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Elise Villemin, Baptiste Lemarque, Thi Thiêt Vũ, van Quynh Nguyen, Gaelle Trippé-Allard, et al.. Improved adhesion of poly(3,4-ethylenedioxythiophene) (PEDOT) thin film to solid substrates using electrografted promoters and application to efficient nanoplasmonic devices. Synthetic Metals, 2019, 248, pp.45-52. 10.1016/j.synthmet.2018.12.010 . hal-02570136

HAL Id: hal-02570136
https://hal.science/hal-02570136

Submitted on 21 Oct 2021

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Improved adhesion of poly(3,4-ethylenedioxythiophene) (PEDOT) thin film to solid substrates using electrografted promoters and application to efficient nanoplasmonic devices

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ABSTRACT

In this work we present a new strategy to enhance poly(ethylenedioxythiophene) (PEDOT) adhesion to solid substrates (Indium Tin Oxide-ITO and gold). Two derivatives, incorporating thiophene or ethylenedioxythiophene moieties, are first electrografted from diazonium salt precursors. The resulting ultrathin layers act as adhesion promoters for ITO and gold electrodes. In a second step, EDOT is electropolymerized on the modified surface. Adhesion tests, using ultrasonication, of the PEDOT layer deposited on bare or on modified ITO electrodes show that the presence of the ultrathin layer leads to an improvement of the PEDOT adhesion while retaining its electronic properties. This strategy was used to prepare stable plasmonic devices with gold nanoparticles surrounded by PEDOT film. We show that their plasmonic properties are not changed by the adhesion layer and that their lifetime are greatly improved.

Keywords: conjugated polymers, poly(3,4-ethylenedioxythiophene), adhesion, electrografting, electropolymerization, electrochemical switching, plasmonic devices, localized surface plasmon resonance

1 Introduction

Among the commercialy available conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is probably one of the most used due to its high chemical and thermal stability.[1,2] Its low oxidation potential, allowing it to switch from an insulating to a highly conductive state (more than 3000 S cm^{-1} under specific conditions[3,4]) and the possibility of coating it as a thin film on various substrates[5,6] make PEDOT and its derivatives[7,8,9] suitable for various applications. Energy conversion and energy storage, organic light-emitting diodes, electrochemical transistors, thermoelectrical materials and sensing devices[10–14] and, more recently, medical applications such as neural prosthesis,[15–21] cardiovascular implants for tissue regeneration,[22] antitumor compounds for metastatic cell adhesion[23] and PEDOT hybrid-based electronic biomedical devices are

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the multiple domains where PEDOT is involved. However, its low adhesion to various inorganic solid substrates constitutes a serious drawback and its frequent delamination from the substrate decreases the device lifetime.[24,25]

Various processes have been used to limit the cracking and delamination of the PEDOT layer. Silane linkers bearing various aromatic units (pyrrole, thiophene, aniline) [26–29] have been used to form covalent bonds with metals, indium tin oxide (ITO) or various inorganic oxide substrates.[30,31] According to this concept, the preparation of adhesive conducting PEDOT films was fulfilled by anchoring an EDOT vinyl derivative onto a disilane-functionalized free-radical initiator followed by copolymerization with EDOT.[32] Electrostatic interactions between carboxylic acids functionalized by EDOT and inorganic solid subtrates were also found to enhance PEDOT adhesion.[33]

In recent years, the electrografting process, where electron transfer is followed by the formation of covalent metal-organic bonds between a substrate and a molecular compound, has been considered as a novel means of improving the adhesion of polymer films.[34,35] Electrografting presents several advantages, such as a high selectivity, high versatility and a significant economy of time. It has been applied to several thiophene derivatives, mixed with various co-monomers[36,37] and recently to generate on various electrodes a thick (a few μm) nonconjugated, cross-linked, and adherent P(EDOT-NH_2)-based polymer coating through electrochemical oxidation of the amine. This thick layer did not block charge transport through the interface, and subsequent electrochemical PEDOT deposition onto P(EDOT-NH_2)–modified electrodes was possible. It was shown that with P(EDOT-NH_2) as the anchoring layer, PEDOT coating adhesion was greatly enhanced.[38]

Diazonium salt electroreduction [34,39] is another effective way of electrografting organic compounds onto a surface, and has been widely used by our group to synthesize adherent thin films of conjugated oligomers on various conductive substrates.[40,41] The technique consists in preparing from an aminophenyl derivative a diazonium salt whose electroreduction leads to the formation of extremely reactive phenyl radicals which, in turn, react with the substrate to form a covalent metal-organic bond. By this technique it is possible generate homogeneous, ultrathin (less than 10 nm in contrast with reference 38). compact and pinhole-free films. We have shown that this latter property is particularly useful and essential for the design of molecular electronic devices. [42–45][46]

Several examples of the diazonium electrografting technique used for enhancing the adhesion of organic films on solid substrates have been described. In the first example a thin layer of diphenylamine (DPA) was grafted by the electrochemical reduction of the 4-aminodiphenylamine (ADPA) diazonium salt. The DPA-grafted layer did not impeded aniline oxidation, and polyaniline (PANI) was easily deposited on the DPA-modified electrodes. The PANI films generated on these electrodes showed electrochemical behavior similar to that of PANI electrodeposited on bare carbon electrodes but exhibited better chemical stability and high resistance to aggressive environments, that is, high temperatures and ultrasonic etching.[47] Electrografting of 4-nitrobenzene groups onto a gold surface and onto a porous silicon substrate using the 4-nitrophenyl diazonium salts, followed by the electroreduction of the nitro group to amine, has also been reported as a means of increasing the adhesion of

PANI.[48,49] In-situ generated pyrrole diazonium derivatives have been electrografted onto nickel surfaces.[50,51] Diazonium-modified flexible substrates have been prepared for the growth of adherent silver/polypyrrole nanocomposite films using surface-confined UV photopolymerization.[52]

In this paper, we used a two-step strategy (Figure 1) to enhance PEDOT adhesion to an ITO surface. The first step consists in electrografting, by diazonium salt electroreduction, ultrathin adhesion layers based on EDOT or thiophene moieties; the second step consists in the electropolymerization of EDOT monomer onto the primer layer. We demonstrate the efficiency of BTB (1-(2,2'-bisthienyl)benzene) and ETB (4-(5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)benzene) as adhesion promoter layers to improve the adherence of PEDOT thin films on ITO. We prove with electrochemical and optical analysis that the particular electronic and optical properties of PEDOT are maintained in the presence of these adhesion-promoting ultrathin layers. Then, we report the plasmonic properties of gold nanoparticles (AuNPs) surrounded by ETB/BTB-PEDOT block polymer as a function of the electronic state of the polymer. We demonstrate that this strategy is an effective way of increasing PEDOT adhesion to plasmonic electrodes and is a useful means of fabricating robust optoelectronic devices.

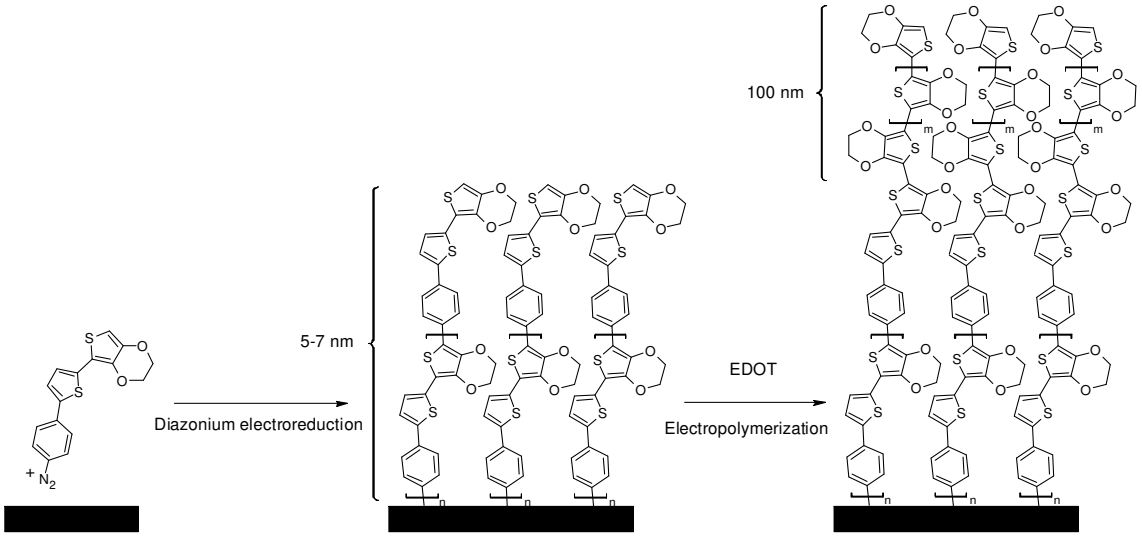


Figure 1. Two-step strategy to enhance PEDOT adhesion to solid substrates: The first step consists in the grafting of an ultrathin layer (5-7 nm) (here oligo(ETB)) acting as an adhesion layers. The second step is the PEDOT deposition from EDOT electropolymerisation on the ETB modified ITO electrode. Note that ETB can be replaced by BTB.

2 Experimental details

2.1 Chemicals and apparatus

1-(2,2'-Bisthienyl)-4-aminobenzene (BTAB) and 4-(5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)aniline (ETAB) precursors were synthesized according to published procedures.[53] All chemicals were used as received. *tert*-Butylnitrite (*t*BuO-NO), ferrocene (Fc), potassium gold(III) chloride ($KAuCl_4$) and sodium carbonate (Na_2CO_3) were purchased

from Sigma-Aldrich. Lithium perchlorate ($LiClO_4$) and tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4) from Aldrich were used as supporting electrolytes. 3,4-Ethylenedioxythiophene (EDOT) from Bayer was distilled before use. Acetone, acetonitrile (ACN) and absolute water-free ethanol were purchased from VWR.

For electrochemical experiments, a conventional three-electrode cell was employed with a CHI 760C potentiostat (CH Instruments, Austin, TX). The auxiliary electrode was a stainless steel grid, and a SCE (4M KCl) was used as reference electrode. Indium tin oxide (ITO)-coated glass plates with resistance of 30-50 Ω/square were purchased from Solems and were used as working electrodes. Before modification, the ITO-coated glass slides were ultrasonically cleaned (BRANSON 1510 ultrasonic cleaner) in acetone, ethanol and deionized water, each for 15 min, then carefully rinsed with distilled water and dried in a stream of N_2 before use.

2.2 Electrografting of adhesion promoters (BTB and ETB)

The *in situ* formation of the diazonium cation from (BTAB) or (ETAB) was performed under acid-free conditions, by adding *tert*-butylnitrite (*t*BuO-NO).[44,54] Briefly, an acetonitrile solution containing 5.10^{-4} M BTAB or 5.10^{-4} M ETAB and Bu_4NBF_4 (0.1 M) as supporting electrolyte was prepared and degassed by argon bubbling for at least 10 min. Then *t*BuO-NO was added in excess to the solution (30 equiv.). As the reaction between an amine and *tert*-butylnitrite is relatively slow, grafting started only after an incubation time of 5 min. After modification the subtrates were rinsed with ACN to remove any residual physically adsorbed moieties from the ITO surface and they were dried in a stream of N_2.

2.3. Electrochemical deposition of PEDOT on bare ITO and on ITO modified by Oligo-BTB and Oligo-ETB layers

PEDOT thin films were deposited at constant current ($0.01\ mA/cm^2 \leq I \leq 0.2\ mA/cm^2$) and for a time calculated to deliver a constant coulombic charge of $20\ mC/cm^2$ corresponding to a PEDOT thickness of around 100 nm. It was carried out in aqueous medium (2.10^{-2} M EDOT and 0.1 M $LiClO_4$) and in the presence of a surfactant (0.1 M sodium dodecyl sulfate-SDS) according to a previous procedure.[55,56]

2.4. AFM Characterization

AFM measurements were performed on a Keysight system (Picoscan 500). AFM images were recorded in the tapping or contact mode with a tip from Budgetsensor (AFM tap 300 G, resonance frequency 300 kHz, force constant 40 nN/m). Experiments were performed to estimate the thickness of the organic layers by the "scratching" procedure.[57] A statistical procedure was devised to average the trench depth over a large fraction of the scratch area.[43]

2.5. Preparation of plasmonic devices

AuNPs were deposited on ITO electrodes at a constant potential according to published procedures[58,59] ITO substrates were dipped into a stirred aqueous solution of 2.10^{-3} M $KAuCl_4$ and 0.25 M Na_2CO_3 as supporting electrolyte, and a controlled total charge of 22 mC/cm^2 was applied. Then, after modification, the plasmonic samples were inserted in a home-made planar electrochemical cell consisting of a standard three-electrode configuration (with a stainless steel counter-electrode grid and a silver (Ag/AgCl) pseudo-reference electrode), the whole placed under an Olympus microscope. All potentials are referenced to this Ag/AgCl electrode. The electrolyte solution was carefully degassed prior to the introduction into the cell. Modulation of LSPR signals was checked by switching the applied potential between a cathodic (–1 V/Ag) and an anodic value (0.5 V/Ag).

2.6. Adhesion of PEDOT tested by ultrasonic stirring in water

Unmodified and modified electrodes, covered with a PEDOT layer, were immersed in a 25 mL glass vial filled with deionized water. The vials were placed in a BRANSON 1510 ultrasonic cleaner with a power of 80–143 W (frequency 40 kHz) for different times (from a few seconds to 15 min).

3 Results and discussion

The electrografting of adhesion promoters (BTB and ETB) was performed by cyclic voltammetry from the electroreduction of the corresponding diazonium compounds. With the ETB-diazonium compound,[54] a first irreversible reduction wave, starting at 0.4 V/SCE with a peak current centered at 0.15 V/SCE (Figure 2a), yields ETB radicals which react with the ITO surface to form a covalent bond. This first ETB monolayer does not impede the reduction of other diazonium salts which then react with the ITO-bonded species to form a multilayer corresponding to an ETB oligomer grafted onto the ITO surface. As of the second cycle, the intensity of the cathodic current decreases and the reduction wave totally vanishes after several cycles. This behavior is associated with the formation of an ultrathin insulating organic layer (less than 10 nm) blocking the surface in the +0.4 V to –0.5 V potential range. Similar results are obtained with BTB-diazonium compounds whose reduction starts at a less positive potential than previously (0.2 V/SCE) with a peak current for the first cycle centered also at a more negative potential, –0.15 V/SCE (Figure S1). The AFM image confirms that the films are homogeneous with no visible pinholes (at the AFM resolution).[42,44] The thicknesses of the ultrathin films formed range from 5 to 7 nm (Figure S2).

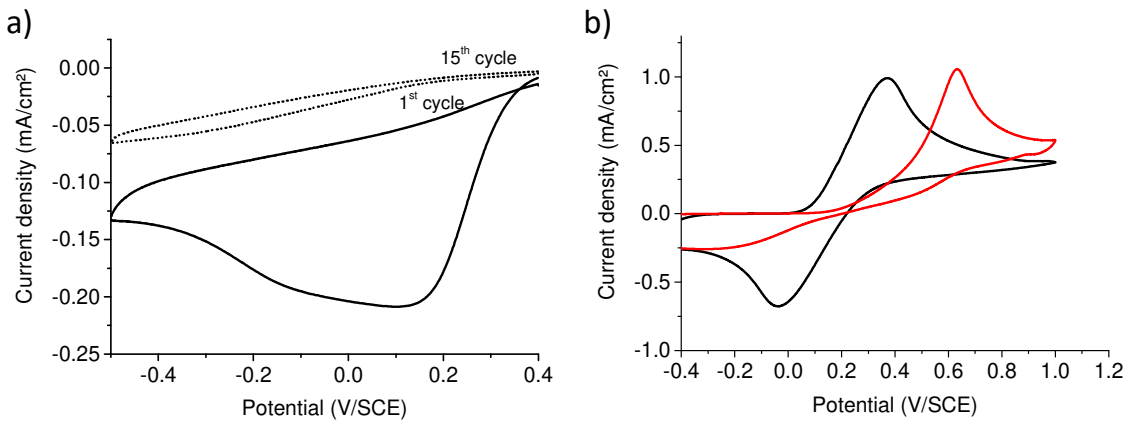


Figure 2. a) Electroreduction by cyclic voltammetry of 5.10^{-4} M ETB-diazonium on ITO electrode in ACN with 0.1 M Bu_4NBF_4. Scan rate 0.1 V/s. b) Cyclic voltammograms of ferrocene redox probe on bare ITO electrode (black line) and on ETB-ITO electrode (red line).

These oligo(BTB) and oligo(ETB) layers grafted onto ITO can switch to a conductive state at a specific potential corresponding to an oxidized-p-doped state of the oligomers.[54,60] This is revealed by the behavior of the redox probes on the modified electrodes.[61] As an example, Figure 2b and Figure S1 compare the voltammograms of 5.10^{-3} M ferrocene in ACN with 0.1 M Bu_4NBF_4, obtained on ITO, ETB-ITO and BTB-ITO electrodes. Ferrocene oxidation currents are maximum at 0.63 V/SCE and 0.95 V/SCE on ETB-ITO and BTB-ITO electrodes, respectively, instead of 0.37 V/SCE on bare ITO. The oxidation peak of ferrocene on BTB-ITO and ETB-ITO electrodes is thus strongly shifted to more positive potentials than that observed on bare ITO, confirming that these layers are conductive when the applied potential is above an anodic polarization threshold but insulating below this threshold. Furthermore, the replacement of a thiophene unit in BTB by the electron-rich 3,4-EDOT unit lowers the insulating-conducting switching potential.

Electrooxidation of EDOT was then carried out on the modified ITO electrodes and compared to that on bare ITO. In a first series of experiments PEDOT film was electrodeposited by sweeping the potential from –0.75 V/SCE to 1 V/SCE. Figure 3a and S3 shows the first electrochemical cycle of EDOT oxidation on ITO electrodes modified by ETB and BTB ultrathin layers, respectively. The CVs on the modified electrodes are similar to those on bare ITO and demonstrate that the presence of ultrathin ETB (or BTB) adhesion layers on ITO does not prevent EDOT oxidation and the deposition of PEDOT film. However, on bare ITO the current intensity grows abruptly at 1 V/SCE while on the ETB-modified electrode the intensity grows more smoothly but at a lower potential (onset at 0.75 V/SCE). All these data confirm that the electropolymerization of the EDOT remains possible on the ultrathin switchable ETB or BTB adhesion layer deposited on ITO.

Note that in a previous study, a minimal amount of EDOT was oxidized on ultrathin BTB layers (by sweeping the potential at the foot of the EDOT oxidation signal). We demonstrated that grafting only a few (less than 3) nanometers of EDOT moieties (5 to 6 units) onto the switchable BTB layer completely changes its switching properties. A range of

new materials covalently grafted onto the underlying electrode, consisting of oligo(BTB)-oligo(EDOT) diblock oligomers with tunable interfacial properties was created.[62]

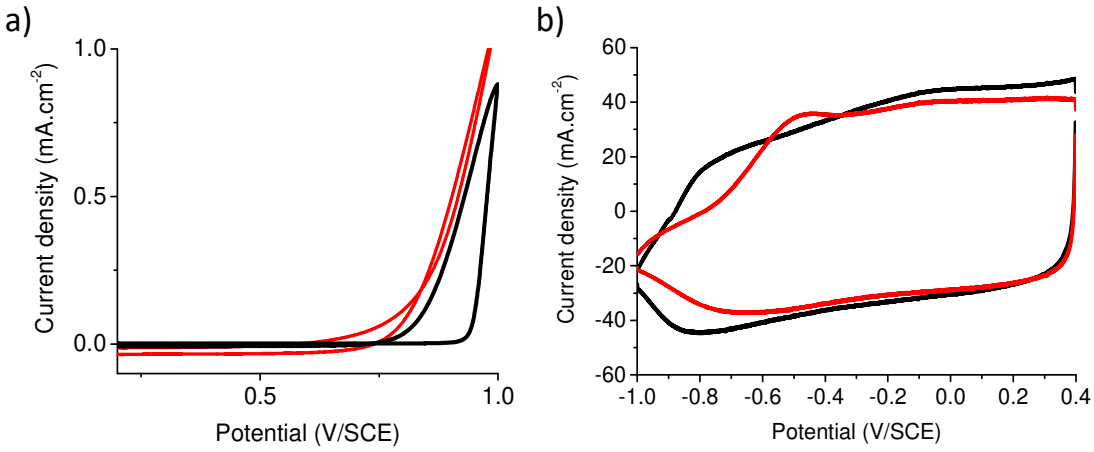


Figure 3. a) First voltammogram of EDOT oxidation on bare ITO electrode (black lines) and on ETB-modified ITO electrode (red line) b). Cyclic voltammograms of PEDOT deposited on bare ITO electrode (black lines), and on ETB-modified ITO-electrode (red line), PEDOT was deposited at constant current (5.10^{-2} mA/cm^2).

In the present studies, we deposited much thicker PEDOT layers on the ETB-modified ITO- or BTB-modifies ITO substrate. To do so, EDOT was electropolymerized at constant current (with intensities between 10^{-2} mA/cm^2 and 2.10^{-1} mA/cm^2) and for deposition times calculated to obtain a charge deposition ($Q_{deposition}$) of 20 mC/cm^2 corresponding to a PEDOT thickness of about 100 nm. Typical chronopotentiometric curves recorded during PEDOT deposition on ITO and ETB-modified ITO electrodes are shown in Figure S4. The potential stabilizes at a constant value during the whole deposition process and the initial potential observed in the first seconds is smaller on modified ETB-ITO electrodes. Then, the electroactivity of the PEDOT films was characterized by cyclic voltammetry (Figure 3b and S5). The same ranges of faradic and capacitive currents are observed for PEDOT deposited on bare ITO and PEDOT deposited on ETB modified ITO, confirming that the same amount of PEDOT is deposited on both electrodes. The PEDOT film on the ETB-modified electrode is characterized by reversible oxidation/reduction peaks centered at –0.50 V/SCE and –0.70 V/SCE, respectively (Figure 3b), while on the BTB-modified electrode a similar reversible oxidation/reduction peak occurs at slightly less negative potentials of –0.40 V/SCE and –0.50 V/SCE, respectively (figure S6).

The charge required to dope the PEDOT film, named Q_{doping} i.e. the charge for the oxidation of the deposited PEDOT film between -1 and 0.4 V, was measured from the cyclic voltammograms (Figure 3b) of the PEDOT deposited on the various electrode (ITO,ETB-modified ITO and BTB-modified ITO electrodes). The $Q_{doping}/Q_{deposition}$ ratio was then estimated. For most conductive polymer and when the deposition yield is close to 100% this ratio is around 10%, since for each monomer 2 electrons are removed in the electropolymerization while 0.2 to 0.3 electrons are used to dope the growing film. As a consequence $Q_{doping}/Q_{deposition}$ is between 9% (0.2/2.2) and 13% (0.3/2.3)[63,64]. This is clearly observed for all PEDOT films generated in this study as long as the current intensities

used during EDOT oxidation are above 2.10^{-2} mA/cm^2. (Table 1), which indicates that deposition is quantitative. However, this ratio drops to 6–10% for lower current intensities (10^{-2} mA/cm^2) which indicates a deposition yield below 100% under these conditions.

	I (mA/cm^2)	Deposition time (s)	Q_{doping} before sonication (mC/cm^2)	$\frac{Q_{doping}}{Q_{deposition*}}$ %	Q'_{doping} after sonication (mC/cm^2)	$\frac{Q'_{doping}}{Q_{doping}}$ (%)
PEDOT deposited bare ITO	1.10^{-2}	2000	1.88	9.5	0.16	8.5
	2.10^{-2}	1000	2.56	12.9	0.70	27.3
	5.10^{-2}	400	2.63	13.2	0.35	13.3
	1.10^{-1}	200	2.75	13.9	0.96	34.9
PEDOT deposited on BTB modified ITO electrodes	1.10^{-2}	2000	1.32	6.6	1.30	98.4
	2.10^{-2}	1000	2.20	11.1	2.00	90.9
	5.10^{-2}	400	2.07	10.4	1.89	91.3
	1.10^{-1}	200	2.20	11.1	1.72	78.1
PEDOT deposited on ETB modified ITO-electrodes	1.10^{-2}	2000	1.68	8.5	1.60	95.2
	2.10^{-1}	80*	1.70	10.6	1.60	94.1

(*) $Q_{deposition}$ = 16 mC/cm^2

Table 1. Comparison of Q_{doping}, $Q_{doping}/Q_{deposition}$ and Q'_{doping}/Q_{doping} for PEDOT deposited on bare ITO, BTB-modified ITO and ETB-modified ITO electrodes before and after ultrasonication.

PEDOT coatings synthesized on ITO, BTB- or ETB-modified ITO electrodes were ultrasonicated to estimate the adhesion strength of the PEDOT layer. These PEDOT films are about 100 nm thick, corresponding to a charge deposition of about 20 mC and their adhesion is estimated by the Q'_{doping}/Q_{doping} ratio where Q_{doping} and Q'_{doping} are the charges corresponding to the doping yield before and after ultrasonication, respectively. This ratio gives an estimate of the percentage of PEDOT which remains attached to the substrate. Poor adhesion was found for PEDOT film deposited on bare ITO (Q'_{doping}/Q_{doping} less than 30%). After a few seconds of ultrasonication, the PEDOT film was partially delaminated; this was established by the sharp decrease in the current density and the disappearance of the capacitive and faradic currents (Figure 4a). On the contrary, the PEDOT films electrodeposited on the ETB- or BTB-modified electrodes remained intact after 15 min of ultrasonication. Their electrochemical activity (Figure 4b) exhibits capacitive and faradic currents similar to those before ultrasonication. Similar behaviors are observed for all current densities but, for the largest current density (10^{-1} mA/cm^2), the PEDOT film on the BTB-modified electrode appears to be less resistant (Q'_{doping}/Q_{doping} = 78%) than at lower current densities, where Q'_{doping}/Q_{doping} is about 90-95% (Table 1). In contrast, the same PEDOT film formed on ITO-ETB at 10^{-1} mA/cm^2 remains adherent after sonication (Q'_{doping}/Q_{doping} = 94%).

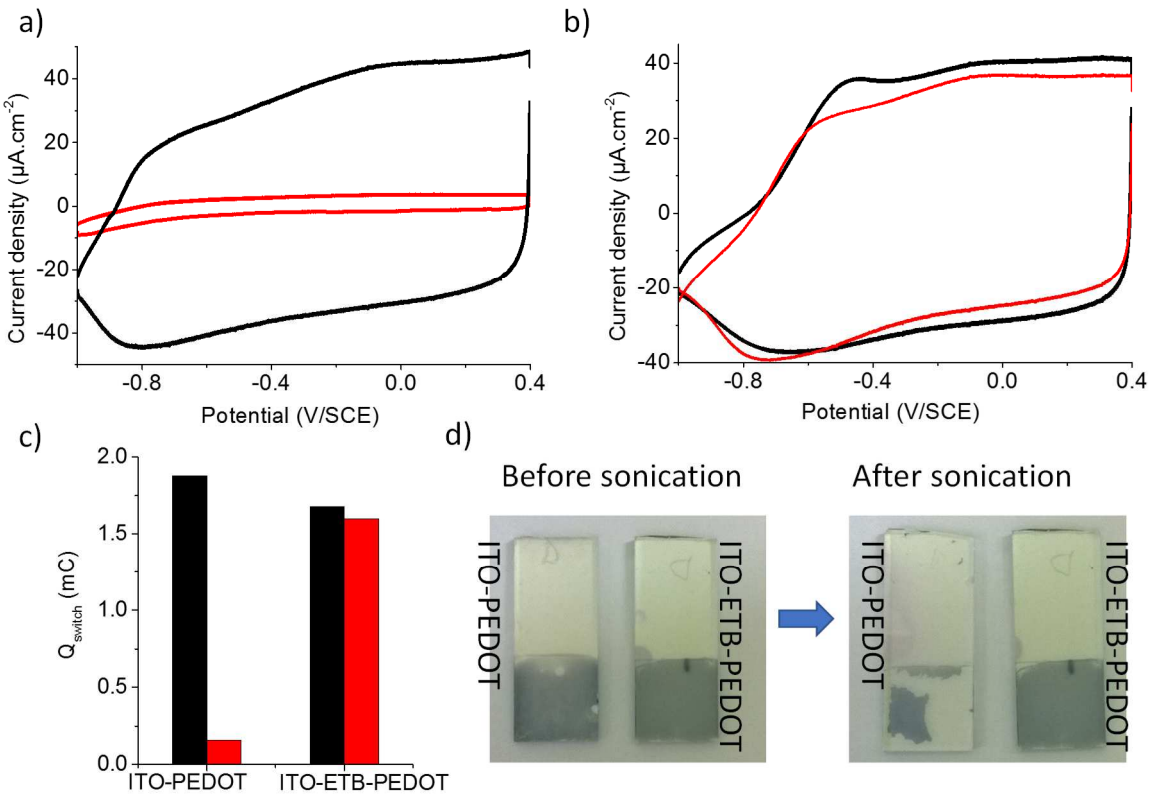


Figure 4. Cyclic voltammograms of PEDOT films obtained at constant current intensity (10^{-2} mA/cm^2) a) on bare ITO electrode before (black line) and after ultrasonication (red line), b) on ETB-modified electrode before (black line) and after ultrasonication (red line). c) Faradic and capacitive charges involved in the doping of the PEDOT film before (black) and after ultrasonication (red) for PEDOT on ITO and PEDOT on ETB-ITO electrodes. d) Optical images of PEDOT films on ITO (left) and ETB-ITO (right) before and after ultrasonication.

Figure 4c summarizes these results and compares Q_{doping} before and after ultrasonication for ITO-PEDOT and ITO-ETB-PEDOT electrodes, while Figure 4d shows images of the electrodes. Both figures indicate that PEDOT grown on ETB-modified electrodes are strongly adherent to the underlying ITO substrate while PEDOT grown directly on ITO is not. Similar curves are shown in Figure S5 and S6 for ETB- and BTB-modified electrodes covered by PEDOT deposited at different current densities.

Overall, these results demonstrate that the grafted BTB and ETB layers considerably increase the adhesion of PEDOT film on the ITO electrode.

This strong adhesion increase can be directly used to enhance the stability of an active plasmonic device [65] consisting of a PEDOT film deposited on a plasmonic electrode (Au NPs deposited on ITO).[66] The plasmonic electrodes were prepared by electrochemical reduction of a gold salt which has been described elsewhere.[59] These substrates show strong extinction spectra around 600 nm due to localized surface plasmon resonance (LSPR). The LSPR is very sensitive to the dielectric function of the surrounding medium. As a consequence, when PEDOT is deposited on Au NPs, the LSPR can be controlled by the

electrochemical reversible redox switch of the PEDOT film, which is accompanied by changes in its color and dielectric function.[55,67–69] However, delamination of PEDOT from Au NPs or from ITO decreases the lifetime of the ITO-AuNPs-PEDOT active plasmonic devices. The use of BTB and ETB as adhesion promoters followed by PEDOT electrodeposition on Au NPs is thus a means of fabricating robust plasmonic devices.

The extinction spectrum of a AuNPs-PEDOT(100 nm) plasmonic device obtained without an adhesion promoter is shown in Figure 5a. The PEDOT film was polarized at –1.0 V/SCE in aqueous $LiClO_4$ solution and dried in air before its spectrum was recorded. A red-shift of 34 nm of the LSPR relative to that of AuNPs in air is clearly observed. Then the device was ultrasonicated for a few minutes and its extinction spectrum recorded again (Figure 5a, red curve). Neither extinction nor absorption of light was measured, which demonstrates that the PEDOT layer and the gold NPs were totally removed by ultrasonication. These results clearly illustrate the poor adhesion of PEDOT on ITO and gold substrates.

The same experiments were then performed on a plasmonic device with the ETB adhesion promoter. ETB was first grafted onto ITO-AuNPs as described above and 100 nm of PEDOT film was then deposited on the ITO-AuNPs-ETB system. With PEDOT in its neutral state (applied potential–1 V/SCE but experiments performed in air) the LSPR is red-shifted by 30 nm, which is similar to that obtained without the ETB layer. The same behavior has already been reported for plasmonic devices with AuNP nanoarrays coated with an ultrathin BTB layer [70] while evidence of the deposition of BTB directly on gold was also directly evidenced by SEM [71]. The presence of an ultrathin layer of ETB (5–10 nm) on the surface of the AuNPs does not significantly modify the optical properties of the plasmonic device formed by an assembly of Au NPs coated with PEDOT. Then the device was ultrasonicated for 30 minutes and its extinction spectra recorded (Figure 5b, red curve). It shows a strong LSPR band, indicating that the whole coating is conserved. These results clearly illustrate the strong adhesion of PEDOT on ETB-modified ITO and gold substrates.

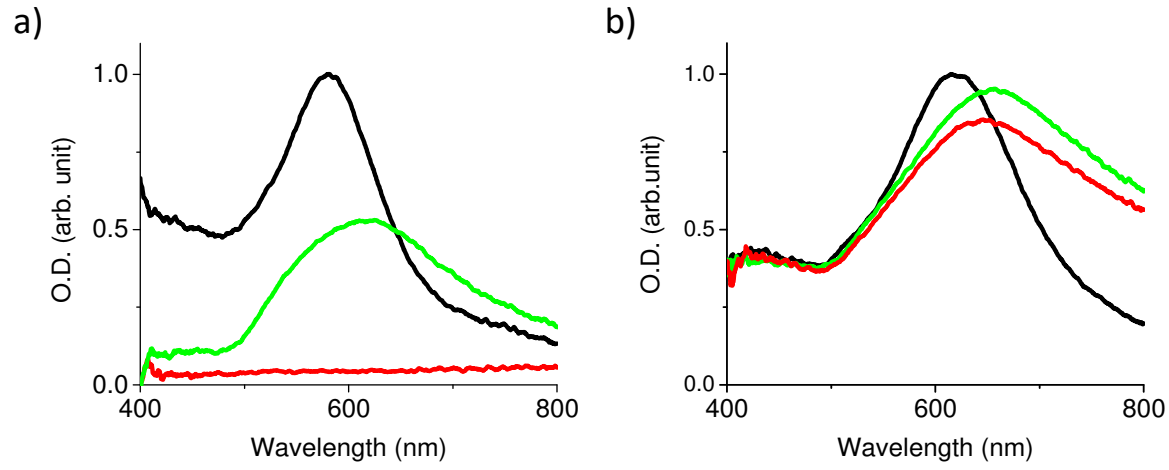


Figure 5. a) Normalized extinction spectra of AuNPs in air (black line), coated with a PEDOT film before (green line) and after (red line) ultrasonication. b) Normalized extinction spectra

of AuNPs in air (black line), coated with ETB-PEDOT before (green line) and after (red line) sonication. All spectra have been shifted on the y axis for better comparison.

The LSPR properties of the ITO-AuNPs-ETB-PEDOT device were then switched. Extinction spectra were recorded in situ while the electrode was polarized in 0.1 M $LiClO_4$ aqueous electrolyte. Figure 6 shows when the polarization is changed at 0.5 V (doped state, green curve) and –1 V/SCE (undoped state, blue curve) the plasmon band is considerably red-shifted, from 589 nm to 711 nm, The plasmonic response of the device is reversible and its properties are maintained over successive polarization cycles between 0.5 V and –1 V and after several ultrasonication cycles. Moreover, this LSPR shift for a disordered assembly of Au NPs is comparable to that obtained with an ordered array of PEDOT-coated Au nanoplots (192 nm).[66]

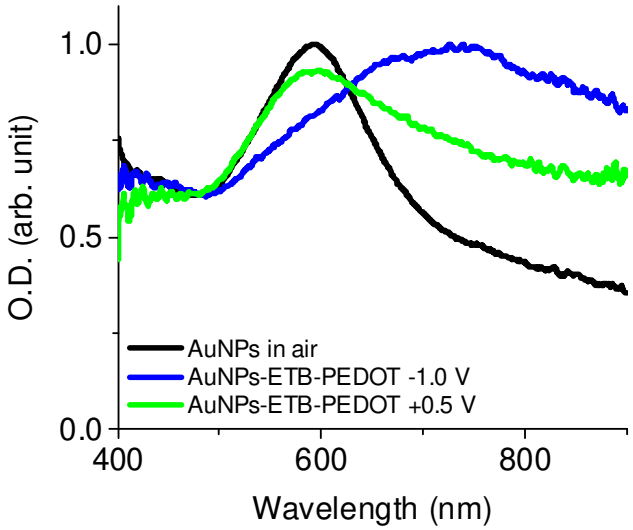


Figure 6. Normalized extinction spectra of AuNPs in air (black line), coated with ETB-PEDOT and polarized at 0.5 V/Ag (green line) and –1.0 V/Ag (blue line) in aqueous electrolyte (0.1 M $LiClO_4$). All spectra have been shifted on the y axis for better comparison.

4 CONCLUSION

Ultrathin layers of oligo(ETB) or or oligo(BTB) generated by electroreduction of diazonium salts considerably enhance PEDOT adhesion to ITO and gold substrates without altering the electrochemical and optical properties of the electrodeposited PEDOT film. This enhancement of PEDOT adhesion on solid substrates can be explained by the formation of covalent bonds at the electrode/oligo(BTB) or oligo(ETB) interface and between oligo(promoter) and the PEDOT layers, giving new structured block polymers firmly anchored to the substrate. This strategy has been used for the preparation of plasmonic devices with AuNPs surrounded by an electrochromic PEDOT film. The plasmonic device is destroyed by ultrasonication when PEDOT is directly deposited on ITO and Au NPs whereas it resists ultrasonication when a BTB or ETB adhesion layer is used. The large reversible shift of the LSPR of the ITO-AuNPs extinction spectra between the reduced state and the oxidized state of ETB-PEDOT film is comparable to that observed on unmodified ITO-AuNPs-PEDOT

plasmonic electrode. This procedure should be an efficient way of preparing robust optoelectronic devices.

From a more general point of view, we anticipate that the two-step method developed in this study to promote PEDOT adhesion will impact the development of organic electronic and bioelectronic research fields, as well as many technologies which use PEDOT.

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on X website at DOI X.

BTB electrodeposition on ITO and ferrocene signal on BTB-ITO electrode, thickness measurement of BTB layer on ITO using a scratch experiment, EDOT electrodeposition on bare ITO and on BTB-modified ITO for current density of 0.05 mA/cm^2 and using cyclic voltammetry (first cycle). Cyclic voltammograms of a PEDOT film deposited on ITO or on ETB-modified electrode at 2.10^{-1} mA/cm^2; CVs are given before and after sonication. Cyclic voltammograms of PEDOT films deposited on ITO and BTB-modified electrode at 10^{-1} mA/cm^2 before and after sonication

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Agence Nationale de la Recherche ANR (France) (ANR-15-CE09 0001-01)

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