

Surface Modification of Indium Tin Oxide via Electrochemical Reduction of Aryldiazonium Cations

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The facile deposition of para-substituted aryl films onto indium–tin oxide (ITO) electrodes by the electrochemical reduction of aryl diazonium salts in acetonitrile is reported. For the deposition conditions used in this report, the aryl film thicknesses are on the order of 1–6 nm, suggesting a multilayer structure. Regardless of the functional group on the aryl diazonium cation, (NO₂, CO₂H, or fluorene) the electrodeposition behavior onto ITO electrodes is similar to that seen on other electrode materials. XPS and UV–vis data support the introduction of organic functional surface groups to ITO. The blocking behavior of the aryl films on ITO toward the Ru(NH₃)₆^{3+/2+} redox couple is in agreement with electron transfer through conjugated organic layers. The facile preparation of patterned aryl films with regular-spaced 700 nm voids on ITO is also described. Atomic force microscopy and scanning surface potential microscopy on patterned NO₂ aryl films are used to assess the molecular structure and orientation. A 100 mV decrease in the contact potential over NO₂ aryl films relative to bare ITO suggests that the aryl films are loosely structured as deposited with the NO₂ groups oriented at a small angle away from the ITO surface.

Introduction

Thin films of indium–tin oxide (ITO) on glass substrates are commonly used electrode platforms for both fundamental (e.g., electroactive optical waveguides¹ and spatially resolved imaging of charge-transfer processes in metal oxides^{2,3}) and applied (e.g., photovoltaics⁴ and organic light emitting diodes (OLEDs)⁵) studies since they are highly transmissive to visible light and electronically conductive. However, the intrinsic heterogeneity of ITO in crystallinity, surface morphology, and surface functional group distribution^{6,7} results in varied local work function/conductivity,⁷ facile diffusion of O and In at the ITO surface,⁵ and a general incompatibility with biological systems,⁸ limiting the effectiveness of ITO for a host of applications. For example, carrier injection rates in OLEDs with ITO anodes suffer from poor matching of the ITO work function and the HOMO of the hole-transporting organic layer, as well as unstable adhesion of the organic layer to the surface of ITO.⁹ To circumvent these interfacial problems, several groups have proposed various surface-modification strategies involving polymer films,¹⁰ thiol-based self-assembled monolayers (SAMs),⁸ cross-linked siloxane films,^{9,11,12} and organic/organometallic moieties.^{13–15} A major

drawback of these approaches is that they typically require lengthy and expensive processing steps performed under nonideal conditions, e.g., high temperature and low pressure. Additionally, these protocols produce either relatively thick films (10–100 nm) or result in irregular or incomplete surface coverage since modification proceeds at spatially nonuniform ITO oxy-hydroxide functionalities.¹⁶ An intriguing alternative approach is to use the self-limiting electrochemical reduction of para-substituted (p-substituted) aryl diazonium salts to deposit conformal, molecularly thin layers. Since the early reports from Ahlberg et al.¹⁷ and Saveant et al.,^{18,19} this approach has been used to modify several different electrode materials, including metals²⁰ and semiconductor surfaces,²¹ but not yet ITO.

Interest in our lab has centered on surface modification of ITO electrodes for study of fundamental electron transport/conductivity²² and chemical sensing investigations.^{23,24} In principle, the deposition of uniform conformal coatings with desired functionality²⁵ onto ITO without excessive or expensive process conditions can contribute tremendously to the aforementioned applications. In particular, electrochemical modification techniques, when coupled with directed patterned film assembly

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methods,²⁶ present the opportunity to fabricate molecularly thin films with regular spaced voids without the use of costly subtractive or additive lithographic steps. The self-limiting electrochemical reduction of p-substituted aryl diazonium salts on ITO is also appealing for gaining insight on the physico-chemical nature of the deposited aryl films. Although several electrode platforms have been used for this deposition route, the influence of the underlying electrode material on the aryl film deposition, as well as on the attachment of the aryl film, has not been fully detailed. Herein, we describe the facile immobilization of functional organic thin films (<6 nm) on ITO substrates via the electrochemical reduction of p-substituted aryl diazonium cations in acetonitrile. The deposition of aryl films on ITO is compared to previously reported studies in this area for other electrode materials. Characterizations of the as-deposited films by electrochemical, spectroscopic, and scanning probe methods are presented, and observations are made which provide insight to the structure and composition of the deposited aryl film. This deposition route enables the facile preparation of complex micropatterned electrodes, which offers promise for fabrication of chemically responsive materials.

Experimental Section

Electrodeposition and Electrochemical Analysis of Aryl Films.

4-Nitrophenyl (NP) diazonium tetrafluoroborate (TFB) and 4-fluorenyl (FP) diazonium chloride were obtained commercially (Aldrich). 4-Carboxyphenyl (CP) diazonium TFB was synthesized according to previously established protocols.²⁷ Briefly, 1.5 g of 4-aminobenzoic acid (Aldrich) was dissolved in 12 mL of 48% aq HBF₄ by gentle heating (<60 °C). The solution was then stirred and chilled at 4 °C. Twenty five milliliters of aq concentrated NaNO₂ were added dropwise. Small aliquots of HBF₄ were added as necessary to prevent unreacted 4-aminobenzoic acid from precipitating out of solution. The solution was then stirred for an additional 30 min. The diazonium product was collected by vacuum filtration. All diazonium salts were stored cold (4 °C) and recrystallized with acetonitrile and ethyl ether prior to use. Glassy carbon (GC) substrates (Alfa Aesar, type 1) were polished stepwise with aqueous alumina slurries of 0.3 and 0.05 μm particles on microcloth (Buehler). The GC substrates were then rinsed thoroughly with and sonicated in NANOpure water (Barnstead, 18 MΩ·cm) for 30 min immediately prior to use. ITO-glass substrates (Delta Technologies Ltd, 15 Ω/□) were cleaned by immersion in aqueous ethanolamine solutions (Aldrich, 30% v/v) for 10 min at 80 °C followed with several rinses in NANOpure water. The ITO substrates were stored in NANOpure water until use, at which time they were rinsed with fresh NANOpure water and/or acetonitrile (Fisher) and dried under a stream of nitrogen. For patterned ITO electrodes, a 1.0% wt/wt solution of 1.71 ± 0.06 μm polystyrene spheres (Microparticles GmbH) in aqueous ethanol 90% vol/vol (Aldrich) was made. A 10 μL aliquot was spread onto precleaned, dried ITO substrates tilted at ca. 15° and was allowed to dry under ambient conditions. After drying in air, the polystyrene layers were annealed in air at 80 °C for 4 h in a muffle furnace, and then the patterned ITO electrodes were used immediately for electrodeposition studies. Following deposition, unpatterned ITO substrates were thoroughly rinsed in acetonitrile followed by NANOpure water and then dried under a stream of nitrogen before further chemical and structural analysis. For patterned ITO substrates, the polystyrene spheres were first removed by sonication in fresh acetonitrile and subsequently rinsed with acetonitrile.

Electrochemical experiments were conducted with a EG&G PAR 276 potentiostat. The ITO substrates were used as the working electrodes in a standard one-compartment, three-electrode cell with

either a flame-cleaned Ag wire (Alfa Aesar) quasi-reference electrode (QRE) or a Ag/AgCl (sat. KCl) electrode and a Au coil as the reference and counter electrodes, respectively. Diazonium salt solutions for electrodeposition studies were prepared from distilled acetonitrile and recrystallized tetrabutylammonium tetrafluoroborate (TBATFB) salt. The solutions were sparged with Ar for 10 min prior to the electrodeposition. ITO electrodes were cycled at 0.2 V s⁻¹ for 20 cycles or biased for 3 min at a potential 0.2 V more negative of the observed voltammetric peak potential. Upon completion, the ITO electrodes were rinsed with copious amounts of acetonitrile followed by NANOpure water. A solution of hexaamineruthenium (III) trichloride (Strem, 99%) was prepared in 0.1 M KNO₃ (Fisher, 99.999%). Cyclic voltammetry was used to measure the apparent heterogeneous electron-transfer rate constant, k_{app}^0 , for the Ru(NH₃)₆^{3+/2+} couple before and after film deposition using the method of Nicholson.²⁸ All electrochemical depositions and measurements were conducted at room temperature (23 ± 2 °C).

XPS Characterization. X-ray photoelectron spectroscopy was conducted with a PHI 5700 ESCA system possessing a scan step size of 0.1 eV and an Al Kα monochromatic line (1486.6 eV), calibrated with the signals for Au 4f_{7/2}, Ag 3d_{5/2}, and Cu 2p_{3/2}. All reported spectra were collected at a scan angle of 45° and a scan rate of 5 eV min⁻¹. The C 1s, In 3d, and Sn 3d spectra were collected with a single scan. N 1s spectra were scan-averaged five times from 390 to 410 eV. For the analysis of the C 1s spectrum, a C 1s spectrum for adventitious carbon was used for background subtraction.

UV-Vis Characterization. UV-vis absorbance spectroscopy was performed with a Varian Cary 5000 instrument with a Hg lamp operating in double-beam mode with a 2.00 nm slit width. Reported spectra are baseline corrected using pristine ITO as a reference.

AFM Characterization. Tapping mode atomic force microscopy was conducted on ITO using a Digital Instruments Bioscope atomic force microscope with a Nanoscope IV controller. All measurements were obtained with either phosphorus-doped (n-type) Si cantilevers (0.01–0.05 Ω cm) with no backside coating (MikroMasch, Ultrasharp tips, length 125 μm, tip radius < 35 nm, resonance frequency ca. 325 kHz, force constant ca. 40 N/m) or Si tips coated with Ti/Pt (MikroMasch, Ultrasharp tips, length 125 μm, tip radius < 35 nm, resonance frequency ca. 325 kHz, force constant ca. 40 N/m, 10 nm Pt/20 nm Ti). For scanning surface potential measurements with bare Si tips, electrical contact was made by applying conductive silver paint to a fresh scratch in the oxide layer²⁹ (Ted Pella, Inc., No. 16034). The ITO substrate was held at ground. Surface potential data were obtained during an interleave trace at a height of 20 nm. All images were acquired at 0.3 Hz.

Results and Discussion

Figure 1 shows the voltammetric response for ITO electrodes immersed in 1 mM solutions of NP, CP, and FP diazonium salts in acetonitrile with 0.1 M TBATFB. All three aryl diazonium cations demonstrate a single irreversible reduction wave that diminishes on successive potential cycles. The observed reduction peak potential, E_p , for each diazonium cation follows the expected shift predicted by Hammett substituent values,^{30,31} with the NP diazonium cation reduced 450 mV more positive than the FP diazonium cation. The voltammetric response at ITO is similar in nature to reported current-potential responses for aryl diazonium reductions at pyrolyzed photoresist films,³² GC,³³ Au,³⁴ Ni,²⁰ Pt,²⁰ Fe,³⁵ Si,³⁶ and B-doped diamond³⁷ electrodes. Although the homogeneous reduction and cleavage of the diazonium group has been proposed to occur in a stepwise fashion

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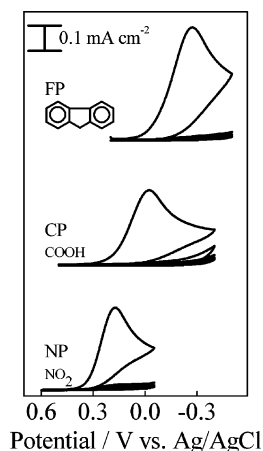
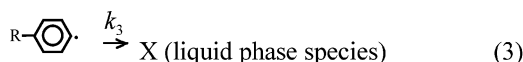
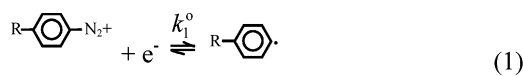


Figure 1. Voltammetric response for ITO electrodes immersed in solutions containing 1 mM FP (top), CP (middle), and NP (bottom) diazonium salts in 0.1 M TBATFB/acetonitrile. The 1st, 5th, 10th, and 15th scans are shown. Scan rate: 0.2 V s⁻¹.

in aqueous solutions,³⁸ the heterogeneous one-electron reduction in aprotic solvents (eq 1) is generally treated as a concerted reduction and cleavage of the N₂ functionality.³¹



Saveant and co-workers^{18,39} previously modeled and described features of the voltammetric response for an electrode surface that is passivated through an irreversible electrochemical reduction (eq 1) followed by a passivating chemical adsorption step (eq 2). A greater rate of the heterogeneous chemical passivation step, k_2 , (eq 2) relative to the rate of a competing homogeneous reaction, k_3 , (eq 3) causes the wave shape to become more symmetric (i.e., indicative of the increasing influence of adsorption) and the cathodic peak current to decrease over successive potential cycles. While increases in film thickness from multilayer formation were not considered in Saveant's voltammetric analysis, we do feel that this approach assesses how readily the pristine electrode surface is initially passivated by adsorbing species. Figure 2 highlights the irreversible reduction of NP diazonium TFB over 20 successive scans. The adsorptive character of the first wave in Figure 2A is more clearly delineated through semi-integration,⁴⁰ as shown in Figure 2B. The distinct peak shape of the semi-integral in Figure 2B rather than a pure sigmoidal form suggests that the reduction of NP diazonium cation in Figure 2A involves an adsorptive step of an electroactive species at the ITO electrode surface and is not a purely outer-sphere process. At -0.22 V vs Ag QRE in Figure 2A, the peak current decreases from 0.32 to 0.03 mA cm⁻² from the first to second cycle, and by the fifth cycle there is no observable faradaic current. The drastic decline in the peak current after the initial

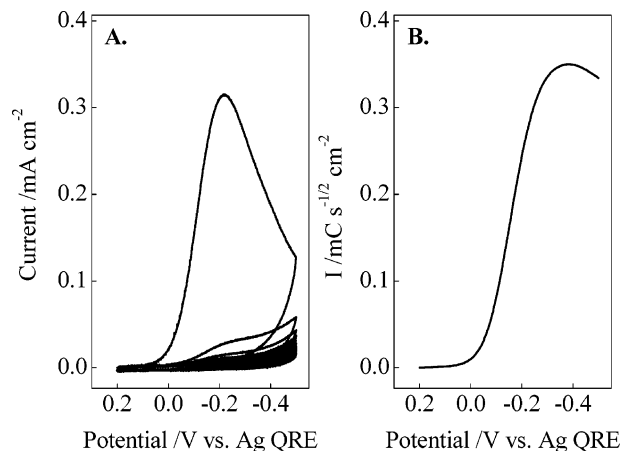


Figure 2. (A) Voltammetric response for an ITO electrode immersed in a solution containing 1 mM NP diazonium TFB in 0.1 M TBATFB/acetonitrile. Twenty successive scans are shown. Scan rate: 0.2 V s⁻¹ (B) Semiintegral convolution of the cathodic portion of the first cyclic voltammogram shown in (A).

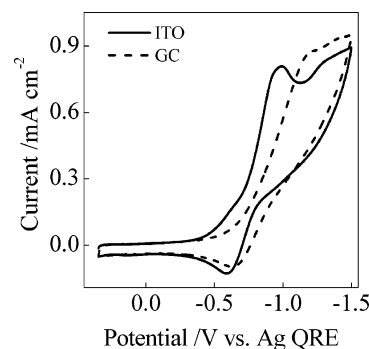


Figure 3. Voltammetric response of NP-modified ITO (solid line) and NP-modified GC (dashed line) electrodes immersed in 0.1 M TBATFB/acetonitrile. Scan rate: 0.2 V s⁻¹.

cycle suggests that the product of eq 1, i.e., the reduced aryl diazonium cation, follows a pathway that leads to adsorption onto the ITO surface much more readily than formation of solution-based reaction products. Bhugun et al.³⁹ introduced the parameter p to assess the competition between the heterogeneous (eq 2) and homogeneous (eq 3) reactions of the aryl radical. In Figure 2A, the trend of decreasing current upon repetitive cycling corresponds to $p \approx 1$ ⁴¹ and translates to ca. 80% electrodeposition efficiency, i.e., the situation where ~80% of the generated aryl radical species react with ITO (eq 2) rather than form solution species (eq 3). The efficiency of NP film deposition is nominally the same as that reported for GC¹⁸ and Au³⁴ electrodes, suggesting that the passivation/deposition process is insensitive to the electrode material.

To determine whether the composition and structure of resultant films on ITO were similar to films deposited on polished GC, we evaluated the voltammetric response for NP films which contain redox-active nitro groups. Following electrodeposition, freshly deposited films were rinsed thoroughly to remove loosely physisorbed diazonium species remaining at the electrode surfaces. A comparison of the voltammograms of NP films on ITO and GC electrodes in deaerated acetonitrile is shown in Figure 3. The voltammetric response of the nitro group at the NP films on the two electrode materials shows similar responses and is consistent with that reported elsewhere for GC,⁴² Au,²⁰ and diamond³⁷ electrodes. The comparable voltammetric sig-

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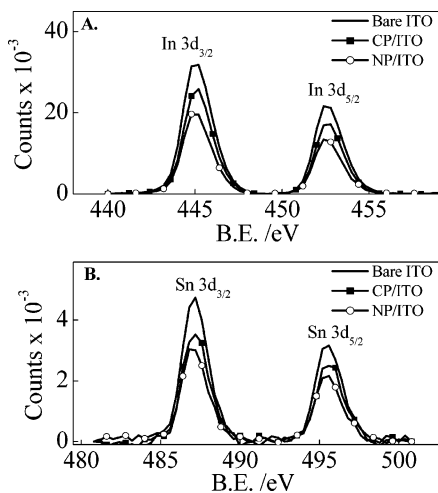


Figure 4. (A) In 3d X-ray photoelectron spectra for (—) pristine ITO, (■) CP-modified ITO, and (○) NP-modified ITO electrodes. (B) Sn 3d X-ray photoelectron spectra for (—) pristine ITO, (■) CP-modified ITO, and (○) NP-modified ITO electrodes. CP- and NP-modified ITO electrodes were deposited through 20 successive voltammetric cycles in 1 mM CP diazonium TFB and 1 mM NP diazonium TFB, respectively.

natures at ITO and GC suggest that the structure and attachment of the NP films are also similar in nature. We do note that subtle differences in the voltammetric responses for redox-active moieties have been seen for films on various electrode materials.²⁰ Gooding et al.⁴³ have recently described aryl monolayers with ferrocene end groups that demonstrate distinctly different electron-transfer behaviors for Au and GC supports, where more reversible and faster electron-transfer rates were seen for Au electrodes. The voltammetric response seen at ITO electrodes in Figure 3 ($\Delta E_p \approx 405$ mV) is most consistent with that reported by Belanger et al.⁴² for multilayer thick films. Integration of the cathodic peak for the modified ITO surface gives a surface coverage of 3.4×10^{-9} mol cm⁻², larger than that expected for a close-packed monolayer of aryl NO₂ units (1.2×10^{-9} mol cm⁻²).²⁷ However, integration of the anodic peak shows that only 0.7×10^{-9} mol cm⁻² are reoxidized. McCreery et al.²⁷ and Saveant et al.¹⁸ have demonstrated reversible voltammetric responses for ultrathin, near-monolayer coverages of NP aryl films on GC, but the voltammetric response in Figure 3 suggest that electron transfer of the nitro groups is quasi-reversible and not all the aryl moieties are in direct contact with the substrate. While we are presently unable to establish the influence of coordination environment, surface coverage, and electrode material on the electrochemical response, studies are underway to elucidate these relationships.

Aryl films from the reduction of diazonium salts are reported to adhere to carbon electrodes through the formation of carbon-carbon (C-C) covalent bonds.^{18,44,45} C-C bonds are not possible for aryl films at ITO interfaces, as covalent bonding with the surface must instead involve In, Sn, and/or O atoms. Figure 4 demonstrates the In 3d and Sn 3d XPS spectra for pristine ITO and ITO after aryl film deposition and subsequent rinsing. For the ITO electrodes modified with NP and CP films, there is no appreciable shift or emergence of sidebands in Figures 4A or B relative to the pristine ITO surface to indicate direct metal-carbon (In-C or Sn-C) covalent bonding, as has been reported

at semiconductor²¹ and Fe³⁵ electrodes. The O 1s spectra (data not shown) of pristine and modified ITO electrodes also do not show evidence of In-O-C or Sn-O-C covalent bonding as suggested by McCreery et al. for Cu-O-C linkages on copper oxide.⁴⁶ However, interpretation of the O 1s spectra is complicated by the existence of up to four different O species on pristine ITO¹⁴ in addition to the carboxylic and nitro groups of the CP and NP films, respectively. Despite no direct spectral evidence that covalent bonds are formed, the strong adherence of the deposited organic films on ITO following copious rinsing and sonication suggests a robust interaction of the organic films with ITO as strong as that seen on GC. Robust attachment of organic molecules onto ITO surfaces is not unprecedented, as functionalized-ferrocene and cytochrome *c* adsorption onto ITO is known. Ferrocene methanol has been shown to adsorb readily at ITO electrodes, presumably through interaction with hydrolyzed oxides and oxy-hydroxides.¹⁴ A similar hydrolysis interaction with the aryl films is unlikely, as the *p*-substituted aryl radicals should not act as proton donors. A purely ionic interaction between the deposited aryl film and ITO as described for cytochrome *c*⁴⁷ is also improbable since these aryl films have weak ionic character (e.g., FP films) yet are as adherent as the more polar films (NP and CP). While the nature of the attachment of the aryl film onto ITO is presently unclear, empirical observations suggest that the aryl films can be regarded as strongly physisorbed.

The attenuation of the integrated In 3d signals in Figure 4A for the modified ITO surfaces is consistent for a uniform coating on ITO following aryl diazonium cation reduction and may be used with the photoelectron escape depth (λ) of In to determine film thicknesses.⁴⁸ For surfaces modified by an organic layer, Seah et al. reported λ may be estimated from the density of the organic layer, the work function of the material, and the binding energy of the ejected electron.⁴⁹ Using a density of 1 mg m⁻² for the aryl layer²⁰ and 4.12 eV as the work function of indium,⁵⁰ λ was estimated to be 3.5 nm for In 3d electrons. From this value, the attenuated In 3d signals correspond to thicknesses of 1.2 and 2.4 nm for CP and NP films, respectively, deposited under identical conditions. Both film thicknesses imply the films are multilayered rather than simple monolayers, as suggested by Downard,⁵¹ McDermott,⁵² and McCreery⁵³ for carbon electrodes. The observation of NP films with a greater thickness under the same deposition conditions as CP films agrees with the previously reported^{32,42} propensity of NP diazonium cations to yield slightly thicker aryl films relative to other aryl diazonium cations.

To determine whether the chemical functionality of the substituted group on the aryl diazonium cation was maintained, UV-vis spectra of FP aryl films were obtained after film deposition from 20 voltammetric cycles (as in Figure 1) was carried out. A representative example of this experiment is shown in Figure 5. The baseline-corrected absorbance spectrum of pristine ITO exposed to ambient conditions does not show measurable absorption between 280 and 320 nm, while the FP aryl film demonstrates a strong absorbance signal of 0.04 with a local maximum at 305 nm, as expected for a film of thickness <10 nm composed of functional groups which are strong

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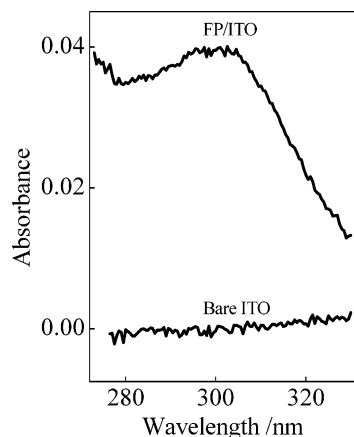


Figure 5. Baseline-corrected UV-vis absorbance spectra for a FP-modified ITO electrode (top) and a bare ITO electrode (bottom). The FP-modified ITO electrode was deposited through 20 successive voltammetric cycles in 1 mM FP diazonium Cl.

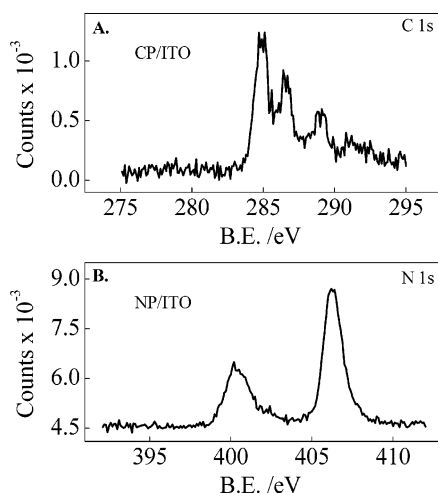


Figure 6. (A) Background-subtracted C1s X-ray photoelectron spectrum (single scan) of a CP-modified ITO electrode. (B) N1s X-ray photoelectron spectrum (5 scan average) of an NP-modified ITO electrode.

chromophores ($\log \epsilon_{\text{fluorene}} = 3.97$ at 300 nm^{54}). The absorbance band in Figure 5 is consistent with the reported absorption of solution-phase fluorene,⁵⁴ although the peak is broader and slightly red-shifted from the reported value for solution-phase fluorene,⁵⁵ similar to that observed for polymerized fluorene chains adsorbed onto polystyrene surfaces⁵⁵ and aggregated porphyrins adsorbed on Au.⁵⁶ Interestingly, those systems had fluorene units with electronic interactions between the ring systems. Hence, the red-shifted and broadened features of Figure 5 support the contention that the film structure is branched with a degree of electronic delocalization, as predicted by McDermott⁵⁷ for multilayer aryl films.

To interrogate the chemical structure of deposited aryl films more directly, high-resolution X-ray photoelectron spectra were obtained of CP and NP films, as shown in Figure 6. FP films were not analyzed by XPS since the C 1s signal of fluorene is not easily distinguishable from the signal from adventitious

carbon. The C 1s XPS spectrum of a CP aryl film after subtraction of the signal from adventitious carbon⁷ in Figure 6A contains signatures for carbonyl and carboxylic functionalities at 286 and 289 eV, respectively,⁵⁸ indicating the carboxylic group of the CP diazonium cation survives the deposition process. The N 1s XPS spectrum for an ITO electrode after reduction of NP deposition and subsequent washing is seen in Figure 6B. Two peaks are evident, located at 400.2 and 406.2 eV. The peak at 406.2 eV denotes the existence of nitro groups at the ITO surface,^{59,60} in agreement with the voltammetric evidence that the functional groups of the diazonium salts retain their chemical nature after deposition. The absence of a signal at 402 eV⁶¹ suggests the complete removal of unreacted aryl diazonium TFB on the ITO after washing, indicative that all of the constituent NP aryl molecules in the deposited film have been reduced. The origin of the signal at 400.2 eV is not as intuitive, as a NP film should only exhibit the one sharp signature peak for the corresponding nitro functionality. A comparable signal at 400 eV has been reported for other similarly treated electrodes surfaces,^{20,60} with several proposed hypotheses to account for this signal. The contamination of adventitious nitrogen-containing species is not likely, as the pristine ITO electrodes that were exposed to ambient conditions did not exhibit any nitrogen signal (data not shown). The reduction of nitro groups and/or diazonium groups to amine groups during the deposition response is also unlikely, as the current densities during the deposition process do not suggest the occurrence of multielectron reductions to amines, as evident in aqueous acidic solutions.¹⁸ The transformation of nitro surface groups to amine groups during exposure to the probe X-rays has been observed on silica surfaces⁶² and has been proposed to occur on aryl films deposited on zinc.⁶⁰ However, because the reported conversion process is slow ($< 12.5\% \text{ h}^{-1}$),⁶² the exposure time used in this study (20 min) would lead to a maximum conversion of 4.2% of nitro groups to amine groups. This amount is insufficient to account completely for the observed signal (37% of the total nitrogen signal) at 400.2 eV. One possibility is that the nitrogen signal at 400 eV may be related to the existence of nitrile-type nitrogen in the deposited films. A case involving acetonitrile, either covalently incorporated into or physically trapped within the aryl layer, is possible, as a signal at 400.4 eV for physisorbed acetonitrile has been reported.⁶³ However, to clarify the effect of the solvent on the N 1s spectra, we performed identical depositions using DMSO instead of acetonitrile as the solvent. For films deposited in DMSO, a strong peak was again observed at 400.2 eV (data not shown), suggesting that the signal ca. 400 eV is not entirely dependent on the use of acetonitrile. Another possible source of this signal is the existence of azo groups. McCreery et al. have suggested azo groups arise from the chemical coupling between diazonium cations and aryl rings.⁴⁶ We have not independently verified the prevalence of azo groups, but their presence is consistent with multilayered films as in this report and those from several other groups.^{20,32,34}

The effect of electrochemically deposited aryl films on the redox behavior of electroactive species in solution has been studied at carbon and Au electrodes.^{34,42,52,57,64} Depending on film thickness, the aryl layer(s) generally slow the voltammetric response of the given redox couple, evidenced by a decrease in

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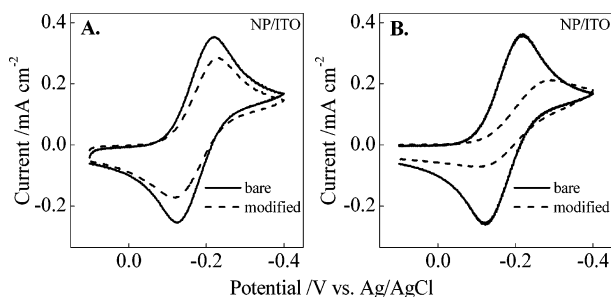


Figure 7. Cyclic voltammograms of bare and NP-modified ITO electrodes immersed in 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ containing 0.1 M KNO_3 . (A) A bare ITO electrode (solid line) and a NP-modified ITO electrode prepared from immersion in 1 mM NP diazonium TFB (dashed line). (B) A bare ITO electrode (solid line) and NP-modified ITO electrode prepared from immersion in 10 mM NP diazonium TFB (dashed line). Scan rate: 0.2 V s^{-1} .

observed currents and an increase in peak splitting for oxidation and reduction. There are conflicting reports regarding the blocking effect on electron transfer of the deposited films on carbon electrodes, as the blocking exhibited for $\text{Fe}(\text{CN})_6^{3-}$ is typically greater than for other redox couples.^{34,57} However, since the reduction of $\text{Fe}(\text{CN})_6^{3-}$ is known to occur at specific sites on carbon and metal electrodes,^{65,66} the diminished voltammetric response for $\text{Fe}(\text{CN})_6^{3-}$ reduction does not exclude the possibility of a substantially uneven film that only blocks certain surface sites. Consequently, because $\text{Ru}(\text{NH}_3)_6^{3+}$ is well-established as an ideal outer-sphere redox probe,⁶⁵ $\text{Ru}(\text{NH}_3)_6^{3+}$ was used as the main redox probe. Figure 7 demonstrates the blocking effect of NP aryl films on ITO on the heterogeneous electron transfer for the redox behavior of $\text{Ru}(\text{NH}_3)_6^{3+}$. An ITO electrode after modification with a NP aryl film exhibits a subtle increase in peak splitting, ΔE_p , relative to a pristine ITO electrode. For three samples, ΔE_p increased from 96 ± 3 to 120 ± 10 mV, corresponding²⁸ to a suppression of the observed charge-transfer constant, k_{app}^o , from $8.6 \pm 0.6 \times 10^{-3}$ to $4 \pm 1 \times 10^{-3} \text{ cm s}^{-1}$. The decrease in k_{app}^o shows that aryl films from these deposition conditions do not impede electron-transfer significantly, as expected on the basis of the nanometer thickness and aromatic character of the constituent molecules of the film. McCreery et al.⁶⁴ previously showed that similar aryl films on GC have a through-bond tunneling constant, β , of 0.20 \AA^{-1} , evidence that supports facile electron transport through aryl films in comparison to alkanethiol layers with larger tunneling constant ($\beta \approx 1 \text{ \AA}^{-1}$).⁶⁴ Assuming aryl films behave as a model tunneling barrier with $\beta = 0.2 \text{ \AA}^{-1}$, the voltammetry in Figure 7A correlates to an average film thickness of 3.8 \AA .

$$k_{\text{app}}^o = k^o e^{-\beta d} \quad (4)$$

XPS analysis yielded a thickness of 2.4 nm, nearly an order of magnitude greater than the voltammetric estimate. Although uncertainties in the photoelectron escape depth (λ) and/or β partially add to the discrepancy in estimated thicknesses, the existence of pinhole defects in the aryl film likely contributes significantly to the observed voltammetric response,⁶⁷ allowing faster electron-transfer rates at bare spots and leading to

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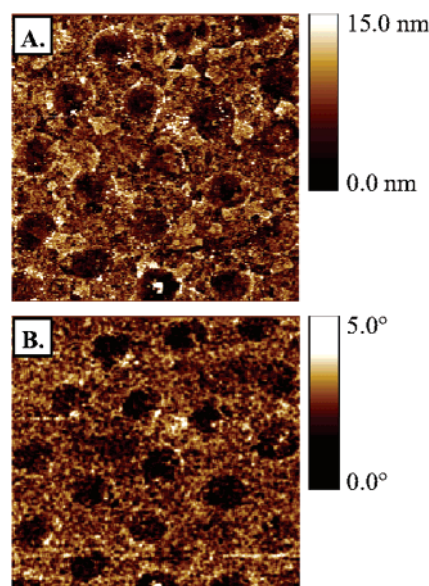


Figure 8. Simultaneously obtained (top) topography and (bottom) phase images of a patterned NP-modified ITO electrode. Scan size $6.8 \times 6.8 \mu\text{m}^2$.

underestimations of film thicknesses. Standard electrochemical analyses⁶⁸ for pinhole defects are not appropriate for these systems, since even defect-free thin films ($d \approx 1 \text{ nm}$) do not completely block electron transfer.⁶⁴ Hence, the direct estimation of pinholes in the aryl films was not possible through electrochemical means. Nevertheless, to minimize the possible influence of pinholes, films were deposited from a 10-fold higher concentration of NP diazonium TFB solution, as Belanger et al.⁴² and McCreery et al.⁵³ have reported that thicker, more compact films (i.e., fewer pinholes) can be produced from more concentrated deposition solutions. Figure 7B shows the effect of an aryl film deposited from a 10 mM NP diazonium TFB solution in acetonitrile on the electrochemical response for $\text{Ru}(\text{NH}_3)_6^{3+}$. Both the peak current and ΔE_p at the modified ITO electrode are more obviously distorted from the response of the same ITO electrode before NP modification. The more blocking nature of the NP film used in Figure 7B is consistent with the contentions of Belanger et al.⁴² and McCreery et al.⁵³ that the film compactness, i.e., pinhole density, can be regulated with increasing diazonium salt concentration in the deposition process. The change in peak separation in the voltammetry in Figure 7B suggests a film thickness of 9 \AA , roughly double that in Figure 7A but still significantly thinner than that measured by XPS.

To assess more accurately the structure of the NP aryl films, tapping mode atomic force microscopy was performed on aryl films deposited on ITO electrodes that were patterned with an overlayer of tightly packed polystyrene spheres using an approach previously demonstrated in our lab.²⁶ Following the deposition of the aryl film, the polystyrene spheres were removed via sonication to expose uncoated regions of ITO. Figure 8 demonstrates the topographic and phase images obtained for a patterned NP aryl film deposited from a 10 mM NP diazonium TFB on ITO using a polystyrene template. Films deposited from 1 mM NP diazonium TFB solutions were too thin to differentiate easily over the root-mean-square (rms) roughness of ITO (ca. 10 nm).⁶⁶ The dark, circular spots shown in Figure 8A correspond to the position of the polystyrene mask that effectively blocked deposits of the NP aryl film and are approximately 6 nm in

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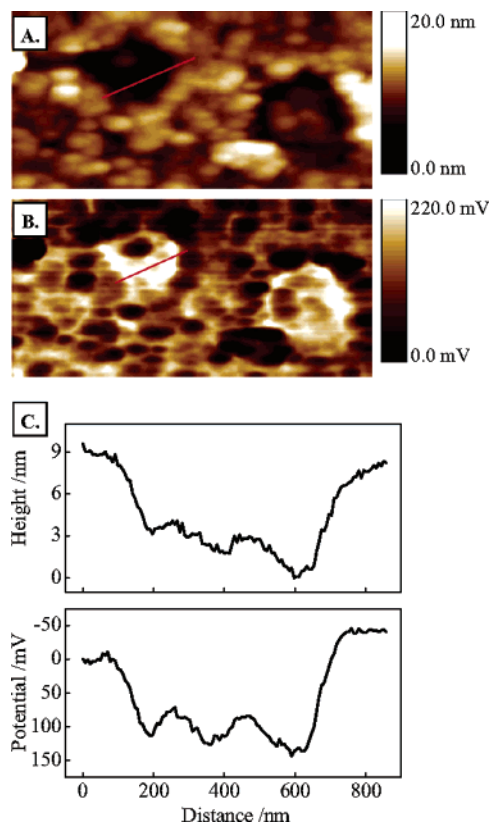


Figure 9. Simultaneously obtained (A) topography and (B) contact potential difference (CPD) images of two ITO voids after patterned deposition of NP followed by removal of polystyrene mask. Scan size $1.4 \times 2.7 \mu\text{m}^2$. (C) Topography profile from cross-section denoted in (A). (D) Contact potential difference profile from cross-section denoted in (B).

depth. A more obvious difference in the contrast between the aryl film and ITO voids is seen in Figure 8B, where there is a 3° phase shift between the film and the bare ITO. Patterning of nanometer-thick films has been reported previously, as Downard et al.⁶⁹ have shown regular grooves in aryl films may be patterned over a small area ($\sim 10^2 \text{ nm}$) by scratching with a scanning probe tip. Figure 8 demonstrates that aryl film deposition through a close-packed polystyrene sphere overlayer is an effective approach to pattern regular ITO voids in nanometer-thick aryl films with a domain size $> \sim 50 \mu\text{m}^2$. Furthermore, since the domain size of the pattern is only limited by the quality of the sphere overlayer and because additional electroactive species (metal, metal oxides, polymers) can be deposited in the voids, this particular approach is more versatile with regards to patterning surfaces of greater size and complexity than the direct scratching method or microcontact patterning approach used by others.⁷⁰

While this patterning approach is interesting in its own right, for the scope of the work discussed in this report, we focus on using the patterning process to facilitate local characterization of deposited aryl films. Figure 9 shows simultaneously acquired topography and scanning surface potential images of two ITO voids. The topographic image (Figure 9A) displays the rough structure of the deposited film with widths of the voids of $\sim 700 \text{ nm}$ and a nodular morphology of the area around the ITO voids. Although this is consistent with the structure of aryl films deposited on HOPG,⁵⁷ the grainy nature of the native ITO surface⁶⁶ prohibits direct correlation of the aryl film topography with

possible film formation mechanisms. However, some structural features of the film can be inferred from Figure 9B as the DC bias applied to the tip (V_{dc}) directly reports on the sample surface potential (eq 5) which is sensitive to the work function of the surface,⁷¹

$$V_{\text{dc}} = -\Delta\Phi_{\text{tip-surface}} = \frac{\Phi_{\text{surface}} - \Phi_{\text{tip}}}{e} \quad (5)$$

where V_{dc} is measured in volts between the probe tip and the interrogated sample, e is the charge of an electron, and Φ_{surface} and Φ_{tip} are the apparent work functions of the surface and probe tip, respectively, measured in electronvolts. The patterning of ITO voids affords the opportunity to estimate in a single image, without additional reference sample(s),⁷² the contact potential difference (CPD) between the NP aryl film and the underlying ITO. The difference between the applied V_{dc} when the probe tip is over the aryl-modified ITO film and the applied V_{dc} when the probe tip is over the ITO voids is a direct measure of the CPD (eq 6).

$$\text{CPD} = \frac{\phi_{\text{NPfilmITO}} - \phi_{\text{tip}}}{e} - \frac{\phi_{\text{ITO}} - \phi_{\text{tip}}}{e} = \frac{\phi_{\text{NPfilmITO}} - \phi_{\text{ITO}}}{e} \quad (6)$$

The CPD between the aryl film and ITO is shown clearly in Figure 9C and 9D by the topography and potential profiles from the cross-sections indicated in Figures 9A and 9B, respectively. The measured -100 mV CPD suggests that the surface work function is lowered by the presence of the NP aryl film. Using an adaptation of the Helmholtz equation for a parallel plate capacitor,⁷³ the molecular orientation of the NP aryl film can be estimated from the CPD by eq 7,

$$\text{CPD} = \frac{\phi_{\text{NPfilmITO}} - \phi_{\text{ITO}}}{e} = \frac{-N\mu_{\text{mol}\perp}}{\epsilon_r\epsilon_0} \quad (7)$$

where N is the density of constituent molecules in the film, ϵ_r and ϵ_0 are the film and vacuum permittivities, respectively, and $\mu_{\text{mol}\perp}$ is the net dipole moment directed perpendicular to the plane of the substrate. Figure 10 displays how the observed work function is expected to change relative to the orientation of NP aryl molecules. For a NP aryl film with a strong dipole oriented toward the ITO substrate (i.e., a positive surface dipole), the electron density is pulled away from the substrate and the removal of an electron from the NP aryl layer becomes easier, i.e., the observed work function of NP aryl film modified ITO is smaller than unmodified ITO. Similarly, a NP aryl film with a strong dipole oriented away from the ITO substrate (i.e., a negative surface dipole) pushes the electron density toward the ITO substrate and the removal of an electron from the NP aryl film/ITO surface becomes more difficult, i.e., the observed work function increases in value over pristine ITO. A modified NP aryl layer without a strong net dipole (i.e., $\mu_{\text{mol}\perp} = 0$) will not show a large change the observed work function relative to the unmodified surface. Hence, for these NP aryl films, the net positioning of the nitro groups toward, away, or randomly with respect to the substrate determines the sign of the observed change in CPD between the film and the ITO regions. The nominal ca. -100 mV change in CPD corresponds to $\mu_{\text{mol}\perp} = 0.03 \text{ D}$ for the NP film, assuming a similar coverage ($N = 3.4 \times 10^{-9} \text{ mol cm}^{-2}$) from the electrochemical response in Figure 3 and $\epsilon_r \approx$

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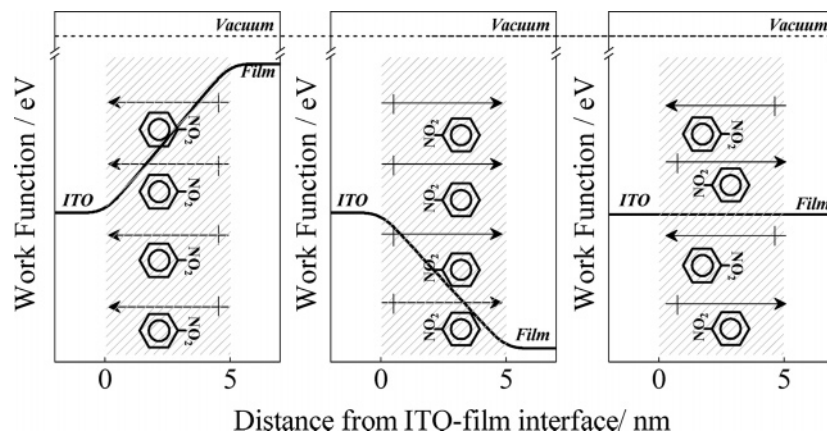


Figure 10. A schematic depiction of the work function change across a 5 nm thin film with a positive (left), negative (center), and zero (right) value of μ_{molL} . The arrows represent the direction of the dipole.

3.⁷⁴ This value is significantly smaller than the reported dipole moment for nitrobenzene of 3.93 D,⁷⁵ which the constituent units of the NP film should closely resemble.

Although bonding interaction of the NP aryl molecules with the surface can change the dipole moment,⁷⁶ we feel that this does not occur, as XPS analysis revealed no spectral shifts to suggest an electronic interaction between ITO and the aryl film. Rather, we feel that the anomalously small aryl film dipole moment measured is reflective of nitro groups that are directed away from the ITO surface but oriented with an extreme tilt angle of ca. 0.4° , i.e., only a small fraction of the NP aryl unit dipole is directed away from the substrate. A nearly parallel orientation of the NP aryl molecules implies the film must consist of numerous stacked, branched layers in order to account for the measured nanometer film thickness. Any preferential aryl film orientation most likely results from weak van der Waals interactions, similar to that observed for the parallel stacking of nitrobenzene molecules in liquid nitrobenzene.⁷⁵ This supposition is substantiated by infrared reflectance studies conducted by Leitner et al.⁷⁷ for similarly prepared NP aryl films on graphite which concluded that aryl films are largely disordered and not rigorously oriented perpendicular to the surface plane.

The electrochemical, XPS, and surface potential measurements support the idea that ITO surfaces can be chemically modified via electrochemical reduction of aryl diazonium salts with comparable properties to that seen on carbon electrodes⁴⁴ and other supports.³⁴ As discussed above, although the presence of covalent linkages involving indium or oxygen, i.e., In–C or In–O–C, was not definitively established, the modified aryl/ITO films are strongly adherent. Importantly, future studies are planned to identify the role of the ITO substrate on structure–property relationships of initial aryl layer(s). For ultrathin monolayer coverages, the substrate should more heavily impact the strength, stability, and dipole character of resultant modifying layer since this system is not chemically equivalent to those aryl monolayers formed on carbon or other metal electrodes. Gooding

et al. have demonstrated that the rates of electron transfer through aryl films with ferrocene end groups are appreciably different at Au and GC.⁴³ Additionally, given the unique nature of the ITO interface, we believe the difference in linkage between the aryl moieties and ITO surface should cause variations in film coverage, pinhole density, and electronic structure.

Summary

Functionalized, nanometer-thick p-substituted aryl films were deposited onto ITO electrodes via the self-limiting electrochemical reduction of aryl diazonium salts. Subtle differences were seen in the electrodeposition and attachment of the aryl films on ITO compared to similarly prepared films on other electrode materials. The as-deposited aryl films decreased the heterogeneous electron-transfer rate constant for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ couple by a factor of 2, indicating facile electron tunneling through the films. In the present report, contact potential difference measurements showed the surface potential of the NP-modified ITO was ca. 100 mV more positive than the pristine ITO surface because of the electron-withdrawing power of the nitro groups, demonstrating the surface potential of an ITO electrode may be regulated through judicious choice of the functional group on the diazonium cation. In this way, the aryl-modified ITO interface may be tuned for the HOMO of an organic hole transport layer in an OLED device to reduce the required turn-on voltage. Contact potential difference measurements also suggested the aryl rings were oriented nearly parallel to the ITO substrate and packed as several multilayers, in agreement with high-resolution XPS spectra. Patterned aryl films with regularly spaced voids were easily prepared which may be useful as chemically responsive gratings utilized in optical-based detection strategies.

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