Fabricating Homochiral Facets on Cu(001) with L-lysine

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Asymmetric adsorption of chiral molecules on chiral crystals may occur, and this kind of phenomenon has been applied to liquid chromatography for chiral separations.[1] Moreover, in terms of the asymmetric adsorption of amino acids on chiral quartz, some scientists tried to explain the dominance of L-amino acids in the living organisms.[2,3] We asked whether asymmetric adsorption as well as related phenomena on achiral crystals, such as on transition metals, may also take place? Recent researches[4,5] have shown that although transition metal crystals are achiral themselves, some high Miller index surfaces may be chiral. In principle, similar to the definition of molecular chirality,[6] a crystal surface can be thought of as chiral if it lacks reflection symmetry and center symmetry[2] because such a surface is not superimposable on its mirror image. Since chirality in some high Miller index surfaces of transition metals exists, it should be possible to observe asymmetric adsorption of chiral molecules on such surfaces. Although this idea has been confirmed by Monte Carlo simulations,[5,7] experimental evidences were just recently provided by Ahmadi and co-workers in the electro-oxidation experiments of D- and L-glucose using the chiral Pt{643} electrodes.[8,9]

Recently, we carried out adsorption studies of amino acids on Cu(001), and unexpectedly found the chiral restructuring phenomenon of steps induced by adsorption of L-lysine [(2*S*)-2,6-diaminocaproic acid, NH_2-$(CH_2)_4$-$CH(NH_2)$-COOH]. Amino acids, as the building blocks of proteins, are typical biological molecules. Investigations on their asymmetric adsorption are of added significance.

The experiment was conducted with an ultrahigh vacuum scanning tunneling microscope (UHV STM) system, which was used in previous work on glycine[10] and L-alanine.[11] The Cu(001) sample was cleaned by repeated cycles of argon-ion sputtering, followed by annealing at 650 K. A monolayer of L-lysine was sublimed in ultrahigh vacuum, and characterized in situ by a scanning tunneling microscope.

There are several points that must be emphasized in advance. Considering that STM is a local surface probing technique and just one or two microscopic observations cannot give one convincing evidences, the whole experiment was repeated for seven runs and in each run 10 positions were randomly observed both on the clean and on the deposited surfaces, respectively. In each position the scanning range is ~3000 × 3000 Å^2. The lateral translation scope of the sample, relative to the STM tip, reaches an area of ~2 × 2 mm^2. Therefore, this experiment is statistically significant.

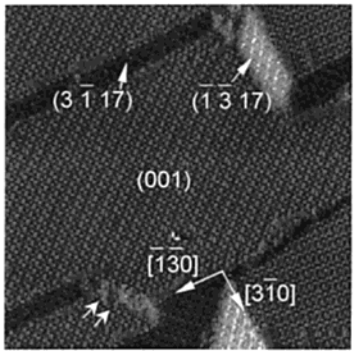

Figure 1. STM image (550 Å × 550 Å, 1.0 V, 0.6 nA) acquired from the L-lysine/Cu(001) surface annealed at 430 K for 20 min, showing coexistence of (001) terraces and {3 1 17} facets formed through bunching of ⟨3 1 0⟩ faceted steps. Note that because of the differential mode, the gray scale has nothing to do with the actual surface height, and the same gray scale represents the same crystal plane. Also note that two neighboring intersection lines of (001) and {3 1 17} planes are always in ⟨3 1 0⟩ directions and thus are perpendicular to each other. As discussed in the text, this is the result of the homochirality of the {3 1 17} facets. (*Notice*: the position where the two parallel arrows point to in the lower left-hand corner is not a regular facet, just some irregularly bunched steps. If annealing time is shorter, such cases can be seen more often.)

At room temperature, L-lysine can form an ordered adsorption structure on Cu(001) terraces. But here we will not consider it. Although in the cases of glycine/Cu(001)[10] and L-alanine/Cu(001)[11] the adsorbates may induce steps faceting to the ⟨3 1 0⟩ directions even at room temperature, L-lysine in the present case only randomly adsorbs on the steps at room temperature. However, the observation shows that although a brief annealing at 430 K is not able to make the steps faceted, an extended annealing such as 20 min at the same temperature can make not only the steps faceted to ⟨3 1 0⟩ directions but also the faceted steps bunched together to form very regular {3 1 17} facets (Figure 1). It is important to note that such facet structures have never been found on the clean Cu(001) surface. The adsorption structure on Cu{3 1 17} is (4 × 1)-L-lysine (see the Supporting Information). After a careful inspection of many images such as Figure 1, it was found that only four kinds of {3 1 17} facets, that is, (−1 −3 17), (3 −1 17), (1 3 17), and (−3 1 17), appeared on the well-annealed surfaces, although in the case of glycine/Cu(001) and L-alanine/Cu(001) all eight kinds of {3 1 17} facets (see below) were observed. The total numbers of the four facets that were observed in the whole experiment are 270, 293, 259, and 285, respectively. However, the other four {3 1 17} facets were *never* observed. We know that the symmetry of the (001) surface of face-centered-cubic copper is C_{4v}. Therefore, there exist eight equivalent ⟨3 1 0⟩ directions on the (001) surface (Figure 2), that is, [1 3 0], [−1 3 0], [−3 1 0], [−3 −1 0], [−1 −3 0], [1 −3 0], [3 −1 0], and [3 1 0], and there also exist eight equivalent {3 1 17} vicinal surfaces around the (001) surface (Figure 2), that is, (3 −1 17), (3 1 17), (1 3 17), (−1 3 17), (−3 1 17), (−3 −1 17), (−1 −3 17), and (1 −3 17). The eight {3 1 17} facets can be divided into two groups: group one consisting of (3 −1 17), (1 3 17), (−3 1 17), and (−1−3 17), and group two consisting of (3 1 17), (−1 3 17), (−3 −1 17), and (1 −3 17). In any group, four {3 1 17} vicinal surfaces are rotationally equivalent, relative to the (001) normal direction, and are of the same chirality, with group one and group two being *R* and *S* configurations,

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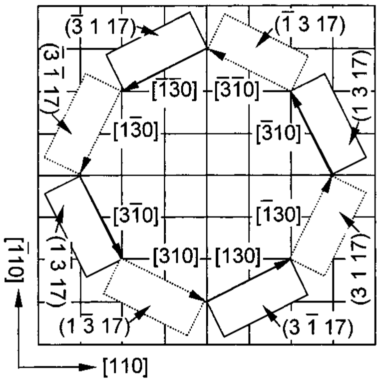

Figure 2. A schematic illustration of the orientational relation between the ⟨3 1 0⟩ steps and {3 1 17} facets. Here, actually the {3 1 17} facets are projected on the (001) plane. The solid and dashed lines denote the ⟨3 1 0⟩ steps and {3 1 17} facets which emerged (*R*-configuration) and did not emerge (*S*-configuration) on the chirally restructured Cu(001) surface, respectively. For the sake of clarity in orientational comparison, a square lattice is used as the background.

respectively, in the nomenclature defined by McFadden et al.[4] Hereafter, group one and group two will be denoted as *R*- and *S*-{3 1 17} facets, respectively.

Here only the *R*-{3 1 17} facets emerged, which clearly indicates that adsorption of L-lysine induces chiral restructuring of steps on Cu(001). From this phenomenon, it is reasonable to suppose that there must exist a difference in adsorption energies of L-lysine on bare (no adsorbates) *R*- and *S*-{3 1 17} facets. According to the reciprocal mechanism[1] of chiral recognition on an independent chiral stationary phase (CSP), that is, the diastereomeric interactions that allow a column derived from chiral A to resolve racemic B also allow a column derived from chiral B to resolve racemic A, further conclusions can be obtained. We know, in the present case, chiral L-lysine resolves "racemic" (*R*- and *S*-) {3 1 17} facets; in turn, chiral (*R*- or *S*-) {3 1 17} facets will resolve racemic lysine. Consequently, this experiment indirectly proves that chiral transition metal surfaces are able to exhibit enantioselectivity.

This experiment, for the first time, demonstrates that a chiral adsorbate can induce an achiral metal surface spontaneously developing intrinsically chiral facets. It is difficult to imagine that such effect is just specific to the L-lysine/Cu(001) system. Schaaff and Whetten have recently reported that gold clusters made using a chiral peptide adsorbate glutathione have unusually strong chiroptical activity.[12] The origin of the optical activity in these clusters has not been firmly established. They interpreted their results in terms of helical structures of Au atoms. According to the present result, an alternative mechanism would be for Au clusters to be close-packed in their cores and to have chiral facets forming their surfaces, induced by the chiral adsorbate glutathione.

In fact, chiral restructuring is a most evident reflection of enantiospecific properties of chiral transition metal surfaces. Many high-index single-crystal surfaces of transition metals have chiral characteristics.[4] Obviously, this experiment further demonstrates that chiral separation and enantioselective heterogeneous catalysis may be carried out directly on them, without participation of any other chiral reagents. By the way, the present experiment would be perfect if two types of control experiments could be performed in future studies. The first is repeating the same experiment on multiple Cu(001) samples to rule out the possibility that the sample used had a net miscut that biased the results toward one crystallographic direction. (In fact, this experiment may be skipped, due to the different *microscopic* local "miscuts" of the sample surface.) The other is repeating the same experiment using D-lysine. This should result in homochiral facets with the opposite chirality to those generated by L-lysine.

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Supporting Information Available: The experimental details and discussion of how the facet index was obtained (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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