

Scanning Tunneling Microscopy and Spectroscopy Studies of Glycine on Cu(100): Inelastic-Tunneling Manipulation of Single Glycine Molecule

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The chemical reaction of a glycine molecule on a Cu(100) surface from the neutral ($\text{NH}_2\text{CH}_2\text{COOH}$) to the glycinate ($\text{NH}_2\text{CH}_2\text{COO}^-$) form via deprotonation, which had been analyzed on the basis of the results obtained by, for example, vibrational spectroscopy and diffraction methods, was studied at the single-molecule level by scanning tunneling microscopy (STM) and spectroscopy. The chemical reaction was successfully reproduced by the inelastic tunneling process through deprotonation. The threshold bias voltage for the reaction process could be attributed to the energy of the O–H stretch vibrational mode, and the asymmetric STM image after the reaction was in good agreement with the structure based on the predicted model. [DOI: 10.1143/JJAP.47.6153]

KEYWORDS: scanning tunneling microscopy, glycine, single molecule, manipulation, Cu, amino-acid, inelastic electron tunneling

1. Introduction

The development of novel devices based on ultrasmall molecular structures, which consist of functional molecules such as biological molecules, is one of the most attractive goals of current research. The glycine molecule is the simplest amino acid with carboxyl and amino groups, which are both common to all amino acids, and is one of the fundamental components of biological molecules such as proteins and peptides. Owing to the basic and practical interest in this material, self-assembled molecular structures of glycine adsorbed on a Cu surface have been widely studied.^{1–7} Recently, an anisotropic two-dimensional free-electron-like electronic structure was realized for glycine on a Cu(100) surface, which has made this system further attractive.⁶

Glycine molecules are evaporated in a neutral form ($\text{NH}_2\text{CH}_2\text{COOH}$). When the substrate is maintained at room temperature (RT), the hydrogen atom in the carboxyl group is removed from the surface and glycine molecules are adsorbed in a glycinate form ($\text{NH}_2\text{CH}_2\text{COO}^-$). Among the amino acids, glycine is the only molecule that does not have chirality, but enantiomeric isomers are observed on the Cu surface depending on the directional relationship of the two groups in the adsorbed form, as schematically shown in Fig. 1. The adsorption properties of this system have been expected to provide us with the basis for the understanding of, and a method of applying, the mechanism of the self-assembly of a polarized molecule with chirality. For further advance, the control and analysis of individual single molecules is of great importance.

Scanning tunneling microscopy (STM) is not only for microscopic observation, but also a novel technique of inducing chemical reactions on the atomic scale using tunneling current, which may not be achieved in an ordinary way, for example, the irradiation of light or electrons, because of the diffraction limit. Although various processes are included in chemical reactions, pinpoint manipulations are realized through inelastic tunneling. Therefore, for the purpose described above, STM has been extensively used these last few decades.^{8–11}

In this study, we analyzed the inelastic-tunneling induced chemical reaction of isolated glycine molecules adsorbed on

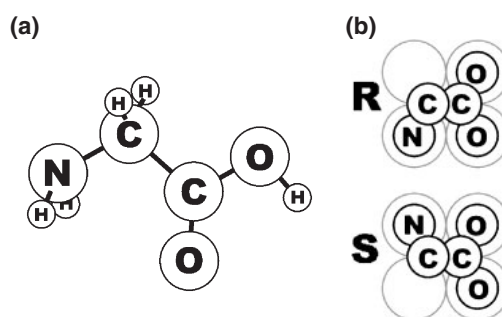


Fig. 1. (a) Molecular structure of glycine molecule. (b) Two conformations of adsorbed glycine molecule on a Cu(100).

a Cu(100) surface by STM at 5 K. The structural transformation of the glycine molecule from its neutral form, $\text{NH}_2\text{CH}_2\text{COOH}$, to a glycinate form, $\text{NH}_2\text{CH}_2\text{COO}^-$, was successfully observed.

2. Experimental

Sample preparation and STM measurements were performed under ultrahigh-vacuum conditions (base pressure $< 1 \times 10^{-8}$ Pa). A clean Cu(100) surface was obtained after several cycles of Ar^+ ion bombardment and annealing at 820 K. After the glycine source was outgassed by heating the Al_2O_3 crucible at 330 K for 5 hours, glycine molecules were adsorbed on the substrate, where the source and Cu sample temperatures were maintained at 370 and 5 K, respectively. Then STM measurements were performed at 5 K using an electrochemically sharpened tungsten tip ($\phi = 0.3$ mm).

3. Results and Discussion

Figure 2(a) shows a typical STM image of the isolated glycine molecules adsorbed on a Cu(100) surface at 5 K. Although molecules form the $c(2 \times 4)$ or $p(2 \times 4)$ periodic structure on the Cu surface when they are adsorbed at room temperature,⁷ molecules are individually observed in this case. Most of the molecules were imaged as an egglike shape as shown by A and B, while a small number of molecules exhibited a bright round shape, as shown by C in Fig. 2(a). The egglike spots had their long axis along one of the four crystal axes, $[010]$, $[0\bar{1}0]$, $[001]$, and $[00\bar{1}]$,

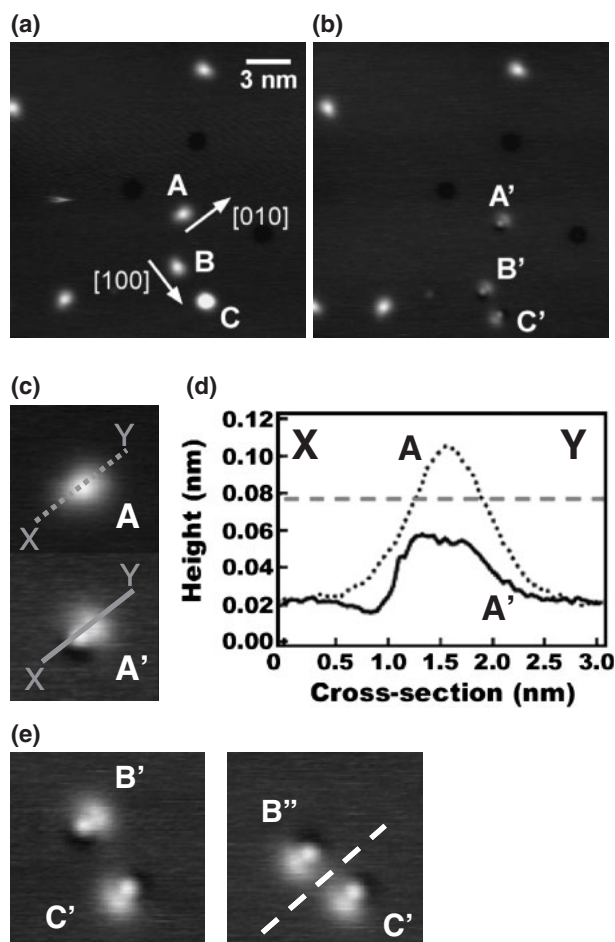


Fig. 2. (a) STM topographic image obtained at 5 K. (b) STM image after excitation of molecules A, B, and C in (a) by applying bias voltage (500 mV, 10 s). (c) Magnified images of a glycine molecule before (upside) and after (downside) excitation. (d) Cross-sections along X–Y in (c). (e) Hopping and sliding of molecule B' (to B'') due to excitation. White dashed line is a mirror plane.

indicating the existence of a specific interaction of the molecules with the Cu(100) surface.

According to a vibrational spectroscopy study, when the Cu substrate is kept a low temperature (<77 K), adsorbed glycine molecules retain the structure of $\text{NH}_2\text{CH}_2\text{COOH}$, while, with increasing substrate temperature, deprotonation from the carboxylic group is induced, resulting in the formation of the glycinate form, $\text{NH}_2\text{CH}_2\text{COO}^-$.¹⁾ This chemical reaction is expected to have occurred in the previous experiments on the formation of self-assembled structures, where molecules were adsorbed at RT.⁷⁾

To study the transformation mechanism of the molecules on the Cu surface, we performed the STM-induced manipulation of single glycine molecules. The STM tip was held over the top of three molecules, A, B, and C, and they were excited by the tunneling current under the condition of a sample bias voltage of +500 mV applied for 10 s for each molecule. After this treatment, the three molecules changed to the same shape, as shown by images A', B', and C' in Fig. 2(b), respectively. A slight positional change caused by hopping of the molecule induced by the application of voltage was observed in the procedure, as shown by B and B' in Figs. 2(a) and 2(b), respectively. Repetitions of this procedure induced changes in the molecular position or the

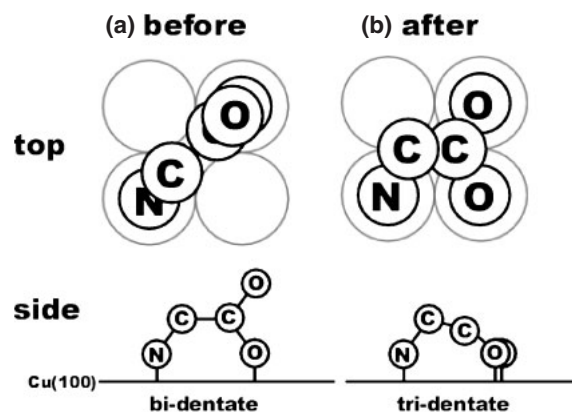


Fig. 3. Schematic illustrations of a glycine molecule adsorbed on a Cu(100) surface (a) before and (b) after the excitation treatment by STM.

direction of its axis, namely, hopping or sliding, but never caused an opposite directional change in the shape, for example, B' to B. Figure 2(e) shows an example of this experiment. A second excitation was applied to B' in Fig. 2(b), resulting in the rotation and hopping of molecule B' to B'', as shown by its positional and directional relationship to C'.

Two marked changes were observed in the molecular images from Fig. 2(a) to Fig. 2(b). One is the change in the shape of the molecule. An internal structure with an asymmetric shape is imaged after the treatment, as clearly shown by the magnified images in Fig. 2(c). This change in the molecule generates chirality, as shown in the schematic model in Fig. 1. The other characteristic is the lowering of the topographic geometry. Cross sections obtained for the STM images along the lines X–Y on molecules A and A' in Fig. 2(c) are shown in Fig. 2(d), where, the dotted line represents the height obtained for a molecule in the $c(2\times 4)$ structure.⁷⁾

Figure 3 shows schematic illustrations of a glycine molecule adsorbed on the Cu(100) surface before and after the excitation treatment by STM. Since the unreacted molecule with hydrogen in the carboxylic group was observed as the achiral egglike shape directed along the $\langle 100 \rangle$ axis of the Cu(100) substrate, its possible structural model is the bidentate structure produced by the binding of a nitrogen atom of the amino group and an oxygen atom of the carbonyl group ($-\text{C}=\text{O}$) with the substrate Cu atoms, as shown in Fig. 3(a), where the hydroxyl group ($-\text{OH}$) is away from the substrate. If the structural change of the molecule induced by the treatment is deprotonation, the glycine molecule has a flat tridentate structure with the one nitrogen and two oxygen atoms in the molecule bonded to the top of the Cu substrate atoms [Fig. 3(b)], then the height becomes lower than the structure before the treatment, as was observed.

Here, the height of the glycine molecule in the $c(2\times 4)$ arrangement is between the heights observed for those before and after the treatment. This result may indicate that molecules have a slightly standing conformation in the $c(2\times 4)$ arrangement owing to the interaction between molecules in the structure. For molecule C in Fig. 2(a), a possible adsorbed structure that produces the observed high geometry is either a carboxylic or an amino group bound to a

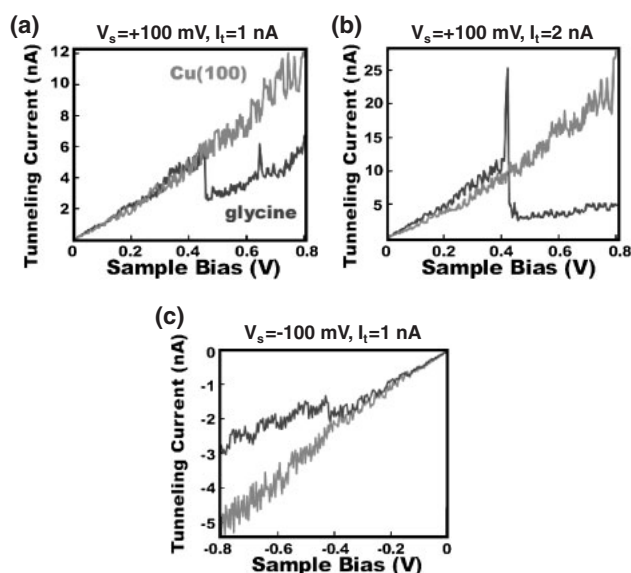


Fig. 4. Typical I - V curves measured for a bare Cu(100) surface and isolated glycine molecules. Rapid change in the tunneling current presents the chemical reaction due to protonation.

substrate Cu atom, with the other groups being away from the substrate.

To confirm the mechanism of deprotonation in greater detail, we analyzed the threshold for the reaction process by changing the set point of the measurement. We placed the STM tip just above the target molecules under various set point conditions and measured current-voltage (I - V) curves by changing the bias voltage from 0 to ± 0.8 V. Since such as hopping and rotation of the molecule were excited by the applied bias voltage lower than that for the deprotonation, it was difficult to determine the vibrational mode in ordinary way. To achieve the chemical reaction, we swept the voltage 100 times faster (500 mV/s) than that for the ordinary IETS measurement (5 mV/s).

Due to hopping and rotation of the molecule excited by the applied bias voltage, the molecular position, therefore, I - V curve measurement was not stable. However, when the chemical reaction was induced, the I - V curve showed a sudden increase or decrease from the linear I - V line. In such a case, we could confirm the occurrence of deprotonation by STM observation. Figure 4 shows typical I - V curves with such changes obtained under different measurement conditions: (a) $V_s = +100$ mV, $I_t = 1$ nA, (b) $V_s = +100$ mV, $I_t = 2$ nA, (c) $V_s = -100$ mV, $I_t = 1$ nA. The bias voltage was increased at from 0 to $+0.8$ V in (a) and (b), and decreased from 0 to -0.8 V in (c). The voltage of the reaction for each set point was (a) 451 ± 4 , (b) 431 ± 4 , and (c) 427 ± 4 mV, respectively, where the uncertainty of ± 4 mV is the sweep step of the bias voltage. The values are close to each other independent of the tunneling current and polarity of the sample bias voltage, suggesting that the reaction is caused by an inelastic tunneling process.

Since it was difficult to determine the exact value of the threshold, measurements were performed several times at each condition, and the lowest bias voltage among those which produced sudden change as shown in Fig. 4 was

defined as the threshold, 427 ± 4 mV. It is well known that chemical reactions are induced by the excitation of specific internal molecular vibrations in inelastic tunneling processes. The threshold energy observed seems closer to the value of the NH_2 symmetric stretch vibrational mode ($3414 \text{ cm}^{-1} = 423 \text{ meV}$) than the O-H stretch vibrational mode ($3566 \text{ cm}^{-1} = 442 \text{ meV}$) of the glycine molecule. However, since the chemical reaction process of a glycine molecule on a Cu(100) surface is the transformation from the neutral ($\text{NH}_2\text{CH}_2\text{COOH}$) to the glycinate ($\text{NH}_2\text{CH}_2\text{COO}^-$) form due to deprotonation,¹⁾ the excitation of O-H vibrational mode is more probable. In fact, the energies of the vibrational modes are those calculated for a free molecule and it was reported that the energy of the NH_2 vibrational mode decreased to 402 meV by the formation of a NH_2 -Cu bonding.¹⁾ Therefore a similar change of the O-H stretch vibrational mode, ~ 20 meV decrease in the energy due to adsorption on a Cu surface, may have an energy close to the observed value.

4. Conclusions

We observed adsorbed isolated glycine molecules on a Cu(100) surface. The chemical reaction process of a glycine molecule from the neutral ($\text{NH}_2\text{CH}_2\text{COOH}$) to the glycinate ($\text{NH}_2\text{CH}_2\text{COO}^-$) form via deprotonation, which had been analyzed on the basis of the results obtained by, for example, vibrational spectroscopy and diffraction methods, was successfully reproduced at a single-molecule level by the inelastic tunneling process induced by STM. The threshold bias voltage for the reaction process could be attributed to the O-H stretch vibrational mode, and the asymmetric STM image after the reaction was in good agreement with the structure based on the predicted model.

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- 1) S. M. Barlow, K. J. Kitching, S. Haq, and N. V. Richardson: *Surf. Sci.* **401** (1998) 322.
- 2) V. Efstathiou and D. P. Woodruff: *Surf. Sci.* **531** (2003) 304.
- 3) X. Zhao, H. Wang, R. G. Zhao, and W. S. Yang: *Mater. Sci. Eng. C* **16** (2001) 41.
- 4) K. Mae and Y. Morikawa: *Surf. Sci.* **553** (2004) L63.
- 5) R. B. Rankin and D. S. Sholl: *J. Phys. Chem. B* **109** (2005) 16764.
- 6) K. Kanazawa, Y. Sainoo, Y. Konishi, S. Yoshida, A. Taninaka, A. Okada, M. Berthe, N. Kobayashi, O. Takeuchi, and H. Shigekawa: *J. Am. Chem. Soc.* **129** (2007) 740.
- 7) K. Kanazawa, A. Taninaka, O. Takeuchi, and H. Shigekawa: *Phys. Rev. Lett.* **99** (2007) 216102.
- 8) S.-W. Hla, L. Bartels, G. Meyer, and K.-H. Rieder: *Phys. Rev. Lett.* **85** (2000) 2777.
- 9) W. Ho: *J. Chem. Phys.* **117** (2002) 11033, and references therein.
- 10) J. I. Pascual, N. Lorente, Z. Song, H. Conrad, and H.-P. Rust: *Nature* **423** (2003) 525.
- 11) Y. Sainoo, Y. Kim, T. Okawa, T. Komeda, H. Shigekawa, and M. Kawai: *Phys. Rev. Lett.* **95** (2005) 246102.