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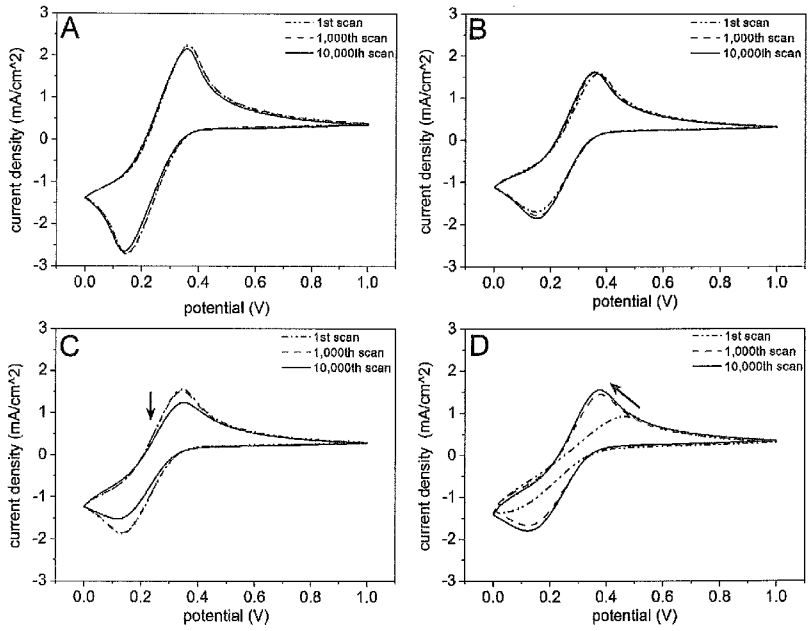
(54) Title: TUNING SURFACE PROPERTIES OF TRANSPARENT CONDUCTIVE OXIDE SURFACES THROUGH THE FORMATION OF ALCOHOL BASED SELF-ASSEMBLED MONOLAYERS

Fig. 1



(57) Abstract: This invention is related to covalent surface modifications of transparent conductive oxide (TCO) films using alcohol containing reagents. More specifically, the present invention is related to alcohol based covalent surface modification of indium tin oxide (ITO) film, as an exemplary TCO, wherein the surfaces of the ITO comprises M-O-R, where M is either In or Sn, and R is an organic group originated from an alcohol based reactant for use, among other applications, in light emitting diodes.

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TUNING SURFACE PROPERTIES OF TRANSPARENT CONDUCTIVE OXIDE SURFACES THROUGH THE FORMATION OF ALCOHOL BASED SELF-ASSEMBLED MONOLAYERS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application claims priority to pending U.S. Provisional Application No. 62/416,923 filed November 3, 2016 which is incorporated herein by reference.

STATEMENT REGARDING FUNDING

[0002] This research was supported in part by the Natural Sciences and Engineering Research Council (NSERC) of Canada (B.D.Gates, Grant No. 1077758), MNT Financial Assistance (CMC Microsystems, Grant No. 3852), and the Canada Research Chairs Program (B.D. Gates, Grant No. 950-215846). This work made use of the 4D LABS (www.4dlabs.ca) shared facilities supported by the Canada Foundation for Innovation (CFI), British Columbia Knowledge Development Fund (BCKDF), Western Economic Diversification Canada, and Simon Fraser University.

FIELD OF THE INVENTION

[0003] This present invention is related to covalent surface modifications of transparent conductive oxide (TCO) films using alcohol containing reagents. More specifically, the present invention is related to alcohol based covalent surface modification of indium tin oxide (ITO) film, as an exemplary TCO, wherein the surfaces of the ITO comprises M-O-R, where M is either In or Sn, and R is an organic group originated from an alcohol based reactant.

BACKGROUND

[0004] Transparent conductive oxides serve a critical function in many organic 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. A common surface modification of TCOs is through the use of self-assembled monolayers. This methodology enables a simultaneous tuning of the properties and performance of this interface, including the surface energy, work function and durability of the TCO. Phosphonic acid and silane based monolayers have been extensively studied and used in devices for their ability to tune the interfacial properties of TCOs.

[0005] The surface modification of TCOs, such as indium tin oxides (ITO), is widely used to tune their surface properties for applications that include light emitting diodes (LEDs), organic light emitting diodes (OLEDs), sensors, solar cells, flat-panel and flexible displays, touch screens, smart windows, and heat reflective coatings. Organic monolayers, such as alkylsilanes and alkylphosphonic acids have been widely pursued for tuning the surface properties of ITO. These coatings are used to tune properties that include the work function and surface energy of TCOs, upon which are deposited other functional materials, such as conductive polymers. However, the modified films using these strategies can compromise the electronic and/or optical properties of the ITO films after prolonged exposure to operational or ambient stresses. These changes can significantly reduce the performance and operational lifetime of devices. For example, OLED devices can experience phenomena referred as vignetting where the corners or

edges of the display appear to prematurely fade or darken. Another challenge can be burn-in or retention of an image on the display. The cause of these phenomena remain contested and are likely the result of multiple sources.A potential source of these phenomena is the introduction of heteroatoms at the ITO interface, such as the silicon or phosphorous containing monolayers. Other exemplary TCO's include ZnO_2 and CdO_2.

[0006] In spite of the ongoing efforts, there is an ongoing desire in the art for improved surface modified transparent oxides and improved methods for forming surface modified transparent oxides. Provided herein is an improved method for forming surface modified oxides and an improved method which allows for efficient formation of monolayers.

SUMMARY OF THE INVENTION

[0007] The present invention is related to surface modification of TCO and specifically ITO.

[0008] More specifically, the present invention allows for tuning of the electronic properties, such as the work function, of the film for improvement of electronic device performance.

[0009] A particular feature of the invention is the ability to selectively and predictably modify the surface properties of TCO

[0010] These and other embodiments, as will be realized, are provided in a modified transparent conductive oxide surface comprising a surface comprising a metal and an organic group attached to the metal by an ether bond.

[0011] Yet another embodiment is provided in a method for forming a modified transparent conductive oxide surface comprising:

providing a transparent conductive oxide surface comprising metal hydroxyl groups; and

reacting an alcohol comprising a pendant group on the alcohol with the metal hydroxyl groups to form an ether bond between the metal and the pendant group.

BRIEF DESCRIPTION OF DRAWINGS

[0012] Fig. 1 is a graphical representation of an embodiment of the invention.

[0013] Fig. 2 is a graphical representation of an embodiment of the invention.

[0014] Fig. 3 is a graphical representation of an embodiment of the invention.

[0015] Fig. 4 is a graphical representation of an embodiment of the invention.

[0016] Fig. 5 is a graphical representation of an embodiment of the invention.

[0017] Fig. 6 is a graphical representation of an embodiment of the invention.

[0018] Fig. 7 is a graphical representation of an embodiment of the invention.

[0019] Fig. 8 is a graphical representation of an embodiment of the invention.

[0020] Fig. 9 is a graphical representation of an embodiment of the invention.

[0021] Fig. 10 is a graphical representation of an embodiment of the invention.

[0022] Fig. 11 is a graphical representation of an embodiment of the invention.

[0023] Fig. 12 is a graphical representation of an embodiment of the invention.

[0024] Fig. 13 is a graphical representation of an embodiment of the invention.

[0025] Fig. 14 is a graphical representation of an embodiment of the invention.

[0026] Fig. 15 is an atomic force microsope image of embodiments of the invention.

DESCRIPTION

[0027] The present invention is related to self-assembled monolayers (SAMS) for modifying the surface properties of TCO, particularly indium tin oxide (ITO), for use in OLEDs and OPVs. The ITO surfaces can be modified by alcohol reagents as particularly exemplified in 1-octadecanol (ODA), 1*H*,1*H*,2*H*,2*H*-perflourooctanol (PFOA), 1,5-pentanediol (PTdiA) or 1,10-decanediol (DCdiA).

[0028] The present invention provides 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. 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, ~4.5 eV, and high transparency, ~90%, within the visible spectrum. There are, however, a number of challenges with the use of ITO in many of these electronic applications. 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. Another challenge exists specifically for OLEDs and OPVs. In these devices, hydrophobic non-polar organic HTLs are often deposited onto ITO. There is an electronic mismatch between these HTLs and ITO as the two materials often exhibit significantly different work functions with a difference of approximately 1.2 to 1.8 eV and surface energies. 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 their surfaces and prepare the ITO films. With 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, UV-ozone, or RCA-1 standard cleaning procedures. 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. These surfaces also undergo rapid changes, including loss of surface hydroxyls and polar oxo groups, under ambient conditions that results in a decrease in the work function. This incompatibility at the interface between 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.

[0029] 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. 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. 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. Carboxylic acid SAMS are not as durable and therefore not as desirable as alcohol based SAMs. 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. 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 after prolonged exposure to operational or environmental stresses. Such degradation can reduce the performance and operational lifetime of the ITO and, in turn, the electronic devices utilizing its properties. 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. Both silanes and phosphonic acid based monolayers do, however, contain potential impurities, such as silicon oxides and phosphonates, that can impair device performance. Silane based monolayers may degrade into a thin layer of silicon oxide over time. Monolayers of phosphonic acid are prone to hydrolytic damage. The rate and extent of this damage varies as a function of how these molecules bind to ITO due to

the varying ratios of their mono-, bi- and tri-dentate structures. In this invention alcohol based monolayers are provided as an alternative to silane or phosphonic acid based monolayers on ITO.

[0030] Described herein is the formation of alcohol based monolayers on the surfaces of ITO. The monolayer 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, such as In-O-R or Sn-O-R. This process is analogous to the formation of silane and phosphonic acid based monolayers having In-O-Si and In-O-P bonds. These surface modifications are directly compared herein with ITO electrodes modified with silanes or phosphonic acids.

[0031] 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. 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.

[0032] 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) were prepared to demonstrate a new approach to preparing SAMs on ITO. These exemplary 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. Previous methods to prepare monolayers on silicon oxides from alcohol based reagents include the use of convective or microwave heating, UV-irradiation, or catalysts. 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). 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. Prior to any molecular modifications to their surfaces, the ITO substrates are preferably cleaned and oxidized using a modified RCA-1 standard cleaning procedure. Each type of monolayer can be grafted onto ITO using specific procedures, which are discussed in detail herein. Monolayers derived from ODA required heating up to 120 °C in neat solutions of alcohol reagents, while ODTS and ODPA monolayers can be grafted at room temperature in hexane and tetrahydrofuran (THF) solutions, respectively. Following the formation of the monolayers, each sample is preferably 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.

[0033] The inventive alcohol based monolayers exhibit a significantly higher stability than the monolayers derived from phosphonic acids and silanes. The optical properties

of the inventive monolayers on ITO are suitable for modifying the properties of these substrates for use in organic based electronics.

[0034] The overall chemical equation is:

$$M\text{-}OH + R\text{-}OH \rightarrow M\text{-}O\text{-}R + H_2O$$

with particularly suitable alcohols represented by: saturated and unsaturated alcohols with 1 to 100 carbons, more preferably 1-50, even more preferably 1-20 and preferably 5 to 12 carbons which can be linear or branched; polyalklene glycols, more preferably polyethylene glycol and more preferably polyethylene glycol with a molecular weight low enough to be liquid at 25°C; fluorinated alcohols and particularly perfluorinated alcohols and even more preferably perfluorinated alcohols which are liquid at 25°C; phenyl alcohols and particularly phenyl alcohols with a formula of $HODC_6H_5$ wherein D represents a bond or a saturated or unsaturated alkyl of 1-6 carbons and more preferably 1-3 carbons; polar alcohols such as alkanolamines with 2-4 carbons and preferably 2 carbons wherein the amine is primary, secondary, tertiary or quaternary; vitamins and particularly thiamine, ascorbic acid, cholecalcifero, riboflavin, vitamin E, ergocalciferol, pantothenic acid, pyridoxal, pyridoxamine or pyridoxine; sugars and particularly n-acetylglucosamine, glucosamine, D-glucose and sucrose; amino acids and particularly serine, threonine and tyrosine; nucleic acids such as adenosine derivatives including adenosine triphosphate, adenosine diphosphate, and adenosine monophosphate; catechols including catechol and catechin and hormones or neurotransmitters including dopamine, norepinephrine, epinephrine, cholesterol, testosterone.

[0035] The present invention provides for improved electrochemical, chemical, and optical stabilities relative to TCO films modified with traditional organic monolayers including organosilanes and phosphonic acids.

[0036] The present invention provides for the surface modification of ITOs using alcohol containing reagents. Unlike traditional organic monolayers, alcohols can covalently bond with hydroxyl containing oxide surfaces via formation of ether bonds, particularly In-O-R or Sn-O-R, analogous to the formation of silyl ether for the modification of silicon oxides, Si-O-R. This invention provides an effective technique to modify surface properties of ITO surfaces.

[0037] ITO films are modified with aliphatic alcohols by immersing the ITO coated substrates into neat solutions of alcohol reagent at elevated temperatures. These modifications to the surfaces of the ITO films are analogous to the preparation of monolayers on silicon oxides. Previous methods to prepare monolayers on silicon oxides from alcohol based SAMs specifically include the use of convective or microwave heating, UV-irradiation, and the assistance of catalysts. Provided herein is the use of reactants to form alcohol based SAMs on ITO and by extension to demonstrate their utility for modifying the properties of TCOs.

[0038] Most TCOs often require additional surface treatment to tune their properties and to minimize thermal, photochemical and diffusive based degradation of the surface. To study the passivation effects of alcohol based SAMs and their electrochemical and chemical properties for comparison with silane and phosphonic acid based monolayers, each of these monolayers was subjected to 10,000 scans by cyclic voltammetry using the modified ITO films as a working electrode while in a 1M KCl solution containing 10

mM $K_4[Fe(CN)_6]$ and 10 mM $K_3[Fe(CN)_6]$. These studies mimicked the use of these ITO substrates while subjected to corrosive electrolytic conditioning and repeated passing of charge relevant to use as electrodes in a variety of applications. Each of the 10,000 scans were obtained over 2.5 days of continuous use. The potential range for these experiments was fixed from 0 to 1 V to avoid the deposition of iron oxide on the ITO at negative potentials. Extensive studies have been performed using silane and phosphonic acid based SAMs to modify the properties of ITO. Examples include octadecyltrichloro silane (OTS) and octadecylphosphonic acid (OPA). In the instant disclosure, ITO surfaces modified with octadecanol (ODA) were compared to ITO surfaces coated with either OTS or OPA as they have the same length of hydrocarbon chain. Additional control experiments included RCA cleaned ITO wherein RCA cleaning is a standard method of cleaning wafers developed by and promulgated by the Radio Corporation of America. Any surface treatment of the ITO with organic molecules can decrease the current passed by these electrodes and can also shift the potential of oxidation and reduction processes. Changes to the monolayers on ITO, such as a restructuring or a decrease in the integrity of these coatings can alter the electronic properties of ITO electrodes. As a result of these changes, the oxidation peak current could increase or the potential of oxidation peak could decrease with a loss of surface passivation. Previous study of n-alkylphosphonic acid monolayers on ITO and their electrochemical stability demonstrated a three-fold increase in peak current after the 60 CV scans. Herein changes to the monolayer modified ITO electrodes are monitored through spectral changes during CV analysis of potassium ferricyanide/ferrocyanide. The instant studies rely on the acquisition of at least 10,000 scans to provide insights

into the electrochemical and chemical stabilities in the electrode potential of monolayers on the ITO surfaces. The ferricyanide/ferrocyanide redox coupled electrolytes were chosen for relatively small dimensions of this electrochemically active species, which can probe molecular scale defects in monolayers covering the electrodes. Fig. 1A illustrates the first, 1,000th and 10,000th scans of the cyclic voltammetry analysis of (A) native ITO, (B) 1-octadecanol coated ITO, (C) octadecyltrichlorosilane coated ITO, and (D) octadecylphosphonic acid coated ITO. These electrochemical studies were performed by immersing the ITO substrates as a working electrode into a solution of 1 M KCl solution containing 10 mM potassium ferricyanide and 10 mM potassium ferrocyanide, and using a scan rate of 50 mV/s. Black arrows indicate the observed shifts in position and peak current of the oxidation processes during this electrochemical aging. Monolayers prepared using ODA exhibited excellent stability, with a change of 0.03 mA in peak current and a shift of 0.01 V in the position of the oxidation peak over the 10,000 CV scans in the oxidation peak as illustrated in Fig. 1B. During the first positive scan of the electrode potential, the peak current and position for the oxidation of the ferrocyanide were 1.59 mA and 0.37 V, respectively. After 10,000 complete scans of the electrode potential, the peak current, 1.62 mA, and its electrochemical potential, 0.36 V, remained relatively consistent. 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 either indium ether (In-O-R) or tin ether (Sn-O-R) linkages through an etherification process. This process would produce chemical structure within these SAMs that is analogous to the structure of alkanethiols on gold

surfaces. On the other hand, the silane or phosphonic acid based monolayers can possess multiple chemical structures as a result of intermolecular polymerization or a series of varying binding mechanisms with the ITO surfaces. Changes to the structure and surface coverage of the monolayers could be introduced under ITO devices' operational conditions. These changes could compromise the fine-tuned properties of the modified ITO substrates. Monolayers formed using OTS initially possessed a similar degree of surface passivation in comparison to monolayers prepared from ODA. The peak current of the oxidation process and its potential at this peak current were 1.56 mA and 0.35 V, respectively as illustrated in Fig. 1C. As the potential was scanned continuously, the overall magnitude of the oxidation peak decreased while the position of this peak remained consistent. After 10,000 scans of the potential, the oxidation peak current decreased to 1.25 mA, a 0.31 mA decrease. This decrease in the peak current could be attributed to restructuring of the OTS coating that originate in the intermolecular polymerization that result during its formation on the ITO surfaces. Electrochemical and chemical stresses during potential cycling could induce structural changes within the OTS monolayers. Monolayers prepared from OPA initially demonstrated a very high degree of surface passivation with a relatively low oxidation peak current, 0.69 mA, and a relatively high oxidation peak potential, 0.50 V, observed during the first scan of electrode potential. Significant changes in both the peak current of +0.65 mA and the position of the oxidative peak potential, -0.13 V, were observed after 10,000 scans as illustrated in Fig. 1D. These significant changes to the oxidative conditions of the ferricyanide/ferrocyanide redox couple can be attributed to restructuring of the OPA coatings, including dissolution of the OPA. Additional studies

were performed to confirm the structural changes and/or dissolution of each of the monolayers on ITO, WCAs were measured.

[0039] The water contact angles (WCAs) of the native ITO and ODA coated, OTS coated and OPA coated ITO surfaces were monitored before and after the electrochemical experiments to assess changes to surface coverage of these passivation layers. Native ITO initially exhibited a WCA of ~0° and after repeated electrochemical tests the WCA increased to 9°. The WCAs were similar for all of the monolayer modified ITO electrodes before electrochemical tests. The ODA coated ITO substrates exhibited WCA values of 100° while OTS and OPA coated ITO substrates exhibited WCAs of 112° and 102° as illustrated in Fig. 2. In Fig. 2 the water contact angles of native and monolayer modified ITO substrates before and after extended electrochemical testing are illustrated. Octadecanol (ODA), octadecyltrichloro silane (ODTS) and octadecylphosphonic acid (OPA). After the electrochemical experiments, changes to WCAs for ITO substrates coated with ODA, ODTS, and ODPA were -3°, -6°, and -20°, respectively. The most significant change was observed for the ODPA coated ITO films, which agrees well with observations made in the electrochemical stability experiments. These changes could be attributed to the strength of ODPA interactions with the ITO and with other ODPA molecules within these monolayers. As anticipated, these WCA results further support the conclusion that the silane molecules undergo structural changes and that the phosphonic acid molecules undergo dissolution. A further assessment of the changes to the chemical composition of each interface was needed after the 10,000 scans of electrode potential to better understand the observed changes to these monolayers.

[0040] Surface composition of the ITO substrates was analyzed by XPS as illustrated in Fig. 3 wherein high resolution O_{1s} XPS of (A) native ITO, (B) 1-octadecanol coated ITO, (C) octadecyltrichloro silane coated ITO, or (D) octadecylphosphonic acid coated ITO is illustrated before and after a series of electrochemical tests. In Fig. 3 the O-In is at 527.7 eV, O-Sn is at 528.8 eV, O-Si is at 529.8 eV, O-P, O=P is at 529.2 eV and O-C is at 529.9 eV. High resolution XPS analysis of the O_{1s} peaks for each substrate were monitored before and after the electrochemical tests. No significant changes in composition were observed for either the native ITO substrates, as illustrated in Fig. 3A, or ODA coated ITO substrates, as illustrated in Fig. 3B, when comparing their XPS spectra before and after the extended electrochemical tests. In contrast, significant changes to the O_{1s} XPS peaks were observed for the substrates coated with either ODTS or ODPA. For the ODTS coated ITO substrates, the O-Si peak is initially dominant but after the electrochemical and potential cycling, these spectra exhibited a significant reduction in O-Si while O-In and O-Sn peaks remain relatively constant as illustrated in Fig. 3C. This change can be attributed to the formation of a multilayer structure and the loss of non-covalently attached polymer chains in the ODTS coatings. The ODPA coated ITO substrates exhibit a spectrum that initially resembles that for the native ITO surfaces. However, after electrochemical stability testing, significant changes in the ratio between the O-P, O-In and O-Sn peaks were observed as illustrated in Fig. 3D. The ratio of the peak intensity between the O-In and O-Sn changed significantly for the ODPA modified ITO surfaces. This phenomenon could be attributed to etching of the ITO surfaces as the ODPA monolayers underwent restructuring and degradation. Previous studies have reported changes to the ratio O-In

and O-Sn following In selective etching of ITO, and phosphoric acid could slowly etch the ITO films, In extraction from solutions could be achieved through the use of phosphonic acids. These XPS results further confirmed that there were significant changes in chemical structure of the ODTS and ODPA monolayers upon prolonged electrochemical testing. In summary, ODA coated ITO substrates demonstrated excellent electrochemical and chemical stability in contrast to ODTS and ODPA coated ITO substrates. Monolayers of ODA could serve as an alternative passivation layer for fine tuning the surface properties of ITO for a variety of applications, such as displays, touchscreens, heat reflective and smart windows. Insight into possible changes to the optical properties of the substrates coated with each of the monolayers was required for further assessing their utility in optoelectronic devices.

[0041] Assessing the changes in the optical properties of the modified ITO films after repeated electrochemical testing was necessary for evaluating these monolayers for potential use in a range of applications utilizing TCOs. The optical transmittance of the monolayer coated ITO substrates was evaluated using ultraviolet-visible (UV-Vis) spectroscopy techniques both before and after the electrochemical experiments. Specifically, transmittance between 350 to 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 native ITO substrates as illustrated in Fig. 4 wherein UV-Vis transmittance spectra of either native, 1-octadecanol (C18-alcohol) coated ITO, octadecyltrichloro silane (C18-silane) coated ITO, or octadecylphosphonic acid (C18-phosphonic) coated ITO films supported on glass slides are illustrated. However, a blue shift was observed for ITO covered with the

monolayers of ODTS after electrochemical testing. This phenomenon is attributed to structural and compositional changes within the ODTS coatings. For example, thin films of silicon oxide prepared from tris-dimethylamino silane exhibit a similar UV-Vis transmission spectrum. Changes to the silane monolayers, such as their decomposition to form silicon oxides, could induce a change in transmittance properties of ITO films. It is speculated that this blue tint observed with ODTS coatings is correlated with the vignetting phenomena observed in OLED devices. Visible blue tints are observable across a typical ODTS coated substrate, while corners and edges of the substrate exhibit a more vivid blue coloration. Repeated electrochemical cycling of the silane monolayers induce changes in the optical properties of the ITO films, while monolayers prepared from phosphonic acids or aliphatic alcohols did not yield any significant changes in their optical transmittance properties.

[0042] An important aspect of monolayers attached to TCO films is in the degree of influence of these films on its ability to pass current as part of an electrochemical device. In order to study the relationship between the electrical properties of these films and the chain length of hydrocarbon in the alcohol based SAMs, a series of electrochemical studies were performed with the modified ITO substrates while monitoring the peak current passed through these monolayers. Molecules with an even number of carbons in their backbone were selected for these experiments to eliminate odd-even effects observed in the formation and electronic properties of monolayers. The degrees of change in current passed through the monolayers during electrochemical studies, specifically the peak faradaic current was evaluated. As the most significant peak shifts occurred within the first 1,000 scans of the CV analyses, the

peak positions were reported at the 1,000th scan. Hydrocarbon chain length and peak current exhibited a linear correlation as illustrated in Fig. 5 wherein a graphical summary of peak currents obtained at a 200 mV/s scan rate after the 1,000th scan of the potential applied to a series of monolayers on ITO is illustrated. Each of these monolayers were prepared from aliphatic alcohols, but with an increasing chain length as depicted by the x-axis. Every two additional carbons in the backbone of the monolayers exhibited an average decrease of ~0.17 mA in the peak faradaic currents. The length of the hydrocarbon chain directly correlated with the observed conductivity of the modified ITO films. The peak faradaic current can be tailored by choice of the appropriate reagent to prepare the monolayers on ITO surfaces to tune the electronic properties for the intended applications. A repeat of the evaluation is illustrated every two additional carbons in the backbone of the monolayers exhibited an average decrease of ~0.18 mA cm^{-2} in the peak faradaic current density or ~0.027 log | *J* | at the faradaic peak. A similar linear relationship has been observed in a study on n-alkanethiols on Au surfaces. The length of the hydrocarbon chain was directly correlated with the observed peak current density recorded for the modified ITO films. The dashed line in Fig. 13 is a linear fit to the observed trend and the error bars for each data point indicate one standard deviation from the mean values. In Fig. 13 average log | *J* | values obtained at faradaic peaks from CV experiments carried out for ITO substrates coated with a series of monolayers. Each of the monolayers were prepared from linear aliphatic alcohols of the specified chain length, as indicated on the x-axis. The results for an RCA-1 cleaned ITO substrate (with chain length of 0) is included for reference. Data were obtained at a 200 mV s^{-1} scan rate. The reported peak current densities are the average values from

three independent samples. These measurements were taken after the 1,000th scan of the applied potential for each of the modified ITO electrodes. The 1,100th scan is illustrated in Fig. 14 wherein the 1,000th profile from a consecutive series of cyclic voltammetry analyses are provided for: (A) RCA-1 cleaned ITO; (B) 1-hexanol coated ITO; (C) 1-octanol coated ITO; (D) 1-decanol coated ITO; (E) 1-dodecanol coated ITO; (F) 1-tetradecanol coated ITO; (G) 1-hexadecanol coated ITO; and (H) 1-octadecanol coated ITO. These electrochemical studies were carried out at a scan rate of 200 mV s^{-1} using the ITO substrates as the working electrode in aqueous solutions of 1 M KCl containing 10 mM of potassium ferricyanide and 10 mM of potassium ferrocyanide.

[0043] The work function of the modified ITO substrates was determined by ultraviolet photoelectron spectroscopy (UPS) to evaluate their use as an anode in device applications. These monolayer modified ITO surfaces were compared with unmodified ITO surfaces, as well as ITO substrates modified with either alkylsilanes or alkylphosphonic acids. The relatively high work function of ITO among TCOs makes it an attractive choice for use as a transparent anode in device applications. There is, however, often a mismatch in the work function between the ITO surfaces and various coatings applied to these electrodes, such as functional polymers. Monolayers on ITO often create a permanent dipole on these surfaces, increasing hole injection efficiencies. Ultraviolet photoelectron spectroscopy (UPS) was used to determine the work functions of the monolayer modified ITO. A series of alcohol containing reagents were evaluated for their ability in tuning the work functions of the ITO. Three separate measurements were obtained to assess the average work function and its variability within each substrate. The work function measured for native ITO, 4.62 eV,

corresponded well with reported values in literature, which ranged between 4.5 and 4.7 eV. Fig. 6 depicts the normalized UPS spectra for each of the samples for various monolayers on ITO coated glass substrates wherein each spectrum shows the secondary electron edge cutoff and the fermi levels associated with each of these monolayers. Table 1 provides the calculated average work functions. Widely reported work functions for ODTS and ODPA monolayers on ITO films were 4.85 eV and 4.5 eV, respectively. The inventive films exhibited much higher values, 5.37 eV and 5.51 eV, respectively, which indicate the formation of multilayers on the ITO surfaces. In contrast, it is anticipated that these values for the monolayers on ITO prepared from the alcohol reagents should be closer to that of a true monolayer as these reagents are less likely to form multilayers. Diols and fluorinated alcohols were also evaluated to assess their ability to further tune the work function of the ITO as the hole-injection transport processes could be enhanced by incorporating terminal electron withdrawing groups to alcohols such as diols and fluorine. Previous UPS studies on phosphonic acid monolayers compared the work functions of native ITO, n-alkylphosphonic acid coated ITO and other phosphonic acids. The n-alkylphosphonic acid monolayers decreased the work function of ITO by 0.6 eV, while the other phosphonic acids, such as fluorinated and phenylated phosphonic acids, exhibited equal or higher work functions to the native ITO surfaces with 1,5-pentanediol, 1,10-decandiol and 1H, 1H, 2H, 2H-perfluoro-octanol monolayers the work function increases from 4.62 eV, for native ITO, to 4.81 eV, 5.34 eV and 5.14 eV, respectively. These values indicate that alcohol based SAMs, such as diols and fluorinated, can be used to fine tune the work functions of ITO.

TABLE 1: Work function obtained from UPS spectra with a He 1 source.

Sample	Work function (eV)
Native ITO	4.62 ± 0.22
OTS	5.37 ± 0.11
OPA	5.51 ± 0.16
pentanediol	4.81 ± 0.24
decanediol	5.34 ± 0.12
octadecanol	5.03 ± 0.17
perfluoro-octanol	5.14 ± 0.13

[0044] As would be realized from the results the formation of monolayers through the condensation of alcohol compounds on TCO surfaces, is demonstrated using ITO as an example. These ITO substrates modified with alcohol based SAMs exhibited superior electrochemical and chemical stability to the surfaces modified with silanes or phosphonic acids, which was further confirmed through XPS and WCA experiments. The optical transmittance of the alcohol based SAMs on ITO films exhibited minimal changes after prolonged electrochemical tests, further validating the overall stability of the alcohol monolayers on ITO surfaces. In addition, alcohol based SAMs of different aliphatic alcohols with variable chain lengths can tune the conductivity and work

function of these surfaces. For example, as the chain length of the aliphatic alcohols in the monolayers increased, the peak current passed through the monolayers progressively decreased, which is consistent with observations made in the field for monolayers of alkanethiols gold films. Work functions acquired from ultraviolet photoelectron spectroscopy (UPS) confirmed that the alcohol based SAMs can increase the work function by up to 0.7 eV through use of diols and the fluorine moiety on the surface of the SAMs in comparison to native ITO.

[0045] Previous studies have demonstrated that interfacial incompatibilities can lead to a non-uniform wetting of the non-polar organic HTL. In OLEDs and OPVs, 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. Monolayers can be used to effectively tune the work function of metals and semiconductors, while increasing the efficiency of the hole injection process. These achievements result from the creation of a new permanently induced surface dipole within the monolayers. The UPS measurements can be used to determine the work function of materials. 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. 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. 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.

[0046] Alcohol based monolayers were specifically evaluated for their ability to tune the work function of ITO. This study included SAMs prepared from ODA, PTdiA, DCdiA, and PFOA. 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. 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 because of its independence from environmental factors, which include 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). 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 (4.73 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. The ITO surfaces modified by SAMs required a more detailed

assessment of their energy levels and the shifts in these levels for an accurate determination of their work functions.

[0047] An accurate determination of the work function for the monolayer modified surfaces requires a consideration of both band bending and shifts in E_F. 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. 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. Depending on the overall direction of the dipole, the energy levels are shifted either upward or downward. 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. 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. The reported work

function values for ODTS and ODPA monolayers on ITO are 4.85 eV and 4.5 eV, respectively. Our coatings prepared from ODTS and ODPA exhibited work function values of 4.07 eV and 4.78 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). Monolayers derived from ODA on ITO exhibited a work function of 4.74 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., $\geq$ 5 eV) is desired to minimize the hole injection barrier, which is sought to improve the performance and lifetime of these devices.

[0048] 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. The work functions of ITO modified with PTdiA, DCdiA and PFOA were determined using the methods described above. Fig. 7 depicts the UPS spectra for each of the samples after normalization to the maximum peak intensity. In Fig. 7 the 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. The average work function values and their associated errors, reported as one standard deviation from the mean values, are summarized in Table 2. The work functions for the ODA, PTdiA, DCdiA and PFOA monolayers were 4.74 eV, 4.58 eV, 4.49 eV and 4.88 eV, respectively. Treatments with either of the diols, PTdiA or DCdiA, decreased the work function by 0.15 and 0.24 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 at the para position. 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 PFOA alcohol based monolayer 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. 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 of the monolayers.

Table 2. Work functions obtained from UPS spectra (He 1 Source).

sample	work function (eV)
RCA-1 cleaned	4.73 ± 0.20
ODA	4.74 ± 0.27
ODTS	4.07 ± 0.05
ODPA	4.78 ± 0.26
PFOA	4.88 ± 0.08
PTdiA	4.58 ± 0.13
DCdiA	4.49 ± 0.16

[0049] 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. 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.

[0050] 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. 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. 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 3. The RCA-1 cleaned ITO sample exhibited contact angle values of ~0° 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 of 23 to 27 mJ m^{-2} for their total surface energy. These results are significantly lower than those for the RCA-1 cleaned ITO substrates, but are consistent with previous values reported for monolayers of ODPA and ODTS which are 29 mJ

m^{-2}. 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 and OPVs. 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.

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

Table 3. 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‡		γ, dispersive component‡		γ, total‡	
	θ*	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	1.7E-3	26	26	26	26
ODPA	102 ± 7	33 ± 4	0.062	3.3E-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

*θ = Average contact angle (degrees).
‡γ = Surface energy (mJ m^{-2}), G = geometric mean, and H = harmonic mean.

[0051] Composition of the monolayers derived from the alcohol based 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 as shown in Table 3. The estimated surface energies were 34, 48 and 46 mJ m^{-2} 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 Fig. 8. In Fig. 8 the surface energies are 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. The results from the ITO substrates modified with the different alcohol based 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 necessary to create a compatible interface for uniform wetting of different 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. This study demonstrated the preparation of monolayers on ITO derived from alcohol based reactants with potential applications in organic based electronic devices, such as OLEDs and OPVs, through designing the ITO interface to exhibit a desirable surface energy and work function. To further evaluate the potential of alcohol based monolayers for use 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.

[0052] In an exemplary analysis ODA, ODTS and ODPA monolayers were prepared on ITO and their electrochemical properties and stabilities were evaluated after extensive CV analyses. The results are presented in Fig. 9 where the 1^{st}, $1{,}000^{th}$ and $10{,}000^{th}$ 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 are presented. These electrochemical studies were performed at a scan rate of 50 mV s^{-1} 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. Fig. 9A 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 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. The CVs obtained for the series of ITO substrates modified with SAMs of ODA, ODTS and ODPA are plotted in Figures 9B to 9D. 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 as illustrated in Fig. 9B. 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. Unlike alcohol based monolayers, the mechanism of formation and the resulting structure is different for the ODTS and ODPA derived monolayers.

[0053] 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. These monolayers are likely to be susceptible to further changes to their structure and surface coverage as a result of induced oxidative and reductive processes at the ITO electrodes. Monolayers formed using ODTS initially possessed a similar degree of surface passivation in comparison to monolayers prepared from ODA. 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 cm^{-2} and 0.35 V, respectively as illustrated in Fig. 9C. 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 cm^{-2}, corresponding to an overall change by -0.31 mA cm^{-2}. 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. Thin silicon oxide films have also been produced from silanes through intermolecular polymerization and hydrolysis of the Si-C bonds. The Si-C bonds are susceptible to hydrolysis as they

exhibit a weaker bond strength than Si-O bonds. 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 of 0.69 mA cm^{-2} and a relatively high oxidative peak potential of 0.50 V. Significant changes in both the peak current density with a change of +0.65 mA cm^{-2} and the position of the oxidative peak potential with a change of -0.13 V were observed after 10,000 scans of the applied potential as illustrated in Fig. 9D. These significant changes to the oxidative conditions of the ferricyanide/ferrocyanide redox couple were attributed to restructuring 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. In addition, it has been shown that In-O-P bonds can be easily hydrolyzed when exposed to moisture. The restructuring of the ODPA coatings likely led to the dissolution of individual ODPA molecules, leaving defects within the monolayers on the ITO surfaces. These changes could significantly compromise the electronic properties of the modified ITO substrates. Additional studies were performed to further assess these structural changes to the monolayers including dissolution of bound species.

[0054] Water contact angle studies can be used to estimate the surface coverage of monolayers. 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 ~0° 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. 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 ~100°, while ODTS and ODPA coated substrates exhibited average WCAs of ~112° and ~102°, respectively s shown in Fig. 10 wherein water contact angles (WCAs) of RCA-1 cleaned ITO, and ITO modified with either ODA, ODTS, or ODPA are illustrated. These average WCA values were calculated using measurements obtained from 8 independent regions on each sample, which were obtained either before or after the series of electrochemical and hydrolytic tests as noted in the legend. 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 the electrochemical stability measurements. These results were also consistent with the hydrolytic sensitivity of ODPA reported in the literature. These changes are 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. 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. The roughness of the ITO modified with ODTS exhibited a decrease of approximately 2 nm as shown in Table 4. Further analyses were required to better understand the observations made regarding the electrochemical and morphological stability of these monolayer modified ITO substrates.

Table 4. Root mean square (RMS) roughness values from the AFM measurements for unmodified and modified ITO substrates.

ITO treatment/modification	RMS (nm)
RCA-1 cleaned	6.11 nm
ODA	6.62 nm
ODPA	6.03 nm
ODTS	4.13 nm

[0055] Potential changes to the composition of the monolayer modified ITO surfaces were assessed by XPS measurements. High resolution XPS analysis of the O_{1s} peaks were monitored before and after the series of electrochemical experiments as provided in Fig. 11. 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 such as In-O-C, In-O-P and In-O-Si. 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. The peak area ratio between the O-In-OH and O-In-O species maintained a value of approximately 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. Fig. 11 illustrates 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. 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, as illustrated in Fig. 11A, or the ODA coated ITO, as illustrated in Fig. 11B. 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, as illustrated in Fig. 11C. This change was attributed to the formation of a multilayer structure within the as-deposited ODTS and the subsequent loss of non-covalently attached ODTS molecules and/or degradation of the monolayers of ODTS. 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 as illustrated in Fig. 11D. This phenomenon was attributed to etching and/or non-specific degradation of the ITO and the ODPA coatings. The ODPA monolayers likely underwent restructuring and degradation from electrochemical and hydrolytic stresses. One example is the hydrolysis of the In-O-P bonds, which produces H_3O^+ and increases the local acidity. Another example is that weakly bound In or Sn atoms coordinate with phosphonic acids and undergo complexation to form an insoluble salt. 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. Another study proposed that phosphoric acid slowly etches ITO and could be used to extract In species from solution. 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. In summary, the ODA coated ITO demonstrated a greater electrochemical and chemical stability in contrast to the ODTS or ODPA coated ITO. The 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. Evaluating these coatings for their potential use in optoelectronic devices required a further assessment of possible changes to their optical properties.

[0056] 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 aa illustrated in Fig. 12 wherein 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 are illustrated. 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. 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 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. Visible blue tint was observed in the ODTS coated ITO films after 2.5 days of exposing these substrates to conditions to simulate their accelerated degradation. 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. 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. Topographies of the ITO surfaces after formation of monolayers using different types of precursors have been imaged by atomic force microscopy (AFM) as shown in Fig. 15. Specifically, AFM images for a series of ITO substrates after the electrochemical and hydrolytic tests were shown in Fig. 15 (A) RCA-1 cleaned ITO; (B) ODA coated ITO; (C) ODPA coated ITO; and (D) ODTS coated ITO substrates. The images show difference in surface roughness for the ITO film coated with ODTS with root mean square (RMS) roughness of 4.1 nm, whereas the surface roughness and topographies of the ITO films that were either cleaned with RCA-1 or coated with ODA or ODPA showed consistency, with RMS roughness of 6.1, 6.6, and 6.0 nm, respectively. The discrepancy in surface topography

resulted from the formation of multilayers of organosilane molecules, which could ultimately compromise the optical characteristics of ITO film. 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.

[0057] 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 m^{-2} 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. Analysis of these alcohol based monolayers on ITO by CV techniques demonstrated their electrochemical and hydrolytic stability relative to surfaces modified with silanes or phosphonic acids. The alcohol based monolayers exhibited a change of only 0.03 mA cm^{-2} 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 in comparison to those derived from silanes or phosphonic acids 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. Of particular note, the silane based monolayers exhibited a degradation in film quality as observed in the optical measurements, which were consistent with the results of the electrochemical tests, AFM measurements, and XPS analyses. The modification of ITO with monolayers prepared from alcohol based reagents is a promising technique for adjusting the properties of the ITO for its use in organic based electronic devices. The alcohol based monolayers on ITO exhibited an exceptional electrochemical and chemical stability, which will be required for a prolonged use in electronic devices. In addition, these surface modifications to ITO can readily incorporate a variety of chemistries, such as a hydroxyl moiety through the use of diol containing reagents. These hydroxyl groups could potentially provide a platform for further chemical reactions and for applications in electronic devices other than OLEDs and OPVs, such as molecular sensors and organic transistors.

EXAMPLES

[0058] Reagent and Materials. All reagents were used as received, which included Sparkleen 1 glassware detergent (Fisher, Catalog no. 04-320-4), propylene carbonate (Sigma Aldrich, 99%, CAS no. 108-32-7), 1-octanol (Sigma-Aldrich, ACS reagent grade, CAS no. 111-87-5), *1H,1H,2H,2H*-perfluoro-1-octanol (Sigma-Aldrich, 97%, CAS no. 647-42-7), hydrogen peroxide (Fisher Scientific, CAS no. 7722-84-1), acetone (Fisher Scientific, reagent grade, CAS no. 67-64-1), and isopropanol (Fisher Scientific, reagent grade, CAS no. 67-63-0), tetrahydrofuran (Calderon, HPLC grade, CAS no. 109-99-9), octadecylphosphonic acid (Sigma-Aldrich, 97%, CAS no. 4727-47-4), octadecyltrichloro

silane (Sigma-Aldrich, ≥90%, CAS no. 112-04-9), 1-octadecanol (Sigma-Aldrich, ReagentPlus® grade, CAS no. 112-92-5), 1-tetradecanol (Sigma-Aldrich, 97%, CAS no. 112-72-1), 1-hexadecanol (Sigma-Aldrich, ReagentPlus®, CAS no. 36653-82-4), 1-dodecanol (Sigma-Aldrich, ACS reagent grade, CAS no. 112-53-8), 1-decanol (Sigma-Aldrich, ≥99%, CAS no. 112-30-1), 1-hexanol (Sigma-Aldrich, reagent grade, CAS no. 11-27-3), n-hexane (ACS, reagent grade, CAS no. 110-54-3), anhydrous ethanol (Commercial Alcohols, product no. P016EAAN), ammonium hydroxide (Fisher Scientific, Reagent ACS grade, CAS no. 1336-21-6) and 1, 5-pentanediol (Sigma-Aldrich, >97%, CAS no. 111-29-5), and 1,10-decanediol (Sigma-Aldrich, 98.0%, CAS no. 112-47-0). Glass slides coated with indium tin oxide (ITO) films (7 ohms/cm^2, polished grade, 75 × 25 × 1.1 mm) were purchased from University Wafer (Item 2290). The polished silicon wafers and glass slides coated with ITO film were diced into either 1 cm × 1 cm or 1 cm × 2 cm pieces that served as substrates for the following experiments.

[0059] Pretreatment of ITO Films on Glass Slides. Each ITO coated substrate was placed into an individual glass test tube (CEM Discover, part no. 908035). The substrates were each sonicated in a detergent solution prepared from 18 MΩ·cm deionized (DI) water (10 mL, obtained from a Barnstead Nanopure Diamond water filtration system) and Sparkleen glassware detergent (1 g). The samples were sonicated sequentially in acetone (5 mL), isopropanol (5 mL) and ethanol (5 mL). The sonication process was maintained over a period of 10 min in each solvent, and subsequently rinsed with DI water (25 mL). A modified RCA-1 cleaning procedure was performed to remove additional surface contaminants and to create hydroxyl groups on the ITO

surfaces.[4] In brief, the RCA-1 cleaning solution was prepared using a glass beaker containing DI water (50 mL) that was heated to 70 °C using a thermocouple controlled hotplate (Corning 720). Upon reading 70 °C, an aqueous solution of NH_4OH (10 mL, 30% v/v) was added to the heated DI water. An aqueous solution of H_2O_2 (10 mL, 30% v/v) was subsequently added to this mixture and heated until re-equilibrating at 70 °C. The freshly prepared, hot RCA solution was transferred to the glass test tubes each containing an individual substrate, which were held at 70 °C for 3 h. The RCA-1 solution was subsequently replaced with DI water (10 mL) and the cleaned substrates were sonicated for 10 min. The rinsed ITO substrates were dried in an oven (Sheldon, model no. 1350GM) maintained at 120 °C for 20 min prior to the formation of the desired monolayers.

[0060] Preparation of the Indium Tin Oxide coated on Glass Slides. Glass slides coated with an ITO film were initially cleaned with approximately 1 g of Sparkleen 1 glassware detergent dissolved in 18 MΩ·cm DI water, acetone, isopropanol, ethanol and DI water under 20 min of sonication in 10 mL glass test tubes. A modified RCA-1 cleaning procedure was performed to remove additional surface contaminants and to create hydroxyl groups on the ITO surfaces. Five parts (~50 mL) of DI water was heated to 80°C, and one part (~10 mL) of a 30% (v/v) NH_4OH aqueous solution was added to the hot DI water. One part (~10 mL) of a 30% (v/v) H_2O_2 aqueous solution was subsequently added to this mixture and the solution was heated until equilibrating at 80°C. The ITO coated substrates were immersed in the hot RCA solution for 3 h at 70°C. These substrates were rinsed by sonicating in DI water for 10 min. The rinsed

ITO substrates were dried at 120°C in an oven for 20 min prior to formation of the monolayers.

[0061] Formation of Alcohol Based Self-Assembled Monolayers (SAMs). Alcohol based SAMs were formed on ITO surfaces. Cleaned ITO coated substrates were placed into a neat alcohol solution, which was heated up to 120°C for 24 h and up to 7 days. Upon removal of the substrates from the alcohol reagents, each substrate was sequentially rinsed with 20 mL of ethanol and 200 mL of 18 MΩ·cm DI water. The rinsed substrates were dried under a steady stream of filtered nitrogen gas.

[0062] Formation of Silane Based SAMs. A solution of octadecyltrichloro silane (OTS) was prepared in n-hexane for use in preparing OTS monolayers following previously published techniques. Cleaned ITO coated substrates were placed into individual 10 mL glass test tubes containing ~5 mL of 0.02 mM OTS solution for 2 h at room temperature. Upon removal of the substrates from the preparing solution, these substrates were sequentially rinsed with 20 mL of ethanol and 200 mL of 18 MΩ·cm DI water. The rinsed substrates were dried under a steady stream of filtered nitrogen gas.

[0063] Formation of Phosphonic Acid Based SAMs. A solution of octadecylphosphonic acid (OPA) was prepared in tetrahydrofuran for use in preparing OPA monolayers following previously published techniques[8]. Each of the ITO cleaned substrates was placed into an individual 10 mL glass test tubes containing ~5 mL of 0.01 mM the solution for up to 15 h at room temperature. Upon removal of the substrates from the preparing solution, these substrates were sequentially rinsed with 20 mL of ethanol and 200 mL of 18 MΩ·cm DI water. The rinsed substrates were dried under a steady stream of filtered nitrogen gas.

[0064] Rinsing the Prepared Substrates. Upon removal of a substrate from the corresponding solution used to prepare each of the monolayers, the substrate was rinsed sequentially with ethanol (20 mL) and DI water (200 mL). To remove any non-covalently attached molecules, the substrates were sonicated in ethanol (5 mL) for 10 min. The sonicated substrates were dried under a steady stream of nitrogen gas filtered with a PTFE membrane containing <200 nm pores.

[0065] Water Contact Angles (WCAs). The WCA measurements were performed with a contact angle goniometer (Dataphysics, model OCA 15) in the Nanofabrication Facility of 4D LABS at Simon Fraser University. A 2 μL droplet of 18 MΩ·cm deionized water was dispensed onto a substrate for each measurement. The WCA was measured as the angle between the air-water interface of the droplet and the interface between the water and the substrate. Where applicable, error bars for the WCA measurements are reported as one standard deviation of at least five independent measurements.

[0066] X-ray Photoelectron Spectroscopy (XPS). A series of XPS measurements were performed to investigate the chemical composition of the SAMs. These studies were conducted using a Kratos Analytical Axis ULTRA DLD system with a monochromatic aluminum source (Al Kα of 1486.7 eV) operating at 150 W with a 90° takeoff angle. Survey spectra (0 to 1200 eV) were acquired using a pass energy of 160 eV, a dwell time of 100 ms, and 1 sweep. High-resolution spectra were obtained using a pass energy of 20 eV, a dwell time of 500 ms, and 10 sweeps. This XPS analysis was performed with the assistance of a charge neutralizer because of significant charging effects for the substrates of interest. An area of 700 μm × 300 μm was analyzed in three separate regions of each sample to check the uniformity of each type of surface

modification. Analysis and fitting of the XPS peaks was performed using Vision Processing software version 2.2.7 beta.

[0067] Cyclic Voltammetry (CV). The CV experiments were performed to investigate the electrochemical and chemical stability of the monolayers on the ITO coated substrates. These experiments were performed using a Biologics Potentiostat (Model SP-150) using a standard three-electrode system with a Ag/AgCl reference electrode (CH Instruments, CHI111), a Pt counter electrode (CH Instrument, CHI115) and the ITO substrates as the working electrode. The electrolyte solution used for these experiments was 100 mL of 1 M KCl containing 10 mM $K_4[Fe(CN)_6]$ and 10 mM $K_3[Fe(CN)_6]$. Acquisition of a series of CV scans was performed using a scan rate of 50 mV/s and over a potential range from 0 to 1 V for up to 10,000 scans.

[0068] UV-Vis Transmission Spectroscopy (UV-Vis). The optical transmittance of the ITO coated substrates, across the UV-Vis region of the electromagnetic spectrum was assessed to characterize the optical properties of monolayer coated ITO substrates, using an Agilent 8453 UV-Vis spectrometer. The spectral range for these studies was 190 to 1100 nm with scan time of 1.5 s. Spectral resolution of the system was 1.5 nm and UV-Visible ChemStation Rev. A.07.01 [52] was used to perform the analyses on these spectra.

[0069] Ultraviolet Photoelectron Spectroscopy (UPS). A series of UPS measurements were performed to assess the work functions of the modified ITO substrates. Before UPS measurements, survey XPS was performed to confirm the composition of each substrate with the incident monochromatized AlKα X-rays, operating at 20 mA at 15 kV. The operating parameters for survey XPS were lens in

hybrid mode, the aperture to slot and the spectrometer pass energy at 80 eV. The data point spacing was 1.0 eV/step. The work function analyses of the monolayers modified ITO substrates were performed using a Kratos Axis Ultra DLD photoelectron spectrometer. The incident radiation was the He 1 line produced by a Kratos UV lamp. The lamp was operated at 10W of power. The spectrometer was operated in UPS mode, pass energy 5 eV, aperture 100 um. Data point spacing was 0.01 eV/step. Calibration was performed using a clean gold film. Data analysis was performed using Casa XPS software version 2.3.15 and data processing was performed using Vision Processing software version 2.2.7 beta.

[0070] Atomic Force Microscopy (AFM). The topography of the ITO surfaces both before and after modification with organic based monolayers was characterized by AFM. These analyses were obtained using an MFP 3D AFM (Asylum Research and Oxford Instruments) operating in AC mode using silicon cantilevers from BudgetSensors (Tap150-G, resonant frequency of 150 kHz, force constant 5 N/m). Scan areas of either 20 μm by 20 μm or 5 μm by 5 μm were used for these measurements, each acquired with a scan speed of 0.4 Hz and a resolution of 512 by 512. The analysis of the images and the evaluation of the root mean square (RMS) roughness were performed using Igor Pro 6.22.

[0071] The invention has been described with reference to the preferred embodiments without limit thereto. Additional embodiments and improvements may be realized which are not specifically set forth herein but which are within the scope of the invention as more specifically set forth in the claims appended hereto.

Claimed is:

1. A modified transparent conductive oxide surface comprising:

   a surface comprising a metal; and

   an organic group attached to said metal by an ether bond.

2. The modified transparent conductive oxide surface of claim 1 wherein said surface comprises at least one of In, Sn, Zn or Cd.

3. The modified transparent conductive oxide surface of claim 2 wherein said surface comprises indium tin oxide.

4. The modified transparent conductive oxide surface of claim 1 wherein said organic group is the residue of a reaction of an alcohol with a metal hydroxide.

5. The modified transparent conductive oxide surface of claim 4 wherein said alcohol is selected from the group consisting of saturated and unsaturated alcohols with 1 to 100 carbons; polyalklene glycols; fluorinated alcohols; phenyl alcohols; polar alcohols; vitamins; sugars; amino acids; nucleic acids and catechols.

6. The modified transparent conductive oxide surface of claim 5 wherein said saturated and unsaturated alcohols have 1 to 50 carbons.

7. The modified transparent conductive oxide surface of claim 6 wherein said saturated and unsaturated alcohols have 1 to 20 carbons.

8. The modified transparent conductive oxide surface of claim 5 wherein said saturated and unsaturated alcohols have 5 to 12 carbons.

9. The modified transparent conductive oxide surface of claim 5 wherein said polyalklene glycols is polyethylene glycol.

10. The modified transparent conductive oxide surface of claim 9 wherein said polyethylene glycol has a molecular weight low enough to be liquid at 25°C.

11. The modified transparent conductive oxide surface of claim 10 wherein said fluorinated alcohols are perfluorinated alcohols.

12. The modified transparent conductive oxide surface of claim 10 wherein fluorinated alcohols are liquid at 25°C.

13. The modified transparent conductive oxide surface of claim 5 wherein said phenyl alcohols have a formula of $HODC_6H_5$ wherein D represents a bond or a saturated or unsaturated alkyl of 1-6 carbons.

14. The modified transparent conductive oxide surface of claim 13 wherein said phenyl alcohols have a formula of $HODC_6H_5$ wherein D represents a bond or a saturated or unsaturated alkyl of 1-3 carbons

15. The modified transparent conductive oxide surface of claim 5 wherein said polar alcohols are alkanolamines with 2-4 carbons.

16. The modified transparent conductive oxide surface of claim 15 wherein said alkanolamines have 2 carbons.

17. The modified transparent conductive oxide surface of claim 15 wherein an amine of said alkanolamines are selected from a primary amine, a secondary amine, a tertiary amine and a quaternary amine.

18. The modified transparent conductive oxide surface of claim 5 wherein said vitamins are selected from thiamine, ascorbic acid, cholecalcifero, riboflavin,

vitamin E, ergocalciferol, pantothenic acid, pyridoxal, pyridoxamine and pyridoxine.

19. The modified transparent conductive oxide surface of claim 5 wherein said sugars are selected from n-acetylglucosamine, glucosamine, D-glucose and sucrose.

20. The modified transparent conductive oxide surface of claim 5 wherein said amino acids are selected from serine, threonine and tyrosine.

21. The modified transparent conductive oxide surface of claim 5 wherein said nucleic acids are adenosine derivatives.

22. The modified transparent conductive oxide surface of claim 21 wherein said adenosine derivatives are selected from adenosine triphosphate and adenosine monophosphate.

23. The modified transparent conductive oxide surface of claim 5 wherein said catechols are selected from the group consisting of catechins, hormones and neurotransmitters.

24. The modified transparent conductive oxide surface of claim 23 wherein said neurotransmitters are selected from the group consisting of dopamine, norepinephrine, epinephrine, cholesterol and testosterone.

25. The modified transparent conductive oxide surface of claim 5 wherein said alcohols are selected from the group consisting of 1-octadecanol, 1*H*,1*H*,2*H*,2*H*-perflourooctanol, 1,5-pentanediol and 1,10-decanediol.

26. A method for forming a modified transparent conductive oxide surface comprising:

providing a transparent conductive oxide surface comprising metal hydroxyl groups; and

reacting an alcohol comprising a pendant group on said alcohol with said metal hydroxyl groups to form an ether bond between said metal and said pendant group.

27. The method for forming a modified transparent conductive oxide surface of claim 26 wherein said surface comprises at least one of In, Sn, Zn or Cd.

28. The method for forming a modified transparent conductive oxide surface of claim 27 wherein said surface comprises indium tin oxide.

29. The method for forming a modified transparent conductive oxide surface of claim 26 wherein said alcohol is selected from the group consisting of saturated and unsaturated alcohols with 1 to 100 carbons; polyalklene glycols; fluorinated alcohols; phenyl alcohols; polar alcohols; vitamins; sugars; amino acids; nucleic acids and catechols.

30. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said saturated and unsaturated alcohols have 1 to 50 carbons.

31. The method for forming a modified transparent conductive oxide surface of claim 30 wherein said saturated and unsaturated alcohols have 1 to 20 carbons.

32. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said saturated and unsaturated alcohols have 5 to 12 carbons.

33. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said polyalklene glycols is polyethylene glycol.

34. The method for forming a modified transparent conductive oxide surface of claim 33 wherein said polyethylene glycol has a molecular weight low enough to be liquid at 25°C.

35. The method for forming a modified transparent conductive oxide surface of claim 34 wherein said fluorinated alcohols are perfluorinated alcohols.

36. The method for forming a modified transparent conductive oxide surface of claim 34 wherein fluorinated alcohols are liquid at 25°C.

37. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said phenyl alcohols have a formula of $HODC_6H_5$ wherein D represents a bond or a saturated or unsaturated alkyl of 1-6 carbons.

38. The method for forming a modified transparent conductive oxide surface of claim 37 wherein said phenyl alcohols have a formula of $HODC_6H_5$ wherein D represents a bond or a saturated or unsaturated alkyl of 1-3 carbons

39. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said polar alcohols are alkanolamines with 2-4 carbons.

40. The method for forming a modified transparent conductive oxide surface of claim 39 wherein said alkanolamines have 2 carbons.

41. The method for forming a modified transparent conductive oxide surface of claim 39 wherein an amine of said alkanolamines are selected from a primary amine, a secondary amine, a tertiary amine and a quaternary amine.

42. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said vitamins are selected from thiamine, ascorbic acid, cholecalcifero, riboflavin, vitamin E, ergocalciferol, pantothenic acid, pyridoxal, pyridoxamine and pyridoxine.

43. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said sugars are selected from n-acetylglucosamine, glucosamine, D-glucose and sucrose.

44. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said amino acids are selected from serine, threonine and tyrosine.

45. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said nucleic acids are adenosine derivatives.

46. The method for forming a modified transparent conductive oxide surface of claim 45 wherein said adenosine derivatives are selected from adenosine triphosphate, adenosine diphosphate, and adenosine monophosphate.

47. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said catechols are selected from the group consisting of catechins, hormones and neurotransmitters.

48. The method for forming a modified transparent conductive oxide surface of claim 47 wherein said neurotransmitters are selected from the group consisting of dopamine, norepinephrine, epinephrine, cholesterol and testosterone.

49. The method for forming a modified transparent conductive oxide surface of claim 29 wherein said alcohols are selected from the group consisting of 1-

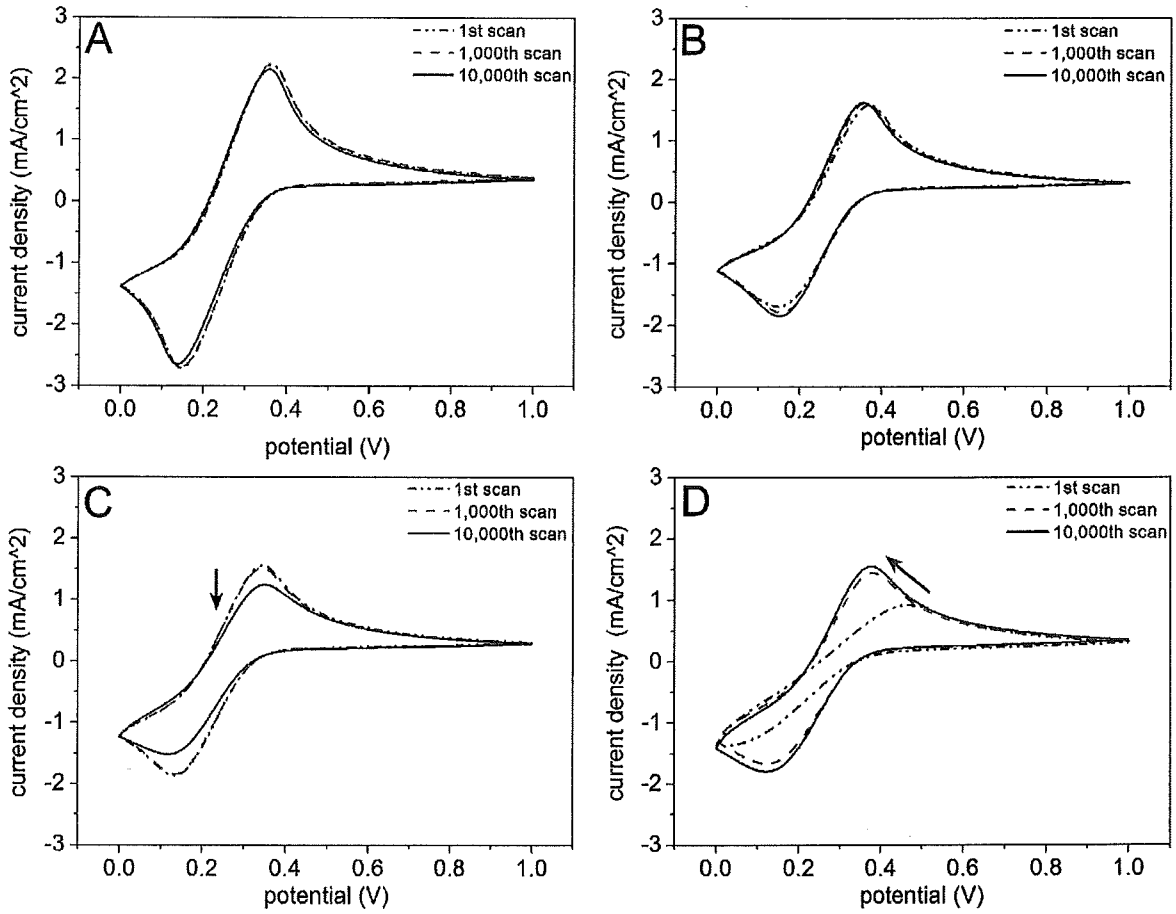
octadecanol, 1*H*,1*H*,2*H*,2*H*-perflourooctanol, 1,5-pentanediol and 1,10-decanediol.

50. The method for forming a modified transparent conductive oxide surface of claim 26 further comprising cleaning said surface.

51. The method for forming a modified transparent conductive oxide surface of claim 26 further comprising oxidizing said surface.

52. The method for forming a modified transparent conductive oxide surface of claim 26 further comprising sonicating said modified transparent conductive oxide surface.

53. The method for forming a modified transparent conductive oxide surface of claim 26 further comprising drying said modified transparent conductive oxide surface.


A
B
C
D
1st scan
1,000th scan
10,000th scan
current density (mA/cm^2)
potential (V)
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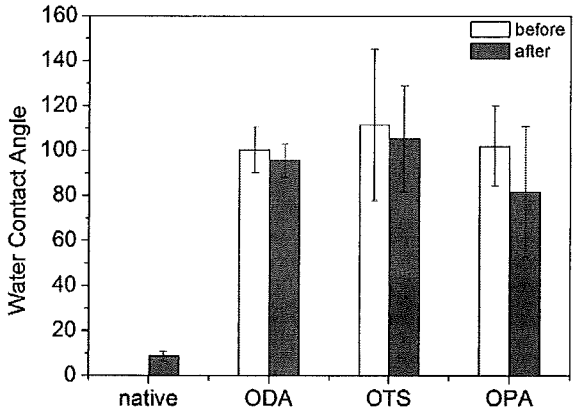
-1
-2
-3
0.0
0.2
0.4
0.6
0.8
1.0

Fig. 1


Water Contact Angle
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100
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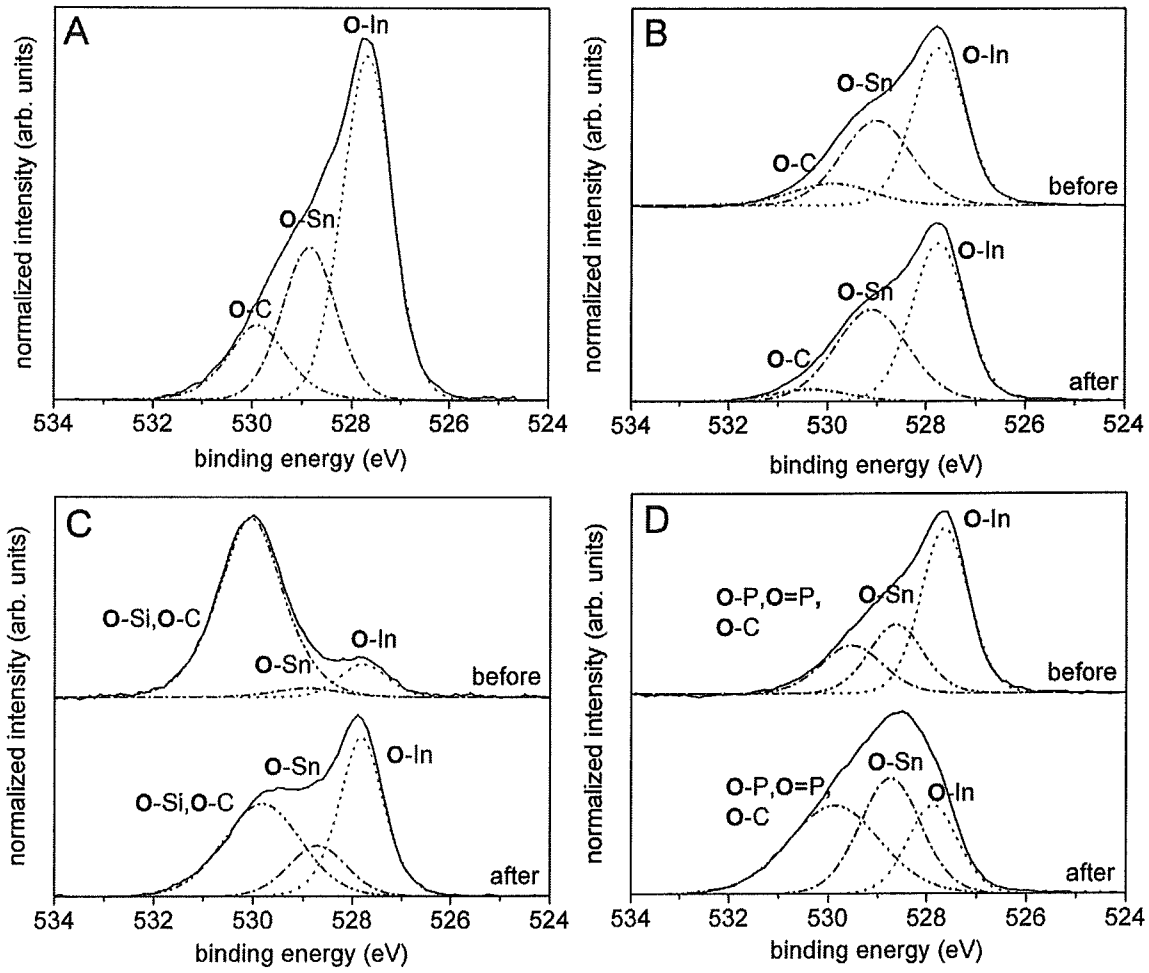
60
40
20
0
before
after
native
ODA
OTS
OPA

Fig. 2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O-In
O-Sn
O-C
normalized intensity (arb. units)
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532
530
528
526
524
binding energy (eV)
B
O-In
O-Sn
O-C
before
after
C
O-Si,O-C
O-Sn
O-In
D
O-P,O=P,
O-C

Fig. 3

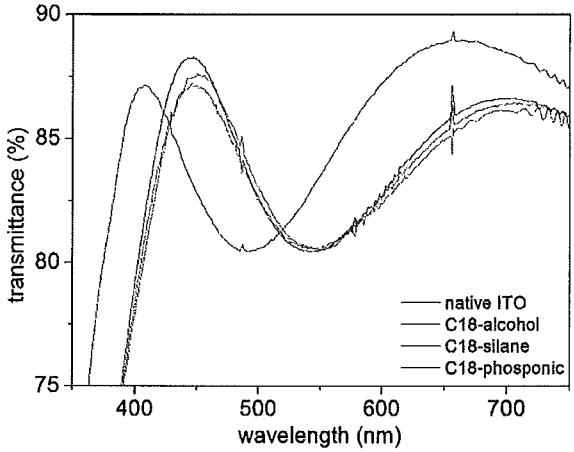
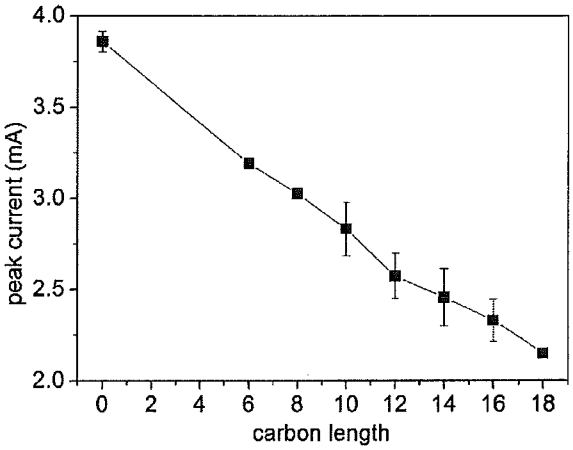

90
85
80
75
transmittance (%)
400
500
600
700
wavelength (nm)
native ITO
C18-alcohol
C18-silane
C18-phosponic

Fig. 4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3.5
3.0
2.5
2.0
peak current (mA)
0
2
4
6
8
10
12
14
16
18
carbon length

Fig. 5

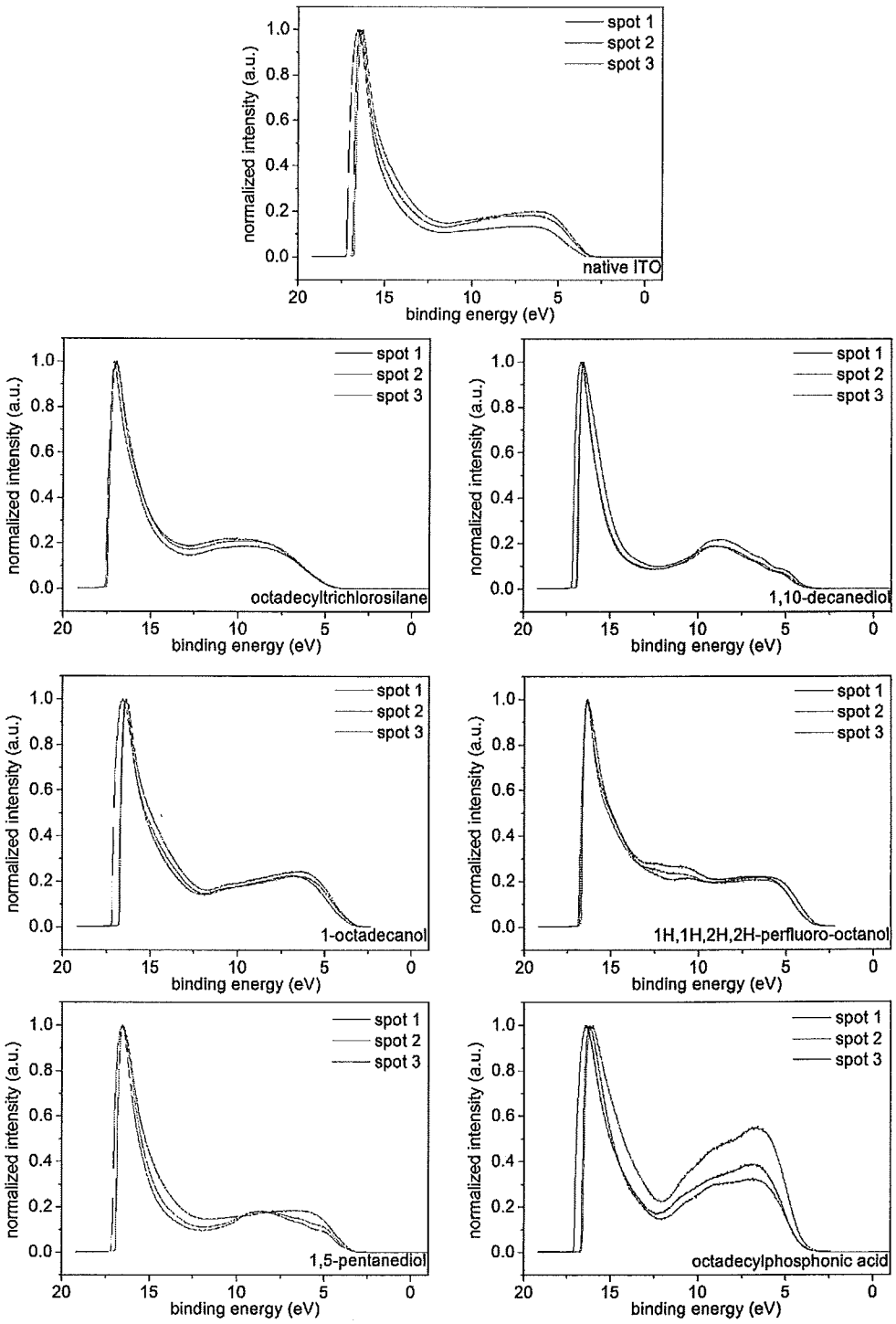
spot 1
spot 2
spot 3
normalized intensity (a.u.)
binding energy (eV)
native ITO
octadecyltrichlorosilane
1,10-decanediol
1-octadecanol
1H,1H,2H,2H-perfluoro-octanol
1,5-pentanediol
octadecylphosphonic acid

Fig. 6

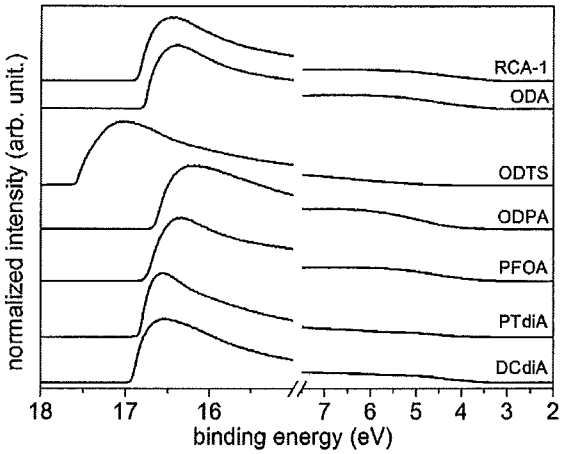
normalized intensity (arb. unit.)
RCA-1
ODA
ODTS
ODPA
PFOA
PTdiA
DCdiA
18
17
16
7
6
5
4
3
2
binding energy (eV)

Fig. 7

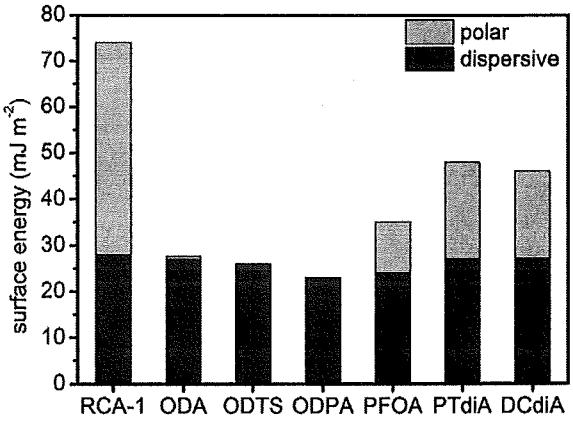
surface energy (mJ m-2)
polar
dispersive
0
10
20
30
40
50
60
70
80
RCA-1
ODA
ODTS
ODPA
PFOA
PTdiA
DCdiA

Fig. 8

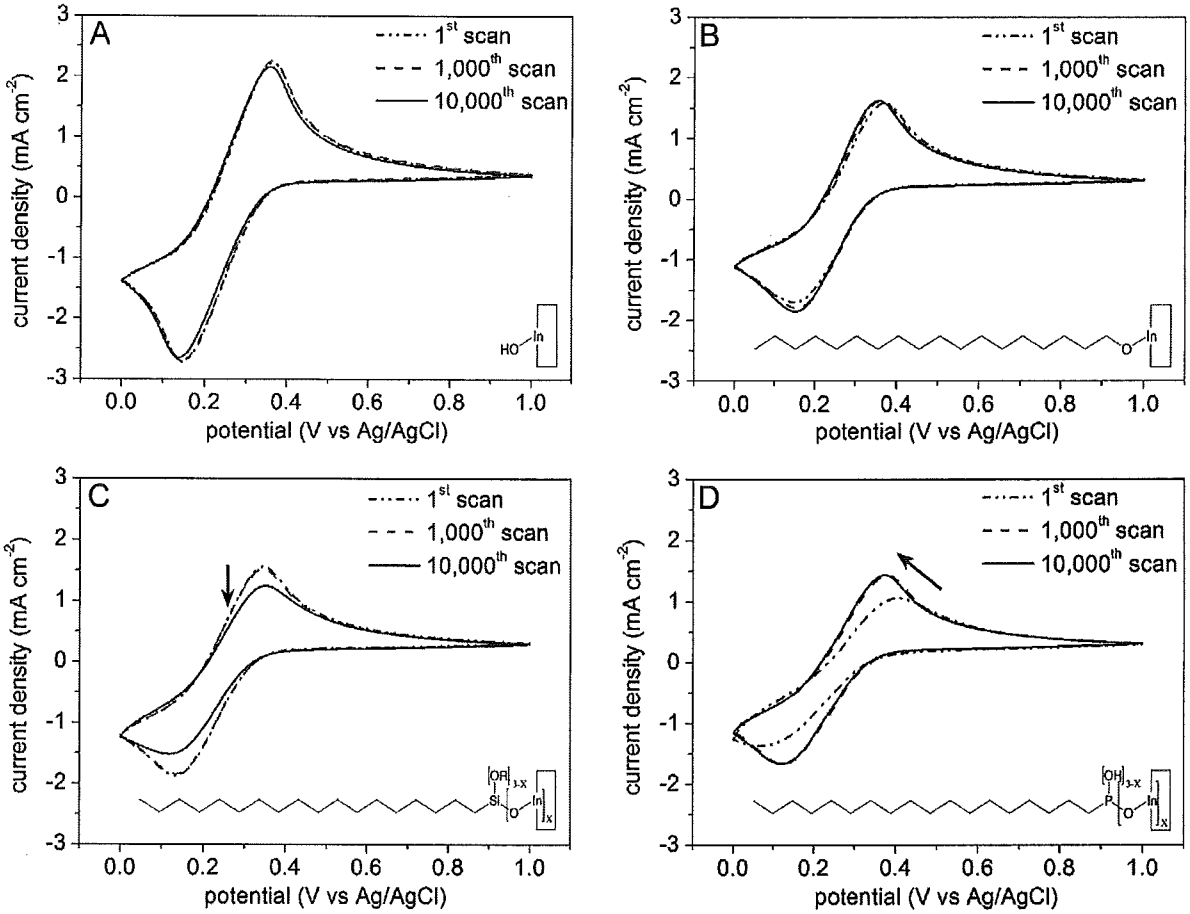
A
B
C
D
1st scan
1,000th scan
10,000th scan
current density (mA cm-2)
potential (V vs Ag/AgCl)

Fig. 9

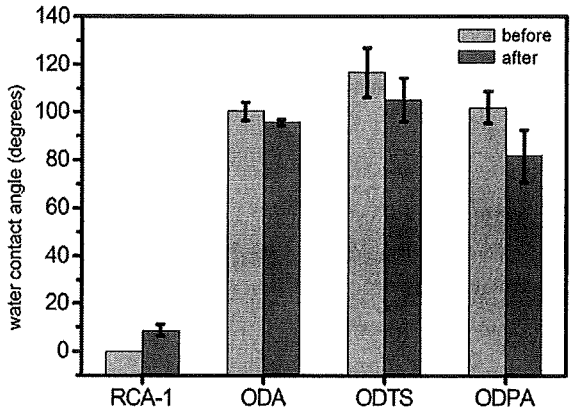
water contact angle (degrees)
140
120
100
80
60
40
20
0
before
after
RCA-1
ODA
ODTS
ODPA

Fig. 10

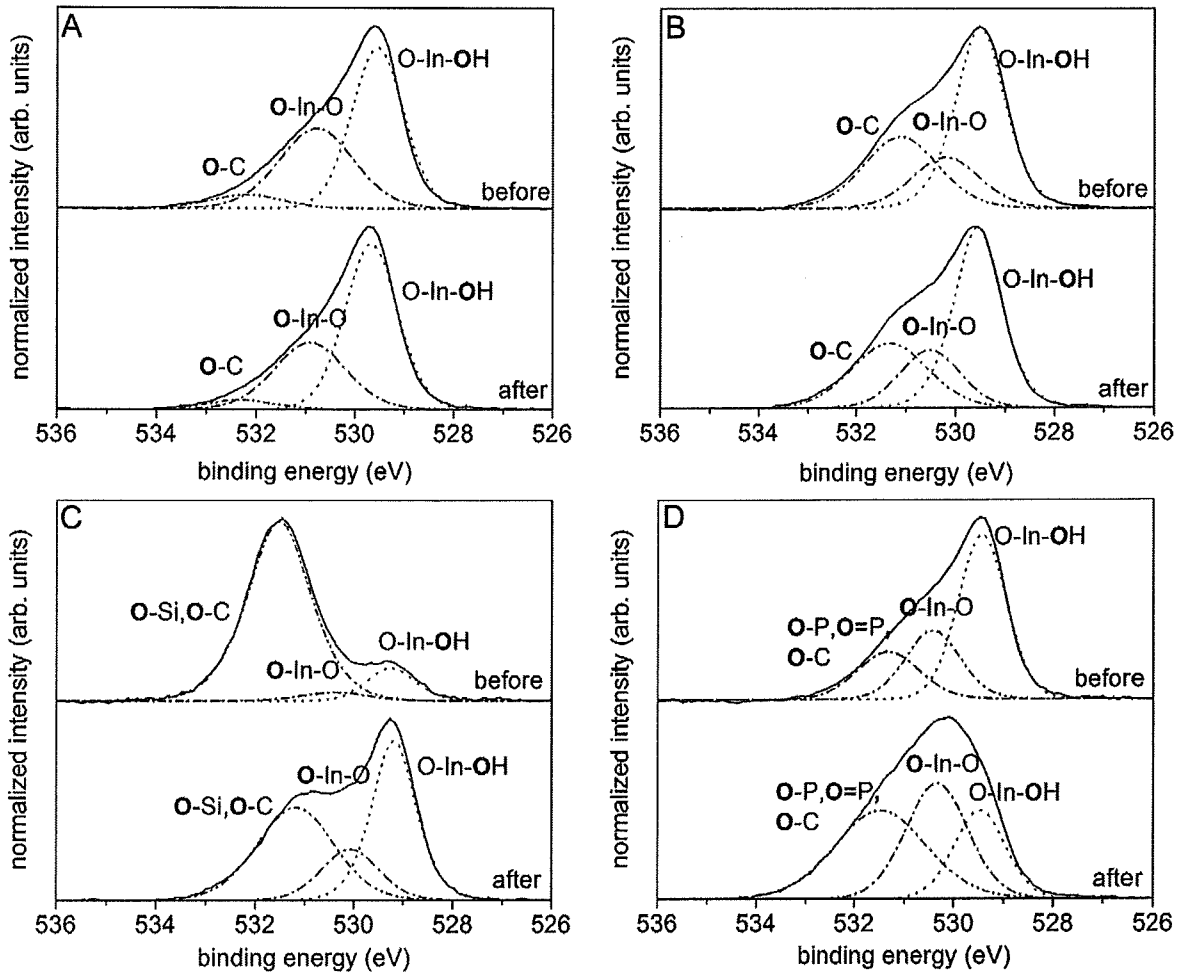
A
O-In-OH
O-In-O
O-C
before
after
B
C
O-Si,O-C
D
O-P,O=P,
normalized intensity (arb. units)
binding energy (eV)
536
534
532
530
528
526

Fig. 11

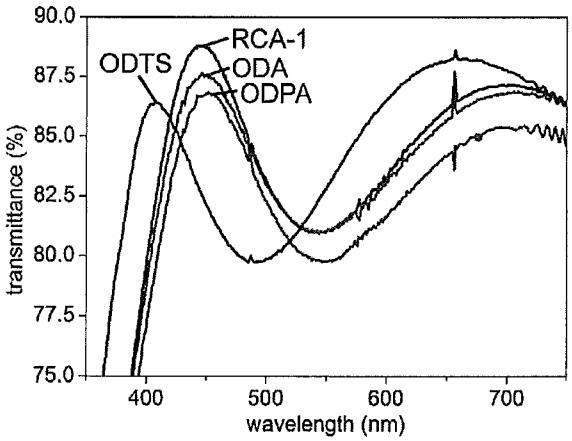
90.0
87.5
85.0
82.5
80.0
77.5
75.0
transmittance (%)
400
500
600
700
wavelength (nm)
RCA-1
ODTS
ODA
ODPA

Fig. 12

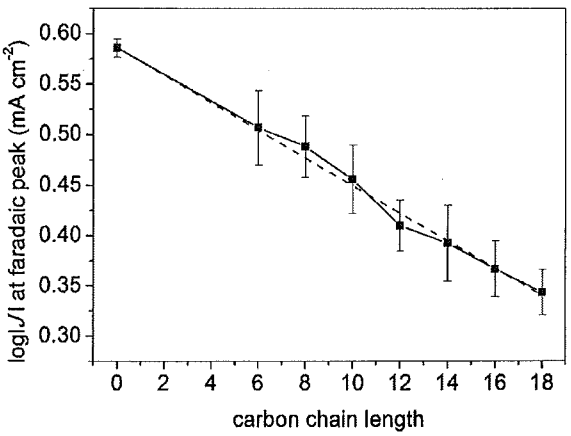
0.60
0.55
0.50
0.45
0.40
0.35
0.30
log|J/I at faradaic peak (mA cm-2)
0
2
4
6
8
10
12
14
16
18
carbon chain length

Fig. 13

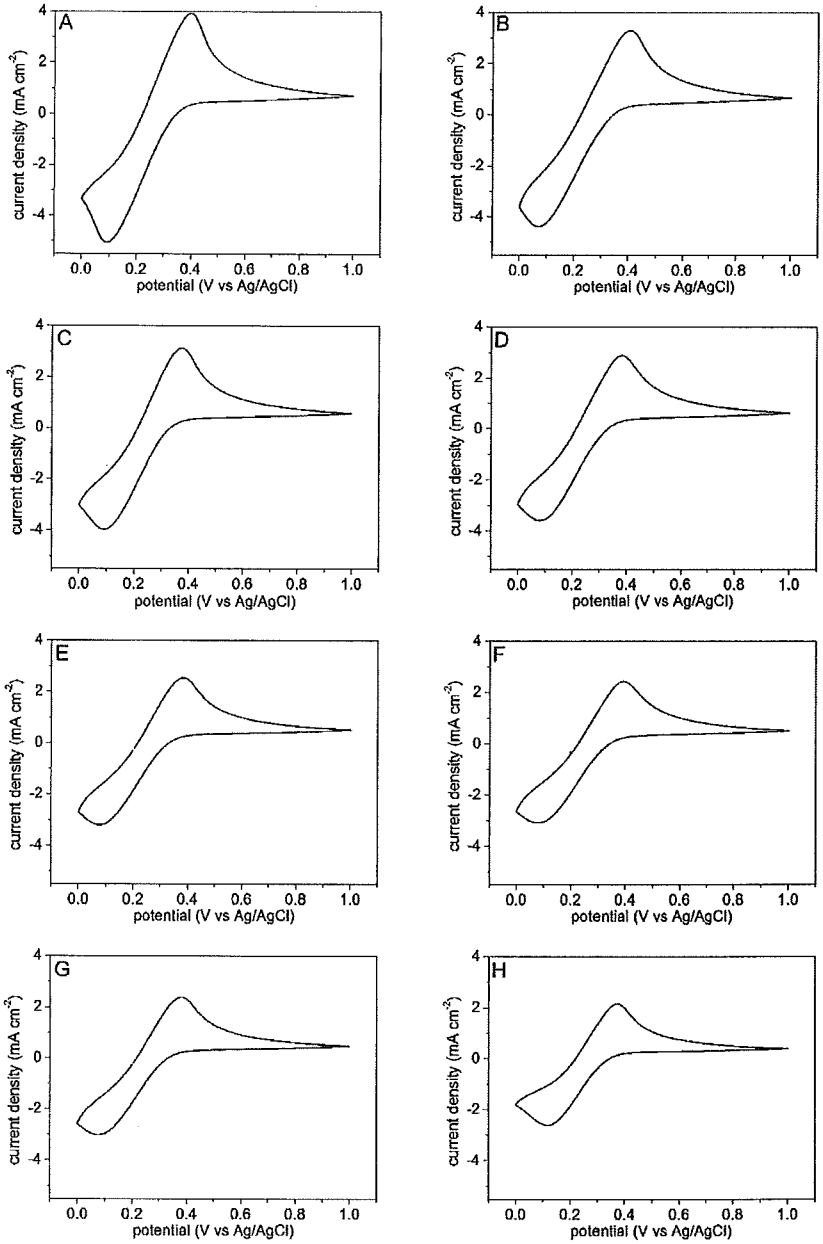
A
B
C
D
E
F
G
H
current density (mA cm-2)
potential (V vs Ag/AgCl)
4
2
0
-2
-4
0.0
0.2
0.4
0.6
0.8
1.0

Fig. 14

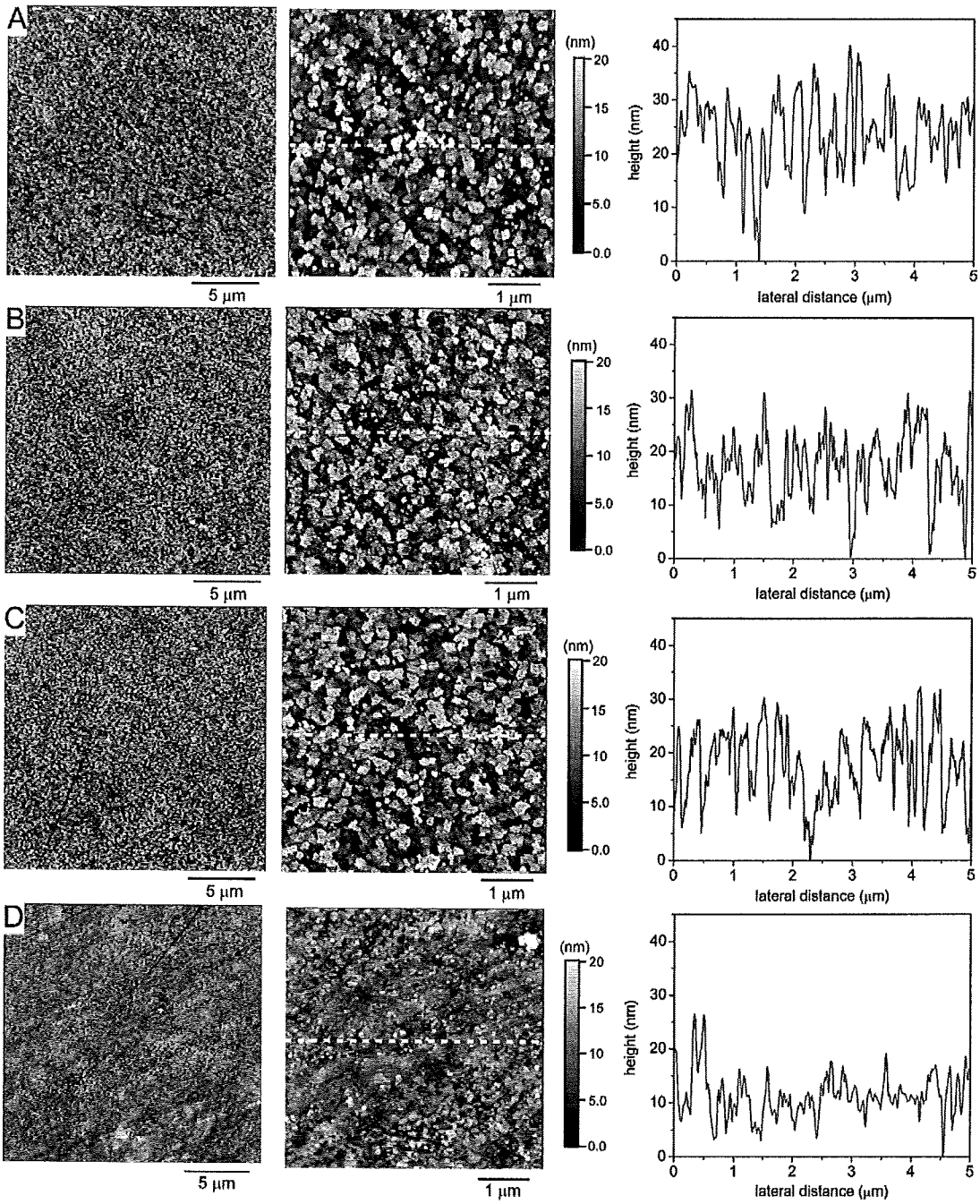
A
B
C
D
5 µm
1 µm
(nm)
20
15
10
5.0
0.0
height (nm)
lateral distance (µm)
0
10
20
30
40
1
2
3
4
5

Fig. 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2017/051312

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C07F 7/22*** (2006.01) , ***H01B 1/08*** (2006.01) , *H01L 51/44* (2006.01) , *H01L 51/52* (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2006.01): ***C07F 7/22***, ***H01B 1/08*** , ***H01L 51/44***, ***H01L 51/52***

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
STN Express (Registry, CAPlus), Canadian Patent Database, Questel Orbit, PubMed
Keywords: TCO, ITO, "transparent conductive oxide", "conductive oxide", "titanium oxide"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WU, Qi-Hui, "Progress in Modification of Indium-Tin Oxide/Organic Interfaces for Organic Light-Emitting Diodes", *Critical Reviews in Solid State and Materials Sciences*, 2013, 38(4), p. 318-352 **see entire document**	1-53
A	WO2016085980A1 (GATES B et al,), 02 June 2016 (02-06-2016) **see entire document**	1-53
X,P	CN106448804A (HAILING Z et al.), 22 February 2017 (22-02-2017) **see the claims**	1, 5-25

☐ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 04 January 2018 (04-01-2018)	Date of mailing of the international search report 10 January 2018 (10-01-2018)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Authorized officer Guillaume Tessier (819) 639-8671

WO2016085980A1	02 June 2016 (02-06-2016)	WO2016085980A1	02 June 2016 (02-06-2016)
		CN107109129A	29 August 2017 (29-08-2017)
		KR20170088957A	02 August 2017 (02-08-2017)
		US2017362256A1	21 December 2017 (21-12-2017)
CN106448804A	22 February 2017 (22-02-2017)	CN106448804A	22 February 2017 (22-02-2017)
		CN106448804B	31 October 2017 (31-10-2017)