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Electronic structure of the pentacene–gold interface: A density-functional theory study

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ABSTRACT

The structural and electronic properties of a pentacene monolayer adsorbed on the Au(1 1 1) surface have been studied with a density-functional theory (DFT) approach. A thermally stable adsorption geometry of the pentacene monolayer on the gold surface is found, from which the adsorption energy per pentacene molecule can be evaluated. Our results illustrate how the electron charge distribution initially present over the clean gold surface is pushed back upon adsorption of the pentacene monolayer; this push-back (pillow effect) leads to a significant work-function decrease for the modified gold surface. The electronic couplings between the highest occupied molecular orbital of pentacene and the Au(1 1 1) surface and between adjacent pentacene molecules within the monolayer, were extracted from the calculated band structures; the pentacene–gold surface electronic coupling is found to be about five times smaller than the electronic coupling between pentacene molecules.

1. Introduction

Organic semiconductors are drawing a great deal of attention due to their impact in new generations of (opto-)electronic devices, such as light-emitting diodes, field-effect transistors, or solar cells. Crystals and thin films of pentacene have been used as the hole-transport material in transistors and solar cells due to their high hole mobility [1,2]. The interface between organic semiconductors and metal electrodes has been studied extensively because charge transfer across the interface is crucial for the performance of organic electronic devices. In general, the energy offset between the metal Fermi level and the highest occupied molecular orbital (HOMO) [or lowest un occupied molecular orbital (LUMO)] level of the organic films plays an important role in controlling the hole [electron] injection from the anode [cathode] to the hole [electron] transport material. Pentacene has been shown to effectively tune the work-function of metal (such as gold) electrodes, used as source and drain in organic field-effect transistors. Experimental investigations of a pentacene monolayer adsorbed on a polycrystalline or single-crystal gold surface have revealed a broad range of work-function modifications of the gold surface, from *ca.* 0.5–0.95 eV [3–9]. In addition, various interfacial structures of the pentacene monolayer on the gold surface were also proposed; scanning tunneling microscopy (STM) and spectroscopy studies point to a flat-lying pentacene geometry with the molecular plane parallel to the gold surface [5,10–13] while near-edge X-ray absorption fine structure (NEXAFS) experiments also show a flat-lying geometry, but with the molecular plane tilted along the molecular short axis at a finite angle [14].

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Quantum–mechanical calculations based on density-functional theory (DFT) have been successful in understanding the interfacial properties of self-assembled monolayers (SAMs) chemically adsorbed on metal surfaces [15–18]; however, fewer DFT studies have been reported on weakly interacting interfacial systems, where the molecules forming the monolayer are physically adsorbed on the metal surface [19–22]. Previous DFT calculations [20,21] optimized the pentacene adsorption geometry on the Au(0 0 1) surface while assuming a flat-lying geometry of the pentacene molecules with their molecular planes parallel to the surface.

Here, we report on a DFT study of the interface made of a pentacene monolayer adsorbed on the Au(1 1 1) surface. The equilibrium structure and adsorption energy of the pentacene monolayer, the work-function change of the Au(1 1 1) surface upon pentacene adsorption, and the energy level alignment at the interface are calculated and compared with recent experimental data [3,5,7,10,12–14]. In addition, the band structures of the pentacene–Au interface are analyzed in detail to extract the electronic couplings between the HOMO level of pentacene and the gold surface and between adjacent pentacene molecules within the monolayer.

2. Methodology

We use a repeated-slab approach and model the Au(1 1 1) surface with a $c(\sqrt{3} \times 6)$ surface unit cell with lateral unit cell parameters $a = 5.11$ Å and $b = 17.71$ Å along the $\langle 11\bar{2}\rangle$ and $\langle 1\bar{1}0\rangle$ directions. The surface unit cell parameters are derived from the optimized bulk gold lattice parameter without taking into account the Au(1 1 1) surface reconstruction [23–28], as discussed in Ref. [15]. In the direction perpendicular to the c-axis ($\langle 1\ 1\ 1\rangle$ direction) of the unit cell, a slab consisting of five layers of gold atoms is used to model the surface, with each layer containing 12 gold atoms (resulting in 60 gold atoms per unit cell). The gold atoms within the top two layers of the slab are fully relaxed while the bottom three layers are frozen (see the lateral view in Fig. 1a). The c lattice parameter of the unit cell is taken to be 45.28 Å; since the thickness of the relaxed gold slab is about 10 Å, this leaves a vacuum gap of about 35 Å between each repeated gold slab along the c-direction (which effectively prevents any interactions from slab to slab).

To model the monolayer coverage, each surface unit cell of the gold is made to accommodate one pentacene molecule. Interestingly, the experimental observed surface lattice parameters of the pentacene monolayer on the gold surface ($a = 5.76$ Å, $b = 15.3$ Å, $\gamma = 79.1°$ [10] or $a = 5.7$ Å, $b = 15.5$ Å, $\gamma = 84°$ [12]) are different from those of the clean gold surface unit cell. However, it would be very difficult to model two sets of non-commensurate lattice parameters in a DFT calculation under periodic boundary conditions; to take into account the lattice parameters for both the gold surface and the pentacene monolayer at the same time, a much larger super cell would need to be adopted, which would be computationally unpractical. Therefore, in the present study where the a lattice parameter is taken to be 5.11 Å, neighboring pentacene molecules are constrained to lay at a distance *ca.* 0.6–0.65 Å shorter than the one experimentally observed; this is expected to slightly affect the optimization of the pentacene adsorption geometry due to the increased steric hindrance, as we will discuss below.

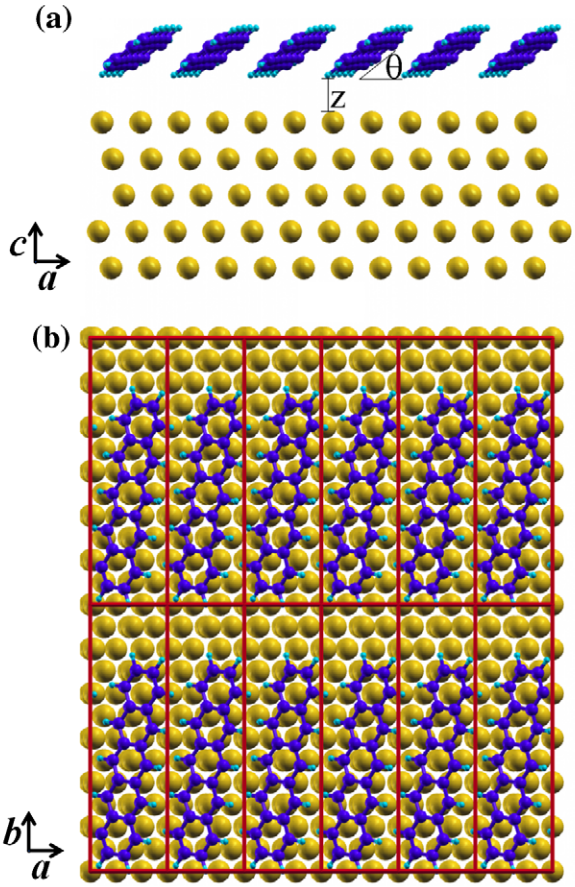

Fig. 1. Side view (a) and top view (b) of the relaxed structure of the pentacene–Au interface. In (a), the adsorption height z (defined as the distance between the lowest hydrogen atom of the pentacene molecule and the average height of the gold atoms in the top layer of the slab, projected along the lattice c-direction) is equal to 3.13 Å; the tilt angle between the pentacene molecular plane and the gold surface θ, is equal to 37.7°. The surface unit cell is indicated by the red contour in (b). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

As a starting geometry, the pentacene molecules were positioned 2.48 Å (measured as the distance between the lowest hydrogen atom of the pentacene molecule and the average height of the gold atoms in the top layer of the slab, projected along the lattice c-direction) above the clean Au(1 1 1) surface, with their molecular long axis parallel to the surface along one of the diagonals in the surface unit cell (see the top view in Fig. 1b), and the molecular plane perpendicular to the Au(1 1 1) substrate. The vacuum gap between the top atom of the pentacene molecule and the next gold slab is then larger than 28 Å. All atoms in the pentacene molecule and in the top two layers of gold surface slab