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Photoelectron spectroscopy study of the electronic structures at CoPc/Bi(111) interface

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ABSTRACT

Self-assembly of functional molecules on solid substrate has been recognized as an appealing approach for the fabrication of diverse nanostructures for nanoelectronics. Herein, we investigate the growth of cobalt phthalocyanine (CoPc) on a Bi(111) surface with focus on the interface electronic structures utilizing photoelectron spectroscopy. While charge transfer from bismuth substrate to the molecule results in the emergence of an interface component in the Co 3p core level at lower binding energy, core-levels associated to the molecular ligand (C 1s and N 1s) are less influenced by the adsorption. In addition, density functional theory (DFT) calculations also support the empirical inference that the molecule-substrate interaction mainly involves the out-of-plane empty Co 3d orbital and bismuth states. Finally, valence band spectra demonstrate the molecule-substrate interaction is induced by interface charge transfer, agreeing well with core level measurements. Charge transfer is shown to be mainly from the underlying bismuth substrate to the empty states located at the central Co atom in the CoPc molecules. This report may provide a fundamental basis to the on-surface engineering of interfaces for molecular devices and spintronics.

1. Introduction

The manipulation of self-assembly of functionalized molecules on solid surfaces has been extensively exploited because it facilitates the convenient fabrication of low-dimensional nanostructures with great flexibility [1]. Furthermore, not only the physical nanostructures but also the related electronic properties, can be tailored as demanded [2,3]. In particular, the family of phthalocyanines, as one of the most widely investigated conjugated ring complex, has been proposed for an increasingly promising range of applications in the field of biological processes, gas sensing, thin-film transistors, photovoltaic devices and so on [4–8]. For example, considerable interests have been paid to the transition-metal phthalocyanines (TMPcs) as a representative model system because of the possibility of tuning both electronic and optical properties, owing to the presence of partially filled d orbitals of the transition metal atom [9–11]. As a result, numerous investigations have proliferated in the past regarding on the adsorption of TMPcs on solid substrates, for example, CoPc and MnPc on Ag(111) [11–15], CoPc on graphene [16], CoPc on Ag/Si(111) [17], CoPc on Cu(111) [18], FePc on Ag(111) and Au [19–21], CoPc on Au [22–25], CuPc on Ag [26], and their application to spintronics and data storage devices has also been demonstrated [27,28].

It has been realized that, the performance of transitional metal phthalocyanines in devices can be strongly affected by interface interaction, which in turn can be altered both in strength and nature by choosing specific substrates [16,22–32]. Bismuth (Bi), a heavy element semimetal, has interesting properties such as strong spin orbital coupling [33] and plays a major role in topological insulators (for instance, Bi_2Se_3 or Bi_2Te_3). Meanwhile, efforts have also been devoted to prepare transition metal phthalocyanines on Bi substrates, based on the relatively inert activity of bismuth as compared to other metals such as Cu, Ni or Ag [34–36]. Because of the strong spin-orbit interaction, Bi surfaces have unusual spin properties [36] and one of the most appealing applications could be the construction of spin-filters for spintronics. Importantly, Bi(111) is the natural cleavage plane of Bi crystal and turns out to be the preferred direction of epitaxial growth [37]. Consequently, the CoPc/Bi(111) interface could be an ideal combination to study the interface electronic and magnetic

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properties. Since the molecule-substrate interaction is expected to be predominantly between the partially filled 3d orbitals of cobalt ion and the spin-orbit coupled bismuth substrate, the investigation of the CoPc/Bi(111) system may also shed new light on the understanding of interfacial interactions between atoms both with strong spin-orbital interactions. Therefore, we focus on the interface exploiting between CoPc and Bi(111) in this work, by carrying out photoelectron spectroscopy (PES) and density function theory (DFT) to understand the interference of the Co 3d states on the interface electronic properties.

2. Material and methods

All the experiments were performed under ultra-high vacuum with the base pressure better than $5*10^{-10}$ mbar at room temperature (RT). Photoelectron spectroscopy measurements were carried out at the Centre for Storage Ring Facilities (ISA) in Denmark at “Matline”, while the valence band spectra were also repeatedly measured in the lab using the helium lamp (He I, hv=21.2 eV). The photon energies were calibrated by comparing the binding energy of Ta 4f and the metal Fermi level (E_f) from the sample holder. The Bi(111) substrate (Mateck) was cleaned prior to organic film deposition by cycles of Ar + sputtering at 800 eV and post annealing to about 400 K while the surface cleanliness was checked by XPS. The CoPc molecule (Sigma-Aldrich, the molecular structure is shown in Fig. 1) was thermally evaporated onto the Bi(111) surface from a temperature controlled evaporation cell after overnight outgassing. The thickness of the CoPc films varies from submonolayer to multilayer as was determined using quartz microbalance together with the attenuation of the intensity of the Bi 4f substrate peak in XPS, suggesting an almost layer-by-layer growth mode of CoPc on Bi(111). Herein, one monolayer is defined to have a thickness of about 3 Å (consistent with other studies for such planner ring macrocycles [18,20,35]). After background subtraction, XPS spectra were fitted using Voigt functions with XPSPEAK software.

Calculations were performed in the framework of Density Functional Theory (DFT) [38,39] by using CASTEP package [40] with the gradient-corrected Perdew-Burke-Ernzerhof (PBE-GGA) exchange-correlation functional [41]. To obtain a more exact description of interaction between CoPc and substrate, the van der Waals (vdW) were included using Tkatchenko-Scheffler method [42]. The convergence criterion for electronic self-consistent relaxation is set to 2×10^{-5} eV/atom. The Bi atoms in the substrate are fixed while the atoms in the adsorbate macrocycles are fully relaxed with a force convergence criteria of 0.01 eV/ Å.

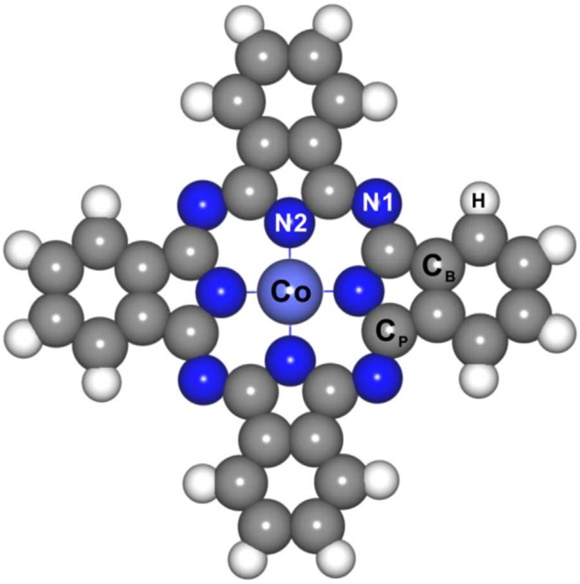

Fig. 1. The molecular structure of CoPc in gas phase. N1 and N2 indicate two different chemically bonded nitrogen sites, while C_B and C_P represent carbon atoms in benzene ring and pyrrole, respectively.

3. Results and discussion

As revealed from previous reports, CoPc is expected to lie flat on metal surfaces for layer thickness of up to a few monolayers, thus maximizing the interaction of the molecule's extended π-electron system and d orbitals of the Co atom with the underlying substrate [23,24,31]. Owing to its high sensitivity to changes of chemical environment, XPS is therefore a powerful tool for monitoring any chemical state change of CoPc upon adsorption on bismuth substrate. To start with, the Co 3p core level was recorded in sequence as a function of coverages and plotted together in Fig. 2. Due to the upper limit of photon energy at the Matline beamline, the monitoring of Co 2p core level was unfortunately not possible even though it has a relatively high photoionization cross section compared to the Co 3p. For the convenience of comparison, the raw Co 3p spectra with background included are plotted and presented separately in Fig. 2a. As seen, the Shirley background feature is apparent for thick CoPc film. However, a liner background is observed at low coverages (below 2.5 ML) due to the fact that the spectrum background (at low CoPc coverage) is mainly dominated by the contribution from the Bi(111) surface, which shows a similar liner background at the binding energy region between 70 eV and 50 eV. The best fitting parameters of Co 3p spectra are listed in Table 1, with the peak position, line width and the relative percentage of peak area included. At first glance, apparent changes can be identified for the cobalt chemical state from submonolayer to multilayer coverage. At the initial stage of about 0.4 ML CoPc deposited onto the Bi(111) substrate, a peak located at about 59.5 eV binding energy can be clearly resolved. Further deposition of another 0.8 ML CoPc (1.2 ML in total) results in a visible change of the Co 3p peak shape with an additional component located at higher binding energy (60.5 eV), which is about one fifth in intensity of the original component at 59.5 eV. When the coverage reaches about 2.5 ML, these two components are still well resolved while the relative percentage of peak intensity of individual component changes significantly: the component at higher binding energy gets 3 times stronger compared to the peak at lower binding energy, meanwhile the line shape of both peaks keeps constant. Furthermore, for thick film of about 4 ML, the component at 60.7 eV becomes absolutely dominant and the one locating at 50.7 eV almost vanishes.

In the case of the free CoPc molecule, the macrocycle has D_{4h} symmetry and Co is divalent (Co^{2+}) [14,18,31]. As compared to previous studies from literature [24,43], the Co 3p peak locating at 60.5 eV should be attributed to the Co(II) oxidation state, and in our case it is assigned to the Co ion in the center of CoPc molecule at thick coverage (Peak T), where the majority of CoPc molecules have no interaction with the Bi substrate and hence the CoPc behaves more or less as in gas phase [22,23,44]. Based on this, it can be concluded now that the appearance of Co 3p component at 59.5 eV at thin coverage of CoPc on Bi(111) should be related to the interface molecular-substrate interaction, which consequently results in a new chemical state for the cobalt ion. As seen in Fig. 2b, when less than one monolayer of CoPc was deposited onto the bismuth substrate, the Co 3p core level presents only one single peak located at 59.5 eV (interface component, Peak I), indicating that the first layer of CoPc is directly contacted with the underlying bismuth surface and the interface charge transfer involves the central Co ion interacting with the underlying bismuth states, as similar behavior has also been reported for the analogous systems of CoPc on Ag(111) and Au(110) [12,23]. In addition, the presence of both the Co(II) state and the interface component in the case of 1.2 ML and 2.5 ML coverages is again an evident proof for the strong molecule-substrate interaction between CoPc and Bi(111). While the first monolayer of CoPc has covered the whole surface, additional layers of CoPc do not contact or interact with the substrate, which in the end gives the pristine Co(II) state for multilayer CoPc.