Polarization-specific adsorption of organic molecules on ferroelectric LiNbO₃ surfaces

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(Received 2 August 2010; accepted 17 November 2010; published online 15 December 2010)

Polarization effect on adsorption of d-cysteine molecules on ferroelectric LiNbO₃ surfaces is studied by a combination of infrared spectramicroscopy and spatially resolved x-ray absorption near edge spectroscopy. It is shown that even in the absence of any electronic excitation (optical or thermal), the adsorption is still polarization-specific with preferential d-cysteine deposition occurring on positive domains. This observation rules out molecular adsorption solely due to pyroelectric or photoinduced charge and suggests possible dipole-dipole interaction between polar d-cysteine molecules and ferroelectric polarization dipoles. The surface chemistry related to polarization-dependent variations in Li/Nb concentration is also implicated as a contributing factor in the domain-specific adsorption of d-cysteine. © 2010 American Institute of Physics.

[doi:[10.1063/1.3525373](https://doi.org/10.1063/1.3525373)]

One of the characteristic features of the ferroelectrics is the presence of electrically reversible polarization. In a properly oriented ferroelectric sample, the polarization can be aligned perpendicular to the surface. In this case, the abrupt change in the normal component of the spontaneous polarization on a surface results in the appearance of a bound polarization charge, which in ambient conditions is compensated by the accumulation of ionic species or dipole molecules and through redistribution of mobile carriers in the bulk.¹ This screening significantly affects the surface charge distribution and the surface potential and results in band bending.² Similarly, charged surface states can pin the surface Fermi level resulting in a change in both the surface charge, the surface potential, and the molecular band offsets.³ It has been recently shown that these electrically switchable properties of the ferroelectrics can be used to tailor surface reactivity. Several examples illustrating the effect of polarization on the photoreduction rate of Ag⁺ ions, the sticking coefficients and interaction energies of alcohol and water molecules can be found in literature,^{4–10} including the selective deposition of virus particles.¹¹ This effect opens a possibility of controlled assembling of complex organic/inorganic nanostructures for hybrid electronic devices.¹²

In spite of sizeable amount of experimental evidence on the effect of polarization on surface reactivity, the physico-chemical mechanism of adsorption on the polar surfaces is not well understood. Band bending and induced redistribution of polarization screening charges was invoked as a mechanism for photoinduced adsorption of metals on ferroelectric surfaces.^{4,13} On the other hand, the photoinduced reduction of silver can occur on domains of both polarities under sufficiently high dose of irradiation. Different physisorption energies and chemisorption modes of CO₂ molecules (dissociative versus associative adsorption) have been reported for opposite domains in barium titanate.¹⁴ The strong effect of the LiNbO₃ polarity on the thermal desorp-

tion of polar acetic acid molecules but not the nonpolar dodecane molecules was explained by electrostatic interactions of polar molecules with uncompensated surface charges arising due to pyroelectric effect.⁶ Nonetheless, polarization-dependent surface chemistry was not excluded in prior studies of molecular adsorption on LiNbO₃ (Refs. 6, 7, and 14) and thus must be considered as another possible mechanism affecting molecular adsorption and desorption.

An investigation of the electronic structure of molecules on ferroelectric surfaces can provide additional information regarding the polarization effect on molecular adsorption. In this paper, we investigate the polarization effect on adsorption of d-cysteine molecules [a chiral isomer of *L*-cysteine (chemical formula C₃H₇NO₂S)] on ferroelectric substrates using a combination of infrared spectramicroscopy and spatially resolved x-ray absorption near edge spectroscopy (XANES). (It is worth mentioning that there is a rich literature of cysteine adsorption chemistry^{15–19} and the characteristics of cysteine adsorption molecules on polar surfaces could be of interest for differentiating amino acid molecules.) We have shown that although experiments were performed in the absence of any external electronic excitation (optical or thermal), the adsorption was still affected by polarization with preferential deposition occurring on the positive domains. This observation allows us to exclude selective molecular adsorption due to the surface charge resulting from, for example, the pyroelectric effect, restricting the possible surface interactions to polarization-dependent surface chemistry and dipole-dipole interaction.

Periodically poled lithium niobate (PPLN) substrates of congruent composition, which are similar to the ones used in Ref. 13, were used as the ferroelectric substrates. At room temperature, lithium niobate exhibits a hexagonal symmetry with polarization along the *c* axis (polar axis), which allows only two possible domain orientations (*c*+ and *c*–). The stripe domain pattern with a period of ~28 μm has been fabricated by depositing a photoresist mask on the +*c* sample face and by applying a voltage of 10 kV through a fixture

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FIG. 1. (Color) The spatial localization of the d-cysteine molecules on a periodically poled lithium niobate detected using an infrared spectramicroscopy with a blue contrast indicating a higher degree of adsorption. The inset at the left shows a PFM phase image of domains (at the same magnification as the infrared microscopy image). Positive domains appear with dark PFM contrast. The inset at right shows a low-resolution infrared microscopy image of a larger ($100 \times 300 \mu\text{m}^2$) portion of the same sample. Darker stripes in the inset correspond to regions covered with d-cysteine molecules.

with an electrolyte solution. The mask has been removed after poling by means of chemical-mechanical polishing leaving behind a bare ferroelectric surface. As a result, periodic domain patterns containing stripes of antiparallel 180° domains, with their dipoles oriented either positive or negative along the surface normal have been produced (left inset in Fig. 1). Atomic force microscopy (AFM) analysis of the surface topography showed that the resulting surfaces were smooth with no features that can be associated with the domain stripes. Polarity of domains was determined by monitoring the phase of their electromechanical vibration using piezoresponse force microscopy (PFM).²⁰

Spatially resolved x-ray absorption near edge spectroscopy (μ -XANES) experiments were performed at the microXAS beamline (X05, Swiss Light Source, Switzerland). A microfocused x-ray beam of $2 \times 2 \mu\text{m}^2$ and a solid-state Si-detector was utilized in order to record the μ -XANES spectra. The energy of the incident x-ray beam was set using a fixed-exit Si(111) double-crystal monochromator, with an energy resolution of about 2 eV at 19 keV.

Deposition of d-cysteine molecules on PPLN has been carried out by immersing the PPLN substrate in aqueous 1M d-cysteine solution for 24 h. Following immersion, the samples were washed in a weak 1M NaOH alcohol-water solution to remove excess molecules followed by rinsing in ethanol using the previously described cleaning process¹¹ and dried. Deposition was carried out in isothermal conditions at room temperature without illumination. Spatially resolved chemical mapping has been performed using infrared spectramicroscopy to determine the domain-specific localization of d-cysteine molecules by means of the IR reflection mode of Thermo Nicolet continuum microscope at the synchrotron of the Center for Advanced Microstructures and Devices at Louisiana State University.^{21,22} With the synchrotron as a light source, the infrared incident light is highly plane-polarized and s-polarized in the geometry of the experiment.

Figure 1 shows IR spatial microscopy images of the d-cysteine coverage of the PPLN surface. Blue contrast in Fig. 1 and darker contrast in the right inset correspond to regions covered with d-cysteine molecules. Comparison of the stripe shape of these regions with the periodical domain structure revealed by PFM indicates that d-cysteine adsorption closely follows the polarization pattern. Combined AFM/PFM inspection of the PPLN surface after deposition showed larger accumulation of substance on the positive ends of domains.

The change in the infrared spectra associated with adsorption of d-cysteine on lithium niobate is shown in Fig. 2.

FIG. 2. (Color) (a) IR spectrum on PPLN surface before d-cysteine deposition. [(b) and (c)] Spectrum of d-cysteine molecules on PPLN (b) as compared to the reference IR spectra of solid d-cysteine (c). (d) The calculated vibrational modes of d-cysteine from density functional theory. Note that in the absence of d-cysteine, LiNbO_3 shows little IR absorption in the reflection geometry, as expected. The molecular scissor mode experimentally determined to be at 775 cm^{-1} and calculated to be at 753 cm^{-1} is schematically shown as an inset. This mode (see arrow) occurs in a region where there is no absorption from LiNbO_3 undecorated by d-cysteine, and was used to construct the IR spatial absorption map of Fig. 1.

In the absence of d-cysteine, absorption on the LiNbO_3 (001) surface is weak [Fig. 2(a)]. The characteristic IR absorption lines of d-cysteine are clearly evident in the IR spectra of d-cysteine deposited on LiNbO_3 [Fig. 2(b)], but the huge increase in the relative absorbance of the dipolar molecular scissor mode is a strong indication of d-cysteine aligned with the long molecular axis normal to the surface. The suppression of the other modes of a different symmetry is also consistent with this interpretation. There is some shift of the dipole modes to higher vibrational energies, as has been seen with other dipolar molecules on ferroelectric substrates.²³ Obtaining the IR absorption spectra of molecular adsorbates on transparent wide band gap oxides is widely recognized to be very difficult and intensity of IR vibrational modes of molecular adsorbates on oxide surfaces tend to be about an order of magnitude weaker than observed for the same adsorbate on a metal substrate.^{24–26} Beyond the obvious surface localization, ascertaining the surface density of d-cysteine molecules is difficult from the data available here.

To verify that selective deposition of the d-cysteine molecules is not a result of the change in bulk composition of lithium niobate, spatially resolved x-ray absorption near edge spectroscopy analysis has been performed [Fig. 3(a)]. The spectra were collected in fluorescence mode, with the sample placed at an angle of 45° relative to the incoming x-ray beam, in order to minimize scattering contributions to the fluorescence spectra. XANES spectra taken at various locations on the LiNbO_3 at the spacing of about $10 \mu\text{m}$ in the direction normal to domain boundaries show no change in the absorption fine structure. The absence of the spatial spectral variations indicates that lithium niobate is compositionally uniform and the bulk composition is not altered by the ferroelectric poling. This data also suggest that the selective deposition of d-cysteine is a surface effect influenced by polarization of lithium niobate.

In prior deposition experiments, employing the particles in solution,^{10,27} it has been assumed that the interaction between the deposited ions or charged particles and the ferro-

FIG. 3. (Color) (a) Spatially resolved near edge x-ray absorption fine structure (XANES) spectra taken at the Nb K-edge at a number of different positions (denoted by five different colors) and spaced apart by roughly 10 μm in vertical and horizontal directions. Fluorescence yields are plotted against photon energy. The Nb K-shell edge is at 18.986 keV. (b) D-cysteine showing the free molecule frontier charge densities. Using the calculated Mulliken charge densities, the nitrogen has -0.7 , each oxygen has about -0.5 excess charge (specifically -0.45 and -0.56), and sulfur has only -0.1 excess charge.

electric surface is electrostatic in nature and results from the fact that the ferroelectric holds a bound surface charge arising from its spontaneous polarization. However, in an aqueous solution, the formation of an electric double layer due to the adsorption of water dipoles or different ionic species should lead to essentially complete screening of the polarization charges. (For lithium niobate, this is the dominant screening mechanism.¹³) Only generation of uncompensated surface charges via band gap illumination or temperature change resulted in polarization-specific adsorption. In present experiment, adsorption of the d-cysteine molecules occurs in the isothermal conditions and without optical excitation. Hence, it cannot be attributed to the effect of pyroelectric or photoinduced charge. The data suggest that polarization-dependent surface chemistry can be implicated in the selective adsorption of d-cysteine. Nonetheless, the indications of a preferential alignment of adsorbed d-cysteine molecules along the surface normal, while not completely inconsistent with a polarization-dependent surface chemistry do suggest that interface dipole-dipole interaction should play a role as well. The d-cysteine molecules largely contain a nonpolar thiol group (-0.1 excess charge on S), a polar amine group (-0.75 excess charge on N), and a polar carboxylate group (-0.45 and -0.56 excess charge on each oxygen, respectively), as derived from density functional theory (the standard B3LYP function) and illustrated in Fig. 3(b). The latter two groups possibly participate in the dipole-dipole interaction with the polar lithium niobate surface and thus cause polarization-dependent adsorption. Polarization-dependent surface reconstructions and surface relaxations are indicated by the apparent variations of Li/Nb concentration ratios at the lithium niobate surface determined from temperature dependent Auger electron spectroscopy, while the possibility of defects at the surface mediated by the polarization are suggested by the changes in the O/Nb ratio.^{28,29} Non-uniformity of surface composition can also explain considerable variations in d-cysteine concentration along the domain stripes.

In summary, the polarization-specific adsorption of d-cysteine on periodically poled lithium niobate during isothermal deposition from solution has been studied by means

of infrared spectromicroscopy and XANES spectroscopy. The reported effect is attributed to dipole-dipole interaction between polar d-cysteine molecules and ferroelectric polarization dipoles. Surface chemistry related to polarization-dependent variations in Li/Nb concentration is also implicated as a contributing factor in the domain-specific adsorption of d-cysteine.

This work was supported by the National Science Foundation (through Grant Nos. NIRT DMR-0403871 and CHE-0909580) and the Nebraska Center for Materials and Nanoscience at University of Nebraska-Lincoln. The authors would like to thank O. Kizilkaya and the staff of the Center for Advanced Microstructures and Devices (CAMD).

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