

The Modification of Indium Tin Oxide with Phosphonic Acids: Mechanism of Binding, Tuning of Surface Properties, and Potential for Use in Organic Electronic Applications

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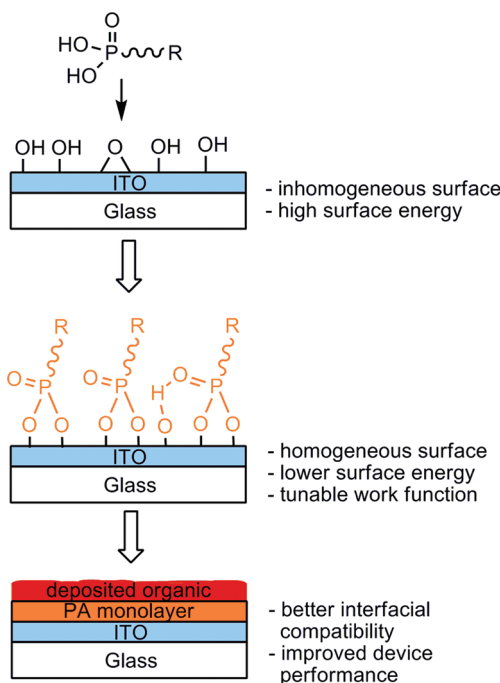
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CONSPECTUS

Transparent metal oxides, in particular, indium tin oxide (ITO), are critical transparent contact materials for applications in next-generation organic electronics, including organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs). Understanding and controlling the surface properties of ITO allows for the molecular engineering of the ITO–organic interface, resulting in fine control of the interfacial chemistries and electronics. In particular, both surface energy matching and work function compatibility at material interfaces can result in marked improvement in OLED and OPV performance. Although there are numerous ways to change the surface properties of ITO, one of the more successful surface modifications is the use of monolayers based on organic molecules with widely variable end functional groups. Phosphonic acids (PAs) are known to bind strongly to metal oxides and form robust monolayers on many different metal oxide materials. They also demonstrate several advantages over other functionalizing moieties such as silanes or carboxylic acids. Most notably, PAs can be stored in ambient conditions without degradation, and the surface modification procedures are typically robust and easy to employ.

This Account focuses on our research studying PA binding to ITO, the tunable properties of the resulting surfaces, and subsequent effects on the performance of organic electronic devices. We have used surface characterization techniques such as X-ray photoelectron spectroscopy (XPS) and infrared reflection adsorption spectroscopy (IRRAS) to determine that PAs bind to ITO in a predominantly bidentate fashion (where two of three oxygen atoms from the PA are involved in surface binding). Modification of the functional R-groups on PAs allows us to control and tune the surface energy and work function of the ITO surface. In one study using fluorinated benzyl PAs, we can keep the surface energy of ITO relatively low and constant but tune the surface work function. PA modification of ITO has resulted in materials that are more stable and more compatible with subsequently deposited organic materials, an effective work function that can be tuned by over 1 eV, and energy barriers to hole injection (OLED) or hole-harvesting (OPV) that can be well matched to the frontier orbital energies of the organic active layers, leading to better overall device properties.



Introduction

One of a variety of transparent conducting oxides (TCOs), indium-doped tin oxide (ITO), is the most widely used transparent electrode for a variety of optoelectronic technologies.^{1,2} ITO materials with In:Sn atomic ratios of ca. 90:10 have electrical conductivities rivaling metal thin films, and good transparency in the visible region. However, ITO must be annealed at high temperatures after sputter deposition, which results in a highly polar and crystalline material, with variable surface roughness, and a surface composition and work function that can be challenging to control.^{2–4} This Account focuses on the functionalization of ITO with phosphonic acids, a class of surface modifiers that have been proven to form robust bonds to the ITO surface, allowing for tunability of work function, wettability, and compatibility with a wide variety of organic electronic materials.

Choice of Phosphonic Acids

Chemical reactions at metal oxide surfaces are typically dominated by reactions of M^{n+} species (often exhibiting Lewis acidic character), O^{2-} species (Lewis basic), and/or $-OH$ groups (with amphoteric character and a tendency to react via condensation and/or hydrogen-bonding mechanisms), allowing for multiple reactivity patterns, as illustrated in several reviews covering typical chemical behavior of TiO_2 ,⁵ ZnO ,⁶ and SiO_2 ⁷ surfaces. Several approaches to surface modification can be envisaged, including acids, bases, plasma treatments to clean and/or alter the surface chemistry,^{1,3,4,8,9} and coatings of thin layers of polymers¹⁰ and inorganic species.¹¹ However, one of the most widely studied methods by which surface properties can be altered has been through the attachment of organic compounds to form close-packed monolayers.¹²

For the formation of robust monolayers on ITO, a variety of different functional groups can be used, such as carboxylic acids, thiols, alcohols, organosilanes (e.g., alkoxy- and chlorosilanes), and phosphonic acids (PAs).^{12–14} Organosilanes have found great utility in the modification of metal oxides in general; they are frequently commercially available and have been widely studied. Organosilanes also have significant shortcomings: they can be difficult to synthesize and isolate, are sensitive to moisture, and can easily self-condense (due to the favorable energy of formation for the Si–O–Si linkage), leading to difficulties in experimental application (e.g., precise control over amount of water content, heat, or other reaction conditions) and decomposition during storage.¹⁵

Several groups have recently explored the utility of PAs as a functional binding group for metal oxides, leading to the

synthesis of unique compounds and studies exploring their mechanism for surface binding and monolayer formation. Particularly attractive features of PAs are that their synthesis and purification is generally not difficult, they are often crystalline solids that can be stored in ambient conditions without undergoing self-condensation reactions, and the surface modification procedures are in many cases robust and easy to employ since they tend to bind strongly to most oxide surfaces and are less prone to self-condensation than organosilanes.¹⁶ As a consequence, rigorous exclusion of water during surface modification is not required to deposit well-packed monolayers.¹⁶ Several studies have confirmed that, once formed, PA-based monolayers are more resistant to hydrolysis than those formed from organosilanes or carboxylic acids,^{17,18} allowing solutions used for modifications to be reused.

Characteristics of PA Binding to Surfaces

Mechanism and Strength of Binding. PAs contain a tetracoordinate phosphorus atom in the +5 oxidation state that is bound to two hydroxyl groups and a double-bonded oxygen (phosphoryl group). PAs are finding an increasingly important role in the field of organic electronics, where they can be used as surface modifiers on a myriad of substrate types. Detailed investigation of the binding of PAs to metal oxide surfaces began in the late 1980s¹⁹ and has developed significantly through the spectroscopic analyses of Reven and co-workers.^{20,21} Extensive studies have been performed to characterize the binding of PAs on Al/ Al_2O_3 ,^{19,22} Ti/ TiO_2 ,^{23–25} and Si/ SiO_2 surfaces.²⁶ Recent work by Schwartz et al. has described a generally applicable protocol for the robust surface modification of metal oxide surfaces with PAs based on a two-step assembly/annealing procedure abbreviated as “T-BAG” (Tethering By Aggregation and Growth).²⁷

The presence of three oxygen atoms allows for covalent binding of the PA to an oxide surface in either monodentate, bidentate, or tridentate modes. Chemisorption via electrostatic interactions and/or hydrogen bonding can also occur. Additionally, the bonds can be either bridging (each acid oxygen binds to a different metal atom) or chelating (two or three of the acid oxygen atoms bind to the same metal atom).^{16,23} All these possibilities lead to a large variety of possible binding configurations (Figure 1).

Though it is difficult to unambiguously identify any single one binding mode present in a particular system, it is possible to distinguish the presence or absence of some of the binding modes. The mechanisms by which PAs bind

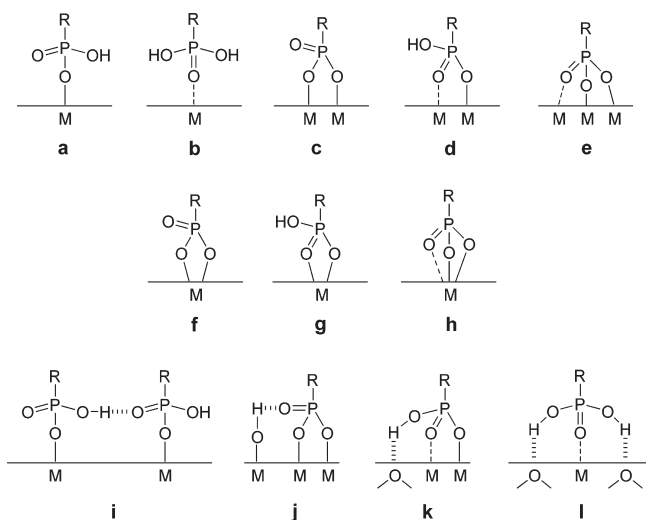


FIGURE 1. Some possible binding modes of phosphonic acids to a metal oxide surface, where M = metal: Monodentate (a and b), bridging bidentate (c and d), bridging tridentate (e), chelating bidentate (f and g), chelating tridentate (h), and some possible additional hydrogen bonding interactions (i–l). Adapted with permission from reference 23. Copyright 2008 American Chemical Society.

differ depending on the nature of the metal oxide surface. Binding of PAs to Lewis acidic metal oxide surfaces proceeds first via coordination of the phosphoryl oxygen to a Lewis acidic site on the surface, followed by heterocondensation with surface hydroxyl groups (Figure 2, upper).^{23,24,28} This heterocondensation is accelerated by the increased electrophilicity of the phosphorus atom after surface coordination of the phosphoryl group. At any point hydrogen bonding may take place instead of heterocondensation and this largely depends on the surface –OH content and the experimental conditions. PAs can still bind to surfaces of low Lewis acidity, although without the initial coordination of the phosphoryl group to the surface (Figure 2, lower).²² While there have been reports of hydroxyl-independent mechanisms,²⁹ it is generally accepted that the surface –OH content is key.²⁴ Heat will increase the extent of heterocondensation and can promote covalent bond formation via hydrogen bonding interactions.

To better understand the binding modes of PAs to ITO, Paniagua et al. employed polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) of octadecylphosphonic acid (ODPA, Figure 3) modified ITO, which was compared with the transmission FTIR spectrum of ODPA powder (Figure 4).³⁰ The presence of strong peaks corresponding to $\nu(\text{P}=\text{O})$ vibrations in the 1230 cm^{-1} region in both spectra, along with the diminished peaks between ca. 955 and 930 cm^{-1} (assigned to $\text{P}-\text{O}(\text{H})$ stretching vibrations) in the surface-bound sample, indicated the presence of mainly bidentate-bound ODPA.

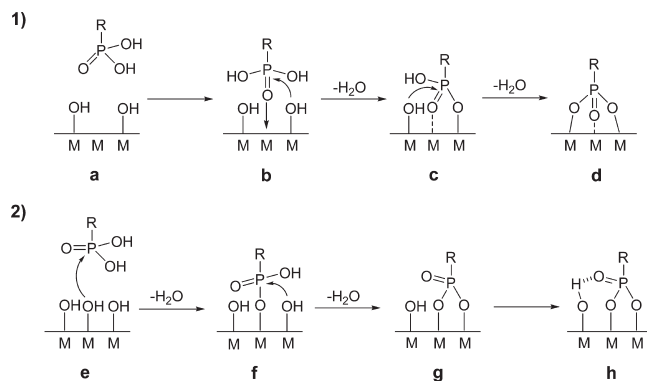


FIGURE 2. (1) Mechanism of phosphonic acid attachment to Lewis acidic metal oxides: (a) initial conditions, (b) coordination of the phosphoryl oxygen to a Lewis acidic site on the surface followed by heterocondensation with the now more electrophilic phosphorus, (c) additional heterocondensation, and (d) final tridentate binding state. (2) Mechanism of phosphonic acid attachment to poorly Lewis acidic metal oxides: (e) heterocondensation with a surface hydroxyl group, (f) second heterocondensation with the surface, (g) bidentate bound state, and (h) hydrogen bonding of phosphoryl group with surface hydroxyl.

Paramonov et al. used density functional theory (DFT) studies of the ITO surface to determine the core–level energies of various atom types that could be used to identify the binding modes of PAs to ITO.³¹ These calculations, in conjunction with high-resolution XPS investigation, allowed for the determination of the specific binding of the adsorption of octylphosphonic acid (OPA) monolayers to ITO, and good correlation with the experimental data was achieved (Figure 5).³¹ Adsorption modes corresponding to bidentate (with and without hydrogen bonding of the unbound oxygen species) and tridentate binding were the modes most commonly obtained as a result of structural optimizations. The XPS spectrum of isolated OPA displays O(1s) peaks at significantly higher binding energies, similar to the calculated oxygen core levels in the $\text{P}-\text{OH}\cdots\text{O}(\text{ITO})$ mode. A comparison of the simulated and experimental XPS spectra indicated the absence of hydrogen bonding and $\text{P}-\text{OH}$ groups as well as the unambiguous identification of bidentate (with and without the phosphoryl oxygen hydrogen bonded to the ITO surface) and tridentate binding modes as the main products of PA adsorption.

Some studies have also determined the relative binding strengths of PAs to ITO. Brewer et al. calculated the binding energy of 12-phosphonoundecanoic acid in the gas phase to the potential energy surfaces of tin or indium to be 98 or 116 kJ/mol, respectively.¹³ Hotchkiss et al. experimentally determined the binding energies of phenylIPA, OPA, and ODPA to ITO as 52 ± 1 , 82 ± 4 , and 159 ± 8 kJ/mol, respectively, illustrating the cooperative effects of the van der Waals forces of long alkyl chains in monolayer formation.³²

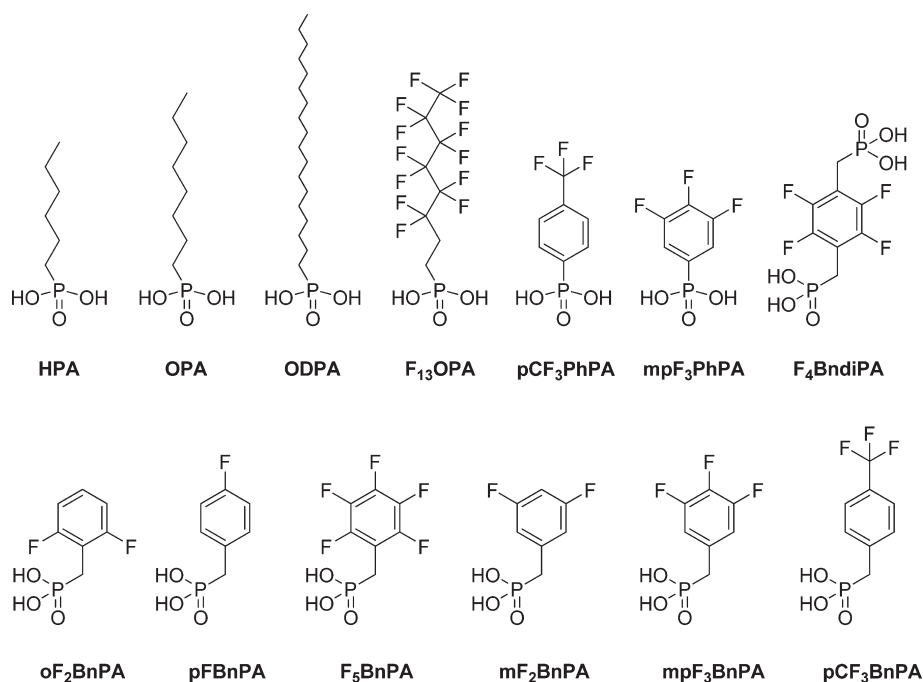


FIGURE 3. Chemical structures of the phosphonic acids used in our studies: hexylphosphonic acid (HPA), octylphosphonic acid (OPA), octadecylphosphonic acid (ODPA), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl phosphonic acid (F₁₃OPA), 4-(trifluoromethyl)phenylphosphonic acid (pCF₃PhPA), 3,4,5-trifluorophenylphosphonic acid (mpF₃PhPA), (perfluoro-1,4-phenylene)bis(methylene)diphosphonic acid (F₄BndiPA), 2,6-difluorobenzylphosphonic acid (oF₂BnPA), 4-fluorobenzylphosphonic acid (pFBnPA), pentafluorobenzylphosphonic acid (pF₅BnPA), 3,5-difluorobenzylphosphonic acid (mF₂BnPA), 3,4,5-trifluorobenzylphosphonic acid (mpF₃BnPA), and 4-(trifluoromethyl)benzylphosphonic acid (pCF₃BnPA).

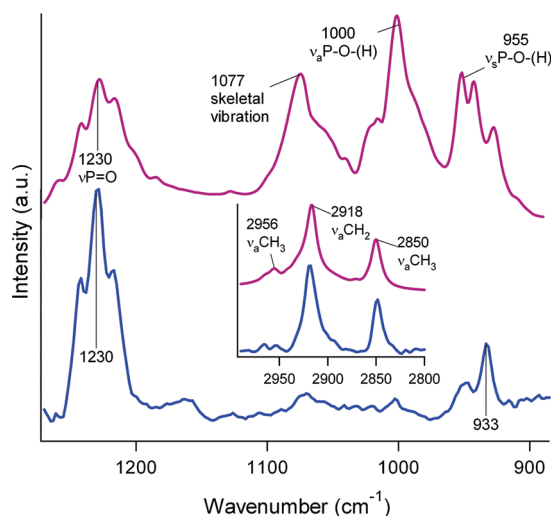


FIGURE 4. Comparison of the ODPA transmission FTIR spectrum (top spectrum) and the PM-IRRAS spectrum for an ODPA modified DSC/OP-treated ITO surface (bottom spectrum) in the ν(P–O) region. Inset: Spectral comparisons for the ν(C–H) region. Reprinted with permission from reference 30. Copyright 2008 American Chemical Society.

Surface Coverage and Kinetics of Binding. The ultimately achievable packing density of PAs on a surface will depend on several factors: the binding area of the PA moiety, the availability of binding sites on the oxide surface, the size of the

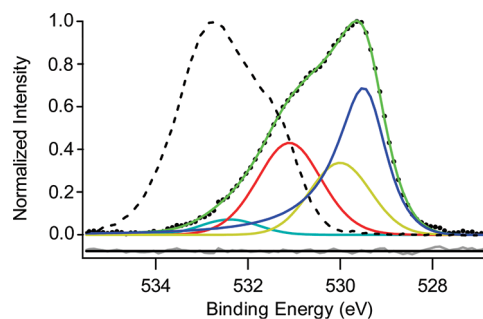


FIGURE 5. Experimental O(1s) core level XPS spectrum for OPA adsorbed on the ITO surface (dots), fitted with components calculated at the DFT level (colored lines); gray baseline corresponds to fit error. The three main components of the fit are at 529.5 eV (bulk O); 530.0 eV (surface In–O–In and Sn–O species); 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. XPS spectrum of isolated OPA powder (dashed line) is shown for comparison. Reprinted with permission from reference 31. Copyright 2008 American Chemical Society.

overall molecules, and the presence of additional stabilizing factors. The binding area of a PA headgroup has been reported as 0.24 nm² (~4 molecules/nm²).²¹ The availability of binding sites depends both on the surface chemistry (as discussed above) and steric conditions, which contribute to the ability to form close-packed monolayers of PAs, as a bulky R group could decrease the packing density.³³ Additional intermolecular

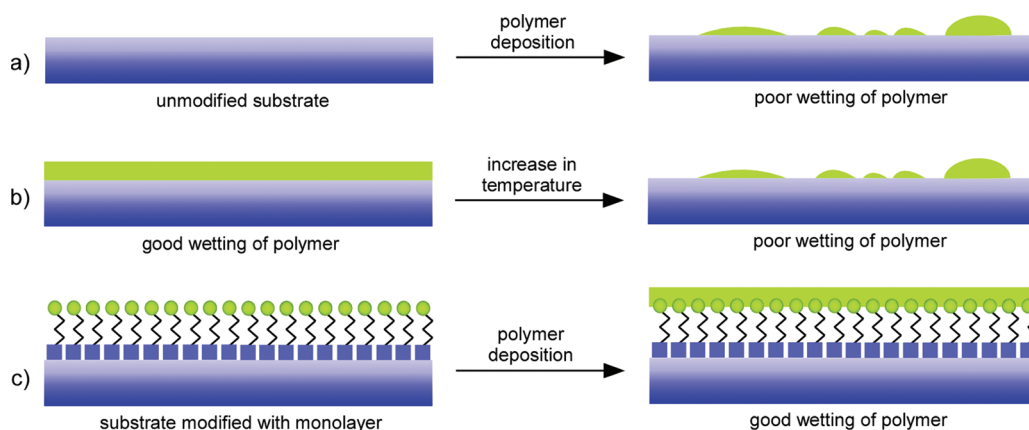


FIGURE 6. Illustration of the physical interactions between a substrate and deposited polymer. (a) Hydrophilic substrate that does not interact well with the deposited polymer, thereby causing inhomogeneous coating of the polymer on the surface. (b) Initial good wetting of the polymer which displays poor wetting after an increase in temperature and/or over time. (c) Substrate modified with a monolayer that changes the surface energy of the material in such a way as to interact more favorably with the polymer, resulting in lasting homogeneous film coverage.

stabilizing factors, such as van der Waals forces or acid–base interactions, can help promote monolayer formation.¹³

There is a paucity of studies in the literature quantifying the surface coverage of PAs on ITO. Cyclic voltammetry has been used to determine a monolayer packing of ferrocene-substituted PAs of ~ 2.5 molecules/nm².³⁴ Koh et al. related the contact angle of ODPA-coated ITO to contact angle data for the analogous thiol-coated gold surface and found that ODPA achieves a coverage slightly below that (87%, or 4.8 molecules/nm²) for a full self-assembled monolayer of octadecanethiol on gold.³⁵ Paniagua et al. used a similar approximation to determine coverages of 5.0, 5.0, and 2.9 molecules/nm² for HPA, ODPA, and F₁₃OPA, respectively, on ITO, indicating dense monolayer formation.³⁰

Related to the degree of surface coverage is the kinetics of formation for PA monolayers on metal oxide surfaces. No reports in the literature were found regarding the kinetics of monolayer formation from PAs on ITO, but there have been a number of studies measuring the rate of monolayer formation on other oxide surfaces. Depending on the oxide and surface pretreatment, full monolayer formation can be achieved in minutes or days.^{22,36} Additionally, the formation of multilayers is possible, but these have been shown to be easily distinguishable from monolayers.³⁷

Tuning the Surface Properties of ITO

Surface Energy Matching. In organic electronic systems, the electronic interactions between two layers of materials can be severely undermined if they are not in good physical contact with one another. The interface between the anode and the hole-transport material (and the cathode and the electron–transport material) in organic light-emitting diodes

(OLEDs) and that between the electrodes and the photoactive layer(s) in organic photovoltaics (OPVs) is critical; if poor physical interaction is seen in any of these interfaces then device performance and/or lifetime could be significantly decreased.³⁸

It has been shown that many common hole-transport materials do not wet ITO properly, due to poor surface energy matching.^{4,8,23,39} The energy for a given surface corresponds to half the amount of energy it would take to cleave a bulk amount of the same material in half. It could also be thought of as the interaction between the forces of cohesion and the forces of adhesion which determines whether or not the wetting of an applied material (usually a liquid) occurs. The importance of surface energy matching between a deposited material on a substrate is illustrated in Figure 6. Several types of weak forces contribute to the surface free energy, including polar components arising from permanent and induced dipoles, and hydrogen bonding and dispersion components arising from induced (instantaneous) dipoles.⁸

Improving the wetting of subsequent organic layers deposited onto ITO can help to enhance the rates of charge transfer in optoelectronic devices, and the device lifetime.³⁸ While ITO often has a high surface energy as a result of surface –OH groups, the surface energy of many organic hole-transport materials (both polymer and small molecule, such as those based on triphenyl 1,4-bis(phenyl-*m*-tolylamino)biphenyl (TPD) and 1,4-bis(1-naphthylphenylamino)biphenyl (NPB)) is considerably lower.⁴⁰ This difference in surface energies can result in poor adhesion characteristics and could ultimately result in delamination of the organic film from the ITO.³⁹ Hence, PAs that can decrease the surface energy of ITO are very attractive for creating monolayers on

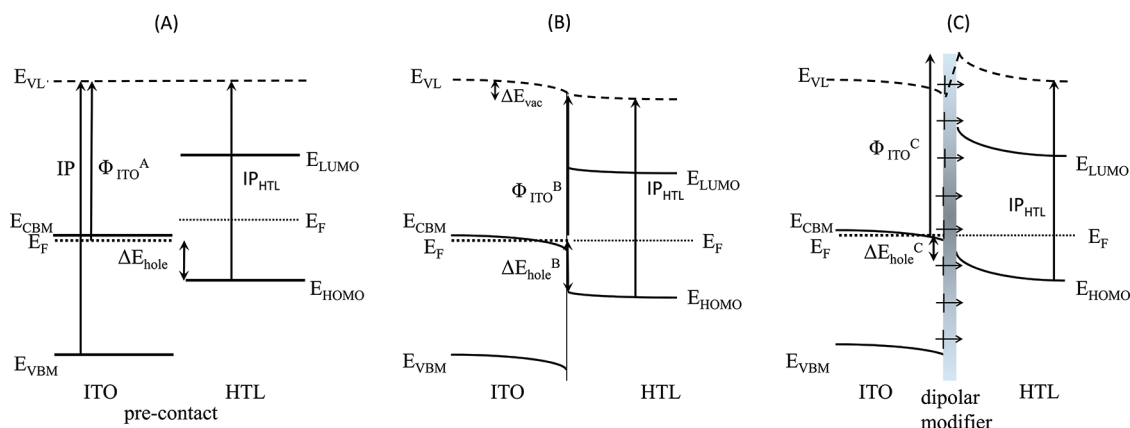


FIGURE 7. Schematic energy level diagrams representing three different heterojunctions: (A) an ITO electrode with an effective work function of ca. 4.5 eV, prior to contact with a prototype HTL, as might be used in OLED applications; ΔE_{hole} is the barrier to hole injection into the HTL; (B) the heterojunction in (A) after electronic equilibrium has been achieved, showing a decrease in effective work function for ITO at the ITO/HTL interface, and movement of $E_{F,\text{ITO}}$ into the conduction band region; (C) as in (B) but starting with an ITO electrode modified with a dipolar small molecule modifier, which increases the effective work function for ITO at the ITO/HTL interface and decreases (ΔE_{hole}).

ITO for compatibilizing organic materials used in optoelectronic device applications with the ITO surface.

Paniagua et al. studied the effects of tuning the surface energy of ITO with PAs (HPA, ODPa, F_{13} OPA, F_5 BnPA, and F_4 BndiPA, Figure 3) and observed a large decrease in the overall surface energy ($\sim 25\text{--}35$ vs $\sim 60\text{--}70$ mJ/m^2), specifically the polar component ($\sim 2\text{--}10$ vs $\sim 30\text{--}45$ mJ/m^2).³⁰ Not surprisingly, the binding to (and replacement of) surface hydroxyl groups by aliphatic and benzylic moieties decreased the polar component of the surface energy although F_{13} OPA resulted in the lowest observed overall surface energy (24 mJ/m^2) due to the highly hydrophobic and oleophobic nature of fluorinated hydrocarbons.⁴¹ Additionally, it was seen that monolayers of the alkyl PAs yielded a lower surface energy on ITO than a monolayer of F_5 BnPA, illustrating the denser packing of aliphatic groups over perfluoroaromatic groups, thereby creating a more hydrophobic surface.⁴² Subsequent work by Hotchkiss et al. showed that differently fluorinated benzyl PAs could also be used to decrease the surface energy of ITO (35–38 mJ/m^2), compared to detergent/solvent cleaned (DSC) and DSC/oxygen plasma (DSC/OP) cleaned ITO (56 and 72 mJ/m^2 , respectively).⁴³

Work Function Matching. Another challenge for optimizing materials systems for organic electronic applications lies in minimizing the charge injection (collection) barriers between the electrodes and the organic layers.⁴⁴ In an OLED, for example, the highest occupied molecular orbital (HOMO) of the hole transport layer (HTL) (which is close to the ionization energy (IP) measured by UPS) is often larger in energy than the effective work function (the difference between the local vacuum level and the Fermi level) of the

anode (usually ITO, with work functions between 4.4 and 5.0 eV, depending upon cleaning/activation). Figure 7A represents precontact for bare (unmodified) ITO and an HTL. The barrier for hole injection from ITO (Fermi level) into the HOMO of the HTL (ΔE_{hole}) is set by these precontact levels, and the system is not yet at equilibrium. Note that the ITO Fermi level could be very close to, or inside, the conduction band if the ITO electrode is sufficiently doped (e.g., In:Sn = 10). Figure 7B shows the heterojunction in (A) after electronic equilibrium has been reached by electron donation from the HTL to ITO, showing some “inversion” in the near-surface energy levels for ITO. The local vacuum level decreases slightly as does the work function for the ITO electrode ($\Phi_{\text{ITO}}^{\text{B}} + \Delta E_{\text{vac}} = \Phi_{\text{ITO}}^{\text{A}}$). “Band bending” (charge redistribution) in the HTL occurs over just a few molecular layers, and the ΔE_{hole} is increased relative to the precontact condition. When the ITO is modified with a strongly dipolar monolayer (with negative pole pointed out, Figure 7C), the local work function is increased by raising the vacuum level at the surface. Assuming only weak interactions between the HTL and the dipolar modifier, the vacuum level shifts down again upon HTL deposition, but ΔE_{hole} has been decreased relative to both the precontact levels and the unmodified ITO/HTL heterojunction. Such schematics assume that the modifiers act as point-dipoles, and depending upon the dipole moment of the modifier (projected along the normal axis) this change in vacuum level and change in effective work function can span ca. 1.5 eV for both metal oxides such as ITO and metals such as Au and Ag.^{45,46}

A few studies have detailed the ability to increase the work function of ITO anywhere from 0.3 to 0.9 eV using

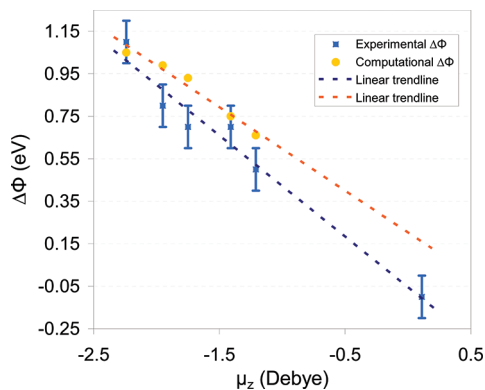


FIGURE 8. Changes in work function as measured by UPS (blue) and evaluated by DFT (orange) as a function of the μ_z value calculated for the PA used to modify the surface. Adapted with permission from reference 43. Copyright 2009 Wiley.

different PAs.^{35,47,48} Guo et al. reported a decrease in the work function of ITO ($\Delta\Phi = -0.28$ eV) upon attachment of a monolayer of quarterthiophene-2-phosphonic acid,⁴⁹ which was found to increase upon doping of this monolayer with tetrafluorotetracyanoquinodimethane (F_4 -TCNQ), ($\Delta\Phi = +0.35$ eV compared to bare ITO).²⁷

Research by Paniagua et al. to investigate work function tuning of ITO using a sequential oxygen plasma (OP)/PA treatment by ultraviolet photoelectron spectroscopy (UPS) revealed some interesting concepts in regards to the origin of the observed change in work function,³⁰ specifically in differentiating induced surface dipole versus band bending contribution to the work function change. The latter could be tracked by following the valence band maximum of the underlying ITO after each treatment. It was determined that band bending accounted for ± 0.2 eV variation in effective surface work function at a maximum, and that induced surface dipoles were responsible for bigger changes. First, an increase in surface dipole from the plasma etching ($+0.4$ eV relative to a non-plasma-treated ITO) occurs, followed by varying results depending on the particular PA used, where the alkyl PAs (HPA and ODPA) seemed to eliminate the surface dipole imparted by the plasma treatment (leaving the electrode with its preplasma treatment work function, 4.5 eV) while the fluorinated PAs (F_{13} OPA and F_5 BnPA) mostly maintained the work function of the plasma treated ITO (5.1 and 4.9 eV, respectively). This can be explained since nonpolar alkyl chains pointing away from the surface and a polar PA binding group pointing toward the surface result in an overall surface dipole toward the surface, while PAs with highly electronegative fluorine atoms pointing away from the surface impart a surface dipole pointing away from the surface.

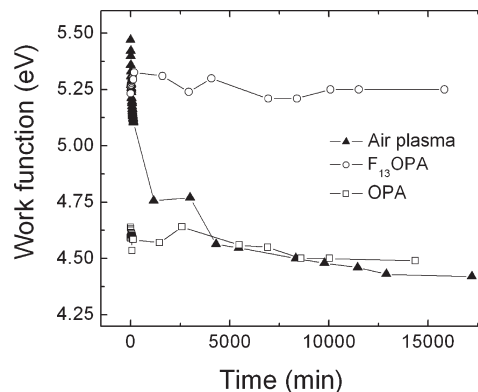


FIGURE 9. Effect of ambient exposure on the stability of the work function over time in differently modified ITO substrates: air plasma (\blacktriangle), OPA (\square), and F_{13} OPA (\circ) treated ITO. Reprinted with permission from reference 53. Copyright 2008 American Institute of Physics.

A subsequent study focused on the synthesis of six fluorinated benzylIPAs (Figure 3) and their use to form monolayers to give a low, relatively constant surface energy on ITO from one monolayer type to another, independent of work function.⁴³ Fluorine substituents were chosen due to the strongly dipolar C–F bonds which allow for the molecular dipole and resultant work function of ITO to be tuned by varying the degree and position of fluorination on the aromatic ring. A maximum overall change of $\Delta\Phi = +1.2$ eV was realized for ITO modified with oF_2 BnPA versus ITO modified with pCF_3 BnPA. Work function changes of PA-modified ITO surfaces with respect to unmodified ITO were also derived through DFT calculations and compared to experimental data (Figure 8), showing good correlation with the slopes of the dipole normal to the surface and the change in work function with similar molecules adsorbed to gold.^{43,46,50} In a similar type of study, Jee et al. were able to raise the work function of ITO by $+0.8$ eV while keeping the surface energy unchanged by modifying the surface with a monolayer of 2-chloroethylIPA.⁵¹

Performance of PA-Modified ITO in Organic Electronic Devices. The ability to control important surface properties of ITO, such as the surface energy and work function, has allowed for concomitant improvements in the properties of organic electronic devices. Several studies have demonstrated the improvements in OLED device performance by modification of the ITO with PA-based monolayers. Monolayers of PAs on ITO have resulted in enhanced hole injection in both single and double layer OLED devices,²⁷ as well as in polymer LEDs.^{49,52}

Sharma et al. have found that, in addition to stabilizing the change in work function of ITO by modification with a PA

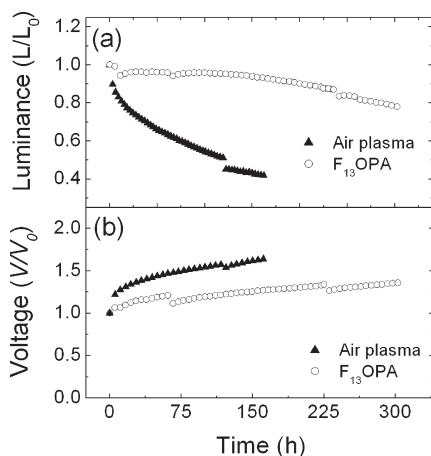


FIGURE 10. Comparison of normalized (a) luminance and (b) voltage under constant current density (6 mA/cm^2) for an air plasma (\blacktriangle) and F_{13}OPA (\circ) modified ITO-based device. The discontinuities correspond to points where operation was stopped and restarted in between measurements. Reprinted with permission from reference 53. Copyright 2008 American Institute of Physics.

for extended periods of time, versus plasma treatment alone (Figure 9), the lifetimes of electrophosphorescent OLEDs can be increased as well.⁵³ Devices incorporating a monolayer of F_{13}OPA showed substantially higher luminance over time versus only air-plasma treated devices (Figure 10). Additionally, the voltage increase over time necessary to maintain the initial current density was higher for air plasma treated OLEDs.

The effect of work function alone on the performance of OPVs and OLEDs has also been studied using a number of the fluorinated benzyl and phenyl phosphonic acids (Figure 3) to modify the surface work function of ITO while minimally affecting the surface energy.^{54,55} Although the work functions of ITO were successfully tuned from 4.9 to 5.4 eV with PAs, both single layer diodes and multilayer molecular OPVs failed to show improvement in a number of important device parameters over air plasma treatments in their initial performance. These results were tentatively assigned to Fermi level pinning effects.

Another study did find increased performance parameters of electrophosphorescent OLEDs due to the use of PAs; however, these do not appear to be work-function related.⁵⁶ Modification of ITO with F_5BnPA in an OLED based on evaporated $\alpha\text{-NPD}$ HTL resulted in a higher efficiency (9.3% at 1000 cd/m^2) than ITO that was only modified by air plasma (7.6% at 1000 cd/m^2). Additionally, pinhole formation as a result of material incompatibilities at the interface in unmodified ITO was not seen in any devices with PA-modified ITO. The PA-based monolayers also helped to keep

turn-on voltages low when compared to films of commonly used PEDOT:PSS material. Though these early studies indicate the benefits of increased ITO work function may be minimized due to the Fermi-level pinning effects hypothesized above, PAs appear to help compatibilize the ITO surface to minimize pinhole formation in subsequent organic material deposition.

Conclusions

A number of fundamental studies have been published showing the means by which PAs can be used to form robust, chemically bound monolayers on ITO that are easily formed and are more hydrolytically and thermally stable than monolayers formed from analogous organosilanes. Monolayers of PAs on ITO can be used to impart unique, tunable properties, such as the ability to control both the surface energy and work function of the surface. Additionally, the use of PAs to modify ITO has proven useful in their application to organic electronics, resulting in longer-lasting work function changes over plasma treatment alone, better compatibility of modified materials with subsequent deposited organic materials, and better overall measurable device properties. It is expected that the use of PAs as surface modifiers will continue to expand as their use in the formation of robust monolayers on a number of metal oxide materials makes them important in the investigation of nonstandard materials for use in organic electronics and other applications.

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FOOTNOTES

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