

Article

Deposition of Polymers on Titanium Nitride Electrodes

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Abstract: The application of titanium nitride (TiN) as an electrode for electrochemical deposition or characterization requires the removal of an insulating layer from its surface. This process was studied and optimized, and the conditions for the complete removal of this layer through treatment with oxalic acid were formulated. The obtained TiN surfaces were used for the deposition of various conducting and non-conducting polymers. Two different approaches were applied: (i) in situ electrochemical synthesis of the main classes of conducting polymers, including polyaniline, polypyrrole, polythiophene, and selected derivatives thereof, and (ii) electrostatically driven layer-by-layer (LbL) deposition of multilayers of oppositely charged polyelectrolytes. The deposited polymers were characterized by electrochemical methods. The electrochemical properties of the deposited conducting polymers and their deposition on the TiN surface were comparable to those of the metallic electrodes. The films produced via LbL deposition exhibited a pronounced influence of the charge of the last deposited polymer on the redox reaction of ferri/ferrocyanide, validating the charge alteration with each successive polymer layer deposition. The studied deposition technologies can be used for the modification of TiN surfaces required in applications of this material in chemical sensors and other devices.

Keywords: titanium nitride; conducting polymer; electrochemical polymerization; layer-by-layer deposition; treatment of TiN; insulating layer on TiN



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1. Introduction

Titanium nitride (TiN) was introduced to the global market in the 1970s as a super-hard material (2000 kg/mm²) for protective coatings [1–5]. Furthermore, TiN has a high melting temperature (3000 °C), corrosion resistance, exceptional mechanical strength, and durability, as well as biological compatibility. Thanks to its electronic properties and high electrical conductivity (4000–55,500 S·cm^{−1} [6,7]), TiN is considered one of the most promising engineering materials for applications in various devices [8,9]. As a transition-metal nitride with a low cost, high molar density, and superior chemical resistance, TiN is used in supercapacitors [10,11]. It provides efficient charge collection [12,13] and fast charge transfer at the interface and therefore is promising for applications in electrochemical devices requiring a high power density [14] and high mechanical stability [15]. It was demonstrated that a TiN coating acts as a mechanical buffering layer that helps to prevent structural deformations during repeated charge–discharge cycling [14]. It facilitates electron transfer at the electrode/electrolyte interface, while its ability to be oxidized on the surface contributes to pseudocapacitance [16]. Examples of TiN applications in microelectronic devices include its uses as diffusion barriers [17,18], decorative coatings [19,20], ohmic contacts for semiconductors [21–23], and Schottky contacts [24,25]. It can also be applied in

photoelectrochemical cells [26,27] and in electrocatalysis [28]. The novel field of possible TiN applications includes chemical sensors [29–31] and biosensors [32,33]. TiN is appealing not only because of its electrical and electrochemical properties but also because of its plasmonic properties, which are comparable to those of metallic gold or silver. An application of TiN as a resonator in refractometric surface plasmon resonance (SPR) sensors with different configurations was previously reported [34].

Many applications of TiN, for example, in electrochemical chemo- and biosensors, require surface modification of this material. Such protocols have been well developed for gold [35,36], silicon oxide [37,38], and a few other surfaces [39]. However, the deposition of designed organic layers on the surface of TiN has not been studied so far. Herein, we describe two approaches to the surface modification of TiN: in situ electrochemical polymerization of the main types of conducting polymers and electrostatically driven layer-by-layer (LbL) deposition of multilayers of oppositely charged polymers.

Conducting polymers belong to organic materials that can switch between insulating and conducting forms. This transition results from the formation of charge carriers in the polymer-conjugated backbone upon oxidation/reduction or protonation/deprotonation. The changes induced by the injection or removal of charge carriers in the polymeric matrix lead to conformational transformation and changes in the electronic structure of the conjugated backbone. This conversion provides the unique electrical, electrochemical, and optical properties of conducting polymers. Such switching is also influenced by the binding of some analytes to the backbone of the polymer or to the receptor connected to the polymer chain, which makes them useful for applications in various chemical sensors [40]. Due to the changes that can be detected by in situ resistance, UV-vis, and NIR or fluorescence, conducting polymers have acquired great potential for the implementation of various intelligent devices. Conducting polymers can be deposited onto various substrates using diverse techniques. The most popular method for the deposition of conducting polymers onto conducting supports is their electrochemical synthesis in situ. This allows one a direct electrical control of the thickness of the deposited polymer. Herein, we describe the first electrochemical synthesis of conducting polymers on the surface of TiN.

Layer-by-layer (LbL) deposition, first suggested by Decher in the 1990s [41], is another general approach to the deposition of thin organic layers of controllable thickness and structure. In thousands of publications, the deposition of various polymers or polymer/nanoparticle and even polymer/cell combinations on diverse surfaces has been described [42,43]. However, according to our knowledge, there are currently no data on the application of these techniques for deposition onto the surface of TiN.

Electrochemical polymerization on the surface of TiN requires the removal of an insulating layer that is formed spontaneously on the TiN surface. For LbL deposition, the removal of this layer is not essential, but it is also important for the application of electrochemical characterization techniques (i.e., cyclic voltammetry (CV) or electrochemical impedance spectroscopy (EIS)) to characterize the deposited organic layers. This is why the initial part of our study was focused on the optimization of the treatment procedure to remove this insulating layer from the TiN surface. This layer, formed by the oxidation of titanium nitride because of its exposure to air, was the subject of an in-depth study by Achour et al. [44]; using high-resolution XPS spectra for Ti 2p and N 1s showed the presence of such chemical species as TiN, TiO₂, Ti₂O₃, and β-N, as well as some poorly defined chemical structures that were indicated to be oxynitride (TiN_xO_y) and nitrogen–oxygen (NO_x, NO, or NO₂). A treatment with oxalic acid was suggested to remove this layer [45].

In this work, we investigated the dissolution of this oxynitride layer on the TiN surface in detail and found the experimental conditions required to remove it completely without damage to the TiN. Then, the pretreated TiN surfaces were used for the deposition of various types of polymers using electrochemical polymerization or layer-by-layer deposition.

2. Materials and Methods

2.1. Materials and Instrumentation

Oxalic acid (98%), aniline, N-methylaniline, pyrrol, thiophene, 3-thienylboronic acid, boron trifluoride diethyletherate (BFEE), 2,6-di-tert-butylpyridine (DTBP), tetrabutylammonium hexafluorophosphate, 20% aqueous solutions of poly(diallyldimethylammonium chloride) (PDDA) with a molecular weight of ~200–350 kDa and poly(allylamine hydrochloride) (PAH) with a molecular weight of 15 kDa, potassium chloride ($\geq 99\%$), potassium hexacyanoferrate II trihydrate ($\geq 99\%$), and potassium hexacyanoferrate III (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA); 50% aqueous solution of poly(acrylic acid) (PAA) with a molecular weight of ~3–5 kDa was from Thermo Scientific (Waltham, MA, USA), and acetonitrile (can) was from Honeywell (Charlotte, NC, USA). All chemicals were used without further purification. All solutions were prepared with deionized water additionally purified by the ELGA-Classic system.

TiN electrodes fabricated by sputtering in argon plasma on silicon plates with dimensions of 30 mm $\times$ 8 mm were generously provided by IHP GmbH (Frankfurt (Oder), Germany). The thickness of the TiN film is ~100 nm; according to [46], the deposition technology used leads to the film growing as a columnar structure.

A conventional three-electrode glass cell was used for the electrochemical experiments. The characterization of the LbL films was performed using a platinum wire 0.25 mm in diameter as the auxiliary electrode, an Ag/AgCl (sat. KCl) electrode with a double salt bridge (Metrohm, Herisau, Switzerland) as the reference electrode, and a PC-controlled Autolab PGstat12 equipped with a FRA32 impedance module and controlled by NOVA 2.1.5 software (Metrohm). The electrochemical polymerization of conducting polymers was performed using the Palm Sens Em Stat³ electrochemical interface, a carbon counter electrode, and a silver chloride reference electrode (Ag/AgCl, sat. KCl in water for aqueous solutions or Ag/AgCl 2M LiCl in ethanol for non-aqueous solutions). All the experiments were performed at room temperature. The potential values are indicated relative to the corresponding reference electrodes.

Optical characterization was performed by spectroscopic ellipsometry using SEN-research 4.0 (SER 850-NIRE, spectral range 190–3500 nm) from SENTECH Instruments GmbH (Berlin, Germany) at three different angles of incidence (60°, 65°, and 70°) for the wavelength range 400 nm $\leq \lambda \leq$ 1700 nm. The values of the complex refractive index were extracted using the software jreftran_rt.m, version 2.1 (Photonics Group ETH Zürich, Zürich, Switzerland) to fit the raw data [47]. For this fit, the optical properties of the TiN layer were taken from previous measurements of the sputtered material [34,48].

2.2. Procedures

Prior to modification, the electrodes were cleaned to remove the insulating layer on the TiN surface by treatment with a freshly prepared solution of 8% oxalic acid. Pyrrol, polyaniline, and thiophene, as well as the derivatives of the latter two, were selected as examples of conducting polymers. The electrochemical synthesis of the conducting polymers was performed by potential cycling at a scan rate of 100 mV/s from either aqueous (polyaniline and its derivative) or organic (polypyrrole, polythiophene, and its derivative) solutions. The scan rate used corresponds to the optimal one for PANI deposition on complex substrates [49] and has been used in many publications for various polymers and electrodes. The solutions used and the potential range are summarized in Table 1. The electrode potentials in this table are indicated relative to the Ag/AgCl reference electrodes described above.

Table 1. Conditions for electrochemical synthesis of conducting polymers.

Polymer	Monomer Concentration	Electrolyte	Potential Range/Number of Cycles
Polyaniline	50 mM aniline	0.5 M H ₂ SO ₄	−0.3~+1.0 V/15 cycles
Poly-N-methylaniline	100 mM N-methylaniline	2 M HClO ₄	−0.3~+0.85 V/10 cycles
Poly-pyrrole	100 mM pyrrole	ACN, 100 mM NBu ₄ PF ₆	−0.2~+1.1 V/7 cycles
Polythiophene	50 mM thiophene	90% BFEE/10% ACN (<i>v/v</i>), 50 mM DTBP	−0.2~+1.8 V/14 cycles
Poly-3-thienylboronic acid	50 mM 3-thienylboronic acid	90% BFEE/10% ACN (<i>v/v</i>), 50 mM, DTBP	−0.2~+1.8 V/14 cycles

LbL deposition was performed by successive immersions of the oxalic acid-treated TiN electrode in solutions of 1 g/L of cationic (either PDDA or PAH) or anionic (PAA) polymers at pH 7.0 (adjusted with either 1 M HCl or 1 M NaOH) for 5 min with continuous stirring. Between immersions in the polymer solutions, the electrode was washed by three immersions in a large volume of pure water. The total number of individual polymer layers varied from 1 to 15. The electrochemical characterization of the synthesized films of conducting polymers was performed by cyclic voltammetry in the same electrolyte that was used for polymerization, but without monomers. Electrochemical characterization of LbL films was performed by cyclic voltammetry or impedance spectroscopy in the presence of 1 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] using 1 M KCl as a supporting electrolyte. Three successive scans were performed for each CV experiment. EIS measurements were performed in the frequency range from 10 kHz to 100 mHz.

3. Results and Discussion

3.1. The Removal of the Insulating Layer from the TiN Surface

Electrochemical deposition on the TiN surface requires the pretreatment of this surface to remove the insulating layer. Electrical access to the surface is also required for the electrochemical characterization of polymer layers that are deposited by non-electrochemical techniques. Therefore, the first part of the current study was the removal of the oxide layer. Several approaches have been proposed for this purpose [50,51]. Iniesta et al. [45] proposed the use of sandblasting, etching in boiling 15% oxalic acid (OA) (for 60 min), and subsequent immersion in concentrated (96%) sulfuric acid before a final rinse with deionized water. After a brief comparative test of different techniques, this approach was selected for further investigation and subsequent implementation in our work. The goal was to find the conditions to remove the oxide layer while keeping the 100 nm TiN film intact. Since sandblasting can cause some scratches on the TiN film, and concentrated sulfuric acid may react with titanium, these two steps were excluded from our procedure. Therefore, the TiN surface treatment was performed using an aqueous solution of 8% OA. The treatment time was extended and optimized. The process was studied at temperatures of 308, 328, 348, and 373 K.

CV monitoring of the OA treatment (the first scan) is shown in Figure 1 and in Figures S1–S3 in the Supplementary Information (SI). In comparison with such measurements using bare gold or platinum electrodes, the CVs before treatment (Figures 1 and S1–S3, black curves) also showed the oxidation and reduction peaks of ferri/ferrocyanide, but these signals were not well pronounced: the peak magnitudes were low, while the potential gap between these peaks was relatively wide. This indicates some hindrances in the electron transfer, which can be attributed to the presence of the insulating layer on the TiN surface. Oxalic acid treatment resulted in dramatic changes in CV (Figures 1 and S1–S3). As the treatment progressed, the currents of the oxidation and reduction peaks increased, while the potential gap between these peaks decreased. According to [52,53], this can be considered a measure of the resistance of the insulating layer. Therefore, the decrease in the gap indicates

the gradual removal of the insulating layer, which provides a better availability of TiN for electrochemical reactions with dissolved species.

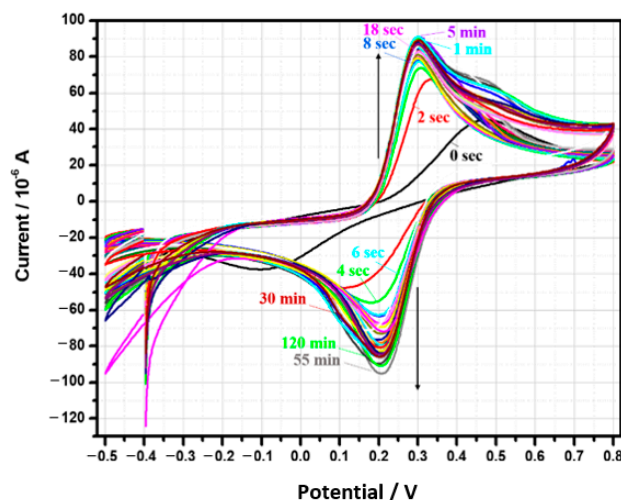


Figure 1. Cyclic voltammetry of the TiN electrode before and during treatment with 8% oxalic acid at 373 K measured at a scan rate of 50 mV/s in 1 M KCl electrolyte containing 1 mM $K_4[Fe(CN)_6]$. The duration of the oxalic acid treatment between measurements was 2 s during the first minute of the treatment, 5 min during the first hour, and 15 min during the second hour. The time indicated on the CVs in the figure corresponds to the duration of OA treatment. The arrows indicate the main direction of the current change in subsequent measurements without consideration of the fluctuations shown in Figure 2.

The evolution of the electrochemical parameters (oxidation current (I_{ox}), reduction current (I_{red}), and potential gap (ΔE)) extracted from the CV curves for different treatment times is shown in Figure 2. Such data obtained at other treatment temperatures are shown in Figures S4–S6 in the SI. In all curves, we observed an increase in the absolute values of the peak currents and a simultaneous decrease in ΔE over some characteristic time, after which these values did not change. This characteristic time (t_0) characterizes the time required for oxide removal. To estimate t_0 , the curves were fitted by the exponential function $A_0 + Ae^{-t/t_0}$ for $\Delta E(t)$ or by $A_0 + A(1 - e^{-t/t_0})$ for $I_{ox}(t)$ and $-I_{red}(t)$, where the values A and A_0 are some constants, while A characterizes the maximal magnitude of the parameter changes. The value $1/t_0$ characterizes the reaction rate of oxide removal at a given temperature. At 373 K, fitting was performed only for the first minute because t_0 was estimated to be very low (Figure 2). At 348 and 328 K, fitting was performed for the first 10 min (Figures S4 and S5). At 308 K, fitting was performed for the whole treatment time (Figure S6). The results show that the temperature increase leads to a faster removal of the oxide layer. However, too long a treatment leads to the partial or complete removal of the TiN layer. This can be detected as an increase in the gap caused by an increase in the ohmic drop. Further treatment resulted in the complete loss of electrochemical activity.

The obtained values of the reaction rate ($1/t_0$) are shown in Figure 3 in the Arrhenius plot. The slope corresponds to the activation of energy of 62 ± 8 kJ/mol (Figure 3). This value is similar to that obtained for the dissolution of various oxides in acidic media, such as the dissolution of CuO in citric acid (69.9 kJ/mol) [54], cobalt oxides in sulfuric acid (70 kJ/mol) and EDTA (60 kJ/mol) [55], and cerium oxides in nitric acid (60–85 kJ/mol) [56].

The kinetics of the removal of the oxide layer from the TiN surface were also obtained from impedance spectroscopy. The measurements were performed in 1 M KCl in the frequency range of 100 mHz–10 kHz before treatment and after treatment in 8% oxalic acid at 373 K for 1 min, 1 h, and 4 h (Figures 4 and S7). The obtained Bode plots of the impedance spectra were fitted by an equivalent circuit (Figure 4, inset) consisting of a series-connected resistor R and capacitor C . The results indicate a monotonous increase in capacitance during the treatment. However, a quantitative analysis of these data was complicated by some slow

process with characteristic time of tens of minutes. According to cyclic voltammetry, the characteristic time of the oxide removal at 373 K is on the time scale of seconds; therefore, one can expect complete removal within 1 min of treatment. At the same time, during the first minute, the specific capacitance (calculated under the assumption that the electrode surface area is equal to its geometrical area) was increased from 32 ± 2 to $49 \pm 2 \mu\text{F}/\text{cm}^2$. The measured capacitance includes the serially connected capacitance of the insulating oxide layer C_{ol} and the electrical double layer (C_{dl}). Considering that $\frac{1}{C} = \frac{1}{C_{dl}} + \frac{1}{C_{ol}}$ and assuming that the oxide layer was completely removed after 1 min of treatment, the value of $49 \pm 2 \mu\text{F}/\text{cm}^2$ can be considered the capacitance of the electrical double layer, while the capacitance of the oxide layer can be estimated to be $92 \pm 2 \mu\text{F}/\text{cm}^2$. The values of the dielectric permittivity of the oxide layer are expected to be close to those of titanium oxide or titanium oxynitride. In the literature, values of 95 [57], 50 [58], and 80–100 [59] have been reported for titanium oxide, while values of 30 [60] and 28–80 [61] have been reported for titanium oxynitride. Assuming that the dielectric permittivity of the studied oxide layer on the TiN surface is ~ 50 , we find that the thickness of this layer is $\sim 0.5 \text{ nm}$.

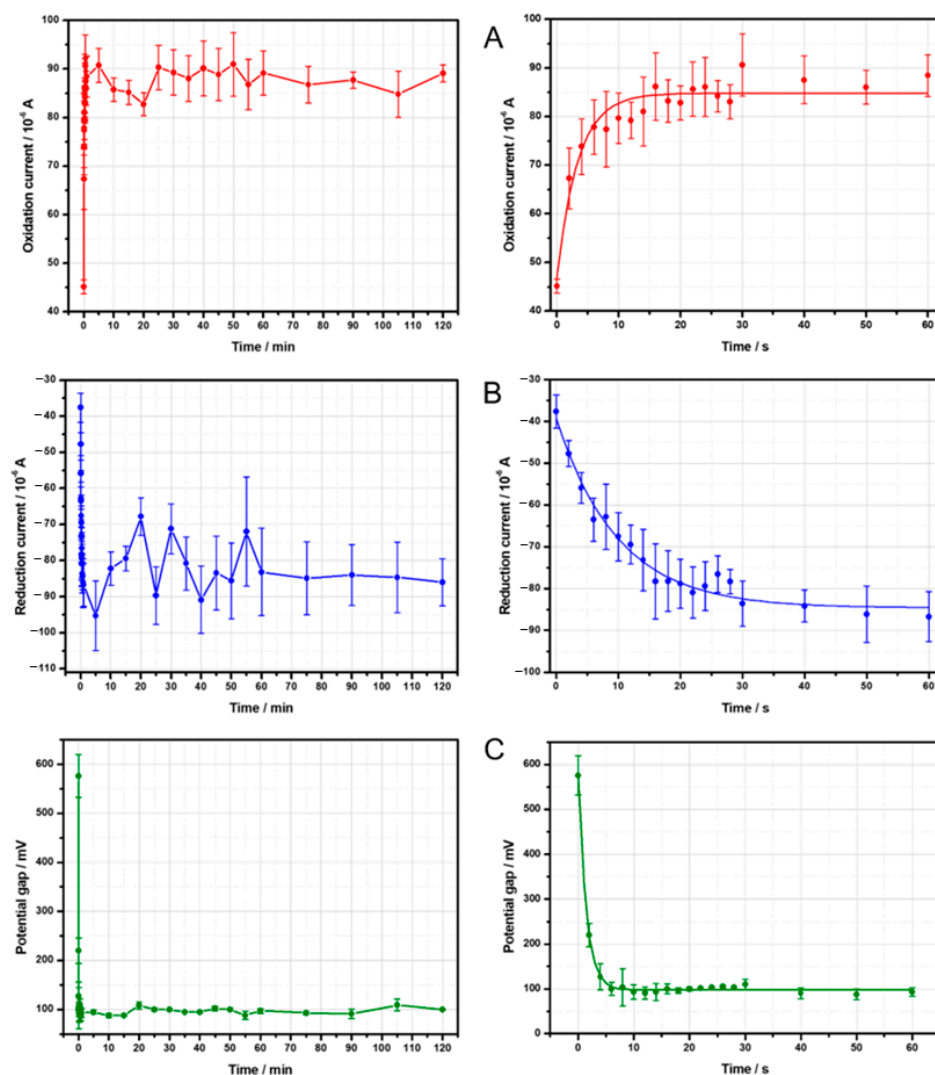


Figure 2. Dependencies of I_{ox} (A, red curves), I_{red} (B, blue curves), and ΔE (C, green curves) extracted from the cyclic voltammetric curves indicated in Figure 1 on the duration of oxalic acid treatment at 373 K for 2 h (left panels) and in the first minute (right panels). Curves in the right panels show exponential fitting performed to obtain the corresponding values of t_0 .

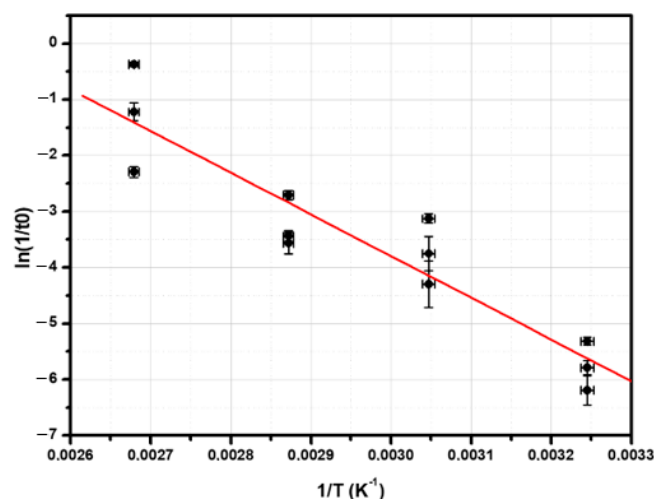


Figure 3. Arrhenius plots of the reaction rates estimated as $1/t_0$ for I_{ox} , I_{red} , and ΔE measured at different temperatures.

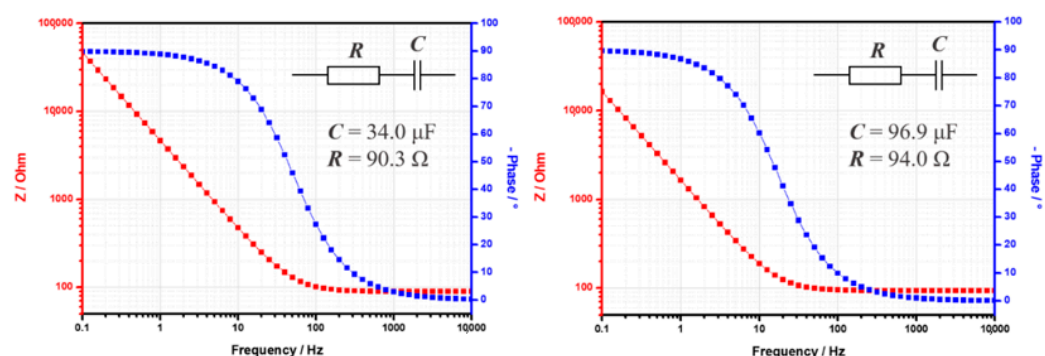


Figure 4. Impedance spectra of TiN electrodes measured before (**left**) and after (**right**) 4 h treatment in 8% oxalic acid at 373 K in 1 M KCl and the fitting of these spectra by a serially connected resistor and capacitor. The data for other treatment times are indicated in Figure S7.

3.2. Layer-by-Layer Deposition of Polyelectrolytes

LbL deposition is an electrostatically driven adsorption process, and the selection of the first polymer (either cationic or anionic) depends on the sign of the surface charge. To determine the sign of the surface charge, the effect of polymer adsorption on cyclic voltammetry in the presence of potassium ferri/ferrocyanide was studied. The results are shown in Figure S8. The cyclic voltammogram recorded on the TiN electrode after incubation in PDDA solution showed no change in the signal corresponding to the oxidation/reduction of ferri/ferrocyanide. However, a decrease in the oxidation and reduction peak currents and an increase in the potential gap between these peaks are observed for the TiN electrode after incubation in PAA solution, which proves that PAA was adsorbed on the TiN surface. Considering that the redox-active compound is present in the anionic form, these data indicate that the TiN surface is positively charged. This conclusion contradicts the polarity of the ζ -potential of TiN nanoparticles reported in [14,62,63], but the discrepancy can be explained by the influence of the oxide layer on the surface charge of these nanoparticles: hydrated surface oxides can be deprotonated, forming a negative surface charge. Therefore, the first polymer layer to be electrostatically deposited on the positively charged surface of the OA-treated TiN should be negatively charged, and in our case, it is PAA.

The process of LbL deposition of polymers was monitored electrochemically by CV and EIS analysis after each deposited polymer layer. Figure 5 shows the evolution of cyclic voltammograms and impedance spectra during the deposition of PAA and PDDA.

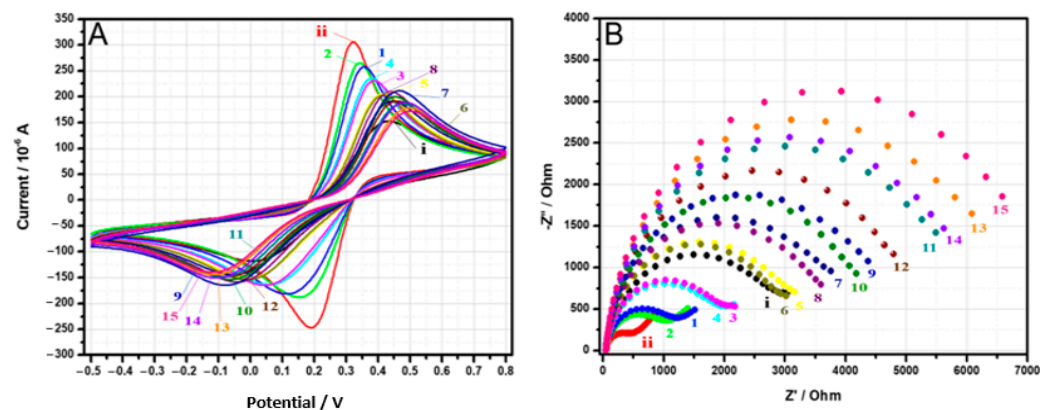


Figure 5. Cyclic voltammetry (A) and impedance spectra (B) measured in the electrolyte containing 1 M KCl, 1 mM $K_3[Fe(CN)_6]$, and 1 mM $K_4[Fe(CN)_6]^-$ with the untreated TiN electrode (curve i), after 1 min cleaning in 8% oxalic acid at 373 K (curve ii), and after the deposition of each polymer layer (either PAA or PDDA, curves 1–15, where the number indicates the number of polymer layers). The colors of the curves in (B) correspond to those in (A).

Consider the dependence of the values of I_{ox} , I_{red} , E_{ox} , E_{red} , and ΔE on the number of polymer layers deposited (Figures 6 and S11, red curves). A decrease in the magnitudes of the oxidation and reduction peak currents and an increase in the potential gap between these peaks can be observed with each deposited bilayer of PAA and PDDA (Figures 6 and S11, red curves). However, a consideration of the changes between each deposited polymer layer demonstrates systematic fluctuations in all these values. These fluctuations show the influence of the outer layer on the electrochemical reaction. When the outer layer is formed by the positively charged polymer (PDDA), the surface concentration of the negatively charged redox-active species ($[Fe(CN)_6]^{3-/4-}$) increases due to electrostatic attraction, leading to an increase in the electrochemical reaction rate. Conversely, when the outer layer is formed by the negatively charged polymer (PAA), the surface concentration of the negatively charged redox-active species decreases due to electrostatic repulsion, resulting in a decrease in the electrochemical reaction rate.

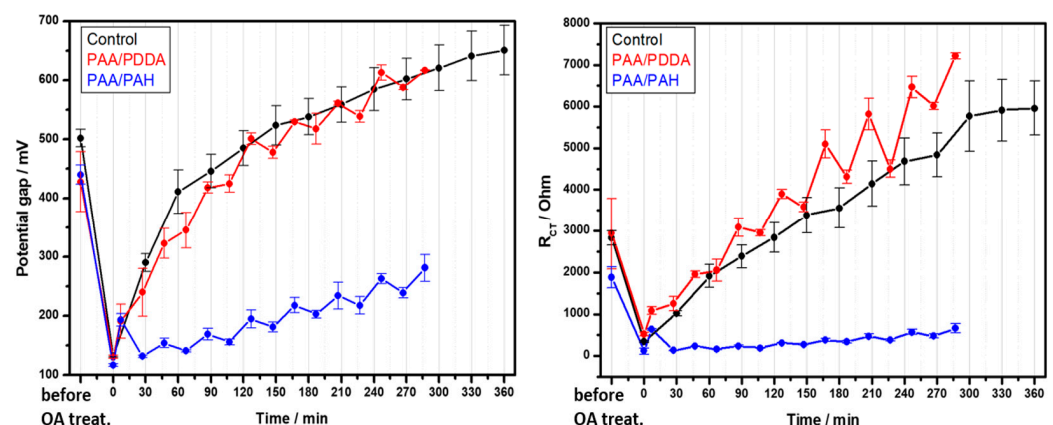


Figure 6. Dependence of ΔE (left) and R_{CT} (right) before, after 1 min cleaning in 8% oxalic acid at 373 K, and after each incubation of the TiN electrode in the polymer solution. Red curves correspond to incubation in PAA and PDDA solutions. Blue curves correspond to incubation in PAA and PAH solutions. Black curves correspond to the control experiment characterizing the evolution of the corresponding electrochemical parameters during the exposure of OA-treated electrodes to air.

The same effect of systematic fluctuations in the dependence on the number of polymer layers deposited, as well as the monotonic increase with the number of polymer bilayers deposited, is observed for the resistance of charge transfer (R_{CT}) extracted from

the impedance spectra (Figure 6, right panel, red curve). These values were estimated by fitting the spectra in Figure 5B using a Randles equivalent circuit.

A very similar dependence of I_{ox} , I_{red} , E_{ox} , E_{red} , ΔE , and R_{CT} is observed for the deposition of PAA and PAH (Figures 6 and S11, blue curves). The data were extracted from the CV and impedance spectra shown in Figure S10. Also, for this polymer film, it is possible to observe systematic fluctuations in these parameters indicating the alteration of the surface charge, but the monotonic changes with each deposited bilayer are lower.

One can also try to attribute the observed systematic increase in the studied values characterizing the blocking of the electrochemical reaction to the formation of the polymer layer, but such an explanation attempt requires the exclusion of the possible reformation of the oxide layer during the experiment. For this purpose, both CVs and impedance spectra were measured on the OA-treated TiN electrodes during the typical deposition time of 15 polymer layers (~6 h) with an interval of 30 min between the measurements (Figure S9). The evolution of the electrochemical characteristics (Figures 6 and S11, black curve) was found to be very similar to that of the PAA/PDDA films (red curve). This may indicate the significant contribution of TiN oxidation during the experiment. This conclusion allows one to suggest that the PAA/PAH polymer film can prevent such oxidation of TiN, and this may lead to lower monotonic changes in the studied electrochemical values with each deposited polymer bilayer (Figures 6 and S11).

Finally, although the systematic increase in the blocking of the electrochemical reaction of ferri/ferrocyanide oxidation/reduction does not allow a definite conclusion on the polymer deposition, the systematic fluctuations in these parameters clearly indicate the alternations of the surface charge, thus proving the polymer deposition.

After several months of storage at room temperature in ambient air, the samples prepared by LbL deposition exhibited no signs of damage or detachment of the polymer layer.

Being motivated by the possible application of the PAA/PAH bilayers as surface functionalization for optical biosensors using TiN-based plasmonic structures [34,48], we also performed measurements of the complex refractive index of the material in the wavelength range of $400 \text{ nm} \leq \lambda \leq 1700 \text{ nm}$ (Figure 7).

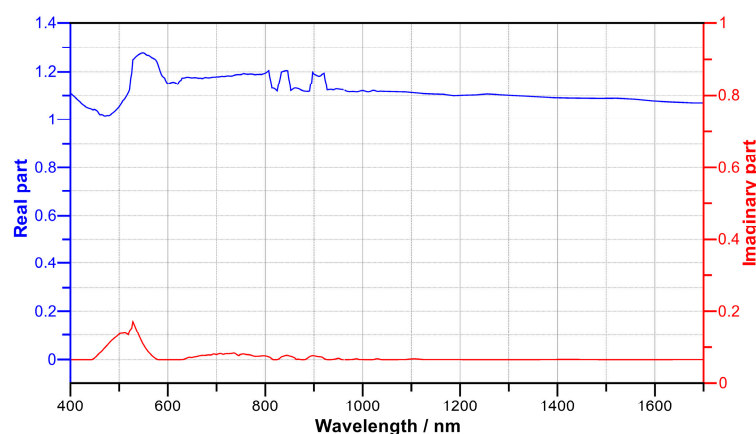


Figure 7. The real and imaginary parts of the complex refractive index of the LbL-fabricated PAA/PAH bilayers on a 100 nm TiN layer.

The thickness of the polymer layer extracted from the fit is 10 nm. The real part of the refractive index is approximately constant at wavelengths above 950 nm but shows a wavelength dependence at wavelengths between 400 and 600 nm, indicating the presence of resonant absorption processes. A possible explanation for the oscillations in the real part of the permittivity at wavelengths between 800 and 950 nm is increased noise resulting from scattering off the micropores in the film at these wavelengths. Furthermore, as can be seen from the imaginary part of the complex refractive index, the absorption in the material is very low above 950 nm, making the PAA/PAH bilayer suitable as dielectric surface functionalization for possible application in SPR sensing. Finally, we note that the

real part of the refractive index is within the range reported in [64]. While higher values have also been reported for selected wavelengths [65,66], on the one hand, we report on the complex refractive index over a wavelength range rather than at a constant wavelength. On the other hand, the real part of the refractive index has been shown to depend on the pH conditions during deposition [64].

3.3. In Situ Electrochemical Synthesis of Conducting Polymers

The electrochemical synthesis of several polymers belonging to different classes of conducting polymers and their derivatives was investigated on the TiN surface: polyaniline and N-methylaniline, polypyrrole, polythiophene, and poly-3-thienylboronic acid. Some polymers require the deposition of an adhesive layer for the adsorption of the synthesized polymer on the surface. For example, the deposition of a sublayer of 4-aminothiophenol was important for the strong binding of poly-N-methylaniline to a gold electrode [67]. However, the study of the formation of all the aforementioned conducting polymers on the surface of the oxalic acid-treated surface of TiN has shown that the adhesion of all the polymers is rather strong, and no adhesive layer is required. The process of electrochemical polymerization on the TiN surface and the subsequent electrochemical activity of the deposited polymers confirm an effective charge transfer through the oxalic acid-treated TiN surface.

Figure 8A shows cyclic voltammograms obtained during the electrochemical polymerization of aniline. The curves are very similar to the cyclic voltammetric curves obtained for the polymerization of aniline on gold [68] and platinum [69] electrodes. It is possible to observe permanently growing characteristic peaks corresponding to the electrochemical activity of the formed polymer, as well as a peak in the anodic region related to the formation of cation radicals of aniline. The origin of these peaks has been discussed in detail previously [70]. Cyclic voltammetry in the same electrolyte without aniline (Figure 8B) shows the same curve but without this anodic peak. The shape of this curve and the good reversibility of oxidation/reduction (the ratio of oxidation to reduction charge is 1.02) are also typical for polyaniline electrochemically synthesized on gold or platinum surfaces [71,72]. The polymer film can be observed visually; increasing the number of cycles to 15 leads to the formation of films with the typical green color of polyaniline. Similar results were obtained by potentiostatic polymerization of aniline at +0.9 V.

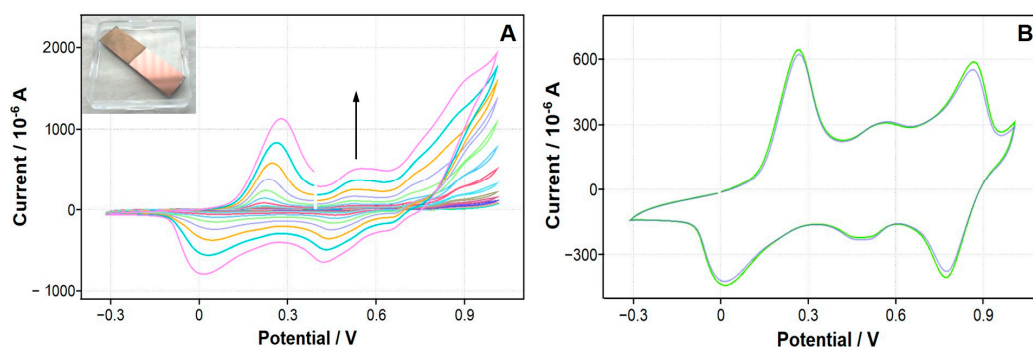


Figure 8. Cyclic voltammograms during the electrochemical synthesis of polyaniline from a 50 mM aniline solution in a 0.5M H₂SO₄ solution (A) and in the same electrolyte without monomers (B). Sweep rate: 100 mV/s; number of polymerization cycles: 15. The arrow indicates the current increase during polymer deposition. Different colors of cyclic voltammograms during polymer deposition in this and subsequent figures were used to separate individual cycles.

Similar results for the electrochemical polymerization of N-methylaniline are shown in Figure 9A. In our work [67], mostly homogeneous films of this polymer on a gold surface were formed when perchlorate was used as the counter ion; therefore, the deposition of poly-N-methylaniline on the TiN surface was performed from perchlorate. Again, the shape of the cyclic voltammetric curve during electrochemical polymerization was very similar to

that obtained on the metallic surfaces [73]. The cyclic voltammograms of the electrodes with deposited polymers measured in the same electrolyte without N-methylaniline showed good reversibility of oxidation/reduction: the ratio of the oxidation to the reduction charge was 0.84. The shape of the curve after polymer deposition was similar to that during the process of electrochemical polymerization, except for the absence of the anodic peak corresponding to the formation of the radical cation [74]. Qualitatively similar results have been reported for platinum and glassy carbon disk electrodes [73,75,76]. Some differences in the gap between oxidation and reduction peaks and the exact peak potentials can be attributed to the partial reformation of the oxide layer on the TiN surface and the influence of anions.

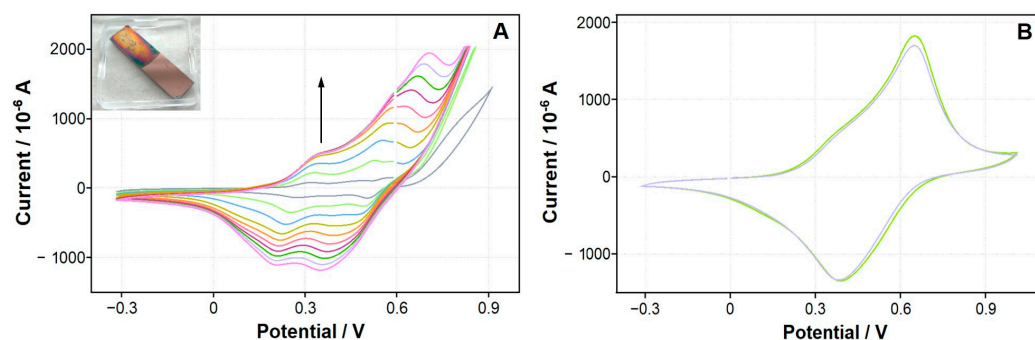


Figure 9. Cyclic voltammograms during the electrochemical synthesis of poly-N-methylaniline from a 100 mM N-methylaniline solution in a 2 M HClO_4 solution (A) and of the deposited layer in the same electrolyte without monomers (B). Sweep rate: 100 mV/s; number of polymerization cycles: 10. The arrow indicates a current increase during polymer deposition.

Polypyrrole belongs to another widely used class of conducting polymers. It has been reported that the use of aprotic solvents is preferable for electrochemical pyrrole polymerization [77]. In our work, electropolymerization was performed from a 0.1 M pyrrole solution in acetonitrile containing 100 mM of NBu_4PF_6 as an organic salt, dissociating into hydrophobic ions and 1% (v/v) water [78]. Potential cycling between -0.6 and $+1.2$ V leads to the formation of dark films on the electrode. One can also observe a permanent increase in the current during polymer growth (Figure 10A). However, its electrochemical activity is more pronounced in the cyclic voltammetry of deposited films, which was performed in the same electrolyte but without pyrrole (Figure 10B). The shape of the curve is similar to the literature data obtained for electrochemical polymerization on metallic electrodes [78]. The potentiostatic electrochemical polymerization of pyrrole on the TiN surface was performed from the same solution at $+1.1$ V.

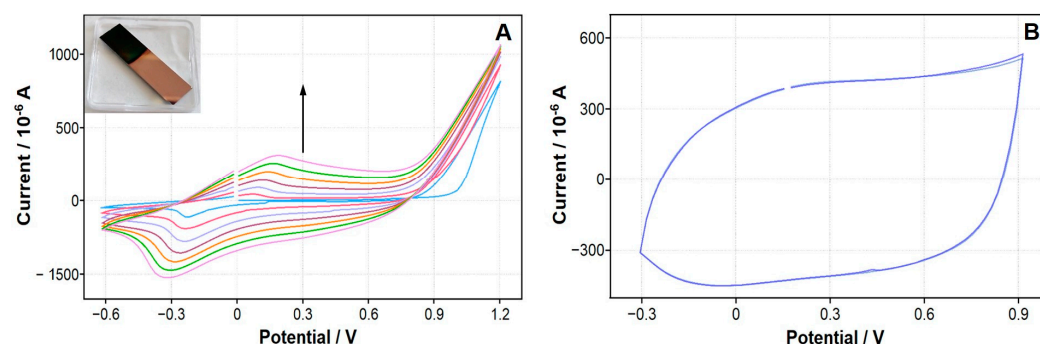


Figure 10. Cyclic voltammograms during the electrochemical synthesis of polypyrrole from a 0.1 M pyrrole solution in acetonitrile containing 100 mM of NBu_4PF_6 and 1% (v/v) water (A) and of the deposited layer in the same electrolyte without pyrrole (B). Sweep rate: 100 mV/s; number of polymerization cycles: 7. The arrow indicates a current increase during polymer deposition.

According to the literature, high-quality polythiophene (PTh) films can be formed by electropolymerization in an organic electrolyte containing 90% BFEE and 10% ACN [79]. ACN is required to increase the solubility of the thiophene monomers. Recently, we optimized the polymer deposition by introducing 0.05 M DTBP into the polymerization mixture [80]; this compound acts as a dehydrating agent. Figure 11A shows cyclic voltammograms during the formation of the PTh film on the TiN electrode. The curves correspond to the literature data obtained for the electrochemical formation of PTh on gold [79] and platinum [81] electrodes. Cyclic voltammetry measured after polymerization in the same solution but without monomers shows the same broad peaks of oxidation (+1.3 V) and reduction (+0.3 V), but without the anodic peak related to the formation of cation radicals during electropolymerization (Figure 11B). A comparison of the polymerization charge and the charge of the oxidation or reduction peaks gives an electrochemical yield of the film deposition of 70%.

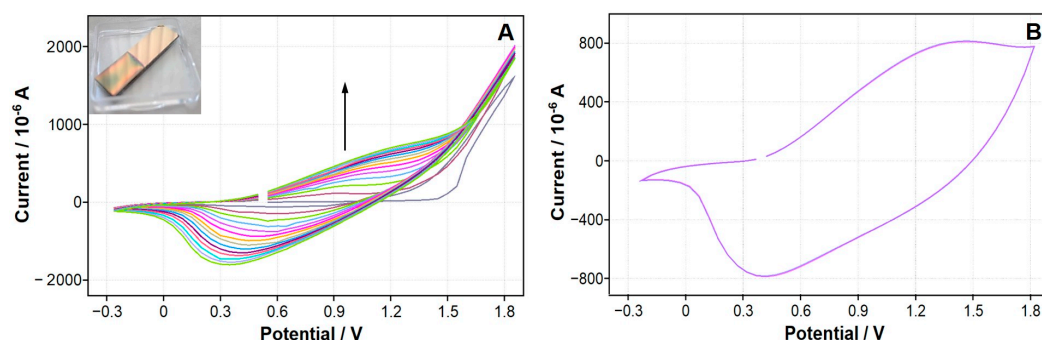


Figure 11. Cyclic voltammograms during the electrochemical synthesis of polythiophene from a 50 mM thiophene solution in the mixture of 90% BFEE and 10% ACN containing 0.05 M DTBP (A) and of the deposited films in the same electrolyte without monomers (B). Sweep rate: 100 mV/s; number of polymerization cycles: 14. The arrow indicates a current increase during polymer deposition.

Poly-3-thienylboronic acid is a new conducting polymer; its synthesis and preliminary characterization were reported in [80]. This polymer has the same backbone as polythiophene, but it is functionalized by the incorporation of a chemosensitive group—boronic acid. This group has an affinity to saccharides and other diol-containing compounds [82]. The chemosensitive properties of its monomer are described in [83]. According to [80], the best films of this polymer on ITO and gold were formed using an electrolyte consisting of a mixture of 90% BFEE and 10% ACN containing 0.05 M DTBP; the same electrolyte was used in the present work. The voltammetric curves obtained during electrochemical polymerization (Figure 12A) and cyclic voltammetry after polymer deposition (Figure 12B) are very similar to those for polythiophene (Figure 11B); therefore, the presence of the boronic acid moiety has only a minor influence on the electrochemical activity of the monomer and polymer. A strong electrochromic effect was observed during potential cycling: the polymer color was changed at potentials above +0.7 V, where the red polymer film became blue. The electropolymerization of PTBA in the potentiostatic mode was performed in the same solution at +1.5 V.

The electrochemical synthesis of conducting polymers in the potentiodynamic mode usually results in more homogeneous polymer films than in the potentiostatic mode [84]. However, the use of the potentiostatic mode provides a direct possibility to measure the polymerization charge. By comparing this value with the electrochemical activity of the deposited polymers and assuming that the entire deposited polymer is electrochemically active, one can obtain the yield of the electrochemical reaction. The charge consumed during polymerization Q_{polym} consists of two parts: the oxidation of the polymer and the formation of cation radicals. The first part depends on the initial and final states of the polymer and is less than 0.5 electrons per monomer (doping level) for a highly conductive polymer state. The second part is 2 electrons per monomer. The oxidation charge after polymerization Q_{ox} can be assumed to be close to the first component. Therefore, the

deposition efficiency (the part of the formed polymer that is adsorbed on the electrode surface) can be estimated as $5 \cdot Q_{ox} / Q_{polym}$ for the doping level of the oxidized state of 0.5 or $9 \cdot Q_{ox} / Q_{polym}$ for the doping level of 0.25. The values of the obtained deposition efficiency are shown in Table 2. These values are close to the literature data on the electrochemical deposition of different conducting polymers, which vary from 15% [85,86] to more than 50% [87].

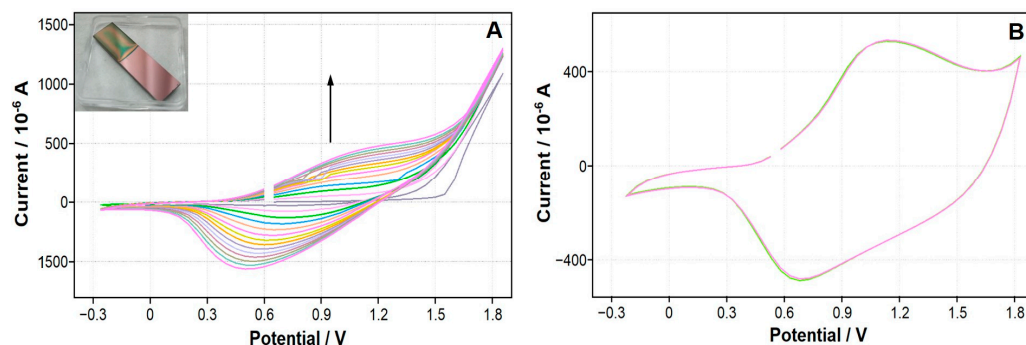


Figure 12. Cyclic voltammograms during the electrochemical synthesis of poly-3-thienylboronic acid from a 50 mM solution of 3-thienylboronic acid in a mixture of 90% BFEE and 10% ACN containing 0.05 M DTBP (A) and for the characterization of the deposited films in the same electrolyte without monomers (B). Sweep rate: 100 mV/s; number of polymerization cycles: 14. The arrow indicates the current increase during polymer deposition.

Table 2. The efficiency of electrochemical deposition of various conducting polymers on TiN in the potentiostatic mode. The data in this table were calculated for doping levels (at the highest anodic potential) of 25% and 50%, while the data indicated in the manuscript text correspond to a doping level of 25%.

Polymer	Q_{polym} , mC	Q_{ox} , mC	Deposition Efficiency, %, Calculated for the Doping Level 0.5	Deposition Efficiency, %, Calculated for the Doping Level 0.25
PANI	78.5	2.5	16	29
PNMA	41.1	3.82	47	84
PPy	54.7	5.7	52	94
PTh	43.9	3.41	39	70
PTBA	51.3	4.3	42	75

The samples synthesized by electrochemical polymerization also showed no signs of damage after several months of storage at room temperature in ambient air.

4. Conclusions

We have demonstrated the ability to deposit various polymeric films on the surface of TiN, which is considered important for different applications. The films of conducting polymers can be deposited by in situ electrochemical polymerization. This process requires an efficient electron transfer through the interface, so it is necessary to remove the insulating layer spontaneously formed on the TiN surface due to exposure to air. The removal can be performed by treatment with oxalic acid. The treatment conditions were optimized to achieve the complete removal of the insulating layer from the TiN surface without dissolving the TiN. The efficiency of the electrochemical deposition of all types of conducting polymers studied was close to that of the deposition on metallic electrodes. The second approach for coating the TiN surface with polymers is based on the electrostatically driven LbL deposition of oppositely charged polyelectrolytes. Both deposition methods allow one to control the thickness of the polymer layer: in electrochemical deposition, it is

performed by varying the polymerization charge, while in LbL deposition, it is controlled only by the number of deposition rounds. The LbL process can be easily automated to perform the deposition of tens of hundreds of monomolecular layers [88]. High adhesion of polymers to the TiN surface was observed, which makes it possible to achieve the formation of stable polymer films without the use of anchor sublayers. The obtained polymer films can be used as receptors or receptor-carried layers for the development of chemical sensors or in other technical applications.

Supplementary Materials: The supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings14020215/s1>.

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