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Modifying the Surface Properties of Indium Tin Oxide with Alcohol-Based Monolayers for Use in Organic Electronics

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Abstract

Transparent conductive oxides serve a critical function in many devices, such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs). To optimize the performances of these devices, it is desirable to tune the interface between the transparent conductive oxide (TCO) and the next functional layer of these devices. Self-assembled monolayers prepared from phosphonic acids and silanes are commonly used to tune the properties and performance of this interface, including its surface energy, work function, and durability. Here, we report a new form of self-assembled monolayers for modifying indium tin oxide (ITO), a standard TCO used in OLEDs and OPVs. The ITO surfaces were modified with a series of distinct alcohol reagents. Stabilities of these alcohol based monolayers were compared with modifications derived from silanes and phosphonic acids, which are commonly used in the literature and industrial processes. Work functions and surface energies of these modified substrates were determined using ultraviolet photoelectron spectroscopy and contact angle measurements. Stability of these monolayers were assessed using cyclic voltammetry, X-ray photoelectron spectroscopy, and transmission spectroscopy techniques. Based on the results of these studies, alcohol based monolayers are promising candidates to modify ITO substrates for use in OLEDs and OPVs.

INTRODUCTION

Surface modifications of transparent conductive oxides, including indium tin oxide (ITO), have been extensively studied to analyze and tune their interfacial properties, such as their surface energy and work function.¹⁻⁸ Here, we demonstrate an alternative class of surface modifications using alcohol based monolayers on ITO to tune the interfacial properties. Commercially, ITO has been utilized in multiple devices, that include light emitting diodes (LEDs), organic light emitting diodes (OLEDs), molecular sensors, solar cells, organic photovoltaics (OPVs), flat-panel and flexible displays, touch screens, smart windows, and heat reflective coatings.^{2, 9-11} For these devices, ITO has become a standard material because of the advantages associated with its intrinsic properties, such as a relatively high work function (e.g., ~4.5 eV) and high transparency (~90%) within the visible spectrum.¹² There are, however, a number of challenges with the use of ITO in many of these electronic applications.^{11, 13-14} One challenge is that the interface between unmodified ITO and the hole transport layer (HTL) can undergo multiple forms of degradation induced by thermal, photochemical, or electrochemical processes. The resulting structural and/or compositional changes to this interface can impede the overall performance of the assembled devices.¹¹ Another challenge exists specifically for organic based electronics, such as OLEDs and OPVs. In these devices, hydrophobic non-polar organic HTLs are often deposited onto ITO.^{1, 4, 7-8, 11} There is an electronic mismatch between these HTLs and ITO as the two materials often exhibit significantly different surface energies and work functions (a difference of approximately 1.2 to 1.8 eV).¹⁵ This mismatch in work functions, called the hole injection barrier, is directly associated with the efficiency of devices incorporating HTLs and ITO. Work functions of clean native ITO can vary from 4.2 to 5.1 eV, depending on the procedures used to clean the surfaces and prepare the ITO films.^{4-6, 15-17} With

the clean native ITO, high work functions are achieved through the polar oxo and hydroxyl surface functional groups, which are often created through specific treatments that include oxygen plasma, ultraviolet (UV)-ozone, or Radio Corporation of America standard cleaning procedures (e.g., RCA-1).^{4, 18-19} These surface functional groups are, however, not well suited for direct contact with the HTL found in many organic based electronics because the polar groups of the native ITO surfaces exhibit an incompatibility due to their high surface energy.^{2, 4, 8} These surfaces also undergo rapid changes—including loss of surface hydroxyls and polar oxo groups—under ambient conditions, which results in a decrease in the work function.²⁰ This incompatibility at the interface between the ITO and the HTL leads to a non-uniform wetting of the organic films, and subsequent changes to the interface can lead to delamination of the HTL. Simultaneously tuning both the surface energy and work function of ITO is, therefore, desired to optimize the performance of organic based electronics.

In an effort to enhance the performance of organic based electronics, the surfaces of ITO have been modified using both inorganic and organic chemistries to adjust the properties of these interfaces. Surface modifications through the deposition of inorganic materials onto ITO films have shown their effectiveness to tune the work function. These surface treatments do, however, often result in the formation of either thick films or discrete islands, neither of which are desirable.^{11, 21} Although atomic layer deposition (ALD) techniques have been demonstrated for modifying ITO as a solution to address this issue through the use of inorganic surface modifications, it is currently too costly to perform this process on large substrates.²² Organic surface modifications, such as self-assembled monolayers (SAMs), are advantageous for their ability to form uniform films, as well as for their ability to tune both the surface energy and work function of the ITO. Monolayers prepared from carboxylic acid, silane, or phosphonic acid based

derivatives have been widely used to tune the surface properties of ITO.^{2-6, 8, 18, 23-28} By inducing a permanent dipole at the surfaces of the ITO electrodes, monolayers have been successfully used to increase the work function of the ITO. Changes in the composition of these monolayers can fine-tune the surface energy of the ITO to enhance its performance and its ability to be adapted for the needs of various electronic devices.^{2, 8, 10-11} Although these strategies can tune the work function and the surface energy of ITO electrodes, studies have shown that the formation of SAMs on ITO can compromise the electronic and/or optical properties of the ITO films upon exposure to operational or environmental stresses.^{11, 29-30} Such degradation can reduce the performance and operational lifetime of the ITO and, in turn, the electronic devices utilizing its properties.^{20, 25, 31-33} Silanes and phosphonic acids have been widely used to form monolayers because of their ability to form covalent bonds with metal oxides in comparison to carboxylic acids, which are only bound through electrostatic interactions.²⁹ Silane based monolayers may degrade into a thin layer of silicon oxide over time.³⁴ Monolayers of phosphonic acid can be prone to hydrolytic damage, depending on the methods used for their preparation. The rate and extent of this damage varies as a function of how these molecules bind to ITO (e.g., based on varying ratios of their mono-, bi- and tri-dentate structures).^{10, 33} An alternative type of precursor was sought that could also tune the interfacial properties of ITO films and that may exhibit an improved durability.

Here, we report the formation of alcohol based monolayers as an alternative strategy to modify the surfaces of ITO. This strategy can simultaneously control the surface energy and work function of these substrates. Similar to other surface modifications using SAMs, alcohols can covalently bond with hydroxyl containing oxide surfaces via the formation of ether bonds (Figure 1). This process is analogous to the formation of silane and phosphonic acid based

monolayers (In-O-Si and In-O-P).^{2-6, 8, 18, 24-25, 35} We sought to understand the effectiveness of tuning the surface properties of ITO through the use of alcohol based monolayers. The properties and performance of these surface modifications were compared with ITO electrodes modified with silanes or phosphonic acids. We also sought to understand the impact of changing the length of the alkyl chains on the alcohol reagents with regards to their passivation of the ITO interfaces. Work functions and surface energies of the modified ITO films were determined using ultraviolet photoelectron spectroscopy (UPS) and contact angle (CA) measurements to better understand the electronic properties of the modified ITO. The stability of these alcohol based monolayers were further characterized using multiple techniques that include prolonged cyclic voltammetry (CV) scans, CA measurements, X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible (UV-Vis) transmission spectroscopy. These techniques enabled an assessment of the electrochemical, optical, and chemical stability of the modified ITO films. These analyses confirmed that the desired interfacial properties were achieved through the use of alcohol based monolayers. These results indicate that alcohol based monolayers with various functional groups could be potentially used to improve the lifetime of electronic devices that rely upon modified ITO substrates.

RESULTS AND DISCUSSION

Electronic devices that utilize organic electronic materials often incorporate ITO or other transparent conductive oxides (TCOs) at an interface within the device. This interface between these dissimilar materials requires further surface modifications to improve their performance and durability.^{14, 36} Numerous surface modifications have been pursued, but many of these modifications have demonstrated drawbacks that include hydrolytic damage and/or a lack of

uniformity across this interface.^{9-10, 36} In this study, we prepared a series of monolayers derived from various alcohol reagents that include 1-octadecanol (ODA), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol (PFOA), 1,5-pentanediol (PTdiA), and 1,10-decanediol (DCdiA) to demonstrate new types of surface modifications for ITO surfaces (Figure 1). These molecules were selected for their ability to establish various types of permanent surface dipole moments that could be used to tune the work function of the modified ITO substrates. These modifications to the surfaces of the ITO films are, in many ways, analogous to the preparation of monolayers on silicon oxides. Previous methods to prepare monolayers on silicon oxides from alcohol based reagents include the use of convective or microwave heating, UV-irradiation, or catalysts.³⁷⁻⁴⁵ The study described herein extends the application of these reactants to form alcohol based monolayers on ITO and to demonstrate their utility for modifying the properties of ITO. Among the alcohol based monolayers prepared in this study, the monolayers derived from ODA were specifically evaluated in a detailed comparison to monolayers that were prepared from octadecyltrichlorosilane (ODTS) and octadecylphosphonic acid (ODPA), following common methods found in the literature.¹⁻⁶ This cross-evaluation was sought to evaluate alcohol based monolayers as an alternative approach to the surface modifications of ITO over current methodologies pursued widely in the literature. The alcohol based monolayers were sought as they could potentially expand the types of surface modifications to the ITO and enable its utilization as an interface to a diverse range of materials and for a variety of applications. All precursor species to these three monolayers consisted of a linear 18 carbon chain. This type of precursor has been previously demonstrated to form well-ordered monolayers due to their extensive van der Waals interactions.^{4-5, 38} Prior to any molecular modifications to their surfaces, the ITO substrates were cleaned and oxidized using a modified RCA-1 standard cleaning

procedure.¹⁷ Each type of monolayer was adhered to the ITO using specific procedures, which are discussed in detail in the Supporting Information. Monolayers derived from ODA required heating up to 120 °C in neat solutions of alcohol reagents, while ODTs and ODPA monolayers were grafted at room temperature in hexane and tetrahydrofuran (THF) solutions, respectively. Following the formation of the monolayers, each sample was sonicated in ethanol and dried with a stream of filtered nitrogen gas. The RCA-1 cleaned ITO substrates (as a control) and substrates coated with the monolayers were subjected to multiple characterization techniques to assess their electronic and optical properties and to cross-evaluate the stability of the monolayers.

Work Function Determination and Electronic Properties. To evaluate the potential utility of alcohol based monolayers in electronic applications, their work function and surface energy must be determined to assess their compatibility with the HTL.⁸ Previous studies have demonstrated that interfacial incompatibilities can lead to a non-uniform wetting of the non-polar organic HTL.^{1-2, 4} In OLEDs, a mismatch in the properties between ITO and the HTL that include their work functions and surface energies must be minimized to optimize their electronic performance. The work function of ITO electrodes at the interface with potential HTLs can be adjusted using SAMs.^{2-5, 11, 15, 46-47} Monolayers can be used to effectively tune the work function of metals and semiconductors, while increasing the efficiency of the hole injection process.^{5, 15, 36} These achievements result from the creation of a new permanently induced surface dipole within the monolayers. Ultraviolet photoelectron spectroscopy (UPS) measurements can be used to determine the work function of a material.^{19, 48-49} Previous UPS studies compared the work functions of monolayers of n-alkylphosphonic acid and other phosphonic acids on ITO to those of Triton™ X-100 cleaned ITO and oxygen plasma treated ITO.^{3-4, 36} The Triton™ X-100 cleaned ITO had a work function of 4.6 eV, and that for the oxygen plasma treated ITO was 5.1

eV.^{4, 19} The n-alkylphosphonic acid monolayers decreased the work function of ITO by 0.6 eV in comparison to the oxygen plasma treated ITO. Other phosphonic acids, such as fluorinated and phenylated species, either had not affected or increased the work function of the plasma treated substrates. These results indicate that the work functions can be tuned through altering the composition of the molecular reagents used to prepare the monolayers. The work functions of a series of ITO substrates, each modified with different alcohol based monolayers, were determined through UPS measurements. Work functions of the alcohol based monolayers were compared with RCA-1 cleaned ITO, as well as to ITO substrates modified with either ODTS or ODPA to validate alcohol based monolayers as an alternative to these more conventional surface modifications.

A series of alcohol based monolayers, which included ODA, PTdiA, DCdiA, and PFOA, were assessed for their ability to tune the work function of ITO. The hydroxylated and fluorinated terminal groups were sought to induce a permanent surface dipole moment and a relatively high electronegativity, which could assist in maximizing the work function of the ITO electrodes.²¹ In this study, three separate measurements were obtained from different regions of each substrate to assess the regularity of each work function. The UPS measurements have a few advantages over other methods to measure work function including its independence from environmental factors, such as contributions from changes in humidity and other atmospheric factors. Important information obtained from the UPS spectra included the width of the spectrum, or the range between the secondary electron edge (E_{sec}) and the Fermi level or E_{F} (0 eV).^{4, 11-12, 15, 19, 49} The difference between the width of the UPS spectrum and the energy of the helium 1 source (e.g., 21.2 eV) was used to determine the work function of the RCA-1 cleaned ITO film (4.7 eV). This value was similar to those reported in the literature for ITO cleaned by

similar techniques, which range from 4.5 to 4.7 eV.^{2-5, 15, 49} The ITO surfaces modified by SAMs required a more detailed assessment of their energy levels and the shifts in these levels for an accurate measurement of their work functions.

An accurate determination of the work function for the monolayer modified surfaces requires a consideration of both band bending and shifts in E_F .^{4, 21, 50-51} Band bending occurs through E_F pinning at the interface of two different materials. This phenomenon can decrease the work function of the ITO, which can result in an increase in the hole-injection barrier when ITO is used as the anode in electronic devices. Monolayers exhibit a permanent surface dipole moment that can shift the vacuum level (E_{vac}) and either increase or decrease the work function depending on the overall direction of the dipole.^{4, 12, 21, 50-52} There are two main components that determine the overall direction of the dipole: (i) the induced dipole at the interface between the ITO and the monolayers; and (ii) the permanent dipole of the molecular constituents of the monolayers.⁵¹ Depending on the overall direction of the dipole, the energy levels are shifted either upward or downward (Figure S1). For example, monolayers prepared from molecules with a negative dipole oriented away from the ITO can raise the level of E_{vac} , increasing the local work function of the electrode. This shift in the energy level of E_{vac} can offset a decrease in work function that results from band bending.^{21, 51} The overall shift in the energy levels from the contributions of the surface dipole and band bending can be measured by monitoring the position of valence band maximum (VBM) and E_{sec} in the UPS spectrum. The onset of the electronic transitions (at ~3 eV) observed for the monolayers on ITO is compared to the onset measured for the RCA-1 cleaned ITO to estimate the relative shift in each spectrum. The width of each UPS spectra, after accounting for these shifts, were used to compute the work functions of the modified ITO substrates.^{4, 10, 12, 52} The reported work function values for ODTS and ODPA monolayers on ITO

in the literature are 4.85 eV and 4.5 eV, respectively.⁴⁻⁵ Our coatings prepared from ODTS and ODPA exhibited work function values of 4.1 eV and 4.8 eV, respectively. The previously reported value for ODTS modified ITO films did not account for the shift in E_F and band bending, which resulted in a higher value than that derived from our measurements. In addition, the reported value was measured using Kelvin probe techniques. The measurements obtained from Kelvin probe techniques under ambient conditions can be influenced by atmospheric conditions (e.g., adsorbed water layers or other species).^{49-50, 53} Monolayers derived from ODA on ITO exhibited a work function of 4.7 eV, which is very close to the value for ODPA monolayers on ITO. These measurements indicate that the alcohol based monolayers had comparable work functions to monolayers derived from alkylsilanes and alkylphosphonic acids. In electronic devices that utilize ITO as an anode, a higher work function for the ITO electrode (e.g., ≥ 5 eV) is desired to minimize the hole injection barrier, which is sought to improve the performance and lifetime of these devices.

A high work function can be achieved through tuning the terminal functional groups of the SAMs. Based on previous studies, electron withdrawing groups can be incorporated into SAMs to increase the work function because of their higher electron affinity in comparison to alkyl chains.^{2-3, 36, 51} The work functions of ITO modified with PTdiA, DCdiA and PFOA were determined using the methods described above. Figure 2 depicts the UPS spectra for each of the samples after normalization to the maximum peak intensity. The average work function values and their associated errors, reported as one standard deviation from the mean values, are summarized in Table 1. The work functions for the ODA, PTdiA, DCdiA and PFOA monolayers were 4.7 eV, 4.6 eV, 4.5 eV and 4.9 eV, respectively. Treatments with either of the diols, PTdiA or DCdiA, decreased the work function by 0.1 and 0.2 eV, respectively, in comparison to the

RCA-1 cleaned sample. This decrease was attributed to the difference in magnitude of the dipoles between the In-O-H and C-O-H terminated surfaces. A previous study with pentafluorobenzyl phosphonic acid exhibited a lower work function than originally anticipated. This decrease in work function was attributed to the fluorine atoms on the phenyl ring. The dipoles formed by each of the fluorine atoms were cancelled by one another, except for the fluorine atoms at the para position.⁴ To increase the work function, a surface dipole created by the monolayers must be larger than the dipole of the native surfaces. The ITO surfaces include both polar oxo and hydroxyl groups (e.g., In-O-In and In-O-H). The monolayers derived from PFOA exhibited a work function that was higher than the RCA-1 cleaned sample. A similar result was previously reported with fluorinated phosphonic acid species used to prepare monolayers on ITO. Monolayers derived from 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl phosphonic acid exhibited a work function of ~5.1 eV.⁴ These results indicate that fluorine containing species in the monolayers can create a stronger surface dipole than the hydrocarbons and can, therefore, increase the work function. The range of values in work function achieved using alcohol based monolayers suggest that the work function of ITO can be tuned through a careful choice of different alcohol reagents. Similarly, the surface energy, which is another important interfacial property of ITO electrodes, can be tuned through adjusting the composition and or the functional group of the monolayers.

The modification of ITO with SAMs can be used to both reduce the surface energy of this electrode and to establish a more stable interfacial chemistry. For example, a higher luminance has been achieved for OLEDs that incorporated ITO modified with silane based monolayers in comparison to unmodified ITO electrodes.⁸ This result was attributed to improvements in the uniformity of the thickness and wetting of the HTL on the monolayer modified ITO substrates.

Surface energy of the ITO can provide an indication of the ability for the HTL to uniformly cover the ITO. It was, therefore, important to determine the surface energy of the modified ITO surfaces as an indication of the utility of the various monolayers for use in organic based electronic devices.

Surface energies of the monolayers on the ITO substrates were derived using the Owen-Wendt model of wetting, which can be used to estimate the total surface energy.⁵⁴ The Owen-Wendt model (Equation 1) can also be used to derive the polar and dispersive components of the surface energy of the ITO substrates. In this equation, θ_c represents the contact angle of the liquid of interest and γ is the surface tensions. The subscripts *LV* and *SV* represent the liquid-vapor and solid-vapor interactions, respectively, while the superscripts *d* and *p* represent dispersive and polar components.⁵⁴ The Owen-Wendt model requires contact angle measurements to be obtained using two distinct liquids. In this study, water and n-hexadecane contact angles were used to derive the polar and dispersive components of the surface energy, as well as the total surface energy of each sample. For all of the substrates, at least four independent contact angle measurements were obtained using each of these liquids. The results of these contact angle measurements are summarized in Table 2. The RCA-1 cleaned ITO sample exhibited contact angle values of $\sim 0^\circ$ for both water and n-hexadecane. Based on these measurements, the total surface energy of the RCA-1 cleaned ITO was calculated to be 73 mJ/m^2 , and the polar and dispersive components were 46 and 28 mJ/m^2 , respectively. Monolayers derived from ODA, ODTS, and ODPA each exhibited similar values for their total surface energy (e.g., 23 to 27 mJ/m^2). These results are considerably lower than those for the RCA-1 cleaned ITO substrates, but are consistent with previous values reported for monolayers of ODPA and ODTS (i.e. 29 mJ/m^2).⁴⁻⁵ The lower surface energies of the modified ITO should enable a more uniform wetting

of the HTL, and are important to achieve the desired efficiencies and lifetimes of OLEDs.³⁶ The other alcohol reagents were also evaluated to better understand the ability to tune the surface energy through altering the composition of the alcohol based monolayers.

$$\gamma_{LV}(1 + \cos \theta_c) = 2 \left(\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \gamma_{LV}^p} \right) \quad (\text{Equation 1})$$

Composition of the monolayers derived from the alcohol reagents were tuned between two extremes. One type of reactant was a perfluorinated species (i.e. PFOA), and the other species were linear diols (i.e. PTdiA and DCdiA). These substrates exhibited slightly higher total surface energies than for monolayers derived from linear hydrocarbon chains (Table 2). The estimated surface energies were 34, 48 and 46 mJ/m² for PFOA, PTdiA and DCdiA, respectively. The total surface energies for each of these monolayers, along with a distinction of their polar and dispersive components, are graphically depicted in Figure 3. The results from the ITO substrates modified with the different alcohol reagents indicated that the composition of these monolayers can be tuned to adjust the surface energies over a wide range of values. This tunability could be beneficial when creating a compatible interface for uniform wetting of various HTLs. These modifications to the ITO surfaces also result in changes to their surface work function as discussed above. Together these alterations to the ITO substrates could lead to further improvements in device performance. To further evaluate the potential use of alcohol based monolayers in organic based electronic devices, a series of accelerated degradation tests were applied to the modified ITO surfaces to predict their long-term stability under hydrolytic and electrochemical conditions.

Electrochemical and Chemical Stability. Surface modifications of ITO are required to tune their properties, as well as to minimize their potential degradation by thermal, chemical, and

diffusive based processes. A common methodology to adjust the interfacial chemistry of ITO, as discussed above, is through the use of SAMs.¹¹ To better understand the potential utility of alcohol based monolayers for modifying ITO and to validate them as a potential alternative coating layer, their stability were compared to commonly used SAMs for ITO surface modifications. The electrochemical and chemical stability of the monolayers were assessed through a series of degradation tests.

The monolayers on ITO were subjected to a series of electrochemical experiments. The SAMs derived from ODA, ODTS and ODPAs reagents were extensively compared to evaluate the relative stability of the alcohol based monolayers. The modified ITO films served as the working electrode submerged in a 1 M KCl solution containing 10 mM $K_4[Fe(CN)_6]$ and 10 mM $K_3[Fe(CN)_6]$. These studies mimicked exposure of the modified ITO substrates while subjected to corrosive electrolytic conditions, which may be experienced by the electrodes after a prolonged use in some electronic devices. Alterations to the composition and structure of the monolayers were indirectly monitored through the use of redox reporters (i.e. $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$) incorporated into the electrolyte used for this process of electrochemical aging. The ferricyanide/ferrocyanide redox couple was chosen for the relatively small dimensions of these redox active species, which can probe molecular-scale defects in monolayers covering the ITO electrodes.⁵⁵ Changes in the electrochemical peak current density and peak potential of the oxidation and reduction processes were assessed as an indication of changes to the SAMs at the ITO interface. The electric potential applied to the ITO electrodes was continuously scanned between 0 and 1 V versus a Ag/AgCl reference electrode for at least 10,000 full scans or approximately 2.5 days. This range of potentials was selected to avoid the deposition of iron oxide onto the ITO at negative potentials, and the electrolysis of water at 1.23 V.⁵⁶ These tests

enabled an assessment of the electrochemical and hydrolytic stability of each type of monolayer on the ITO substrates.

Multiple studies have previously investigated electrochemical properties of SAMs on ITO. In these studies, the most extensively studied SAMs on ITO include those prepared from ODTS and ODPA.^{2, 4-5, 35, 46} To the best of our knowledge, previous studies have not investigated the prolonged hydrolytic and electrochemical stability of these monolayers. In this study, ITO surfaces modified with ODA were directly compared to ITO surfaces coated with either ODTS or ODPA. Additional control experiments included a comparison to the properties of RCA-1 cleaned ITO. The modification of the ITO surfaces with organic molecules can decrease the current passed through these electrodes, and can also shift the potentials of the oxidation and reduction processes that take place at the surfaces of these electrodes.⁵⁷⁻⁵⁸ Changes to the monolayers on the ITO, such as a restructuring of the assembled coatings or any decrease in the integrity of these coatings, can further alter the electrochemical properties of the ITO electrodes. The measured current could increase or the measured potential could decrease for the oxidative processes due to the loss of the surface passivation. A previous study also analyzed the electrochemical properties of monolayers on ITO derived from n-alkylphosphonic acid.⁴⁶ The results of this prior study demonstrated a three-fold increase in the oxidative peak current within only 60 consecutive CV scans of the applied potential. Similar results were observed in our CV experiments with ODPA monolayers, where the oxidative peak current almost doubled within the first 100 CV scans.

The ODA, ODTS and ODPA monolayers on ITO were prepared and assessed for their electrochemical properties after extensive CV analyses to confirm the integrity of the alcohol based monolayers. Figure 4A includes plots of the 1st, 1,000th and 10,000th CV scans for an

RCA-1 cleaned ITO electrode. The RCA-1 cleaned ITO exhibited a subtle decrease in the peak current density (a change of -0.24 mA/cm^2) without a significant change in the peak position of the oxidative processes. This decrease in current density was attributed to thermal, chemical and diffusive based processes and their impact on the unmodified ITO interfaces.^{11, 13} The CVs obtained for the series of ITO substrates modified with SAMs of ODA, ODTS and ODPA are plotted in Figures 4B to 4D. The peak current density nominally increased by 0.03 mA/cm^2 and the peak position changed by -0.01 V over the 10,000 CV scans for ITO electrodes coated with ODA monolayers (Figure 4B). During the first positive scan of the electrode potential, the peak current density and position of the oxidation of the ferrocyanide were 1.59 mA/cm^2 and 0.37 V , respectively. After completing 10,000 complete scans of the applied potential, the peak current density (1.62 mA/cm^2) and peak potential (0.36 V) remained relatively consistent. Changes to the CV profiles indicated the degree of molecular-scale changes to the electrode surfaces as a result of the electrochemical processes. The results suggested that the ODA monolayers exhibited a high degree of electrochemical and hydrolytic stability under the conditions used in this study. This stability could be attributed to the mechanism by which these monolayers form and the structure of the ODA when covalently bound to the ITO. The hydroxyl group of ODA and terminal hydroxyl groups on the ITO surfaces likely form indium ether (In-O-R) or tin ether (Sn-O-R) linkages through an etherification process. This process could produce monolayers with a chemical structure that is analogous to that of alkanethiols assembled onto gold surfaces.⁵⁹ Unlike alcohol based monolayers, the mechanism of formation and the resulting structure is different for the ODTS and ODPA derived monolayers.

The CV analyses of ITO substrates coated with silane and phosphonic acid based monolayers demonstrated a distinct progression of the signal when compared to the samples of RCA-1

cleaned ITO and ODA monolayers on ITO. The silane or phosphonic acid based monolayers can possess multiple chemical structures on the surfaces of the ITO as a result of intermolecular polymerization or a series of varying binding mechanisms.¹¹ These different binding mechanisms and the potential intermolecular polymerization leads to different degradation mechanisms, which can be seen in the different outcomes of the electrochemical analyses. The peak current density of the oxidation process for the ODTS modified ITO electrodes and its potential at this peak current were 1.56 mA/cm² and 0.35 V, respectively (Figure 4C). During the consecutive scans of the applied potential, the overall magnitude of the oxidative peak decreased, but the position of the peak remained consistent. After 10,000 CV scans, the oxidative peak current density decreased to 1.25 mA/cm², corresponding to an overall change by -0.31 mA/cm². This decrease in peak current density was attributed to restructuring of the ODTS coating. Previous studies demonstrated the susceptibility of silane based monolayers to thermal, hydrolytic, and other forms of chemical damage.^{30, 60-61} Thin silicon oxide films have also been produced from silanes through intermolecular polymerization and hydrolysis of the Si-C bonds.³⁴ The Si-C bonds are susceptible to hydrolysis as they exhibit a weaker bond strength than Si-O bonds.⁶² We hypothesize that the ODTS monolayers decomposed to form thin silicon oxide films on the ITO surfaces through a process of electrochemical, hydrolytic, and other chemical stresses. This additional passivation increased the interface resistance between the ITO and the electrolyte. Monolayers prepared from ODPA initially demonstrated a very high degree of surface passivation with a relatively low oxidative peak current density (0.69 mA/cm²) and a relatively high oxidative peak potential (0.50 V). Significant changes in both the peak current density (a change of +0.65 mA/cm²) and the position of the oxidative peak potential (a change of -0.13 V) were observed after 10,000 scans of the applied potential (Figure 4D). These significant changes

to the oxidative conditions of the ferricyanide/ferrocyanide redox couple were attributed to degradation of the ODPA coatings. The phosphonic acids interact through three distinct denticities with the ITO surfaces, and structural changes can alter in their binding denticity.¹⁸ In addition, it has been shown that In-O-P bonds can be easily hydrolyzed when exposed to moisture.¹⁴ The degradation of the ODPA coatings likely led to the dissolution of individual ODPA molecules, leaving defects within the monolayers on the ITO surfaces. According to previous studies, annealing after the formation of phosphonic based monolayers can enhance their stability by consolidating the In-O-P covalent bonds.⁷⁻⁸ We anticipate that stability of ODPA monolayers could be improved through annealing. Additional studies were performed to further assess these structural changes within the monolayers including dissolution of bound species.

Water contact angle studies can be used to estimate the surface coverage of monolayers.⁶³ In this study, changes in WCA values were used to infer changes in their surface coverage. The WCA values for all of the as-prepared and electrochemically tested substrates, including the RCA-1 cleaned ITO, were assessed for changes to their surface passivation. The RCA-1 cleaned ITO electrodes initially exhibited a WCA value of $\sim 0^\circ$ and after the series of electrochemical tests the WCA increased to 9° . This increase in WCA was attributed to an increase in the surface coverage of O-In-O bonds through condensation of In-OH bonds, accumulation of organic contaminants, and/or leaching of indium species from the surfaces that could expose an underlying layer of oxygen deficient In.^{11, 19-20} The WCA values for each of the as-prepared monolayers on the ITO electrodes were similar. The ODA coated substrates exhibited average WCA values of $\sim 100^\circ$, while ODTS and ODPA coated substrates exhibited average WCAs of $\sim 112^\circ$ and $\sim 102^\circ$, respectively (Figure S18). After the electrochemical experiments, changes to

the average WCAs for the ITO substrates coated with ODA, ODTS, and ODPA were -3° , -13° , and -20° , respectively. The change in WCA and an increase in the associated errors observed for the ODPA monolayers agrees well with observations made in our electrochemical stability experiments. These results were also consistent with the hydrolytic sensitivity of ODPA reported in the literature.¹⁴ These changes were attributed in part to a change in the binding states of the ODPA molecules, which could result from exposure to moisture through hydrolysis of In-O-P bonds.¹⁴ The WCA measurements further supported the findings that the electrochemical tests and their hydrolytic conditions resulted in structural changes to the silane molecules and dissolution of the phosphonic acid molecules from the ITO surfaces. A matched-pair t-test was performed to assess the statistical significance of the observed changes in the WCA values. The changes observed for the ODA coated ITO had a 95% statistical significance, while the ODTS coated ITO and ODPA coated ITO both exhibited a 97.5% significance. To confirm that the changes in the WCA values did not originate from changes in surface morphology, atomic force microscopy (AFM) was performed for both the unmodified and modified ITO surfaces. The AFM measurements indicated that the roughness of the ITO substrates modified with monolayers derived from ODA and ODPA were relatively consistent with the RCA-1 cleaned ITO after the CV analyses (Figure S20). The roughness of the ITO modified with ODTS exhibited a decrease of approximately 2 nm (Table S1). Further analyses were required to better understand the observations made regarding the electrochemical and morphological stability of these monolayer modified ITO substrates.

Changes to the composition of the monolayer modified ITO surfaces were assessed by XPS measurements. High resolution XPS analysis of the O_{1s} peaks (Figure 5) were monitored before and after the series of electrochemical experiments. The O_{1s} species were selected for this

analysis because the monolayers would be formed from specific interactions between the molecular species and the ITO through oxygen containing bonds (e.g., In-O-C, In-O-P and In-O-Si).^{15, 18} Three O_{1s} peaks were consistently observed for each of the substrates, which were attributed to O-In-OH, O-In-O and O-C at binding energies of 529.5 eV, 530.4 eV and 531.5 eV, respectively. The binding energies of these species were consistent with previously reported values.^{4, 10, 16, 24, 27} The peak area ratio between the O-In-OH and O-In-O species maintained a value of approximately at 2 for all of the samples. The binding energies of the oxygen atoms within the silane or phosphonic acid based monolayers (O-Si, O-P or O=P) overlapped with the O-C peak position. A shift in the binding energy for the O-C species was observed after preparation of the monolayers when compared to the RCA-1 cleaned ITO substrates. This shift was attributed to a change in E_F at the interface between the ITO and the monolayers. When comparing the XPS spectra before and after the extended electrochemical tests, no significant changes in composition were observed for the RCA-1 cleaned ITO (Figure 5A) or the ODA coated ITO (Figure 5B). The XPS spectra obtained from ODA monolayers before and after the CV analyses suggested that the chemical composition of the ITO surfaces experienced minimal changes after the extended electrochemical and hydrolytic testing. In contrast, significant changes were observed in the XPS spectra of the substrates coated with either ODTS or ODPA. For the ODTS coated ITO, changes were observed in the relative intensity of the O-Si species. After repeatedly cycling the applied potential, the spectrum exhibited a significant reduction in the intensity of the O-Si species in comparison to the O-In-OH and O-In-O species (Figure 5C). Analysis of the survey spectra for the ODTS modified ITO substrates before and after the electrochemical and hydrolytic tests (Figures S7 and S8) indicated that the C_{1s} content of the ODTS modified substrates decreased by ~70% relative to the Si_{2s} species following these tests.

In contrast, the relative peak intensities of the O_{1s} to Si_{2s} species increased by 60% while the O_{1s} to In_{4s} peak intensities remained approximately unchanged and the In_{4s} species increased relative to the Si_{2s} species by ~90%. These results suggest the removal of a significant amount of the ODTS from the ITO substrates, exposing the underlying ITO substrate (as indicated by the increased O-In-OH, O-In-O and In_{4s} species) and the simultaneous formation of SiO_x species on the ITO surfaces. These changes were attributed to the formation of multilayer structures within the as-deposited ODTS and the subsequent loss of non-covalently attached ODTS molecules and/or degradation of the monolayers of ODTS during the electrochemical and hydrolytic tests. The ODPA coated ITO substrates also exhibited a significant change in their high resolution XPS spectra when comparing the plots obtained before and after the extensive electrochemical testing. The high resolution O_{1s} spectrum for the as-prepared ODPA monolayers exhibited similar peak intensities to those observed for the RCA-1 cleaned ITO surfaces. After evaluating the electrochemical stability of the ODPA monolayers, the peak intensity of the O-In-OH species significantly decreased relative to the O-C or O-In-O species (Figure 5D). This phenomenon was attributed to etching and/or non-specific degradation of the ITO and the ODPA coatings. One example is the hydrolysis of the In-O-P bonds, which produces H₃O⁺ and increases the local acidity.¹⁴ Another example is that weakly bound In or Sn atoms coordinate with phosphonic acids and undergo complexation to form an insoluble salt.^{9,64} Previous studies have reported that changes in the relative content of In and Sn on the surfaces of ITO can result from selective etching of the In species with an acid.^{17,65} Another study proposed that phosphoric acid slowly etches ITO and could be used to extract In species from solution.^{14,66} The results of these XPS analyses confirmed the observations made from the CV and WCA analyses, which suggested that changes to the chemical composition and structure of the ODTS and ODPA monolayers

could result from prolonged electrochemical and hydrolytic testing. These results further suggest that alcohol based monolayers on ITO could serve as alternative passivation layers for fine tuning the surface properties of ITO for a variety of applications, such as displays, touchscreens, heat reflective coatings, and smart windows.⁹⁻¹¹ Evaluating these coatings for their potential use in optoelectronic devices required a further assessment of possible changes to their optical properties.

Optical Properties. The optical properties of the modified ITO films were evaluated after repeated electrochemical and hydrolytic testing. The optical transmittance of these substrates was evaluated using UV-Vis transmission spectroscopy. Specifically, transmittance between 350 and 750 nm was investigated to monitor changes in the desired optical properties of the ITO films. Substrates coated with monolayers of either ODPA or ODA did not exhibit any spectral shift in comparison to the RCA-1 cleaned ITO substrates (Figure 6). A blue shift was, however, observed for the ODTS modified ITO after electrochemical testing. This phenomenon was attributed to structural and compositional changes to the ODTS coatings. Thin films of silicon oxide prepared from the decomposition of tris-dimethylaminosilane exhibit a similar UV-Vis transmission spectrum.³⁴ Decomposition of silane based monolayers, such as through the formation of silicon oxide, could induce the observed changes in the transmittance properties of the ITO films. It was speculated that the blue tint observed for the ODTS coatings was due to the formation of a thin silicon oxide layer. The growth of a silicon oxide film was consistent with the observed changes to the morphology and the relative increase in O-Si species observed by XPS analyses for the ODTS modified ITO as a result of the evaluation of their electrochemical and hydrolytic stabilities. The observed change in the dielectric properties at the ITO surfaces could lead to the shift in the features observed within the transmission spectrum.⁶⁷ Figure 7 shows the

visible blue tint to the ODTS coated ITO films after 2.5 days of exposing these substrates to conditions to simulate their accelerated degradation. For the ODTS modified ITO substrate, the corners and edges exhibited a more vivid blue coloration. Non-uniformities in the current density between the edges and center of the ITO electrodes could lead to this differential growth of the silicon oxide films.⁶⁸ The monolayers prepared from phosphonic acids or aliphatic alcohols did not exhibit a significant change in their optical transmittance, further validating the potential utilization of the alcohol based monolayers to modify ITO for use in organic based electronic devices, and specifically OPVs and OLEDs.

CONCLUSIONS

The modification of ITO surfaces with alcohol based monolayers has been demonstrated for the first time to tune the properties of the ITO for use in a variety of organic based electronic devices. Several alcohol containing reagents were successfully grafted onto ITO surfaces through a condensation reaction. The electronic properties of each of the monolayers, which include their work function and surface energy, were analyzed using UPS techniques and the Owen-Wendt model of wetting. The work function was adjusted from 4.49 to 4.88 eV and the surface energy was tuned from 27 to 48 mJ/m² through changes to the composition of the alcohol based monolayers. The results indicated that alcohol based monolayers can be used to simultaneously tune both the surface energy and work function of the ITO. The alcohol based monolayers were evaluated against surfaces modified with silanes or phosphonic acids to confirm the potential use of the alcohol based monolayers as an alternative surface modification for ITO substrates. The alcohol based monolayers exhibited a change of 0.03 mA/cm² and -0.01 V in the faradaic peak current density and peak position after a series of accelerated degradation tests carried out over

the course of ~2.5 days. The observed stability of the alcohol based monolayers was further confirmed through WCA measurements and XPS analyses. The optical transmittance of the alcohol based monolayers on ITO also exhibited minimal changes after these electrochemical and hydrolytic tests. Silane and phosphonic acid based monolayers are advantageous as they can readily form coatings on ITO at room temperature. Our findings indicate that the silane based monolayers are prone to the forming multilayers, as well as decomposing into thin silicon oxide layers, and the phosphonic acid based monolayers can lead to etching of the ITO and/or formation of insoluble precipitates through degradation processes. As the alcohol based monolayers do not exhibit these potential mechanisms of degradation, the modification of ITO with monolayers prepared from alcohol based reagents is a promising alternative for adjusting the properties of the ITO for its use in organic based electronic devices. The alcohol based monolayers on ITO exhibited electrochemical and chemical stability when compared to conventional surface modification techniques. Another benefit of this new approach to modifying the surfaces of ITO is that it can overcome some of the limitations present when using phosphonic acids and silanes. For example, alcohol reagents with different functional groups can be synthesized in a relatively simpler manner. Therefore, alcohol based monolayers can readily incorporate a variety of chemistries, such as a hydroxyl moiety through the use of diol containing reagents. These hydroxyl functional groups could potentially provide a platform for increasing the diversity of the surface chemistry. It can also be used as a platform for further optimizing and tuning the chemical properties of these surfaces for applications in electronic devices other than OLEDs and OPVs, such as molecular sensors and organic transistors.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

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Materials and methods, peak faradaic current densities, cyclic voltammetry scans, XPS survey scans, high resolution XPS spectra, UV-Vis transmission spectra, WCA measurements, and AFM images.

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Figures

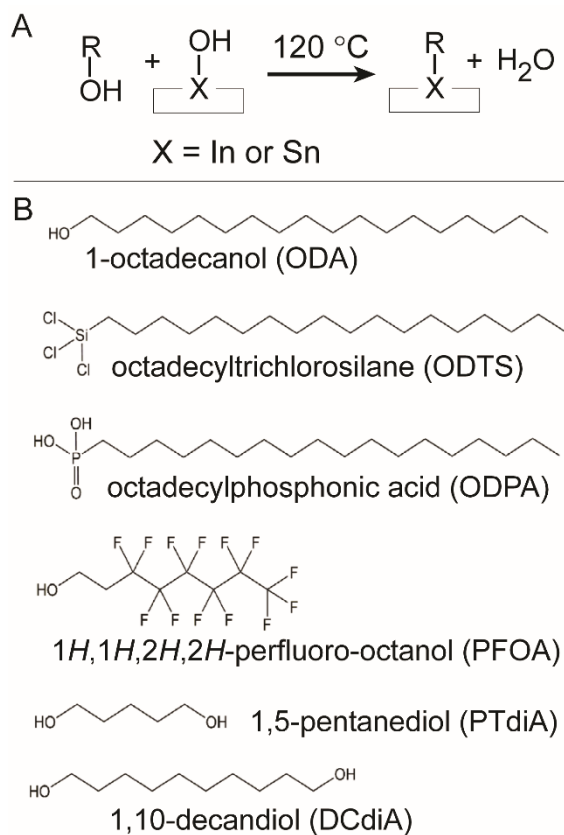


Figure 1. (A) Schematic representation of the alcohol condensation reaction on the surfaces of indium tin oxide (ITO) substrates. The variable, R, denotes the variable composition of the alcohol reagents that could be used in this process. (B) Reagents used in this study to prepare self-assembled monolayers (SAMs) on the ITO substrates.

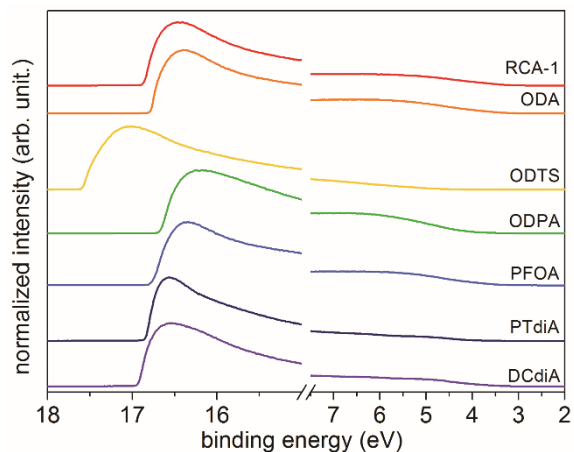


Figure 2. The ultraviolet photoelectron spectroscopy (UPS) spectra for an RCA-1 cleaned ITO and ITO substrates modified with a series of different SAMs. The composition of the SAMs are indicated above each spectrum. The reagents included 1-octadecanol (ODA), octadecyltrichlorosilane (ODTS), octadecylphosphonic acid (ODPA), 1*H*,1*H*,2*H*,2*H*-perfluoro-octanol (PFOA), 1,5-pentanediol (PTdiA), and 1,10-decandiol (DCdiA). The spectra are plotted to depict the secondary electron edge (E_{sec}) and the Fermi levels (E_{F}) associated with each of these substrates.

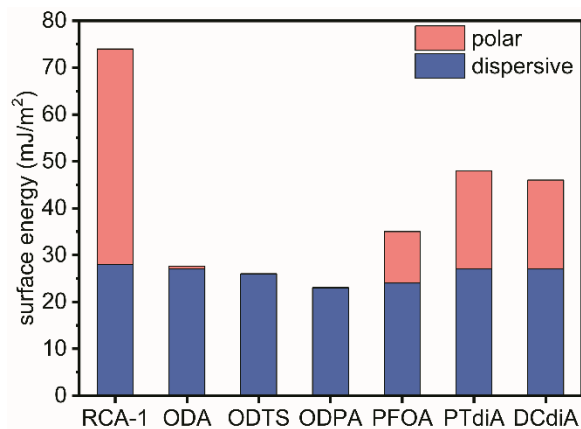


Figure 3. Surface energies derived using the Owen-Wendt model of wetting for RCA-1 cleaned ITO, and ITO substrates modified with SAMs derived from silane (ODTS), phosphonic acid (ODPA), or alcohol (ODA, PFOA, PTdiA and DCdiA) containing reagents. The polar and dispersive components of the surface energy are represented by the light grey (upper) and dark grey (lower) columns, respectively.

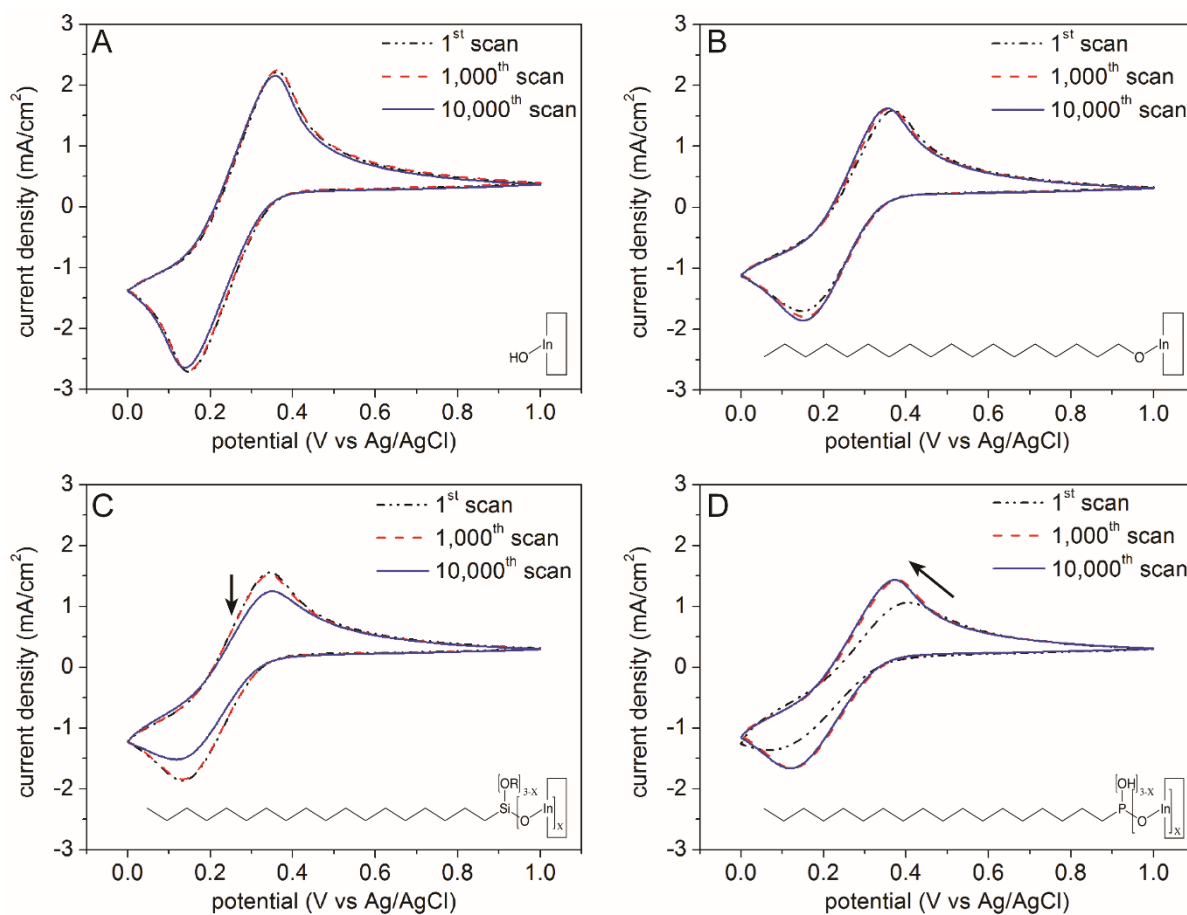


Figure 4. The 1st, 1,000th and 10,000th scans of the cyclic voltammetry analyses of (A) RCA-1 cleaned ITO, (B) ODA coated ITO, (C) ODTS coated ITO, and (D) ODPA coated ITO. These electrochemical studies were performed at a scan rate of 50 mV/s using the ITO substrates as the working electrode in 1 M KCl solutions containing 10 mM potassium ferricyanide and 10 mM potassium ferrocyanide. Black arrows indicate trends observed in the change in position and peak current of the oxidation processes over the course of these experiments.

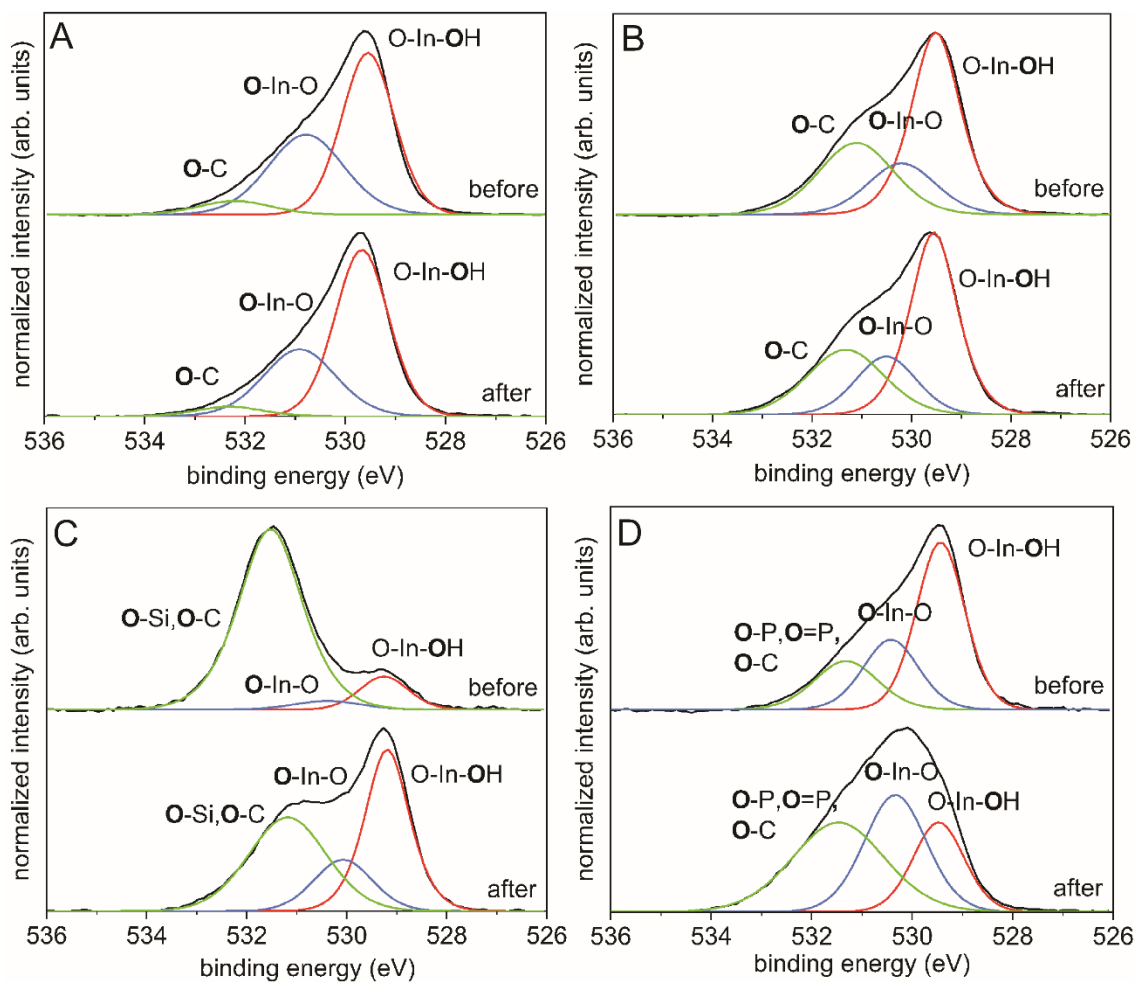


Figure 5. High resolution X-ray photoelectron spectroscopy (XPS) data for O_{1s} species associated with: (A) RCA-1 cleaned ITO; (B) ODA coated ITO; (C) ODTS coated ITO; and (D) ODPA coated ITO. Representative spectra are plotted for each type of surface modification, which were obtained either before or after the series of electrochemical and hydrolytic experiments as noted above each plot.

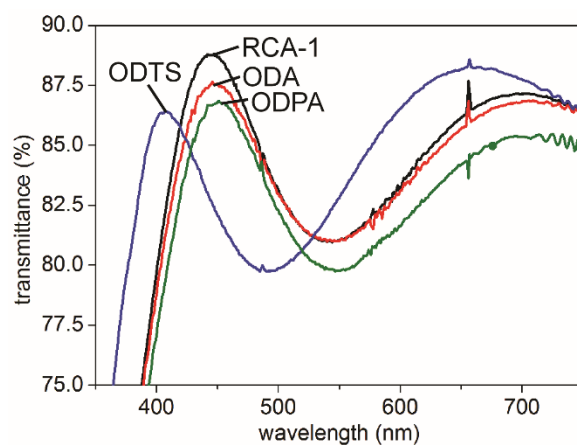


Figure 6. Ultraviolet-visible (UV-Vis) transmittance spectra of RCA-1 cleaned ITO, ODA coated ITO, ODTS coated ITO, and ODPA coated ITO substrates obtained after a series of electrochemical and hydrolytic tests.

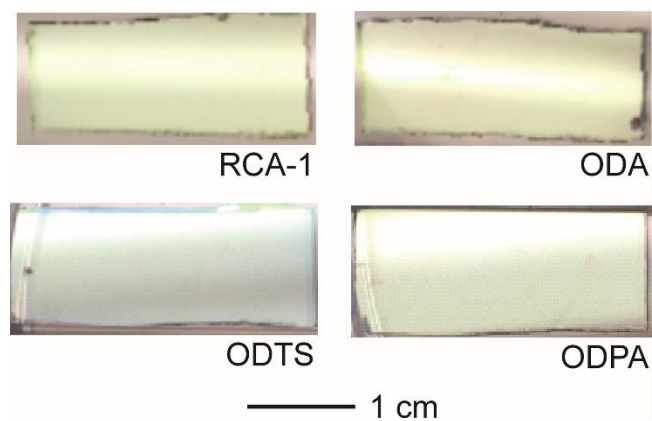


Figure 7. A blue tint was observed for the ODTS modified ITO substrates in comparison to RCA-1 cleaned, ODA coated and ODPA coated ITO substrates after the prolonged electrochemical and hydrolytic tests.

Tables

Table 1. Work functions obtained from UPS spectra (He 1 Source).

sample	work function (eV)
RCA-1 cleaned	4.7 ± 0.2
ODA	4.7 ± 0.2
ODTS	4.1 ± 0.1
ODPA	4.8 ± 0.3
PFOA	4.9 ± 0.1
PTdiA	4.6 ± 0.1
DCdiA	4.5 ± 0.2

Table 2. Average contact angle values for the ITO substrates and their corresponding surface energies derived using the Owen-Wendt model of wetting.

ITO treatment/modification	water	n-hexadecane	γ , polar component ⁽ⁱⁱ⁾		γ , dispersive component ⁽ⁱⁱ⁾		γ , total ⁽ⁱⁱ⁾	
	$\theta^{(i)}$	θ^*	G	H	G	H	G	H
RCA-1 cleaned	0 ± 0	0 ± 0	46	46	28	28	73	73
ODA	100 ± 2	13 ± 2	0.6	0.55	27	27	27	27
ODTS	111 ± 7	19 ± 3	0.021	1.7 E-3	26	26	26	26
ODPA	102 ± 7	33 ± 4	0.062	3.3 E-5	23	23	23	23
PFOA	75 ± 4	31 ± 3	11	10	24	24	34	34
PTdiA	55 ± 2	5 ± 1	21	21	27	27	48	48
DCdiA	58 ± 1	9 ± 2	19	19	27	27	46	46

⁽ⁱ⁾ θ = average contact angle (degrees).

⁽ⁱⁱ⁾ γ = surface energy (mJ/m²); G = geometric mean; and H = harmonic mean.

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