# Significant Enhancement of PEDOT Thin Film Adhesion to Inorganic Solid Substrates with EDOT-Acid

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S *Supporting Information*
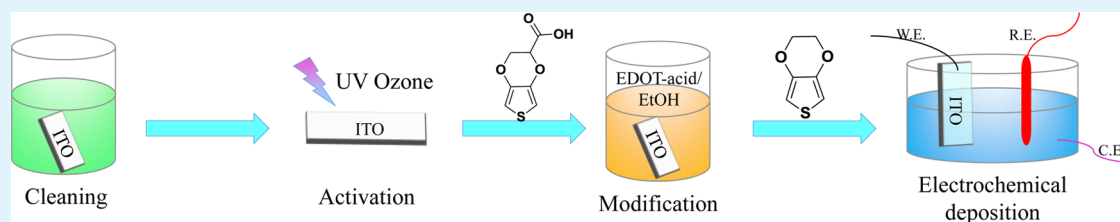
ABSTRACT: With its high conductivity, tunable surface morphology, relatively soft mechanical response, high chemical stability, and excellent biocompatibility, poly(3,4-ethylenedioxythiophene) (PEDOT) has become a promising coating material for a variety of electronic biomedical devices. However, the relatively poor adhesion of PEDOT to inorganic metallic and semiconducting substrates still poses challenges for long-term applications. Here, we report that 2,3-dihydrothieno(3,4-b)(1,4)dioxine-2-carboxylic acid (EDOT-acid) significantly improves the adhesion between PEDOT thin films and inorganic solid electrodes. EDOT-acid molecules were chemically bonded onto activated oxide substrates via the chemisorption of the carboxylic groups. PEDOT was then polymerized onto the EDOT-acid modified substrates, forming covalently bonded coatings. The adsorption of EDOT-acid onto the electrode surfaces was characterized by cyclic voltammetry (CV), contact angle measurements, atomic force microscopy, and X-ray photoelectron spectroscopy. The electrical properties of the subsequently coated PEDOT films were studied by electrochemical impedance spectroscopy and CV. An aggressive ultrasonication test confirmed the significantly improved adhesion and mechanical stability of the PEDOT films on electrodes with EDOT-acid treatment over those without treatment.

KEYWORDS: adhesion, EDOT-acid, PEDOT, neural electrode, conjugated polymers

1. INTRODUCTION

Conjugated polymers have been widely investigated for applications in bioelectronics[1,2] and biomedical devices,[3] especially neural electrodes.[4−7] These conjugated polymeric materials can play an important role in bridging between neurons and electrodes due to their high electronic and ionic conductivity. Among the currently available conjugated polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has received considerable interest because of its low oxidation potential, relatively high chemical and thermal stability, and high conductivity.[8,9] PEDOT has been shown to significantly lower the impedance and increase the charge-injection capacity of metallic neural microelectrodes.[10,11] Despite these advantages, certain limitations still exist. One major challenge is the relatively low adhesion of PEDOT polymer on various inorganic substrates. Detachment of PEDOT coatings from the inorganic substrate under chronic neural recording or stimulation conditions has been associated with the loss of device performance.[12−15] Limiting the cracking and delamination of PEDOT coatings from substrates is necessary to improve their long-term performance.[16]

Many efforts have been previously directed toward improving adhesion of conjugated polymers on metallic substrates.

Mekhalif et al. found that adhesion of polybithiophene to platinum was improved by thiol-modified phenyl monolayers.[17] You and co-workers increased the stability of poly(3-methylthiophene) (P3MT) films on indium−tin oxide (ITO) surfaces using surface-initiated Kumada catalyst-transfer poly-condensation (SI-KCTP) from surface-bound arylnickel(II) bromide initiators.[18] Smela reported the use of thiol-modified pyrrole derivatives to increase the adhesion of polypyrrole coatings on gold.[19,20] Jerome et al. enhanced the adhesion of polypyrrole via copolymerizing polypyrrole with other polymers that can be grafted onto metal surfaces.[21]

However, only a few studies have investigated the adhesion and mechanical stability of PEDOT coatings.[5,22] Cui significantly improved the mechanical stability of PEDOT coatings on Pt electrodes via polymerizing PEDOT with carbon nanotubes (CNTs). Carli and co-workers made PEDOT films that are more mechanically robust using an EDOT substituted silane (APTES-EDOT) as adhesion promoter. These methods have provided thoughtful insights in optimizing adhesion and

Scheme 1. Chemisorption of EDOT-Acid (Red) onto ITO (black) and Electrodeposition of PEDOT (Blue)
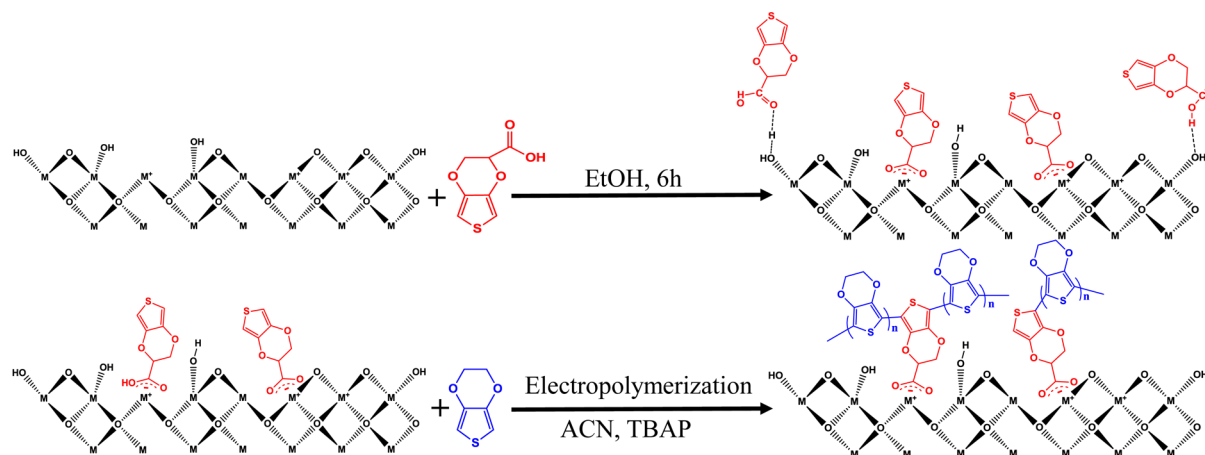
mechanical stability of PEDOT coatings, but not yet a perfect protocol has been set for this problem. Therefore, new and more facile approaches for improving stability of PEDOT still remain an ongoing topic of interest.

In this paper, EDOT carboxylic acid (EDOT-acid) self-assembled monolayers were used to improve the adhesion between PEDOT coatings and metallic substrates. EDOT-acid[23] was designed to create functional conducting polymer films that could be covalently modified with biomolecules such as peptides through the carboxylic acid side group. Employing the carboxylic acid chemistry, this molecule can also act as an adhesion promoter. Carboxylic acids have long been studied and used to tune the surface properties of metals and metal oxides via chemisorption. For example, ferrocene dicarboxylic acid and 3-thiophene acetic acid were used to modify ITO electrodes.[24] Although many different reagents have been developed to modify metals and metal oxides, EDOT-acid is a particularly attractive option as its EDOT moiety allows convenient copolymerization with PEDOT.[25] Furthermore, EDOT-acid is more chemically and thermally stable than its pyrrole-acid and thiophene-acid counterparts. We hypothesized that PEDOT coatings on EDOT-acid modified electrodes might preserve the established advantages of PEDOT, and would also exhibit enhanced long-term mechanical stability and adhesion to substrates. In this work, PEDOT films were electrochemically coated on EDOT-acid modified ITO and stainless steel electrodes, and their morphologies and electrochemical properties were characterized. The mechanical stability and adhesion of the coatings were investigated by ultrasonication tests.

2. EXPERIMENTAL SECTION

2.1. Materials. Tetrabutyl ammonium perchlorate (TBAP), 3,4-ethylenedioxythiophene (EDOT) and 2,3-dihydrothieno-(3,4-b)(1,4)-dioxine-2-carboxylic acid (EDOT-acid) were purchased from Sigma-Aldrich. All other chemicals were of analytical grade, and Milli-Q water from a Millipore Q water purification system was used throughout. All reagents and solvents were used without further purification, unless otherwise noted. ITO-coated glass slides were purchased from Delta Technologies with a surface resistivity of 4−8 Ω/sq.

2.2. Cleaning, Activation, and Surface Modification of ITO Coated Glass Slides. The ITO-coated glass slides (with 0.15−0.20 μm thick ITO coatings on 0.7 mm thick glass substrates) were ultrasonically cleaned (Kendal HB-23, 220 W) in acetone, 2-propanol, and deionized water, each for 15 min. After drying in a stream of N_2, the substrates were then treated in UV Ozone (Novascan PSD UV

Ozone cleaner) for 30 min to activate the ITO surface. The ITO coated glass substrates were dipped into a 10 mM ethanol solution of EDOT-acid at room temperature for 12 h in order to ensure the formation of a densely packed monolayer on ITO surface. The substrates were then rinsed with acetonitrile to remove any residual EDOT-acid molecules from the ITO surface and finally dried in a stream of N_2.

2.3. Surface Characterization. Static water contact angles were measured by applying a 5 μL drop of deionized water to a film set on a leveled base. Photographs were taken of the drops, and their contact angles were measured using NIH ImageJ software with a Drop Shape Analysis plug-in and DropSnake method.

X-ray Photoelectron Spectroscopic (XPS) characterization of both the bare electrodes and EDOT-acid modified electrodes were performed using a Kratos Axis Ultra 165 XPS system equipped with a hemispherical analyzer.

Scanning electron microscopy images of PEDOT films deposited on both unmodified and modified ITO substrates were acquired using a Zeiss Auriga 60 Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) operating at 3 kV.

The surface morphologies of unmodified ITO and EDOT-acid modified ITO substrates were investigated using a Bruker BioScope Catalyst atomic force microscope (AFM) in air in tapping mode. Silicon cantilevers with a spring constant of 5 N/m were used. The heights and root-mean-squared roughnesses of features were calculated from image sections with a size of 5×5 μm^2 using the Gwyddion software.

The surface coverage and adsorption kinetics were studied by quartz crystal microbalance with dissipation (QCM-D) from Q-sense using a stainless steel coated sensor. The fundamental resonant frequency of the crystal was 5 MHz. The crystal was mounted in a fluid cell with a flow rate of 50 μL/min and a solution concentration of 2 mM.

2.4. Electrochemical Polymerization and Characterization. The electrochemical polymerization and characterization were performed with an Autolab PGstat12 Potentiostat/Galvanostat (EcoChemie) using the Nova 1.8 electrochemical software in a three-electrode cell. PEDOT was electrochemically polymerized on both unmodified and modified ITO glass slides (~0.5 cm^2) under galvanostatic conditions (0.075 mA/s) from a dilute (5 mM) acetonitrile solution containing 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. For CV, the EDOT-acid monomer (5 mM) and EDOT-acid modified ITO or stainless steel substrates were scanned between −0.6 V and +1.4 V in acetonitrile solution (0.1 M TBAP) with a Ag/AgNO$_3$ reference electrode. The PEDOT films were scanned between −0.9 V and +0.5 V in a phosphate buffered saline (PBS) buffer solution free of monomer. For EIS, the sample acted as the working electrode, a platinum plate was the counter electrode, a saturated Ag/AgCl electrode was the reference electrode, and PBS was the electrolyte. A 5 mV sinusoidal AC signal was applied over a frequency range of $1-10^5$
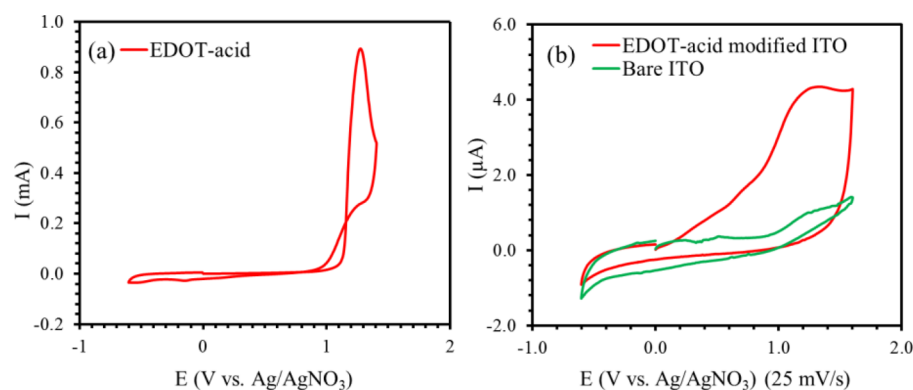
Figure 1. CV of EDOT-acid monomer (a) and CV of bare (green curve) and modified electrodes (red curve) (b).

UV Ozone treated ITO, 5°

ITO after 12 h EtOH exposure, 32°
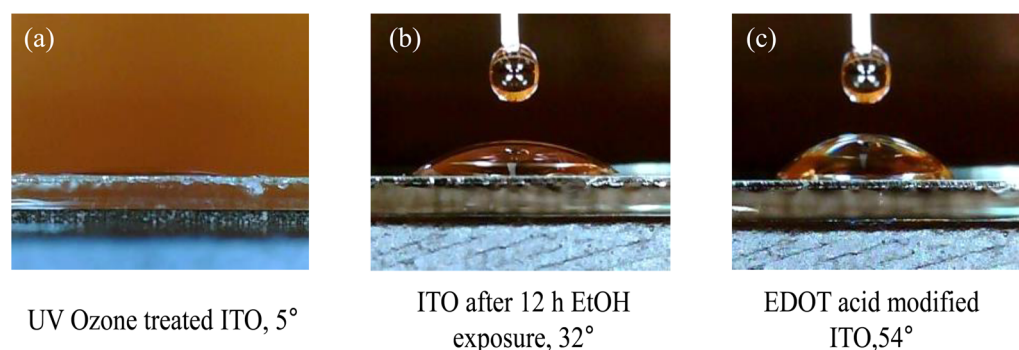
EDOT acid modified ITO, 54°

Figure 2. Contact angle measurements of (a) UV Ozone cleaned ITO slides; (b) ITO slides after 12 h EtOH exposure; and (c) EDOT-acid modified ITO slides.

Hz. Both impedance and phase angle data were collected over the entire frequency range.

2.5. Ultrasonic Testing. To test the adhesion of PEDOT on both modified and unmodified electrodes, the PEDOT-coated electrodes were immersed in a 20 mL glass vial that was filled with DI water. The vials were put in a Kendal HB-23 ultrasonic cleaner with a power of 220 W for specified periods of time (from a few seconds to several minutes).

3. RESULTS AND DISCUSSION

3.1. Chemisorption of EDOT-Acid on Activated ITO. The ITO glass slides were first ultrasonically cleaned and then activated in UV Ozone for 30 min since the as-received ITO slides are expected to be contaminated with ambient organic species and the density of surface hydroxyl group is low.[26] The EDOT carboxylic acid (EDOT-acid) is commercially available (now available from Tractus-chemistry) and can be directly synthesized as well.[22] The chemisorption of EDOT-acid and subsequent electropolymerization of PEDOT are shown in Scheme 1. After UV ozone activation, the ITO glass slides were immediately immersed into vials containing fresh 10 mM EDOT-acid ethanol solution for up to 12 h to ensure that a closely packed monolayer was formed during the chemisorption.[27] It has been previously reported that carboxylic acid derivatives are readily chemisorbed onto ITO surfaces and other conducting substrates, such as stainless steel, without significantly changing the surface roughness of the substrates. Figure 1a shows the cyclic voltammogram of EDOT-acid monomer solution (5 mM in acetonitrile), and the voltammograms for both modified and unmodified ITO surfaces are shown in Figure 1b. A sharp anodic peak corresponding to the oxidation of the EDOT-acid was observed at +1.25 V in Figure

1a, and an oxidation peak with similar potential was also found for the EDOT-acid modified substrates as shown in Figure 1b. In contrast to the sharp peak of the EDOT-acid monomer solution, the oxidation peak of modified substrates was rather broad even after a full day of immersion.[28] The broad peak was also irreversible; it only occurred in the first cycle with no oxidation peaks found in the following cycles. In addition, no reduction or oxidation peaks associated with polymerization of the thin layer of EDOT were ever observed. The surface coverage of the adsorbed molecule was estimated to be 1.7×10^{-10} mol/cm^2 as determined coulometrically,[27] and is only one-third of the expected saturated monolayer coverage (4×10^{-10} mol/cm^2).[29] Presumably, the reason that the electrochemically determined coverage is so low is that only a fraction of the ITO surface is capable of supporting electron transfer to the adsorbed molecule. The successful adsorption of EDOT-acid on metal or metal oxide was also confirmed via QCM measurement with a stainless steel coated sensor, and the adsorption kinetics was studied as well. The frequency change and corresponding mass change calculated via Sauerbrey eq were shown in Figure S1 (Supporting Information, SI).[30] After the initial equilibration step with pure ethanol, introduction of the EDOT-acid solution (point A in SI Figure S1) caused a sudden drop in the resonant frequency signal, followed by a slower frequency decrease. The whole adsorption lasted for 15 min until it reached a steady state. No obvious frequency change was found after rinsing with PBS buffer solution, indicating that the EDOT-acid molecules were strongly adhered to the metal oxide surface.

3.2. Surface Characterization of EDOT-Acid Modified ITO Electrodes. The formation of the adsorbed EDOT-acid thin layer could also be confirmed via static contact angle

measurements. Figure 2 shows the static contact angles of UV Ozone cleaned ITO, ITO exposed to ethanol, and EDOT-acid modified ITO. The UV Ozone treated ITO was extremely polar and had a water contact angle less than 5°. The water contact angle of ITO increased to 32° after 12 h ethanol exposure and the EDOT-acid modified ITO had a contact angle of 54°. The topographies of both clean ITO substrates and EDOT-acid modified ITO substrates were characterized by AFM, as shown in SI Figure S2. Polycrystalline grains with an average diameter of ~36 nm and a root-mean-square roughness on a $5 \times 5~\mu m^2$ regions of ~4.1 nm could be found on the clean, unmodified ITO substrates, as reflected in SI Figure S2a. The EDOT-acid modified surface still showed the same polycrystalline nature of the unmodified ITO substrate with only a small decrease in the surface roughness (rms ~3.9 nm), indicating that the chemisorbed EDOT-acid thin film was smooth and homogeneous. These results show that the thin EDOT-acid layer did not significantly change the surface morphology and texture of the ITO films. XPS analysis was used to study the composition of the adsorbed EDOT-acid thin layer. Figure 3 presents the
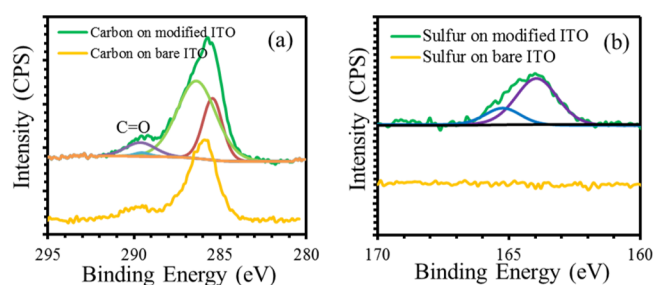

Figure 3. High-resolution XPS spectra of 295−280 eV carbon (a) and 170−160 eV sulfur (b) regions for both unmodified ITO electrodes and EDOT-acid modified ITO electrodes.

high resolution XPS data of the carbon (a) and sulfur (b) regions from both unmodified ITO and EDOT-acid modified ITO electrodes. The presence of carboxylic acid groups in the EDOT-acid coated films was clearly demonstrated by a strong peak at 288.5 ev (Figure 3a). The major peak at 285.8 ev corresponds well with the C(1s) peak from PEDOT.[27,31] S(2p) peaks were also detected near 164 eV, as shown in Figure 3b. No sulfur signal was observed from the unmodified ITO electrodes. The C(1s) peaks in the unmodified ITO are from contaminants and can be easily distinguished from the chemisorbed EDOT-acid thin layer with carboxylic acid side groups.

3.3. Electrochemical Properties of PEDOT on EDOT-Acid Modified ITO. PEDOT was electrochemically polymerized onto unmodified and EDOT-acid modified ITO slides under constant current ($0.15~mA/cm^2$) with tetrabutylammonium perchlorate (TBAP, 0.1 M) as electrolyte in a standard three-electrode cell. The electrochemical behavior of PEDOT coated electrodes and bare ITO glass slides were studied using cyclic voltammetry, as shown in Figure 4. PEDOT coatings on both electrodes showed reversible oxidation and reduction peaks during electrochemical scanning between −0.9 V and +0.5 V (vs Ag/AgNO₃). One benefit of using PEDOT as coating is the greatly improved charge storage capacity (CSC) as compared with the bare electrode. It is clear from Figure 4 that depositing PEDOT on bare ITO and EDOT-acid modified ITO dramatically increased the CSC of the electrodes. The magnitude of the increase of CSC was similar for both
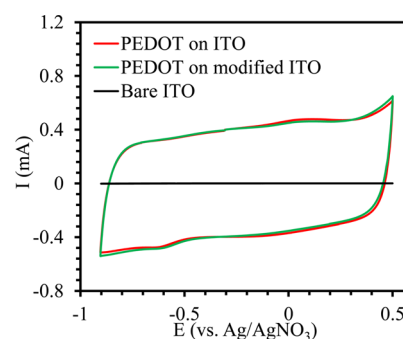

Figure 4. Cyclic voltammetry of bare ITO, PEDOT on ITO, and PEDOT and EDOT-acid modified ITO. (Both PEDOT films were electrodeposited under constant current (0.075 mA) for 12 min).

substrates. The shapes of the CV curves of PEDOT on EDOT-acid modified ITO were nearly identical to those on unmodifed ITO. This indicated that the EDOT-acid thin layer did not have a significant effect on the redox behaviors and charge storage capacity of the PEDOT-coated electrodes.

The electrochemical properties of PEDOT-coated electrodes were further investigated using EIS in 0.1 M PBS buffer solution. After PEDOT deposition, the amplitude of the impedance of the electrodes decreased by 2−3 orders of magnitude at frequencies between 1 and 1000 Hz as seen in Figure 5. This dramatic drop in impedance has been associated
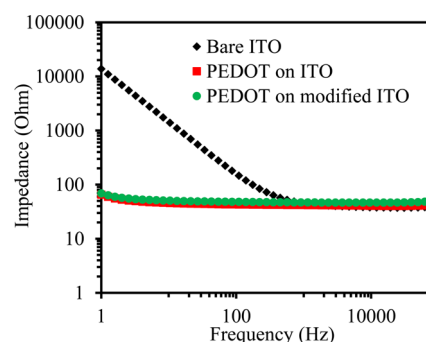

Figure 5. Electrochemical impedance spectroscopy of bare ITO, unmodified, and modified ITO electrodeposited with PEDOT.

with the increase in effective surface area and ability of the PEDOT to facilitate both electronic and ionic transport. It was found that the low frequency impedance of PEDOT coated onto the EDOT-acid modified electrode was only just slightly higher than that of PEDOT coated unmodified ITO (Figure 5), again indicating that the thin EDOT-acid adhesion promoter layer did not significantly block charge transport through the PEDOT−ITO interface.

3.4. Adhesion Testing. The adhesion strength of the PEDOT coatings on both EDOT-acid modified and unmodified substrates were investigated by a simple but effective ultrasonic test. The PEDOT coated electrodes were first immersed into a 20 mL vial that was filled with DI water. The vials were put in a Kendal HB-23 ultrasonic cleaner with a power of 220 W for a specified time during the test. Optical images of the electrodes before and after the sonication test are shown in Figure 6. The PEDOT films on unmodified ITO electrodes could only sustain up to 5 s of sonication. After sonication, these PEDOT films were fragmented into many small pieces, and the nearly the whole film was dispersed into

Figure 6. Optical images of PEDOT films on ITO and modified ITO before and after ultrasonication adhesion test. PEDOT on ITO was tested for 5 s and PEDOT on modified ITO was tested for 2 min.
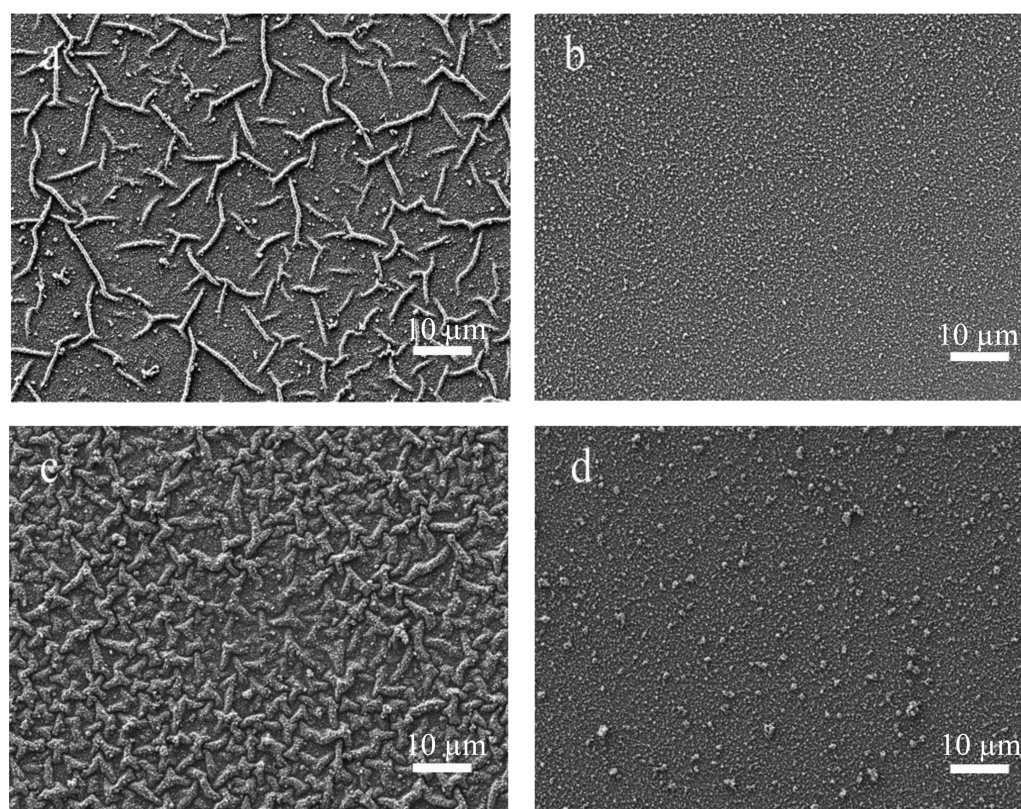

Figure 7. SEM images of PEDOT films on pure ITO electrode (a,c) and EDOT-acid modified ITO electrode (b,d) in acetonitrile for 9 min (a,b) and 12 min (c,d) at constant current mode (0.15 mA/cm^2). Scale bar represents 10 μm.

the solvent. However, the PEDOT films coated onto EDOT-acid modified ITO remained intact even after 2 min of sonication. The excellent mechanical stability of the PEDOT films on EDOT-acid modified ITO indicates that there are significantly stronger interactions between the polymer and the ITO electrodes. The substantially improved adhesion of PEDOT on metals and metal oxides with EDOT-acid coatings suggests that this modification may be important for optimizing performance in long-term recording or stimulation applications.

3.5. Surface Morphology of PEDOT Films. The morphologies of the PEDOT thin films electrochemically deposited onto bare ITO and EDOT-acid modified ITO electrodes were studied using SEM as shown in Figure 7. For SEM studies, PEDOT films were grown in acetonitrile under a constant current (0.075 mA) with varying deposition times (9 and 12 min). Clearly, the morphologies of the films were affected by the interfacing interactions with the underlying substrates. When coated onto bare ITO, which has no specific interactions with PEDOT, the PEDOT film showed a bumpy and rough surface where star-shaped patterns formed by buckling were found (Figure 7a,c).[32]

Buckling delamination is a common phenomenon in thin film materials. Delamination of a weakly bonded thin film from its substrate can occur spontaneously when the strain energy in the film exceeds the interfacial energy resisting separation.[33−35] It has been reported that acetonitrile can cause modest swelling of PEDOT.[36] During swelling, the internal strain energy that built up in the PEDOT film during electropolymerization was evidently larger than the interfacial energy with the bare substrate, thus leading to the observed buckling delamination. When the substrate was modified with EDOT-acid, the stronger interactions between the film and the substrate

suppressed the formation of buckling. This observation is similar to previous studies showing less film buckling when cross-linking agents were introduced into electrochemically deposited PEDOT copolymers.[14] As the film became thicker, the buckling pattern became denser and closer together. The size of the bulking ridges also increased. The bulking effect is consistent with PEDOT having limited adhesion on unmodified ITO. However, only flat and uniform films with no such buckling features were formed on EDOT-acid modified ITO substrates (Figure 7b,d). At the smallest length scales (~100 nm), both films showed the bumpy surface structure commonly observed in electrochemically deposited PEDOT. Evidently, the thin adhesion layer of EDOT-acid increases the interactions between the film and inorganic electrode, eliminating the mechanical buckling seen on the unmodified substrates.

4. CONCLUSIONS

ITO electrodes were successfully modified by EDOT-acid via chemisorption. PEDOT thin films could be electrodeposited onto the EDOT-acid modified electrodes. The electrochemical impedance spectra showed that the impedance of PEDOT-coated EDOT-acid modified ITO electrodes was much lower than that of the bare ITO electrode. The charge storage capacity of PEDOT coated modified electrode were much higher than that of bare ITO characterized by CV. The mechanical stability and adhesion of the PEDOT coatings on modified ITO were tested by aggressive sonication tests. The morphologies were characterized by SEM, and verified the elimination of mechanical buckling of the films on EDOT-modified substrates. These characteristics demonstrate that EDOT-acid has the ability to serve as an adhesion promoter from improving the performance of PEDOT, and presumably other conjugated polymers, as electrochemically deposited coatings on inorganic biomedical devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Quartz Crystal Microbalance plots and Atomic Force Microscopy images. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03350.

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Notes

The authors declare the following competing financial interest(s): DCM is a Co-Founder and Chief Scientific Officer of Biotectix LLC, a University of Michigan spin-off company working to develop conjugated polymers for interfacing a variety of electronic biomedical devices with living tissue..

■ ACKNOWLEDGMENTS

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