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ScienceDirect
Surface Science 601 (2007) 5433–5440
SURFACE SCIENCE
www.elsevier.com/locate/susc

Geometrical characterization of adenine and guanine on Cu(1 1 0) by NEXAFS, XPS, and DFT calculation

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Received 30 April 2007; accepted for publication 5 September 2007
Available online 14 September 2007

Abstract

Adsorption of purine DNA bases (guanine and adenine) on Cu(1 1 0) was studied by X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine-structure spectroscopy (NEXAFS), and density-functional theory (DFT) calculation. At coverages near 0.2 monolayers, Angular-resolved NEXAFS analysis revealed that adenine adsorbates lie almost flat and that guanine adsorbates are tilted up on the surface with the purine ring parallel to the atom rows of Cu(1 1 0). Referring to the previous studies on pyrimidine DNA bases [M. Furukawa, H. Fujisawa, S. Katano, H. Ogasawara, Y. Kim, T. Komeda, A. Nilsson, M. Kawai, Surf. Sci. 532–535 (2003) 261], the isomerization of DNA bases on Cu(1 1 0) was found to play an important role in the adsorption geometry. Guanine, thymine and cytosine adsorption have an amine-type nitrogen next to a carbonyl group, which is dehydrogenated into imine nitrogen on Cu(1 1 0). These bases are bonded by the inherent portion of –NH–CO– altered by conversion into enolic form and dehydrogenation. Adenine contains no CO group and is bonded to Cu(1 1 0) by participation of the inherent amine parts, resulting in nearly flatly-lying position.

Keywords: Nucleic acids; Copper; Near-edge extended X-ray absorption fine structure (NEXAFS); Soft X-ray photoelectron spectroscopy; Density functional calculations; Molecular orientation

1. Introduction

Functionalization of solid surfaces with biological molecules is a recent prevalent topic concerning technological applications such as biocatalysis and biosensors. Basic surface science on the adsorption structure of amino acids [1,2] and the DNA base molecules [3,4] is important in developing such biological molecular science and technology. Surface-scientific methods will be capable of assisting the interpretation of more complicated biological systems, such as DNA-protein bindings [5,6].

Fundamental analysis on the adsorption of the DNA purine bases (guanine, adenine) and pyrimidine bases (cytosine, thymine) was performed on graphite [3], Au(1 1 1) [7,8], Cu(1 1 1) [9] and Cu(1 1 0) [10–15] by means of low-energy electron diffraction (LEED), scanning tunneling microscope (STM), electron energy-loss spectroscopy (EELS), angular-resolved ultraviolet photoemission spectroscopy (ARUPS), and infrared absorption spectroscopy (IRAS). On Cu(1 1 1), the STM study showed the formation of self-assembled superstructures of these molecules through hydrogen-bond-aided dimerization of adsorbed DNA bases [9]. All of four DNA bases are attached on Cu(1 1 1) with their molecular planes parallel to the substrate. As the molecular planes accompany π orbitals, they are called "π planes". On Cu(1 1 0) on the other hand, the

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doi:10.1016/j.susc.2007.09.009

orientations of adsorbed DNA bases are often not parallel to the substrate and DNA bases are chemically altered upon adsorption.

Using X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine-structure spectroscopy (NEXAFS), we previously showed that pyrimidine DNA bases (cytosine and thymine) are configured upright on Cu(1 1 0) with their π planes parallel to the Cu atom row well below the monolayer coverage [16]. These upright-standing positions have also been suggested by IRAS study given by McNutt et al. [12] and Yamada et al. [15] We further assumed from XPS analysis that these molecules can interact with Cu(1 1 0) surfaces through their nitrogen atom (lone-pair) next to the carbonyl group (C=O), which is followed by removal of a hydrogen atom from this site [16].

There is a controversy with the results on purine DNA bases (Fig. 1) on Cu(1 1 0). For adenine, McNutt et al. proposed the upright-standing model using IRAS technique [13]. A process of dissociation of H(9)–N(9) bond is proposed upon adsorption, and adenine is adsorbed through the interaction of N(3) and N(9) atoms. On the other hand, Chen et al. [14], Yamada et al. [15] and recently Preuss et al. [17] derived a nearly flat-lying configuration adsorbed through the $N(6)H_2$ group. In Yamada et al.'s study [15], the flatly-lying position was concluded judging from the surface selection rule in IRAS and the coverage estimation using carbon Auger signals. Chen et al. [14] concluded by STM, LEED, and HREELS that both molecular and $N(6)H_2$ planes are almost parallel to the substrate and the $C-N(6)H_2$ bond tilted slightly out of this plane. Their theoretical calculation, however, indicates that the interaction is exclusively through the $N(6)H_2$ group and the tilting angle of molecular plane to be 25° from the substrate. Under the same assumption, Preuss et al.'s calculation also reached a similar conclusion and the tilt angle of 26.4° was obtained [17].

For guanine on Cu(1 1 0) system, the IRAS characterization by Yamada et al. [15] suggests that the molecule is nearly upright on the surface and that the C(6)=O part is near the surface. The detailed molecular orientation, however, was not given.

In this report, we show the adsorption scheme of adenine and guanine on Cu(1 1 0) surfaces based on the present XPS and NEXAFS studies combined with the calculations on the basis of density-functional theory (DFT). NEXAFS characterization shows a nearly flat position for adenine on Cu(1 1 0) and a nearly upright geometry for guanine. Furthermore, XPS results indicate that guanine is favored to interact with the surface through its imine nitrogen and carbonyl oxygen sites. Referring our previous studies for cytosine and thymine [16], we propose a general rule for the adsorption scheme of DNA bases on Cu(1 1 0) surfaces.

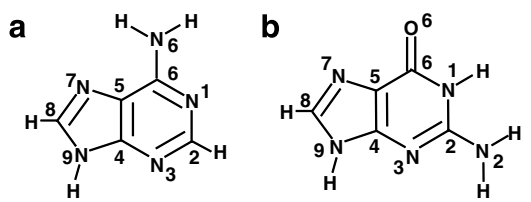

Fig. 1. Molecular structure and atom numbering of (a) adenine and (b) guanine.

2. Experimental

2.1. NEXAFS and XPS measurements

NEXAFS and XPS measurements were performed at undulator beamline I511 at the National Electron Accelerator Laboratory for Nuclear Physics and Synchrotron Radiation Research (MAX-Lab, Lund, Sweden) using the surface science endstation (UHV condition with a base pressure of 10^{-10} Torr). This endstation was equipped with an electron spectrometer (Scienta SES-200; Ref. [18]) and a partial electron-yield detector for NEXAFS. Two Cu(1 1 0) single crystals were mounted with the azimuthal orientation perpendicular to each other. The incoming light was aligned at a few degrees from the surface to achieve grazing incidence. Both the spectrometer and the sample could be turned around the axis of incoming light. The geometry allows NEXAFS measurements in the highly symmetric crystal directions, such as [1 $\bar{1}$ 0], [0 0 1], and [1 1 0] (Refs. [19,20]) for the molecular orientation analysis. All spectra were recorded at room temperature with resolutions better than 0.1 eV and 0.3 eV for NEXAFS and XPS measurements, respectively. For NEXAFS spectra of nitrogen and oxygen K-edges, the partial yield of Auger electron was detected. The XPS and NEXAFS measurements were carried out right after the sample was freshly prepared. By optimizing the beam flux intensity, radiation damage of molecules was avoided.

The Cu(1 1 0) substrates were cleaned by repetitive cycles of Ar ion bombardment and annealing. The cleanness and perfection of surfaces were tested by XPS and LEED. XPS C 1s photoelectron peaks were hardly observed on this surface. Powders of guanine and adenine (Sigma Co. Ltd., purity 99%) were evaporated from a resistively-heated stainless-steel cell onto the clean Cu(1 1 0) surfaces kept at room temperature in UHV. The distance between the substrate and the evaporation cell was approximately 150 mm. The evaporation source temperature was always monitored with a K-type thermocouple. The source temperature for evaporation was controlled at 450 K for adenine and 530 K for guanine. The sample preparation procedure was in general similar to that of the IRAS study by Yamada et al., in which they estimated the surface coverage of adsorbed molecules using an Auger electron spectroscopy (AES) [15]. In the present case the coverage was confirmed in our XPS measurement by analyzing the relative photoelectron intensity of copper, nitrogen, and oxygen core levels. In this report, we show the NEXAFS and XPS data when the coverage θ was estimated to be ~0.2 ML (well be-