Improving the electrode interface in organic electronics

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New theoretical understanding of the geometric and electronic structure of interfaces between transparent electrodes and organic layers could enhance device functionality.

Indium tin oxide (ITO) is the most widely used transparent electrode in organic light-emitting devices and solar cells, and in liquid-crystal displays. The electronic and geometric structure of the interface between ITO and the organic material strongly affects the charge-injection characteristics, and thus largely determines the overall efficiency of these organic electronic devices. Two common issues are the large barrier for charge-carrier injection from ITO into the organic layer, which limits the electrical current, and the lack of compatibility between the hydrophilic surface of the oxide and the hydrophobic organic surface, which leads to poor adhesion between the materials.

Researchers have solved these problems by chemically modifying the ITO surface using small-molecule organic adsorbates. Among various compounds that can self-assemble on OH-terminated surfaces, phosphonic acids (PAs) are especially promising for surface modification of various oxides, including ITO. PAs form robust monolayers without a need for the cross-linking that is common, for example, in silane surface modification. However, the impact of these self-assembled monolayers on the interfacial electronic and geometric structure is not well characterized.

Our group at the Georgia Institute of Technology (Georgia Tech) has developed a theoretical approach to enable investigation of the ITO-PA interface. Our goal was to gain a detailed understanding of the interfacial structure and to provide guidelines for synthetic efforts aimed at lowering the charge-injection barrier via PA deposition. Our first step was, to our knowledge, the first theoretical characterization of a model ITO surface using density-functional theory (DFT). Based on the bulk indium oxide structure, a periodic supercell was chosen that includes examples of all structurally inequivalent surface sites. Each oxygen atom located above the top layer of metal atoms was saturated with hydrogen, to model a realistic, OH-terminated surface. The ratio of tin to indium atoms was set to 0.14, which lies within the typical doping range, 0.1–0.2, found in commercial ITO.

Figure 1. Top view of an OH-terminated indium tin oxide (ITO) surface slab, optimized at the density-functional theory level of calculation. The rectangle indicates the supercell, which is periodically repeated in the calculation. Tin substitutions were randomly distributed over the cationic positions throughout the slab.

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resulting supercell is shown in Figure 1. Two types of potentially chemically active sites were found on the ITO surface: metal ions with oxygen coordination numbers lower than that of the bulk cationic sites, and surface hydroxyl groups.

Our next step was to investigate the adsorption of a PA monolayer on the ITO surface at the DFT level of calculation. The calculation used the surface slab shown in Figure 1 and a representative PA compound, \( n \)-octylphosphonic acid. We characterized more than 20 adsorption possibilities. Among the possible adsorption modes illustrated in Figure 2, (c) and (d) were most frequently obtained as a result of structural optimizations. These binding modes are consistent both with earlier experimental assessments and with recent x-ray photoelectron spectra measured by Neal Armstrong’s group at the University of Arizona on samples synthesized by Seth Marder’s group at Georgia Tech. Interestingly, in the case of phenyl PAs, for which \( R \) in Figure 2 represents a phenyl group, adsorption modes (c) and (d) require that the phenyl groups be oriented nearly perpendicular to the surface.

This work has provided the first theoretical description of a reliable model for the ITO surface and of the binding modes with a PA monolayer. On this basis, our group explored substitutions of the PA phenyl groups with various electron-acceptor functionalities. We are now evaluating the effect of these substitutions on the ITO work function and on the energetic barrier for charge injection from ITO into the organic layer (through the PA monolayer). Several such substituted PAs are being synthesized in Seth Marder’s group and tested in device configurations in Bernard Kippelen’s group at Georgia Tech.

Fine tuning of the interfacial properties in organic electronic devices is becoming a reality. Our modeling capability should be useful in suggesting and evaluating further chemical interface modifications for improving the performance of organic electronic devices.

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