Theoretical Characterization of the Indium Tin Oxide Surface and of Its Binding Sites for Adsorption of Phosphonic Acid Monolayers

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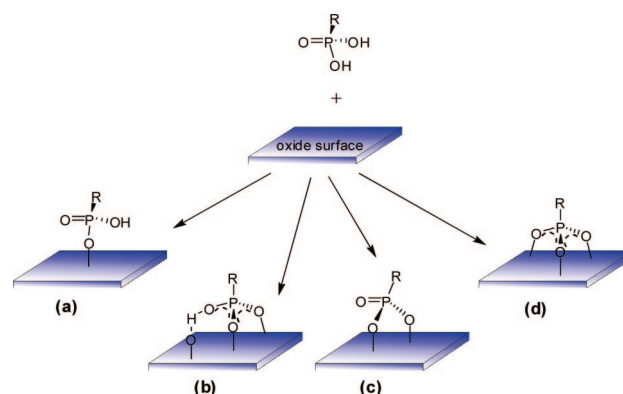
Indium tin oxide (ITO) is currently the most widely used transparent electrode in organic light-emitting devices and solar cells as well as in liquid-crystal displays. The electronic and geometric structure of the interface formed between the ITO surface and the organic overlayer strongly affects the charge injection characteristics and the overall efficiency of the organic electronic devices.[1] Controlling the composition of this interface can be challenging, since there is often a complex mixture of the stoichiometric oxide, hydroxides, and even oxy-hydroxides in the near surface region, whose ratios strongly depend upon the source of the ITO, cleaning and activation procedures, and modification protocols using chemisorption of small molecules.[2]

Chemical modification of an ITO surface via small-molecule organic adsorbates provides a means for tuning interfacial charge injection and constitutes a promising route toward increasing device efficiency in both organic light emitting diodes and solar cells.[2c] Among various small-molecule compounds capable of self-assembling on OH-terminated surfaces, phosphonic acids (PAs) are especially promising for surface modifications of various oxides including ITO,[3] TiO$_2$,[4] ZrO$_2$,[5] Al$_2$O$_3$,[6] and BaTiO$_3$,[7] since they form robust monolayers without the need to resort to cross-linking,

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Scheme 1

as is common, for example, in silane surface modification.[2a,b] Several binding scenarios have been proposed for PA adsorption on transition metal oxide surfaces, which differ in the number of oxygen atoms bound to the surface and the involvement of hydrogen bonding. The type of adsorption mode can change the orientation of the modifier and the net surface dipole at the ITO/modifier interface, which can be important in determining both wettability and effective surface work function; therefore, it is important to be able to describe the possible adsorption modes and to differentiate among them.

Typical proposed PA adsorption modes on metal oxides are shown in Scheme 1. The predominant adsorption modes depend on the type of oxide surface as well as on the reaction conditions. For example, modes (a) (monodentate) and (b) (bidentate + electrostatic) have been suggested for PA adsorption on TiO$_2$,[4a] Al$_2$O$_3$,[6a] and BaTiO$_3$,[7b] while tridentate mode (d) has been proposed to dominate on ZrO$_2$[5] and SiO$_2$.[8] PA adsorption on ITO has been described to occur via multiple modes, with a predominance of bidentate and tridentate modes (c) and (d), as indicated by a combination of X-ray photoelectron spectroscopy (XPS) and FT-IR studies.[3a,c] There remains some uncertainty in the reported spectroscopic studies, in particular XPS studies, that have been used to discern among PA adsorption modes due to a lack of precise knowledge of the spectroscopic features specific to each binding mode.

Here, we present what we believe to be the first theoretical characterization, based on density functional theory (DFT),

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of a model indium tin oxide surface and of the nature of the binding sites that determine the adsorption of phosphonic acid monolayers. We assess the validity of our theoretical description by comparing our first-principles results to XPS data on the ITO surface modified by PA monolayers. The advantage of our approach is to provide from the theory side core-level energies calculated at the quantum-mechanical level for specific atom types, which leads on the experimental side to unambiguous assignments of the various peak components in the XPS spectra.

Crystalline ITO can be viewed as an indium oxide cubic lattice with Sn-substitutions at cationic sites.[9] This model is used as the starting point for our structural description of the ITO surface. We selected the (222) surface since magnetron sputtering,[10] molecular beam epitaxy,[11] and chemical vapor deposition[12] data indicate that face to be the most abundant. The bulk In_2O_3 unit cell is depicted in Figure 1, where the (222) lattice plane is highlighted (upper panel).

Based on the bulk In_2O_3 structure, a periodic supercell (with a rectangular surface) was chosen to be able to sample all structurally nonequivalent surface sites, while maintaining manageable computer times/costs. All oxygen atoms located above the top layer of the metal atoms were saturated with hydrogens to model a realistic OH-terminated surface. The Sn/In ratio was set to 0.14, which lies within the typical doping range, 0.1−0.2, found in commercial ITO.[13] A random number generator was used to distribute Sn substitutions over the cationic positions. The resulting supercell composition corresponds to $(In_{84}Sn_{12}O_{144})H_{24}$.

The atomic positions in the periodic ITO surface slab were optimized at the density functional theory (DFT) level with the PBE exchange-correlation functional,[14] a planewave basis set of 300 eV cutoff, and PAW potentials to describe the valence-core electron interactions,[15] as implemented in the VASP code.[16] The optimized surface cell is presented in Figure 1 (lower panel). Two types of (potentially) chemically active sites were found on the ITO surface: (i) metal ions with oxygen coordination numbers lower than for the bulk cationic sites and (ii) surface hydroxyl groups.

Adsorption of a phosphonic acid monolayer on the ITO surface was studied at the DFT level by using the surface slab shown in Figure 1 and a representative compound, *n*-octylphosphonic acid (OPA). In order to characterize
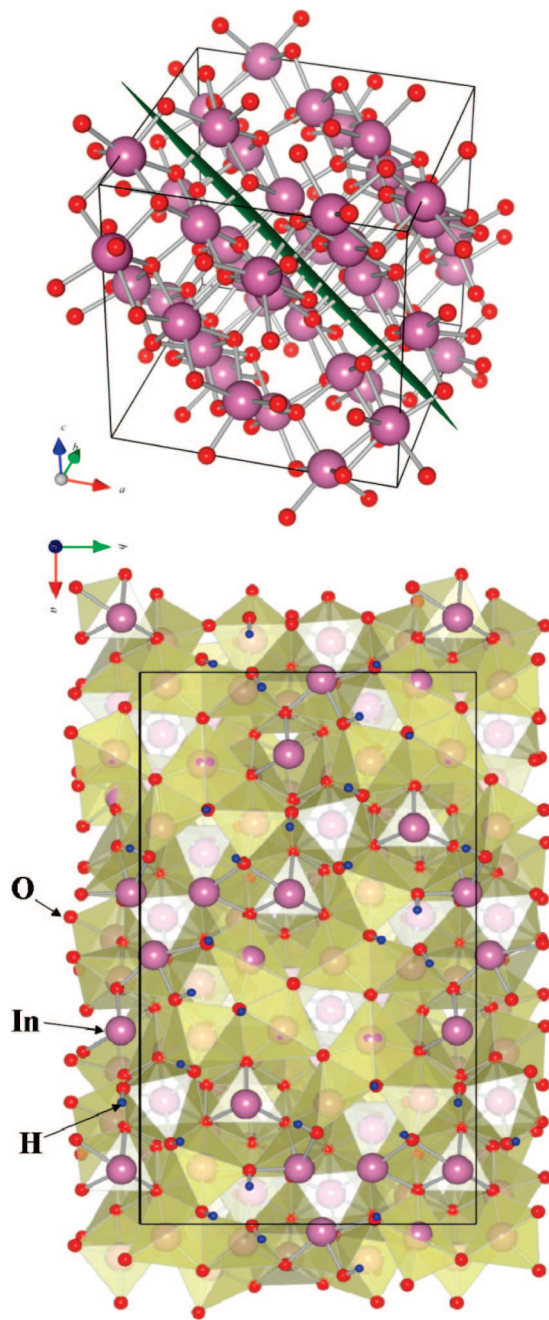

Figure 1. Upper panel: Bulk In_2O_3 unit cell (cubic) with the (222) lattice plane highlighted in green. Lower panel: Top view of a rectangular, OH-terminated ITO (222) surface slab, optimized at the DFT level. The periodic rectangular supercell is indicated. Sn substitutions were randomly distributed over the cationic positions throughout the slab. Chemically active surface sites include under-coordinated metal ions (not shaded by bulk-like coordination polyhedra) and surface OH groups.

various adsorption possibilities, a large number (>20) of initial geometries were generated, sampling the under-coordinated metal sites and surface hydroxyl groups expected to participate in OPA binding. Geometry optimizations were then performed for each initial configuration, allowing elimination of up to two water molecules to accompany OPA chemisorption.

Adsorption modes of types (b), (c), and (d) (see Scheme 1) were most commonly obtained as a result of structural optimizations. Since the core level energies of the oxygen atoms belonging to the phosphonic/phosphonate moiety are

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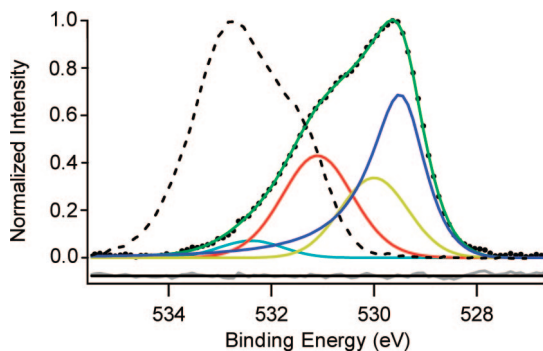
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Figure 2. Experimental O(1s) core level XPS spectrum for *n*-octylphosphonic acid adsorbed on the ITO surface (dots), fitted with components calculated at the DFT level (colored lines); the fit error is indicated by the gray baseline. The three main components of the fit are at 529.5 eV (bulk O, with asymmetry due to energy-loss processes[20]); 530.0 eV (surface In—O—In); and 531.1 eV (P—O—In, P=O···In, and surface In—OH). An additional peak at 532.6 eV was used to complete the fit (not accounted in the model OPA/ITO system). Sn—O species are also included in the 530.0 eV component.[20c] The XPS spectrum of the isolated OPA powder (dashed line) is shown for comparison. H-bonded configurations (POH···O(ITO)) have a calculated O(1s) peak at ca. 534 eV (similar to core levels in isolated OPA); they are absent in the XPS spectrum of the OPA/ITO system, indicating that modes (c) and (d) (Scheme 1) are the main products of OPA adsorption on ITO.

sensitive to their chemical environment, we proceeded to calculate the DFT binding energies of the O(1s) levels. A two-step procedure was used, consisting of (i) the evaluation of the influence of the valence electron distribution on the core electronic states within the *initial-state* approximation (as implemented in the VASP code[16]) and (ii) the use of the *final-state* approximation to estimate the electronic screening of a core hole.[17] The resulting core-level energies were referenced to that of the bulk-like O(1s) levels in the middle of the ITO slab; they are detailed in the caption of Figure 2.

To better identify experimentally which binding mode(s) is (are) predominant under realistic adsorption conditions, monolayers of OPA were prepared on ITO and their XPS spectra recorded. The ITO surface was first subjected to a cleaning procedure involving the use of detergents and organic solvents, followed by an oxygen plasma treatment to both clean and activate the surface. The substrate was then immediately submersed in a 1 mM solution of OPA (Alfa-Aesar) in ethanol, as described elsewhere.[3c] This was followed by an ethanol rinse, heating in a nitrogen environment at 140 °C for 48 h, and a final wash with a 5% TEA solution in ethanol. The O(1s) XPS spectrum of ITO modified with OPA, at 70° takeoff angle (which reduces the information depth to ca. 3 nm instead of the usual 9 nm[18]), is presented in Figure 2. The spectrum was fitted at best when considering three simulated components based on the *cal-*

culated O(1s) core level energies, and an additional adjusted low-intensity component to account for various defects and impurities, present in an actual ITO sample but not included in the model slab calculations. The XPS spectrum of isolated OPA was recorded separately and calibrated using the C(1s) level at 284.9 eV;[19] it displays O(1s) peaks at significantly higher binding energies, similar to the calculated oxygen core levels in the P—OH···O(ITO) mode (b). Importantly, using the procedure described above, the comparison between the simulated and experimental XPS spectra in Figure 1 indicates the absence of hydrogen bonding and P-OH groups in the PA monolayers formed on ITO. Thus, these results allow us to unambiguously identify modes (c) and (d) as the main products of PA adsorption.

Interestingly, adsorption modes (c) and (d) require that, in the case of arylphosphonic acids, the aryl groups be oriented nearly perpendicular to the surface. This is consistent with recent data from reflection infrared spectroscopy of *p*-nitrophenylphosphonic acid on ITO,[3b] which provides additional support for the validity of our results.

To summarize, we have developed the first atomistic model describing the ITO surface and studied the PA adsorption on ITO at the quantum mechanical level. The capability of our methodology to describe the PA binding was demonstrated through a comparison with experimental XPS spectra. Our results confirm that, under the typical reaction conditions we described, PA adsorption on ITO takes place predominantly via bidentate/tridentate binding that involves P—O—In bonds. On the basis of the model developed here for the ITO surface and of the identified adsorption modes, first-principles calculations are currently underway to characterize the work-function modifications induced by self-assembly of various PA molecules on ITO.

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