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Adsorption structures of tetracene on the $Ru(10\overline{1}0)$ surface

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Abstract

Adsorption structures of tetracene on the Ru($10\bar{1}0$) surface has been investigated by means of ab initio density functional theory (DFT) calculations. Several adsorption geometries of tetracene on Ru($10\bar{1}0$) were examined in details. The optimized structures have an adsorption energy of 4.23 eV for tetracene adsorbed between the top and the second Ru atoms rows with its long molecular axis along the $[1\bar{2}10]$ direction, and a slightly smaller adsorption energy of 4.19 eV for tetracene adsorbed with its long axis perpendicular to $[1\bar{2}10]$, consisting well with the adsorption structures observed in the scanning tunneling microscopy (STM) measurements for tetracene overlayer on Ru($10\bar{1}0$). By Comparing DOS before and after tetracene adsorption, we suggest that the coupling of the substrate d-band and the filled p-orbitals of tetracene determines tetracene adsorption on the Ru($10\bar{1}0$) surface. \bigcirc 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Organic semiconductors have been shown to be attractive candidates for both passive and active roles in electronic devices, such as gas sensors [1], heterojunctions [2], ultrafast optical switches [3] and so on, because of their compatibilities with high-throughput, lowcost processing techniques and their capabilities to be precisely functionalized through the techniques of organic synthesis to afford desired performance attributes [4]. In all the case, the molecule–surface interaction plays a vital role, since the binding and ordering of organic molecules on surfaces are generally controlled by the delicate balance between the molecule–substrate and the intermolecular interactions [5]. It is therefore, important to understand in details the binding geometries and the interactions of organic molecules on the well-defined surfaces.

In general, the diffusion barriers for aromatic molecules on metal surfaces are comparable to the thermal energies of these molecules at room temperature. Therefore, it is very likely to form ordered organic structures on metal surfaces at room temperature. Previous studies have shown that many aromatic

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organic materials form ordered structures on a variety of metal substrates [6-8]. Tetracene, one of the simplest and most promising aromatic molecules for its high charge carrier mobility and good luminescence properties, has been widely used as an active layer of field-effect transistor [9], and also as photoconductive material [10]. Investigation of growth behavior of tetracene on single-crystal surfaces, such as Cu (1 1 0) [11], Si (1 0 0) [12], and Ag (1 1 0) [13] have already been reported. At submonolayer coverages, tetracene molecules are expected to be very mobile and can choose proper bonding sites to form ordered phase. However, recent research for tetracene growth on $Ru(10\overline{1}0)$ at monolayer regime showed that no distinct nucleation and ordering were observed [14]. Apparently, transition metals have large densities of states (d-bands) near the Fermi level, in comparison with small densities of states of noble metals near $E_{\rm F}$, different adsorption behaviors for organic adsorptions on transition and noble metal surfaces can be expected. Therefore, knowledge of the adsorption geometries and interaction of tetracene on transition metal surfaces will help to better understanding of the growth mechanism of organic semiconductors.

In the present work, we report our theoretical investigations of tetracene adsorption on the transition metal $Ru(10\bar{1}0)$ surface by using ab initio DFT calculations (periodic DMol³). The densities of states (DOS) before and after tetracene

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adsorption were explored, and the results showed the bonding behavior of tetracene on $Ru(10\bar{1}0)$, and the optimized adsorption structures are in reasonable agreement with STM experiments.

2. Calculational details

The ab initio DFT calculations for tetracene adsorption on $Ru(10\overline{1}0)$ were performed with the program package of DMol³ [15] (Materials Studio (version 3.1) of Accelrys Inc.). This method is reliable on the adsorption system of typical organic molecules on transition-metal (TM) surfaces [16,17]. The physical wave functions were expanded in terms of accurate numerical basis sets. The double-numeric quality basis set with polarization functions (DNP) was used. The size of the DNP basis set is comparable to Gaussian 6-31G**, but the DNP is more accurate than the Gaussian basis set of the same size. We used density functional semicore pseudopotentials (DSPP s) for the Ru substrate. The pseudopotentials are intended for use with density functional local orbital methods such as the DMol³ [18]. The gradient-corrected GGA functional of Becke 1988 exchange [19] and one-parameter progressive (OP) correlation (BOP) [20] was employed. The accuracy of the BOP has been verified by a variety of calculations to determine, for example, the chemical properties of molecules [21], the optimized structures, dissociation energies of first- to third-row transition metal dimers [22], and other properties of molecules [23]. A Fermi smearing of 0.003 Hartree (1 Ha = 27.21 eV) and a real-space cutoff of 4.7 Å were used. For the numerical integration, we used the FINE quality mesh size of the program.

The Ru(10 $\overline{1}$ 0) surface was modeled by periodic slabs of four Ru layers with a 20 Å of vacuum region between the slabs, and the adsorbed tetracene molecule was placed on one side of the Ru slab. Both tetracene molecule and the top two layers of substrate were allowed to relax. A (6 × 4) unit cell was chosen to model tetracene molecule adsorbed with its long axis along the [1 $\overline{2}$ 10] and [0001] azimuth of Ru(10 $\overline{1}$ 0).

The tolerances of energy, gradient, and displacement convergence were 1×10^{-5} Ha, 2×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively. Adsorption energies were determined by subtracting the energies of the molecule alone and the substrate from the energy of the adsorption system as shown in Eq. (1):

$$E_{\rm ad} = -[E(\text{tetracene/surface}) - E(\text{tetracene}) - E(\text{surface})]$$
⁽¹⁾

Where E (tetracene/surface) is the energy of the adsorption system, E (tetracene) the energy of the free molecule, and E (surface) is the energy of the substrate.

Tetracene is a large conjugate organic molecule with all its components in one plane, having two symmetric axes as showed in Fig. 1(a). For free tetracene molecule, the C–C bond length at the molecular center is determined to be 1.42 Å with DMol³. As shown in Fig. 2, For tetracene adsorption on $Ru(10\bar{1}0)$, 12 adsorption sites were examined with attaching a



Fig. 1. Schematically shown (a) tetracene molecular structure, and (b) the electronic structures of tetracene molecule.

tetracene molecule to the surface. The sites are classified by the symmetric axis and the position of the molecular mass-center on the substrate, e.g., for tetracene molecule at the site 6, the long molecular axis is along the $[0\ 0\ 0\ 1]$ azimuth of the substrate, and the molecular mass center is on the top of the first-layer Ru atom, and for tetracene molecule at the site 8, the long molecular axis is along the $[1\ 2\ 1\ 0]$ azimuth of the substrate, and the molecular mass center is on the bridge site of the Ru surface. Since the lateral molecule–molecule interaction is rather weak [14], only a single tetracene molecule is put on the surface.

3. Results and discussions

Fig. 1(a) shows the molecular structure of teteracene. For free tetracene molecule, the typical C–C bond length at the molecular center is determined to be 1.42 Å with DMol³. The molecular plane has a rectangular shape with van der Waals dimension of 13.6 Å × 7.0 Å. The real space electronic structures of tetracene molecule, e.g., the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) are shown in Fig. 1(b). Figs. 2 and 3 schematically show the top views and the side views of the optimized structures for tetracene adsorption on Ru(10 $\overline{10}$)



Fig. 2. Schematically shown the top views of 12 (optimized) adsorption structures of tetracene on Ru(10 $\overline{10}$), the molecule aligned with its long axis either (a) along [0 0 0 1], or (b) along [1 $\overline{210}$].

with the different geometries, respectively. The adsorption energies for tetracene adsorbed on $Ru(10\bar{1}0)$ at different sites are summarized in Table 1.

The most stable adsorption structure of tetracene on $\operatorname{Ru}(10\,\overline{1}\,0)$ occurs at the site 11, in which tetracene molecule is located between the top and the second Ru atomic rows, with its long axis along the $[1\,\overline{2}\,1\,0]$ direction, and its mass-center at the hollow site. The adsorption energy is evaluated to be 4.23 eV. The molecular plane, about 2.37 Å above the top layer of substrate, is slightly distorted, but lies parallel to the surface. The nearest C–Ru distance is about 2.27 Å. The four Ru atoms of first layer just under the four carbon atoms of tetracene

molecule are lifted up obviously, two Ru atoms closing the molecular center lifting upward 0.11 Å, and the other two atoms lifting upward 0.18 Å. The C–C bond length at the molecular center is 1.45 Å, a little bit larger than that for free tetracene molecule (1.42 Å). The C–H bonds tilt outward from the surface, with an bond length of 1.09 Å.

The second stable adsorption structure occurs at the site 3, with an adsorption energy of 4.19 eV, slightly small than that at the site 11. At this site, tetracene molecule is aligned with its long axis along $[0\ 0\ 0\ 1]$, and its mass-center at the short bridge site. The molecule plane is about 2.52 Å above the top layer of substrate, and the nearest C–Ru distance is 2.31 Å. The six Ru



Fig. 3. Schematically shown the side views of 12 optimized adsorption structures of tetracene on $Ru(10\bar{1}0)$, the molecule aligned with its long axis either (a) along [0001], or (b) along $[1\bar{2}10]$.

Table 1 Adsorption energies of tetracene molecule at different sites of $Ru(10\bar{1}0)$

Adsorbed site	E (eV)	$\Delta E_{\rm ad}~({\rm eV})$
Site 1	Move to site (4)	
Site 2	Move to site (3)	
Site 3	4.19	-0.04
Site 4	3.80	-0.43
Site 5	0.70	-3.53
Site 6	0.76	-3.47
Site 7	3.74	-0.49
Site 8	0.05	-4.29
Site 9	0.32	-3.91
Site 10	4.09	-0.14
Site 11	4.23	-0.00
Site 12	0.23	-4.00

atoms of first layer just under tetracene molecule are lifted up from substrate plane, two Ru atoms under the molecular center lifted upward about 0.3 Å, and the other four Ru atoms under the molecule lifted upward about 0.2 Å. The C–C bond length at the molecular center is 1.46 Å, and the C–H bonds also tilt away from the surface, with an bond length of 1.09 Å. The other adsorption configurations result in either much more distorted molecular structures, e.g., for tetracene adsorbed at the site 4 and the site 8, or the molecule far away from substrate, e.g., for tetracene adsorbed at the site 6, the adsorption energies for these configurations are smaller than those of the above mentioned most stable adsorption structures.

Almost the equal adsorption energies for tetracene molecule adsorbed at the site 11 and site 3 suggest an almost equal orientational distributions with the long axes of tetracene molecules aligned in the $[1\bar{2}10]$ direction (at site 11) and perpendicular to the $[1\bar{2}10]$ direction (at site 3) for tetracene overlayer on $Ru(10\overline{1}0)$ in submonolayer regime, in the case of the molecule-substrate interaction is relatively strong and the lateral molecule-molecule interaction is weak. Actually, our STM investigations for tetracene growth at submonolayer regime [14] reveal that the growth of tetracene is controlled mainly by the molecule-substrate interaction, tetracene molecules is flat-lying on the $Ru(10\overline{1}0)$ surface with their long molecular axes mainly either aligned in $[1\bar{2}10]$ or perpendicular to $[1\bar{2}10]$. The present theoretical results of slightly higher adsorption energy (4.23 eV) for tetracene molecule adsorbed at the site 11 than that (4.19 eV) at the site 3 are consistent well with the orientational distributions of 51% of tetracene molecules aligned with their long axes along $[1\bar{2}10]$ and 45% of them adsorbed with their long axes perpendicular to $[1\bar{2}10]$ at submonolayer tetracene coverage on $Ru(10\overline{1}0)$ observed in this STM measurement.

Fig. 4 shows a typical STM image taken for tetracene overlayer on Ru(10 $\overline{1}$ 0) at a coverage of about 0.2 ML (at room temperature), demonstrating the internal molecular structures and the adsorption geometries in details [14]. The image was recorded with a tunneling condition very near to the Fermi level ($V_s = -2 \text{ mV}$, $I_t = 0.71 \text{ nA}$), and the substrate structures, especially the Ru atomic rows are clearly resolved, which makes it possible for us directly to determine the adsorption geometries. The internal structures of the flat-lying tetracene



Fig. 4. High resolution STM image of tetracene overlayer on Ru(1010) at a coverage of about 0.2 ML, taken at room temperature with a tunneling condition of $V_{\rm s} = -2$ mV, $I_{\rm t} = 0.71$ nA, showing the internal molecular structures and adsorption geometries in details.

molecules in the STM image at present tunneling condition should be the reflection of the local density of the HOMO in the molecule, and all the internal features of tetracene are roughly comparable with the density of the HOMO of free tetracene molecule as shown in Fig. 1(b). Of course, mixing between the molecular orbitals and the local states of substrate in strongly chemisorbed systems will modify this local densities of states. The slight discrepancies among the images of the molecules labeled as A and B in different adsorption configurations, and the slight differences of the images from the HOMO structure of tetracene, should be related to the local interactions between tetracene molecules and the Ru substrate. Actually, as discussed above, Ru atoms, especially those under tetracene molecule, are reconstructed due to this molecule-substrate interaction. The interesting point is that, as the schematic tetracene molecules inserted in Fig. 4, the molecule A is just the tetracene molecule adsorbed at the site 11, with its long axis along the $[1\bar{2}10]$ direction and its center between the top and the second Ru atomic rows, while the molecule B, riding over three Ru atomic rows, is just the tetracene molecule adsorbed at the site 3, with its long axis along [0 0 0 1] and its center at central row. As shown in Fig. 4, the molecules tilted away from $[1\bar{2}10]$ have miner contribution (about 3%) in the orientaional distributions for tetracene overlayer on $Ru(10\overline{1}0)$ in the submonolayer regime [14].

Fig. 5 shows the densities of states for the above two most stable adsorption structures with the long molecular axis along $[1\bar{2}10]$ (the site 11) and $[0\ 0\ 0\ 1]$ (the site 3) of the substrate, with which one can understand the bonding behavior of tetracene on Ru $(1\ 0\ \overline{1}\ 0)$. In order to line up the energy levels of free molecule and the molecule-derived levels in the adsorption systems, the DOS of free tetracene molecule for the both adsorption configurations (see the curves for tetracene in



Fig. 5. Densities of states (DOS) for tetracene adsorption on $Ru(10\bar{1}0)$ (the DOS of the clean substrate, molecule in vacuum, the tetracene/ $Ru(10\bar{1}0)$ systems, and the PDOS onto the tetracene molecule) (a) at the site 11, with the long molecular axis along $[1\bar{2}10]$, and (b) at the site 3, with the long molecular axis along $[0\ 0\ 0\ 1]$, the dotted line indicates the Fermi level.

vacuum in Fig. 5) was obtained by placing tetracene molecule far away (10 Å away) from the Ru(10 $\bar{1}$ 0) surface to avoid bonding with substrate. The total DOS for the both adsorption configurations shown in Fig. 5 are dominated by the mayor contribution of the Ru substrate. The width of the d-band is approximately 7.0 eV, in well agreement with the results reported [24,25]. The total DOS also showed the tetracene derived features bellow -6.5 eV in binding energy. The projected DOS (PDOS) onto tetracene molecule, i.e., the electronic states belong to tetracene molecule in Fig. 5 for the both adsorption configurations, show the contributions from s and p-orbitals. The features above -6.5 eV mainly have p characteristics, while the features below -10.0 eV mainly come from s-orbitals.

There are obvious stabilization energies for tetracene molecule adsorbed on $Ru(10\bar{1}0)$ at the site 11 and site 3 (in both adsorption configurations) by comparing the molecule-derived characteristic peaks for tetracene molecule in vacuum with that in the adsorption systems. The main peaks of tetracene shifted downward about 3.6 eV after adsorption. By comparing the DOS of tetracene in vacuum with the PDOS onto tetracene molecule in Fig. 5, it is also clear that the molecule-derived features, especially those from p-orbitals

near to the Fermi level, are apparently modified due to the interaction between the molecule and the substrate. The densities of states from the p-orbitals in the both adsorption configurations are increased, suggesting that the coupling between the substrate d-band and the filled p-orbitals of tetracene molecule determines tetracene adsorption on the Ru(10 $\bar{1}$ 0) surface [26]. This coupling can be understood that, since in the both adsorption configurations, especially for tetracene molecule adsorbed at the site 11, in which the flatlying molecules adsorbed between the top and the second Ru rows with four carbon atoms at one side of tetracene molecule nearly on the top of Ru atoms of the outermost Ru layer, the π -d interactions could be maximized.

4. Conclusions

We carried out ab initio density functional theory (DFT) calculations for tetracene adsorption on the Ru(10 $\overline{1}0$) surface. Several adsorption geometries of flat-lying tetracene molecule with its long axis parallel and perpendicular to the $[1 \overline{2} 1 0]$ direction were investigated in details. The most stable adsorption structures are determined to be for the molecule adsorbed between the top and the second Ru atomic rows, with

its long molecular axis along the $[1\bar{2}10]$ direction and an adsorption energy of 4.23 eV, and for tetracene adsorbed with its long molecular axis perpendicular to $[1\bar{2}10]$ with a slightly smaller adsorption energy of 4.19 eV. The adsorption energy difference of about 0.04 eV between these two adsorption configurations consists well with the statistic orientational distributions (51 and 45% for tetracene aligned with their long axes parallel and perpendicular to $[1\bar{2}10]$) observed in the STM measurements), and the both adsorption configurations match very well with the STM experiments for tetracene overlayer on Ru(10 $\bar{1}0$). By comparing densities of states before and after tetracene adsorption, we conclude that tetracene adsorption on the Ru(10 $\bar{1}0$) surface is determined by the coupling of the Ru d-band and the filled p-orbitals of tetracene.

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