

Anisotropic Free-Electron-Like Dispersions and Standing Waves Realized in Self-Assembled Monolayers of Glycine on Cu(100)

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Knowledge and control of the self-organization of materials are the essential foundations not only for understanding the mechanism of the phenomenon but also for the development of functional materials and devices for practical applications. In fact, among the recent developments in nanoscale science and technology, the realization of new functions via self-organization is the basis of many brilliant innovations and is one of the main goals of researchers. Efficient use of the multifold characteristics of organic materials plays important roles.^{1–12}

The formation of nanostructures is achieved, in general, by controlling the direct and indirect interactions between building blocks, originating from, for example, electronic and conformational structures, strains, and chemical reactions. Recently, a selective supramolecular assembly of adsorbed molecules, for example, has been successfully produced through the chemical modification of functional groups.¹ For the further advance of the nanostructure-based functional devices, the understanding and control of the electronic properties of self-organized structures based on such a modification of interactions are key factors for success.

Here, we demonstrate a two-dimensional (2D) anisotropic electronic structure produced through the formation of a self-assembled monolayer (SAM) of glycine molecules on a Cu(100) surface. A standing wave originating from the 2D electronic structure was visualized, for the first time, for the SAM of organic molecules, and the anisotropic dispersion relations reflecting the structure of the SAM were obtained.

Glycine is the simplest amino acid and does not have any active functional groups except for the carboxyl and amino groups, which are common to all amino acids, and one of the fundamental components of biological molecules such as proteins and peptides. 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 ($\text{NH}_2\text{CH}_2\text{COO}^-$).^{12,13} The two oxygen atoms in the carboxylate group and the nitrogen atom in the amino group, which are located on the top sites of Cu(100), are bonded to the Cu atoms, where the carboxyl and amino groups are negatively and positively polarized, respectively. 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 Figure 1c. The adsorption properties of this system are well characterized, indicating the importance of this material for understanding and application of the basic mechanism of the self-organization of a polarized molecule with chirality.

In addition to sample preparation, scanning tunneling microscopy and spectroscopy (STM/STS) measurements were performed under ultrahigh vacuum conditions (base pressure $< 1 \times 10^{-8}$ Pa). A Cu(100) clean surface was obtained after three cycles of Ar^+ ion

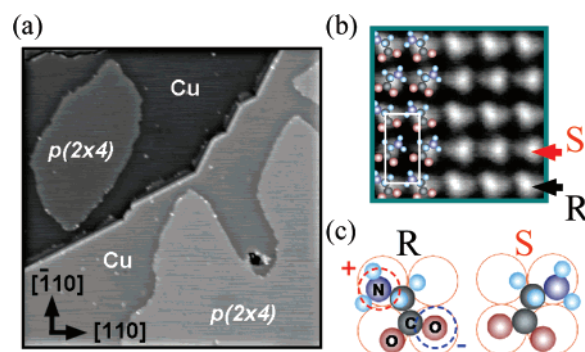


Figure 1. (a) STM image obtained at 5 K ($V_s = -100$ mV, $I_t = 1.0$ nA, 0.4 ML, 150×150 nm²). (b) Magnification of a $p(2 \times 4)$ area with molecular arrangement. (c) Two conformations of an adsorbed glycine molecule.

bombardment and annealing at 820 K. After the glycine source was outgassed by heating the Al_2O_3 crucible at 330 K for 5 h, glycine molecules were adsorbed on the substrate, where the source and Cu sample temperatures were maintained at 370 K and RT, respectively. Then STM/STS measurements were performed at 5 K using a tungsten tip.

Figure 1a is an STM image observed at 5 K of the surface prepared by the adsorption of 0.4 monolayer (ML) glycine. As illustrated in the magnified image (Figure 1b), there is a phase with a $p(2 \times 4)$ periodicity. While the $p(2 \times 4)$ structure is unstable at RT, isolated molecules are stable when the molecules are adsorbed at 5 K. Therefore, the $p(2 \times 4)$ phase structure is formed during the cooling of the sample after molecular deposition.¹⁴ The $p(2 \times 4)$ structure consists of alternately ordered two molecular rows along the $[110]$ direction, which have two different molecular conformations as indicated by red (S) and black (R) arrows in Figure 1c, showing the existence of heterochirality for this structure.

This result indicates that the $p(2 \times 4)$ phase has the pseudo-(2×2) structure.¹⁵ As presented in Figure 1b, the STM image of molecular arrangement is in good agreement with that predicted by the theoretical simulation, and the molecular arrangement is shown (Figure 1b).

Figure 2a shows the $I-V$ (inset) and its derivative spectra obtained for a bare Cu substrate and the $p(2 \times 4)$ structure at 5 K. The $p(2 \times 4)$ structure exhibits a sharp peak near +130 mV. In order to investigate the origin of this signal, we measured the dI/dV images over the area presented in Figure 1a (lock-in modulation = 8 mV, 2.74 kHz, scan speed = 3 ms/pixel, 512×512 pixels).

As shown in the images in Figure 2b, a modulated local density of states (LDOS) is observed, which has a clear bias dependence.

From the bias dependence of the autocorrelations of the modulated LDOS (Figure 3a,b), we obtained nearly free-electron-like dispersion relations, as plotted in Figure 3c. Unlike the substrate symmetry, the dispersion relations are anisotropic, and the effective

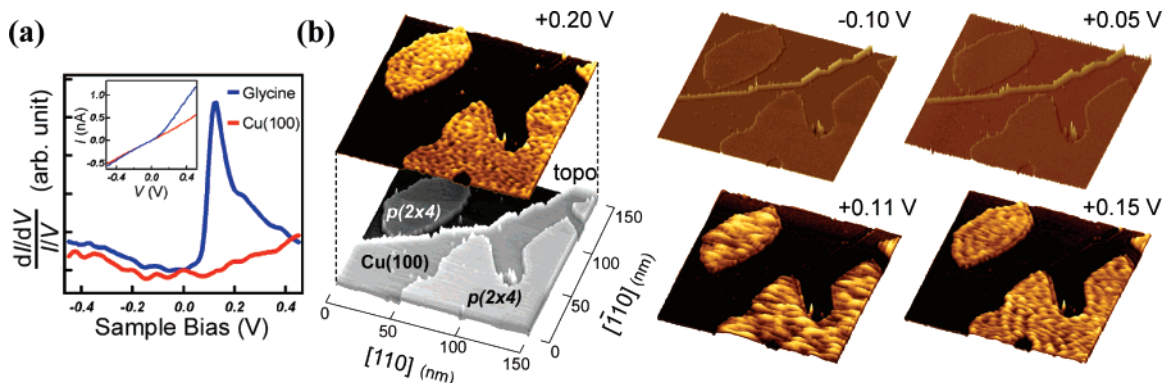


Figure 2. (a) I - V and STS spectra for the glycine $p(2 \times 4)$ structure and bare Cu(100) surfaces obtained at 5 K. (b) STM topographic and dI/dV images obtained at different bias voltages over the same area (set point: $V_s = -100$ mV, $I_t = 1$ nA, 150×150 nm 2).

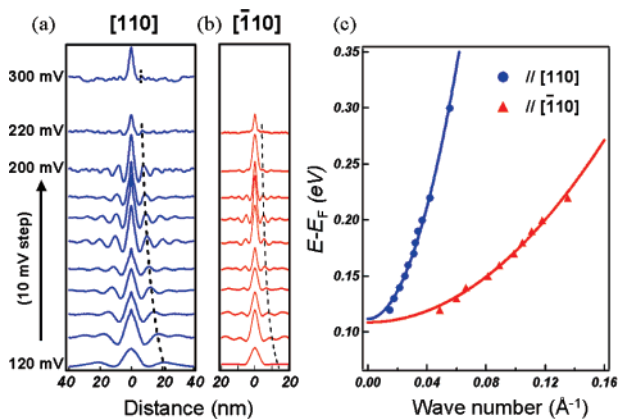


Figure 3. (a) Autocorrelations along (a) $[110]$ and (b) $[\bar{1}10]$ directions, obtained from the 2D autocorrelation of the dI/dV images. (c) Dispersion relations obtained from the autocorrelations in (a) and (b).

masses obtained from the dispersion relations are $(0.061 \pm 0.002)m_e$ for $[110]$ and $(0.61 \pm 0.04)m_e$ for $[\bar{1}10]$ directions.

The observed electronic structures are different from those that may be caused by the Cu(100) substrate, such as simple resonance. Therefore, the observed modulated LDOS can be attributed to the standing wave produced by the electronic states originating from the interaction between the glycine SAM and the Cu substrate. As have been observed, for example, on the (111) surface of noble metals, standing wave, the long-range modulation of LDOS, originates from the quantum interference of low-dimensional free electrons.^{16,17} However, this is the first result that demonstrates the formation of an anisotropic 2D electronic structure in the SAM of an organic material, reflecting the characteristics of the molecular arrangement.

The 10-fold difference in the effective masses is attributed to the anisotropy of the molecular interactions in the SAM; that is, the interaction along the molecular rows in the $[110]$ direction is stronger than the interaction between the molecular rows. In fact, although it is not shown here, the $p(2 \times 4)$ arrangement exhibited some phase defects formed by the substitution of a molecular row of one chirality with a molecular row of the other chirality (appearance of SSS or RRR ordering instead of SRS or RSR as in Figure 1b). This is likely because of a larger overlap of electronic states in molecules along the $[110]$ direction, originating from the carboxyl or amino groups in the molecules (Figure 1b).

The ability to control the electronic structures through chemical modification, for example, by changing functional groups and side chains, is a significant improvement in the design of interactions for producing desired electronic structures.

In summary, an anisotropic 2D electronic structure was formed using the self-organization of glycine molecules on a Cu(100) surface. From the analysis of the standing wave, observed for the first time in the SAM of organic molecules, anisotropic dispersion relations originating from the structure of molecular rows were successfully obtained.

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Supporting Information Available: Procedure of the standing wave analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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