tip between K^+ and Na^+ on the substrate. In order to confirm that the enhanced FFM contrast is caused by the host–guest interaction of 15-crown-5 on the tip, we carried out similar imaging in the presence of free K^+ ions in ethanol. The obtained FFM image showed no clear contrast, while circular holes, distributed irregularly, were observed in the AFM image. The brighter parts in the FFM image disappeared in the presence of free K^+. The comparison between the histograms of the FFM signal inside and outside the holes demonstrates definitely that added K^+ caused significant reduction of their difference (Figure S2).[17] The reduced contrast can be explained in terms of the competitive complexation and the ion exchange at Na^+ regions by K^+ in solution. This result strongly supports our conclusion that the K^+ selective contrasts in Figure 2b can be ascribed to the cation-recognition force detected by the 15-crown-5-modified tip.

It is well known that 15-crown-5 derivatives show higher affinity with Na^+ than K^+. Apparently, the K^+ selectivity of our 15-crown-5-modified tip contradicts this general ion selectivity of crown ethers. A plausible reason is that the 15-crown-5 moieties bound to the tip can be assembled with its high surface density. Such a situation of host molecules in preorganized states might result in preferential formation of their sandwich complexes like bis(crown ethers),[13] leading to the K^+ selectivity in FFM. In previous studies, similar K^+-selective responses have been also observed for 15-crown-5-SAM-modified Au electrode,[14] nanoparticle,[15a] nanorod,[15b] and CdSe/ZnS quantum dot.[15c]

Assuming that the surface density of the thiolates on our patterned substrate is similar to that of SAMs with a $(\sqrt{3} \times \sqrt{3})R30°$ structure on Au(111),[16] the amount of K^+ inside one of the holes (ca. 250 nm in diameter determined from Figure 2a) can be estimated to be roughly 4×10^{-19} mole. Therefore, the results shown in Figure 2 indicate that detection of K^+ at the subattomole level was accomplished by our nanopatterned substrate and 15-crown-5-tip. This may suggest that such AFM-sensing system has a potential for ultrasensitive and efficient detection of trace metal ions, since the nanopatterned sulfonate-SAM can act as a nanoscale adsorbent.

In conclusion, we have successfully utilized the 15-crown-5-modified tip to obtain the chemical image of potassium ion distribution at the submicrometer scale. The frictional force image showed clear contrasts between K^+ and Na^+ nanopatterns fabricated on Au substrate. Higher frictional force was observed on K^+ regions, suggesting the K^+ affinity attributable to the cation-binding interaction of 15-crown-5 assembled on the tip. Finally, we believe that the AFM system using host-molecule-modified tips and nanopatterns could afford ultrasensitive and selective detection of specific guest species. Investigation of such application and development is currently in progress.

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17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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