Molecular orbital imaging of cobalt phthalocyanine on native oxidized copper layers using STM

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ABSTRACT

To observe molecular orbitals using scanning tunneling microscopy, well-ordered oxidized layers on Cu(001) were fabricated to screen the individual adsorbed cobalt phthalocyanine (CoPc) molecules from the electronic influence of the metal surface. Scanning tunneling microscope images of the molecule on this oxidized layer show similarities to the orbital distribution of the free molecule. The good match between the differential conductance mapping images and the calculated charge distribution at energy levels corresponding to the frontier orbitals of CoPc provides more evidence of the screening of the oxidized layer from interactions between the metal surface and supported molecules.

1. Introduction

The concept of atomic orbital and consequently molecular orbital (MO) are used to describe the wave-like electrons in atoms or molecules. MO gives us a direct picture of how atoms are bonded together. Shape and orientation of frontier orbitals, i.e. the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), play key roles in chemical reactions and properties of molecules. Theoretically, these can be computed in quantum chemistry, for example, using the linear combination of atomic orbitals (LCAO) method. Towards the end of the last century, scientists were beginning to observe MO images by various advanced methods [1–3], such as observing the d-orbital holes and Cu–Cu bonding in Cu_2O directly by quantitative convergent-beam electron diffraction combined with X-ray diffraction [1], tomographic imaging of the N_2 MOs by using high harmonics generated from intense femtosecond laser pulses focused on aligned molecules [2], and imaging the d-orbitals of Zn atoms as an impurity in cuprate superconductor using a scanning tunneling microscope (STM) [3].

Although scanning tunneling microscopy is a powerful tool enabling surface structure to be characterized at atomic scale, in most cases, the images (in both modes of constant current and constant height) are convolutions of the density of states (DOS) of the surface of all energy levels between the Fermi level and the applied bias voltages. When a molecule is adsorbed on a metal or semiconductor substrate, the image of the molecule depends not only on the configuration but also on the DOS of the molecule–substrate assembly [4,5]. Due to electron gas scattering of the metal surface and the difference between the energy level of MOs and the Fermi levels of the metal, we could not get the MO images by STM, especially for small molecules with σ-bond.

To get orbital images of quasi-free molecules, Repp and Meyer employed an ultra-thin insulating layer of NaCl on metallic surface to eliminate the scattering effect from the metallic surface [6–8]. They obtained the conjugated π MO images of some organic molecules [6]. Generally, frontier orbitals with energy levels beyond the work function of the substrate and the tip (like small molecules with σ-bond) are not suited for STM measurement. To probe these orbitals, we must set high voltages so that the electron can pass through the vacuum gap of an STM via field emission rather than tunneling, which results in lower resolutions.

In our study, we grow a more native oxidized layer of copper to investigate the MOs of CoPc, which not only has conjugated multiple π rings, but also has centered d-orbital binding to the four nitrogen atoms in the rings. We tried to obtain detailed molecular images and then compare to those of the free molecule as well as those of molecules on metal substrate. Quantum simulation was also performed to further understand the CoPc MOs on such surfaces.

2. Experimental

We used a commercial ultra-high vacuum, low-temperature STM (UHV-LT STM, Unisoku Co., Ltd., Japan) equipped with an

e-beam evaporator. All data shown were obtained at 77 K. The Cu(001) substrate was cleaned through repeated Ar^+ sputtering (1 KeV, 30 min) followed by annealing at 750 K. The oxidized layers were prepared by oxidation in which Cu(001) was kept at ~ 500 K under an O_2 pressure of 1×10^{-7} Torr for 10–600 s. A few CoPc molecules were deposited from a heated crucible onto the oxidized layer at a slow rate of ~ 0.01 ML. STM tips were electrochemically-etched from polycrystalline tungsten and the STM images were obtained in constant-current mode. Differential conductance (dI/dV) measurements and mappings were obtained with the help of a lock-in amplifier (Model 830, Standford Research) with internal modulation source. The modulation of the lock-in amplifier for dI/dV mapping was 15 mV at 880 Hz. Since in our case bias voltages were applied to samples, the modulation probes the unoccupied states of the sample in positive biases.

3. Theoretical methods

Density functional theory (DFT) calculations were performed using the Quantum-ESPRESSO/PWSCF computer package [9] with the Perdew–Burke–Ernzerhof generalized gradient-corrected approximation (GGA) [10] for the exchange and correlation functional. The electron–ion interactions are described by ultrasoft pseudopotentials [11], whereas the wave function and the electron density representation are described with a plane–wave basis set limited by kinetic energies of 30 and 300 Ry, respectively. Brillouin-zone sampling is performed with only the Γ point because a large cubic box with lattice constant of 25 Angstroms was used to contain one CoPc molecule.

4. Results and discussion

4.1. Oxidized copper layer preparation and STM characterization

Fig. 1(a) shows an STM image obtained from a copper surface that has been oxidized, and O_2 exposure was 2 L (1 L=1×10^{-6} Torr s). A previous investigation showed that oxygen dissociatively chemisorbed on Cu(001), and theoretical results revealed that dissociated O atoms reside randomly on four-fold hollow sites (FHSs) at the initial stage of oxidation [12–14]. Due to the small local DOS of the oxygen atoms near Fermi level, the areas adsorbing O atoms appear dark in STM images. With increasing O_2 exposure (~ 10 L), more oxygen atoms are adsorbed onto the surface and form two types of phases, both with ordered structures; the phases are marked A and B in Fig. 1(b).

Atomically-resolved images of phase A (see Fig. 2(a)) indicate that the oxygen atoms reside on the second nearest FHS [15] that finally form c-(2 × 2) structures over a 0.5 monolayer (ML)
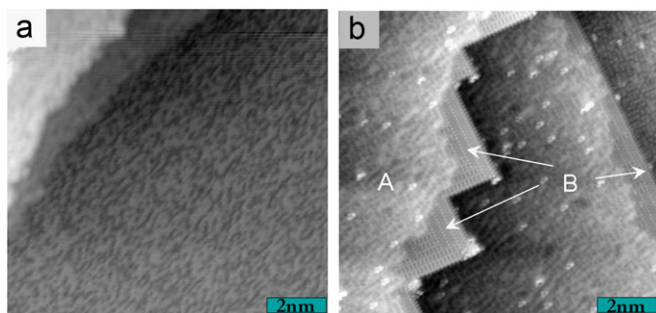

Fig. 1. STM image of structures of the oxidized layer at various oxygen concentrations. (a) at low doses (2 L, 1 L=1×10^{-6} Torr s), the oxygen atoms reside atop sites of Cu(001) and (b) with oxygen exposure of 10 L. There are two kinds of ordered phases (A and B) formed, i.e., c-(2 × 2) and $\sqrt{2} \times 2\sqrt{2}$ R45°−2O.
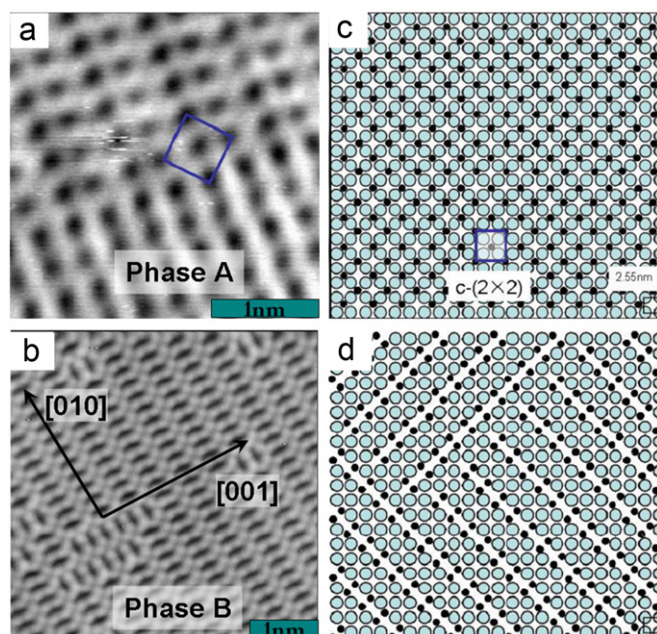

Fig. 2. (a) and (b) STM images of structures of phase A and B in atomic resolution. (c) and (d) the proposed structural models for phases A and B, respectively.

coverage, as depicted in Fig. 2(c). In contrast theoretical results found that the c-(2 × 2) structure is not stable, and every fourth [001] or [010] surface row of Cu would be "squeezed out" resulting in another structure, $\sqrt{2} \times 2\sqrt{2}$ R45°−2O [16], the phase B shown in Fig. 2(b). In this ordered structure, the copper atoms are resolved and the copper atoms in every fourth row along both the [001] and the [010] directions are missing as depicted in the image of phase B in Fig. 2(d). The Cu–O–Cu chains formed spearhead the oxygen-induced reconstruction on Cu(001) surfaces [17].

4.2. CoPc adsorption and its topographic images

The stable reconstructed $\sqrt{2} \times 2\sqrt{2}$ R45°−2O structure is atomically flat and well reproduced, and therefore is a suitable template to position molecules in our STM study. When a few CoPc molecules are deposited on this substrate at room temperature, most of these are trapped by the lattice steps (Fig. 3(a)). After the steps are fully occupied, the molecules can be found on the terraces (Fig. 3(b)). During the STM scanning at 77 K, the molecules are able to rotate, diffuse, or even desorb from the surface. For instance, the circled molecule in Fig. 3(b) was rotating during the scanning, resulting in a fuzzy contour. According to the STM image in Fig. 3(c) where CoPc and substrate lattice were resolved simultaneously, CoPc molecules are determined to lie on the surface with their lobes forming an angle of 22.5° with respect to the Cu[010] and [001] directions; the orientation is similar to CoPc adsorbed on bare Cu(001) [18]. Close observations reveal that the central Co^{2+} ions are located atop sites of O atoms rather than atop sites of Cu atoms possibly resulting from weak coupling between the p state of an outermost O atom and d state of a Co^{2+} ion.

The oxidized layer could decouple the strong interaction between the metallic surface and the molecules despite weak coupling between the O atom and Co^{2+} ion. Fig. 3(d) shows an STM image obtained at a bias voltage of $+1.5$ V under good-performing tip conditions so that the inner structure of the CoPc molecule was resolved. In contrast, the molecules adsorbed on the pristine Cu(001) appear cross-like as seen in the left inset image of Fig. 3(d). Comparing the behaviors of CoPc molecules adsorbed