Formation of homochiral glycine/Cu(111) quantum corral array realized using alanine nuclei

2015 Jpn. J. Appl. Phys. 54 08LB05

(http://iopscience.iop.org/1347-4065/54/8S2/08LB05)

Japanese Journal of Applied Physics **54**, 08LB05 (2015) **REGULAR PAPER**
http://dx.doi.org/**10.7567/JJAP.54.08LB05**

Formation of homochiral glycine/Cu(111) quantum corral array realized using alanine nuclei

Miki Nakamura, Hui Huang†, Ken Kanazawa, Atsushi Taninaka, Shoji Yoshida, Osamu Takeuchi, and Hidemi Shigekawa*

Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Received November 18, 2014; accepted January 13, 2015; published online July 13, 2015

Glycine has enantiomeric isomers on a Cu(111) surface through the dissociation of hydrogen from the carboxyl group and forms an array of quantum corrals of ~1.3 nm diameter. Stable homo-chiral glycinate trimers are formed in the first step, which subsequently form a network with a hexagonal arrangement. However, domains with R- or S-chirality coexist with the same probability. On the other hand, α-alanine has D- and L-chirality in nature and forms a similar quantum corral array on Cu(111) with R- and S-chirality, respectively. Here, by using α-alanine molecules as nuclei, the chirality of glycine molecules was controlled and a homochiral quantum corral array was successfully formed, which indicates the possibility that the optical isomers can be separated through a method such as preferential crystallization.

1. Introduction

The understanding and control of self-organization is a key factor for the development of functional devices based on a variety of molecular characteristics. Among them, chirality plays an important role, for example, in molecular recognition, polymerization, optical functionalization and catalytic reactions.[1–4] On the other hand, with the advancement of surface science techniques, analyses of the molecular dynamics on solid surfaces have provided important bases for the development of molecular technologies as well as for understanding the elemental interactions producing a variety of molecular functions. Scanning tunneling microscopy (STM) is a promising technique because of its capability to analyze the electronic structures of target materials together with their atomic and/or molecular structures. Many interesting results have been obtained in studies on self-assembled monolayers (SAMs).[5–21]

Recently, STM has been applied to study SAMs of glycine and alanine molecules on Cu(110),[12,13] Cu(111),[14–18] and Cu(001)[19–21] surfaces and has shown the importance of chirality in their self-organization mechanisms and in producing their characteristic electronic structures. Glycine and alanine are interesting molecules because of their specific characteristics regarding chirality. Among the naturally occurring α-amino acids, glycine is the only molecule that does not have chirality [Fig. 1(a)], although enantiomeric isomers appear on a Cu surface at room temperature (RT) through the dissociation of hydrogen from the carboxyl group owing to the freedom of the directional relationship between the two groups in the adsorbed form [the R- and S-figures in Fig. 1(c)]. On the other hand, alanine has two isomers, α- and β-alanine. β-alanine has a structure with an additional methylene group ($-CH_2-$) in its main chain compared with glycine and does not have chirality, similarly to glycine, while α-alanine naturally has R- or S-chirality (D- and L-alanine, respectively) as shown in Figs. 1(b) and 1(d).[15,16]

For the cases of glycine and β-alanine molecular structures on a Cu(001) surface, two-dimensional electron gas (2DEG) states with standing waves have only been observed for the $p(2 \times 4)$ arrangement consisting of both R- and S-glycine molecules.[19] The anisotropic ratios of the effective masses were 10 for glycine[19] and 3.6 for β-alanine.[20] In contrast, in the cases of glycine and α-alanine on a Cu(111) surface, glycine forms homochiral domains consisting of R- or S-chirality through the formation of enantiomeric isomers,[15,17] and similar quantum corrals with R- and S-chirality are formed by D- and L-alanine, respectively.[16] However, the experimental results show the observed confinement energies formed by glycine and alanine molecules to be slightly different, 0.3 eV for glycine[17] and 0.5 eV for alanine.[16] These results indicate that the control of interactions based on chirality and the modification of molecules, the addition of a methylene group to glycine in this case, play key roles in the formation and control of the molecular and electronic structures of SAMs. However, few analyses have been carried out so far on the combination of these factors.

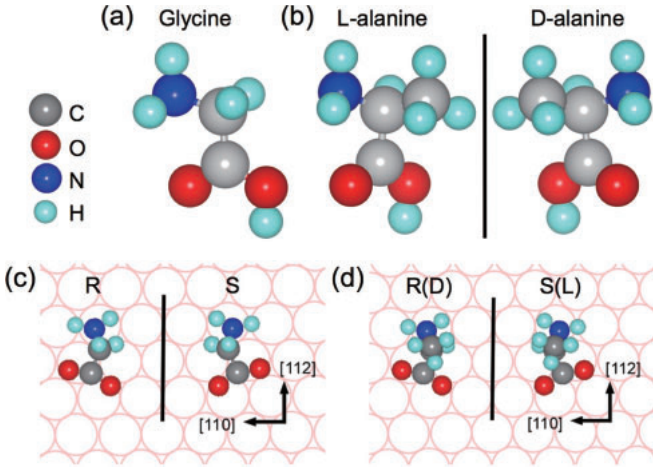

Fig. 1. (Color) Schematic structures of (a) glycine and (b) α-alanine molecules, and their conformations on a Cu(111) surface (c, d).

Here, as a first step to achieving a new methodology for controlling the electronic structures of SAMs, we attempted to control the chirality of quantum corrals formed by glycine on a Cu(111) surface by adding α-alanine as nuclei using the ability of chirality recognition, which was confirmed in this study, between glycine and alanine molecules.

2. Experimental procedure

A clean Cu(111) surface was prepared by three cycles of Ar^+ ion bombardment and annealing at 820 K. The glycine and α-alanine sources were outgassed by heating an Al_2O_3 crucible at 330 K for 5 h. Glycine and/or α-alanine (D- or

†Present address: Hefei University, China.

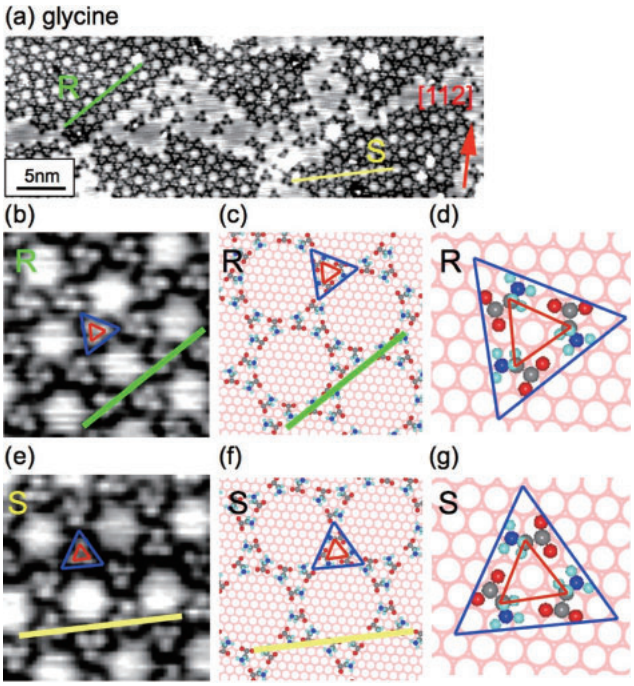

Fig. 2. (Color) (a) Quantum corral domains with R- and L-chirality formed by glycine molecules ($V_s = -0.5$ V, $I_t = 0.5$ nA). Magnified images of quantum corrals consisting of six trimers with (b) R- and (e) L-chirality. Schematic models of quantum corrals (c, f) and trimers (d, g), with R- and L-chirality, respectively. Green and yellow lines indicate the directions used to discriminate between the R- and S-arrangement, respectively.

L-alanine) were adsorbed on the Cu(111) substrate depending on the experiment, where the source and Cu sample temperatures were maintained at 370 K and RT, respectively. After molecular deposition on the clean Cu(111) surface, the sample was annealed at 350 K for 1 h. Then, STM measurements were performed in ultrahigh vacuum ($<1 \times 10^{-8}$ Pa) at 77 K using a tungsten tip.

Experiments were carried out in four steps: (1) formation of quantum corrals by glycine molecules to compare the results with those in Ref. 17, (2) formation of quantum corrals by each of D- and L-alanine molecules to compare the results with those in Ref. 16, (3) formation of quantum corrals by co-adsorption of D- and L-alanine molecules, and (4) control of the chirality of glycine molecules by using D- or L-alanine molecules as a nuclei. The last two steps show new results obtained in this work.

3. Results and discussion

Figure 2(a) shows a typical STM image of quantum corrals formed by the glycine/Cu(111) structure where R- and S-glycine domains exist separately, as was observed in our previous study.[17] Figures 2(b) to 2(g) show magnifications and schematic models. For both chiralities, the array of quantum corrals is formed by homochiral ring structures [(b, c) and (e, f)] with six glycine trimers (d, g), which consist of three of the homochiral glycinate molecules shown in Figs. 1(a) and 1(c). The green and yellow lines indicate the directions used to discriminate between the R- and S-arrangements, respectively.

Next, as the second step, we formed quantum corrals by the deposition of pure D- and L-alanine molecules, which respectively resulted in the formation of quantum corrals with R- and L-chirality, as expected. Figure 3 shows a typical STM image obtained for the case of L-alanine. Quantum corrals with S-chirality were clearly observed. In contrast to the case of glycine, there are white images in some quantum corrals, as indicated by red arrows, reflecting the temporally averaged images of the motion of extra alanine molecules trapped in quantum corrals.[16]

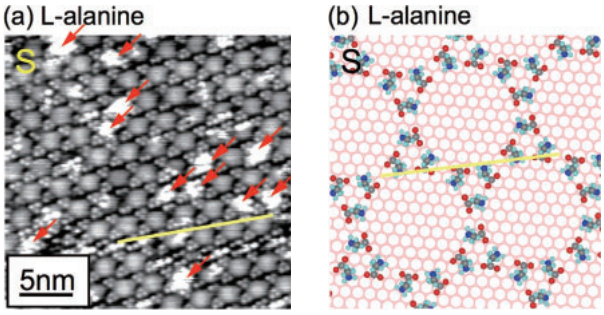

Fig. 3. (Color) (a) STM image ($V_s = -0.5$ V, $I_t = 1.0$ nA) and (b) schematic model of quantum corrals consisting of L-alanine. Yellow lines indicate the directions used to show the S-arrangement. White images indicated by the red arrows show the temporally averaged motions of alanine molecules trapped in the quantum corrals.

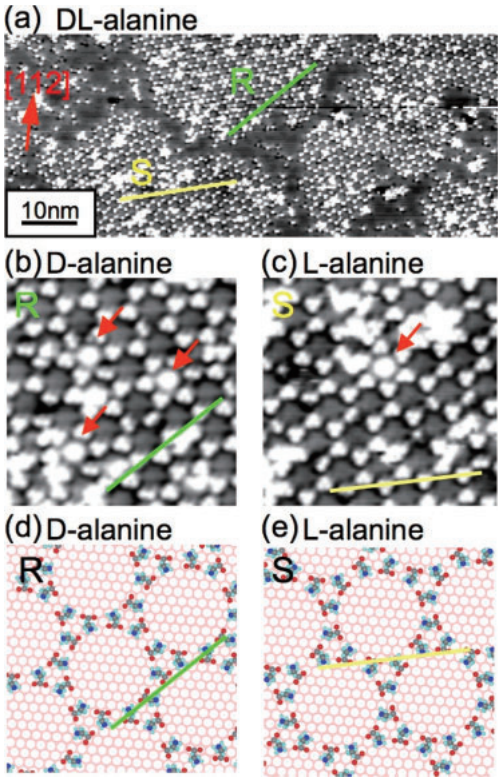

Fig. 4. (Color) (a) Quantum corral domains formed by the co-adsorption of D- and L-alanine molecules with R- and L-chirality, respectively ($V_s = -1.0$ V, $I_t = 0.1$ nA). Magnified images of quantum corrals with (b) R- and (c) L-chirality and their schematic models (d, e). Green and yellow lines indicate the directions used to discriminate between the R- and S-arrangement, respectively. White images indicated by the red arrows show the temporally averaged motions of alanine molecules trapped in the quantum corrals, corresponding to those in Fig. 3(a).

Subsequently, as the third step, quantum corrals were formed by the co-adsorption of D- and L-alanine molecules. Figure 4(a) shows a typical STM image of the alanine/Cu(111) surface. Figures 4(b) to 4(e) show magnifications of

the two types of domains and their schematic models. As shown in Fig. 4(a), the D- and L-alanine molecules recognized chirality, and homo-chiral domains with D- and L-alanine molecules were separately formed, as was observed for the case of glycine molecules shown in Fig. 2(a). The red arrows indicate the temporally averaged images of the movement of alanine molecules trapped in the quantum corrals, as was pointed out for those in Fig. 3(a). Although glycine molecules formed a racemic body because they have chirality upon self-organization, since domains with R- and S-chirality appear, the body is not a general racemic compound but a racemic conglomerate in which both enantiomers are crystallized separately. On the other hand, a racemic conglomerate is also formed when D- and L-alanine molecules are co-adsorbed. These results indicate the possibility that a racemic compound can be changed into a racemic conglomerate by self-organization on a Cu surface.

Although the structures shown in Figs. 2(a) and 4(a) are similar, α-alanine naturally has R- or S-chirality (D- and L-alanine, respectively), in contrast to the enantiomeric isomers of glycine. Namely, in the formation of a homochiral domain by glycine molecules, the chirality may change between the D- and L-conformations during the annealing; however, alanine maintains its chirality after adsorption. Therefore, the diffusion of molecules must be sufficient to form domains whose size is as large as those of glycine. On the other hand, there are some defects in the trimers, as shown in Figs. 4(b) and 4(c). This is considered to be due to the fact that even single and dimer structures are stable on the Cu(111) surface for the case of alanine, whereas only the trimer structure is stable for the case of glycine.

Considering the experimental results obtained for glycine and α-alanine molecules, we attempted to control the chirality of glycine molecules by blending a small amount of D- or L-alanine molecules to act as nuclei to form homochiral quantum corrals of glycine, the forth step described above. Namely, if alanine and glycine molecules recognize the chirality of each other and glycine molecules change their chirality, if necessary, to form homochiral pairs and trimers when they make contact with alanine molecules or reach the edge of glycine molecules trapped by the nuclei of alanine molecules, quantum corrals with the chirality of the blended alanine molecules, thereby their domains are supposed to be formed.

Figures 5(a) and 5(b) show the L-alanine molecules adsorbed on a Cu(111) surface in a wide area and a high resolution image and its magnification of the area indicated by the yellow square, respectively. As shown in Fig. 5(b), the image has the characteristic of trimers consisting of glycine molecules, i.e., bright spots and three regions of depression that are darker than the original substrate, suggesting the electronic structure similar to that of glycine.[17] In addition to the trimer structures, however, there are some structures consisting of single and double alanine molecules, indicating the fact that alanine molecules are stable even in those forms.

After confirming the structure shown in Fig. 5(a), glycine molecules were adsorbed on the surface and Fig. 5(c) shows the quantum corrals formed after the adsorption. As indicated by the yellow lines, all domains consist of molecular structures with S-chirality. Since glycine molecules are expected to have R- and S-chirality with the same probability

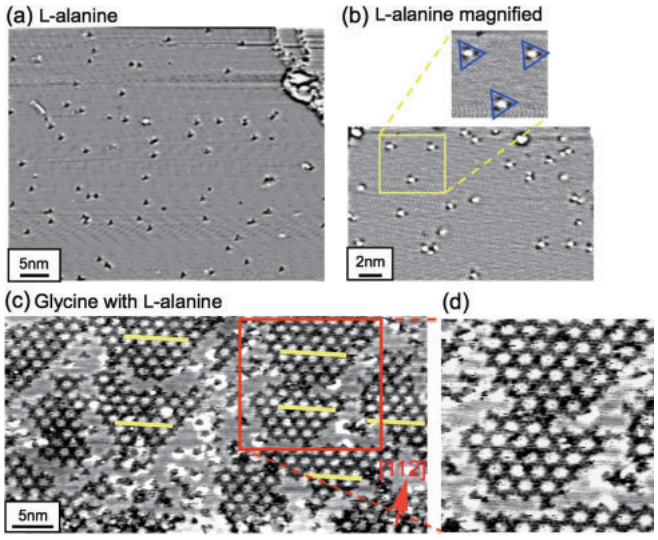

Fig. 5. (Color) (a) STM image of L-alanine molecules on a Cu(111) surface and (b) a high resolution image and its magnification of the area indicated by the yellow square ($V_s = -0.5$ V, $I_t = 1.0$ nA). (c) STM image of quantum corrals formed by glycine molecules deposited onto the surface shown in (a). (d) Magnification of the red square area in (c). Yellow lines indicate the directions used to show the S-arrangement.

when they are adsorbed onto the Cu(111) surface, as was observed in Fig. 2, they are considered to change their chirality when they make contact with L-alanine or reach the edge of a domain grown with S-chirality around the nuclei of L-alanine, as discussed above.

These results indicate first the ability of chirality recognition between glycine and alanine molecules, and the possibility that the optical isomers can be separated through a method such as preferential crystallization, in which a crystal consisting of molecules with the same chirality is grown by introducing an optical isomer to a racemic compound. In addition, as shown in a magnified image of the red squared area in Fig. 5(c) [Fig. 5(d)], quantum corrals mostly do not seem to have alanine molecules inside, which makes this structure more applicable compared to the cases by D- and L-alanine described above.

4. Conclusion

As a first step to achieving a new methodology for controlling the electronic structures of SAMs, we attempted to control the chirality of quantum corrals formed by glycine on a Cu(111) surface by adding α-alanine as nuclei using the ability of chirality recognition between glycine and alanine molecules, and an array of homochiral glycine quantum corrals was successfully formed.

Acknowledgement

Support from the Japan Society for the Promotion of Science in the form of Grants-in-Aid for Scientific Research is acknowledged (22226003).

1) N. Liu, S. Haq, G. R. Darling, and R. Raval, Angew. Chem. **119**, 7757 (2007).
2) M. Lingenfelder, G. Tomba, G. Costantini, L. Colombi Ciacchi, A. De Vita, and K. Kern, Angew. Chem. **119**, 4576 (2007).
3) A. Mugarza, N. Lorente, P. Ordejón, C. Krull, S. Stepanow, M.-L. Bocquet, J. Fraxedas, G. Ceballos, and P. Gambardella, Phys. Rev. Lett. **105**, 115702

(2010).
4) J. Seibel, O. Allemann, J. S. Siegel, and K. H. Ernst, J. Am. Chem. Soc. **135**, 7434 (2013).
5) G. E. Poirier, Chem. Rev. **97**, 1117 (1997).
6) J. V. Barth, J. Weckesser, G. Trimarchi, M. Vladimirova, A. De Vita, C. Cai, H. Brune, P. Gunter, and K. Kern, J. Am. Chem. Soc. **124**, 7991 (2002).
7) T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, and S. Mashiko, Nature **413**, 619 (2001).
8) J. V. Barth, G. Costantini, and K. Kern, Nature **437**, 671 (2005).
9) J. J. A. W. Elemans, S. Lei, and S. Feyter, Angew. Chem., Int. Ed. **48**, 7298 (2009).
10) S. Weigelt, C. Busse, L. Petersen, E. Rauls, B. Hammer, K. V. Gothelf, F. Besenbacher, and T. R. Linderoth, Nat. Mater. **5**, 112 (2006).
11) L. Bartels, Nat. Chem. **2**, 87 (2010).
12) D. I. Sayago, M. Polcik, G. Nisbet, C. L. A. Lamont, and D. P. Woodruff, Surf. Sci. **590**, 76 (2005).
13) D. A. Duncan, W. Unterberger, D. C. Jackson, M. K. Knight, E. A. Kröger, K. A. Hogan, C. L. A. Lamont, T. J. Lerotholi, and D. P. Woodruff, Surf. Sci. **606**, 1435 (2012).
14) X. Zhao, H. Yan, R. G. Zhao, and W. S. Yang, Langmuir **19**, 809 (2003).
15) D. A. Duncan, M. K. Bradley, W. Unterberger, D. Kreikemeyer-Lorenzo, T. J. Lerotholi, J. Robinson, and D. P. Woodruff, J. Phys. Chem. C **116**, 9985 (2012).
16) E. Yitamben, L. Niebergall, R. Rankin, E. Iski, R. Rosenberg, J. Greeley, V. Stepanyuk, and N. Guisinger, J. Phys. Chem. C **117**, 11757 (2013).
17) K. Kanazawa, A. Taninaka, H. Huang, M. Nishimura, S. Yoshida, O. Takeuchi, and H. Shigekawa, Chem. Commun. **47**, 11312 (2011).
18) V. Efstathiou and D. P. Woodruff, Surf. Sci. **531**, 304 (2003).
19) 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**, 740 (2007).
20) K. Kanazawa, A. Taninaka, O. Takeuchi, and H. Shigekawa, Phys. Rev. Lett. **99**, 216102 (2007).
21) K. Kanazawa, M. Nakamura, H. Huang, A. Taninaka, and H. Shigekawa, Surf. Sci. **632**, L1 (2015).