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Density functional theory calculations of tetracene on low index surfaces of copper crystal*

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This paper carries out the density functional theory calculations to study the adsorbate–substrate interaction between tetracene and Cu substrates (Cu (110) and Cu (100) surface). On each of the surfaces, two kinds of geometry are calculated, namely 'flat-lying' mode and 'upright standing' mode. For 'flat-lying' geometry, the molecule is found to be aligned with its longer molecular axis along close-packed direction of the substrate surfaces. For 'upright standing' geometry, the long axis of tetracene is found to be parallel to the surface normal of the substrate on Cu (110) surface. However, tetracene appears as 'tilted' mode on Cu (100) surface. Structures with 'flat-lying' mode have much larger adsorption energy and charge transfer upon adsorption than that with 'upright standing' mode, indicating the preference of 'flat-lying' geometry on both Cu (110) and Cu (100) surface.

Keywords: density functional theory, adsorbed geometry, adsorption energy, density of state
PACC: 8265, 7115M, 7115V

1. Introduction

In recent years, electronic devices constructed with organic materials are becoming increasingly important. The properties of organic layers allow the preparation of inexpensive, light-weight, and flexible thin film for the realization of, e.g., flexible display. Organic field effect transistors[1,2] are also an essential component of an organic integrated circuit. However, the low mobility of charge carriers has become the bottle-neck for the applications of organic materials in electronic devices. It has been suggested that improved internal ordering of the organic thin films could enhance field-effect carrier mobility, together with increasing the electrical conductivity and reducing activation energy for electrical conduction.[3−7] This property has inspired many investigations on the ordered structures of organic materials on different substrates, especially on metal surface.[8−11]

Generally, it is believed that the ordered structure in the first organic layer will substantially affect the packing structure of organic molecules in overlayer. Therefore, self-assembly monolayer structures of organic materials on metal surfaces are extensively studied. The most frequently studied linear aromatic molecules for growth on metal single-crystal are pentacene ($C_{22}H_{14}$) and tetracene ($C_{18}H_{12}$). Detailed studies of initial organic layer growth were performed for pentacene on Au(111)[12−14] and Cu (110)[15−17] and for tetracene on Ag(111),[18] Ag(110),[9] Cu (110),[19,20] and Cu (100).[21] Depending on the coverage and deposition parameters, one often observes more than one stable two-dimensional structure.

For tetracene on low index surface of copper crystal (e.g. Cu (110) and Cu (100)), earlier angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) results indicated ordered structures with the molecular plane perpendicular to the substrate surface ('upright standing' mode).[22−24] However, recent scanning tunnelling microscopy[19,21] and ARUPS[20] experiments confirmed the general idea that tetracene molecules intend to be arranged with the molecular plane parallel to the substrate surfaces on active metal surface ('flat-lying' mode). This contradiction can be cleared up by determining which interaction is dominated in the process of adsorption, say molecule–molecular (M–M) interaction and molecule–substrate (M–S) interactions. The interaction near interface is of great importance for the arrangement pattern of organic materials adsorbed on metal surface. In this article, the adsorption geometry of tetracene on Cu (110) and Cu (100) surface is studied by using density functional theory

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(DFT) calculations. The work is intended to get a better understanding about the interaction between molecule and substrate.

2. Calculation details

DFT calculations of tetracene molecule on Cu (110) and Cu (100) surface were carried out by using the Dmol3 package integrated in the Material Studio program of Accelrys Inc.[25,26] This package employs density functional Hamiltonian for molecules and three-dimensional periodic solid and approximates true wavefunctions through an expansion of crystalline orbitals as a linear combination of atomic orbitals. Generalized gradient approximation[27] and Perdew–Wang (PW91)[28] exchange–correlation functional were used throughout. The DFT semicore pseudopotential (DSPP) was used to describe electron–ion interaction.

The lattice constant of the face-centred cubic (fcc) copper crystal, $a_{\mathrm{Cu}} = 0.3615\,\mathrm{nm}$ which was obtained from an optimization with Dmol3 code, was in good agreement with the previously measured value of 0.361 nm.[29] The sampling k-point set was generated automatically in the approach of Monkhorst–Pack scheme.[30−33] Concerning the accuracy and computational cost, we employ the basis set of double numerical valence functions plus a polarization p-function on hydrogen atoms and d-functions (dnp basis) on non-hydrogen atoms, the local basis cut-off was set as $R_{\mathrm{c}} = 0.44\,\mathrm{nm}$.

We used periodic slabs to model the Cu (110) and Cu (100) surface. Generally, a thick slab (i.e., with 6 layers of Cu atoms) will increase the precision of the calculation, but at the same time increase the calculation time and need larger memory. For test, slabs with six layers of Cu atoms were used, and the upper four layers of Cu atoms were allowed to be relaxed during the structural optimization. The calculated results are almost the same as the ones if a four-layer slab was used. For efficiency and precision, slabs with four layers of Cu atoms were used for all the calculations. Vacuum layers of 1 nm (for 'flat-lying' mode) and 2.5 nm (for 'upright standing' mode) were used to mimic the real surface. The molecule and the upper two layers of copper atoms were allowed to be relaxed during the process of structural optimization. The convergence criteria of the geometrical optimizations is set as $5.44 \times 10^{-4}\,\mathrm{eV}$ for energy, 1.09 eV/nm for energy gradient and $5.0\times10^{-4}\,\mathrm{nm}$ for displacement of the ionic step.

The proposed models from the published experimental results[19−24] are shown in Fig.1. Different adsorption sites were calculated. The adsorption site is defined as the positions at the first layer of the substrate where the centre of the tetracene molecule is located. One thing that should be mentioned is the units of tetracene with 'flat-lying' mode on Cu (100) surface (see Fig.1(b)). Tetracene tends to be aligned along two chemically identical directions, [011] and $[01\bar{1}]$, due to the symmetric nature of (100) surface of fcc crystals. A large unit cell with dimensions of $1.02\,\mathrm{nm} \times 1.53\,\mathrm{nm}$ is used, which is large enough to avoid the VdW (Van der Waals)-like M–M interaction. Structures with the molecule being aligned along [011] direction was only calculated for 'flat-lying' mode of tetracene on Cu (100) surface. The rest unit cells were built according to the experimental result.

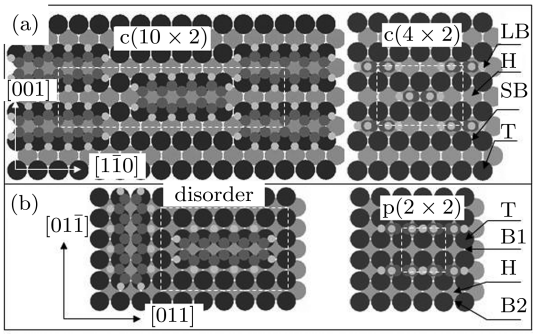


Fig.1. Proposed models of tetracene on (a) Cu (110) surface and (b) Cu (100) surface with 'flat-lying' (left panel) and 'upright standing' (right panel) mode. The adsorption sites are indicated by the initials, where LB indicates long bridge site, SB indicates short bridge site and H indicates hollow site. In (b), B1 indicates the bridge site between adjacent copper atoms in $[01\bar{1}]$ direction, while B2 indicates the bridge site between adjacent copper atoms in the [011] direction.

3. Results and discussions

The most stable structures of tetracene with 'flat-lying' mode on Cu (110) and Cu (100) are shown in Figs.2(a) and 2(b). The unit cell for each substrate is indicated, respectively, by the rhomb and rectangle. Tetracene molecule tends to be aligned with its longer molecular axis along the close-packed direction of the substrate surface. The molecular centre of tetracene is located at bridge site for both Cu (110) and Cu (100) surface (LB site for Cu (110) surface and B1 site for Cu

(100) surface). On both surfaces, tetracene molecule shows a common feature that the carbon atoms always tend to be located between the surface copper atoms and not directly over them in order to reduce the repulsive interaction and increase the attractive force. The molecular plane of tetracene remains almost planar although it is slightly bent with magnitude of less than 0.02 nm. The hydrogen atoms are raised upward, indicating a repulsive interaction between H atoms and Cu substrate, which may account for the bending of the tetracene molecule.

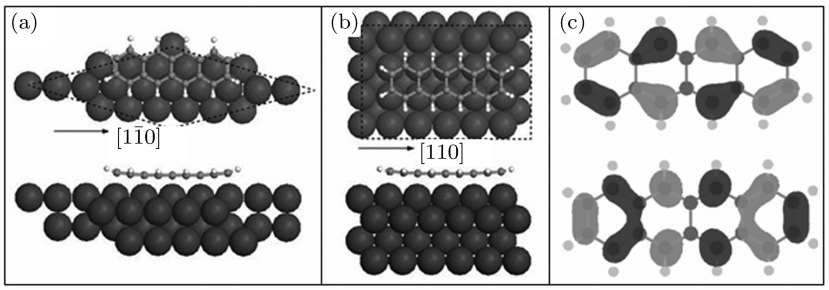


Fig.2. Optimized structures of tetracene on (a) Cu (110) and (b) Cu (100) with 'flat-lying' mode. Upper panel: top view. Lower panel: side view. The rhomb and rectangle represent the unit cell for the calculation. (c) HOMO (upper) and LUMO (lower) of tetracene in gas phase.

In Fig.2(c), the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are shown. Both the HOMO and LUMO are π-conjugated states. The distance between tetracene molecule and the substrate surface is $\sim$0.22 nm, which will contribute to the overlap between the π orbital of the molecule and the d electronic band of the substrate. The short M–S distance favours the M–S interaction. Several previous ultraviolet photoelectron spectroscopy (UPS) experiments show that the HOMO and other states with π character experience large energy shift during the vacuum deposition of tetracene on metal surface,[20,34] which indicates a strong M–S interaction.

The overlap between molecular orbitals of tetracene and d-band of substrate will be small if the molecule is adsorbed with 'upright-standing' mode on Cu substrate, which may indicate very weak M–S interaction. In Fig.3, the most stable structures of tetracene on Cu substrate with 'upright standing' mode are shown. On each surface, the molecule of tetracene is located at bridge sites, which is consistent with that with 'flat-lying' mode. On the Cu (110) surface (see Fig.3(a)), the molecular plane of tetracene is almost perpendicular to the substrate surface, and the shorter axis is aligned along [1$\bar{1}$0] direction of substrate surface. While on Cu (100) surface, tetracene molecule appears as a 'tilted' geometry. The tilted angle, defined as the angle between the molecular plane of tetracene and the surface normal of Cu (100) substrate, is 17°, which is approximately agreed with the earlier ARUPS founding of Yannoulis. Furthermore, the shorter axis is not aligned along the close-packed direction of substrate surface but along the less closed packed [010] direction of substrate surface.

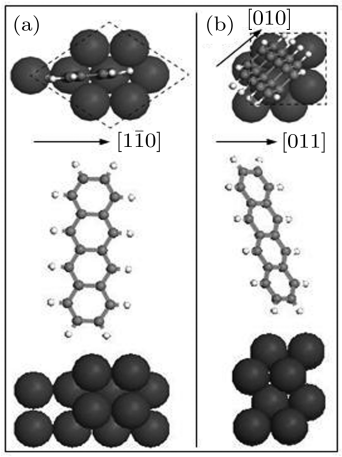


Fig.3. Optimized structures of tetracene on (a) Cu (110) and (b) Cu (100) with 'upright-standing' mode. Upper panel: top view. Lower panel: side view. The rhomb and rectangle represent the unit cell for the calculation.

The 'tilted' geometry of tetracene can be attributed to the competition between adsorbate–adsorbate interaction and the adsorbate–substrate interaction. And the former interaction seems to be overwhelmed. The adsorbate–substrate interaction is very weak for the 'upright standing' mode since the shortest distance between carbon atoms of tetracene molecule and Cu atoms at substrate surface is as large as 0.403 nm (see Table 1). However, the shortest C–Cu distance is much short in the 'flat-lying' cases, where the adsorbate–substrate interaction is dominated.

Table 1. Calculated results of tetracene on Cu (110) surface and Cu (100) surface.

	on Cu (110) surface		on Cu (100) surface	
	parallel	perpendicular	parallel	tilted
shortest C–Cu distance/nm	0.225/0.224[a]	0.402	0.227/0.225[a]	0.403
adsorption energy/eV	2.20/2.22[a]	0.54	2.44/2.45[a]	1.02
total charge transfer/e	0.59	0.06	0.57	0.03

[a] Calculated results using a six-layer slab.

For better understanding the interaction between tetracene and Cu substrate, the adsorption energy and total charge transfer upon adsorption are calculated and summarized in Table 1. The adsorption energy is defined as, $E_{\text{ads.}} = (E_{\text{subs.}} + E_{\text{mol.}}) - E_{\text{sys.}}$, where $E_{\text{subs.}}$ indicates the total energy of Cu substrate, $E_{\text{mol.}}$ indicates the total energy of one single tetracene molecule in gas phase and $E_{\text{sys.}}$ indicates the total energy of adsorbate/substrate system. The positive values of the adsorption energy indicate the exothermic reaction during the process of adsorption process. Clearly geometries with 'flat-lying' mode bear larger adsorption energy than that with 'upright standing' mode, it indicates that the former geometry is more stable than the later.

The charge transfer upon adsorption is obtained by carrying out Mulliken population analysis of tetracene molecule before and after the adsorption. The charge transfer between adsorbate and substrate is much larger for 'flat-lying' geometry than that of 'upright standing' geometry. The 'flat-lying' geometry bears large overlap between molecular orbitals (mainly π states) and substrate surface, therefore it is in favour of the electron transfer between them. However, this geometry will hinder the electron transfer between tetracene molecules where 'hopping' scheme dominate.[35] While tetracene molecules with 'upright standing' geometry experience little orbital overlap with the substrate surface, and therefore have neglectable amount of transferred charge.

Figure 4 shows the density of state (DOS) of tetracene and Cu substrate before and after the adsorption. In Figs.4(c) and 4(d), the DOS lines of Cu d state are shifted in vertical direction for comparison.

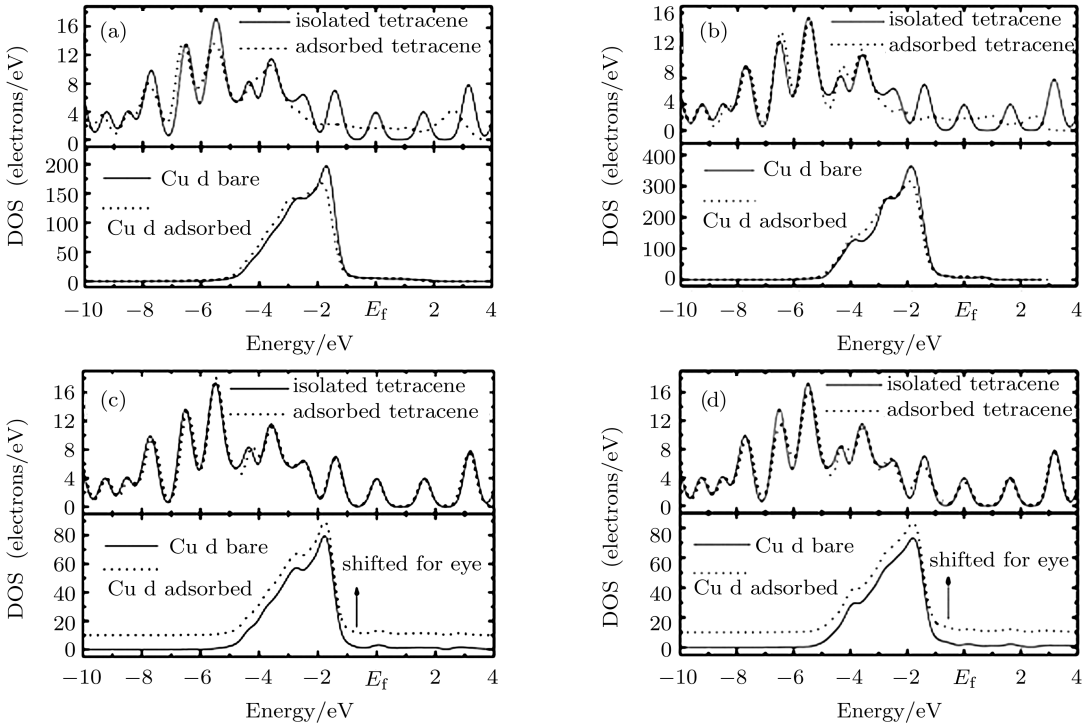


Fig.4. Density of state of the tetracene and the substrate: (a) parallel geometry on Cu (110); (b) parallel geometry on Cu (100); (c) perpendicular geometry on Cu (110); (d) perpendicular geometry on Cu (100).

For parallel geometries, in comparison with DOS of isolated molecule, the DOS of tetracene after adsorption shows tremendous changes in line shape and energy positions of electronic states (π characterized), especially at energy region near to Fermi level. The Cu d electronic band experiences similar changes, indicating the domination of π-d interaction between tetracene and Cu substrates. This is consistent with the previous UPS results.[20] For perpendicular geometry, on the contrary, both DOS of tetracene and the substrate do not experience obvious changes, revealing the very weak M–S interaction if tetracene is adsorbed with 'upright standing' mode.

Considering the active nature of Cu substrate, tetracene favours the parallel geometry on both Cu (110) and Cu (100) surfaces at low coverage (e.g., monolayer (ML) or sub-monolayer). This conclusion is in contradiction with the earlier ARUPS findings.[24] A clue to understand this discrepancy is the difference in coverage, which was estimated to be 1–2 ML in the earlier work. It should be noted that 1 ML with 'upright standing' mode is much thicker that of 'flat-lying' mode. Therefore, 'upright standing' geometry will exist at multilayer coverage since the interaction from Cu atoms is covered by the pre-adsorbed tetracenes.

4. Summary

The adsorbed structures of tetracene on Cu (110) and Cu (100) surface were calculated in frame of DFT. The M–S interactions for both 'flat-lying' and 'upright standing' mode were studied. Larger M–S interaction of parallel geometry than that of perpendicular geometry is found and the preference of the former geometry is concluded at ML tetracene coverage.

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