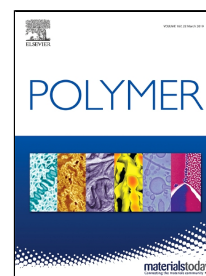# Accepted Manuscript

Comparative Study of Polyaniline (PANI), Poly(3,4-ethylenedioxythiophene) (PEDOT) and PANI-PEDOT Films Electrodeposited on Transparent Indium Thin Oxide based Electrodes

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Comparative Study of Polyaniline (PANI), Poly(3,4-ethylenedioxythiophene) (PEDOT) and PANI-PEDOT Films Electrodeposited on Transparent Indium Thin Oxide based Electrodes

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Abstract

Polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT) and PANI-PEDOT composite films were electrochemically deposited by potential cycling on indium tin oxide (ITO) modified glass slide (glass/ITO) from a water-based solution. PANI-PEDOT, PANI and PEDOT films were characterized and compared using atomic force microscopy, scanning electron microscopy, electrochemical methods, optical techniques and Raman spectroscopy. Synthesis of PANI in the presence of EDOT allowed to improve conductivity of the deposited film. A charge diffusion coefficient of PANI and PANI-PEDOT films was estimated to be 4.7×10^{-10} and 2.1×10^{-8} cm^2 s^{-1}. PEDOT, PANI and PANI-PEDOT (aniline and EDOT monomers ratio 20:1) conductivity values calculated from electrochemical impedance spectroscopy measurements were equal to 1.8×10^{-6}, 2.3×10^{-9} and 3.3×10^{-7} S m^{-1}, respectively. The position of absorption peaks maximum of PANI-PEDOT film can be controlled by changing the concentration ratio of aniline and EDOT. Absorption peaks at 602 and 895 nm tended to shift toward the shorter wavelength region when initial aniline concentration was reduced. The pH sensing capability of PANI-PEDOT film, which was based on changes in optical absorption spectra, was evaluated. Absorption at the maximum of the three peaks (448, 602 and 895 nm) of PANI-PEDOT film depended linearly on the solution pH value in the range from 3.8 to 7.4. Electrochemically deposited PANI-PEDOT film was 6.6 times thicker than PANI film (496 ± 14 *vs* 75 ± 2 nm) deposited under similar electrochemical conditions, but despite this the response time of PANI-PEDOT film was 6 times shorter. Therefore, glass/ITO/PANI-PEDOT structure could be applied in the design of pH sensors and/or some gas (e.g. CO_2 and/or NH_3) sensors.

Keywords: Polyaniline; Poly(3,4-ethylenedioxythiophene); Electrochemical deposition; Optical pH sensor.

1. Introduction

Conducting polymers (CPs) belong to an important class of organic materials, which is widely used in the fabrication of many devices such as transistors, biosensors and fuel cells [1-4]. Furthermore, some CPs possess unique electrochromic and electrochemical properties; thereby they are perfect candidates for designing smart windows, displays, optical sensors and electrochromic color-changing textiles [5-7].

Polyaniline (PANI) is one of the most studied and attractive conducting polymers. It is a perfect candidate for a broad spectrum of applications due to good electrical conductivity, simple synthesis, high environmental stability and optical properties [8-10]. The doping-dedoping process and oxidation-reduction reactions affect conductivity and optical properties of PANI, therefore PANI is suitable for the fabrication of sensitive sensors. For instance, sensors based on PANI film can be used for the detection of NH_3 [11, 12] and CO_2 [13] or solution pH [14]. In addition, some PANI nanostructures can improve sensing characteristics [15]. Optical pH sensors based on PANI can be used for the determination of pH in the range from 2 to 12 [16]. Sensing of pH can be performed using PANI dispersion in water [17] or a thin film of PANI can be deposited on a transparent substrate [18]. Moreover, PANI nanofibers deposited on channels of microfluidic devices were applied for optical pH determination [19].

One of polythiophene derivatives poly(3,4-ethylenedioxythiophene) (PEDOT) is a well-known conducting polymer. PEDOT is hydrophobic and not sensitive to pH changes [20]. Despite this fact, PEDOT was earlier employed in a design of potentiometric pH sensors for improvement of electrical signal transfer [20, 21]. Moreover, PEDOT: pH dyes based on organic electrochemical transistors were used for pH sensing [22]. PEDOT possesses good thermoelectric properties. ZT values of PEDOT and its composites with nanostructures, organic and inorganic materials can reach up to 1 [23, 24] which is comparable to older generation inorganic thermoelectric devices. PEDOT is highly conductive (*ca*. 300 S/cm^{-1}), stable in the oxidized state and features electrochromic properties in visible and infrared regions [25, 26]. PEDOT is one of the most widely used CPs for the practical applications and is often used doped with poly(styrene sulfonate) (PSS) [27].

A new application of CPs can be found by using various strategies for improvement of their specific properties. One of the ways is to nanoscalle CPs, which can have a significant impact for obtaining new or modifying existing properties of these polymers. Another way is based on the functionalization and doping of CPs. The incorporation of different (bio)molecules may allow to reach better biocompatibility, stability and mechanical properties of CPs [28]. Another possibility is to use CPs in composition with nanoparticles. Polymers are most commonly used as a matrix for the incorporation of other components such as carbon nanotubes, metallic nanoparticles or ceramic

nanostructures [29]. Likewise, nanocomposites consisting of two or more polymers can be employed for the formation of materials with desired properties. PANI nanocomposites with other polymers such as polyvinyl acetate, polymethyl methacrylate and polyvinyl alcohol have been reported [30].

PANI and PEDOT have been used together in a form of copolymer [31], hybrid layers and nanocomposite. Application of PANI and PEDOT in a form of hybrid layers improved electrochromic characteristics of individual polymers. The increase of contrast ratio, stability and faster switching between colored and bleached forms were observed [32, 33]. PANI nanofibers can be used as a template for the formation of PEDOT nanorods. PANI-PEDOT nanocomposite was successfully employed in the design of electrochemical sensor for the determination of ascorbic acid [34]. An improvement of thermoelectrical properties of PANI and PEDOT nanocomposite in comparison with PANI was demonstrated [35]. A possible joint utilization of PANI and PEDOT in the design of pH electrochemical microsystem sensor was shown [20].

In this work PANI-PEDOT film electrodeposited on a transparent indium tin oxide (ITO) modified glass (glass/ITO) from a water-based polymerization bulk solution was characterized and applied for pH sensing. Optical properties and optical response time of the developed PANI-PEDOT film-based sensor were compared with that of PANI film. In addition, film thickness, surface activity, charge density, conductivity and diffusion coefficient of PANI-PEDOT, PANI and PEDOT films formed on glass/ITO electrodes were calculated and compared.

2. Materials and methods

2.1. Materials

3,4-Ethylenedioxythiophene (EDOT), hydrogen peroxide, sodium chloride and glass/ITO slides (15-25 Ω cm^{-1}) were purchased from Sigma-Aldrich (Steinheim, Germany). Aniline (ANI), ortho-phosphoric acid and sodium dihydrogen phosphate monohydrate were bought from Fluka (Buchs, Switzerland). Sulfuric acid and ammonium hydroxide were obtained from Roth (Karlsruhe, Germany). Acetic acid and potassium chloride were purchased from Merck. Lithium perchlorate was bought from Alfa Aesar (Karlsruhe, Germany), acetone from LabScan and boric acid from Scharlab (Sentmenat, Spain). Aniline was distilled once before use. All aqueous solutions were prepared with deionized water (18 MΩ cm^{-1}).

2.2. Pre-treatment of glass/ITO slides

All electrochemical measurements were performed using a three-electrode cell and a potentiostat/galvanostat PGSTAT30-Autolab from ECO Chemie with GPES 4.9 software. Glass/ITO slide, which was cut to required size rectangles, was used as a working electrode. Platinum electrode served as a counter electrode and Ag/AgCl$_{(3M\ KCl)}$ electrode from CH Instruments was used as a reference electrode. Before the synthesis of polymers, glass/ITO slides were cleaned with acetone and then sequentially sonicated for 15 min in acetone and water. Additionally, glass/ITO slides were cleaned by potential cycling between 0 and +1 V in 50 mM PBS with 0.1 M KCl and rinsed with water.

2.3. Formation of PANI, PEDOT and PANI-PEDOT films

PANI, PEDOT and PANI-PEDOT polymer films were electrochemically deposited by potential cycling method using a three-electrode cell (Scheme 1). Electrochemical deposition was performed from the aqueous solution containing 0.2 M H$_2$SO$_4$, 0.1 M LiClO$_4$ as the supporting electrolyte and (i) 0.2 M aniline for the formation of PANI film, (ii) 0.01 M EDOT for the deposition of PEDOT film and (iii) different ratio of aniline and EDOT for the synthesis of PANI-PEDOT films. Voltage was swept between 0 to +1.1 V with the potential sweep rate of 50 mV s^{-1} for 10 cycles. After electrochemical deposition, the synthesized polymer films were gently rinsed with deionized water to remove the oligomers and inorganic salt from the surface of polymer film.
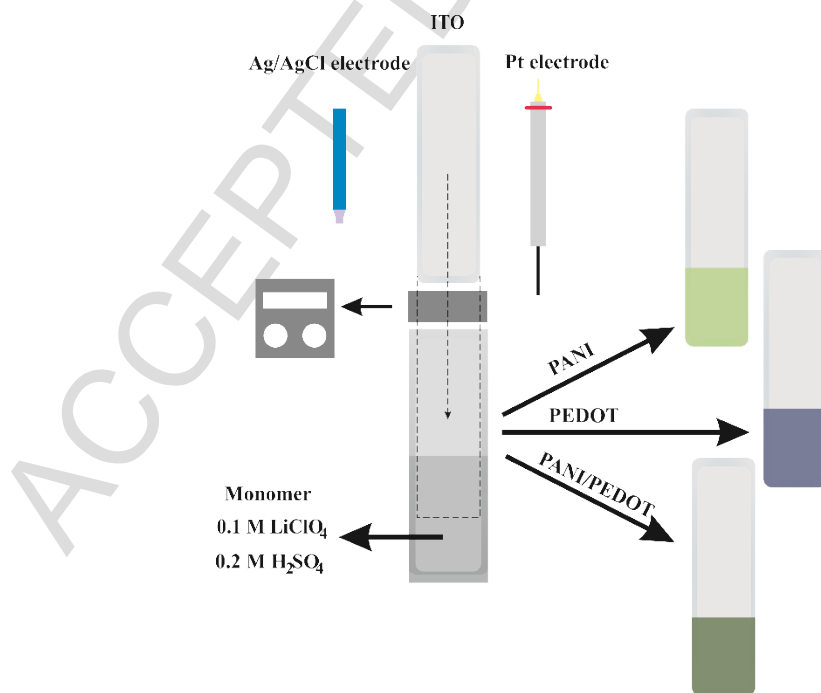
Scheme 1. Electrochemical deposition of polymer films on a transparent glass/ITO electrode.

2.4. DFT calculation methods

The structure of proposed copolymer was optimized by hybrid B3LYP functional and 6-31G(d,p) basis set followed by calculations of their harmonic vibrational frequencies to verify their stability. Vibration frequencies of the Raman spectrum were estimated by employing the suitable for IR spectra estimation EDF2 functional [36] and a 6-31G(d,p) basis set. Spartan'14 program (Spartan'14 for Windows, Version 1.1.2., 1840 Von Karman Avenue, Suite 370, Irvine, CA) in a gas phase at 298 K condition was carried out.

2.5. Characterization of PANI, PEDOT and PANI-PEDOT films

The morphology of PANI, PEDOT, PANI-PEDOT films was studied by using a high-resolution field emission scanning electron microscope SU-70 from Hitachi. The thickness of the electrochemically synthesized PANI, PEDOT and PANI-PEDOT films was evaluated by using atomic force microscope BioScope Catalyst from Bruker. Films synthesized on glass/ITO electrodes were firstly scratched by a soft plastic stick and later scanned in air by AFM in contact mode. A gold coated silicon nitride cantilever (spring constant 0.06 N m^{-1}, resonant frequency 24 kHz) was used for these measurements and surface area of 50×50 microns of each sample was scanned.

Evaluation of polymer films color was performed using Flame Spectrometer from Ocean Optics. Tungsten halogen light source HL 2000 was used as a light source. The angle of measurements was fixed at 45° by adjustment of reflection probe QR400-7-VIS-NIR in fixture for holding RPH-1. Calibration was done using white standard WS-1-SL. The CIELAB 1976 color space coordinates were used for evaluation of polymers film color. In this system, L* represents the lightness of a color, $L^* = 0$ for black and $L^* = 100$ for white colors. a* and b* parameters reflect the relative saturation of green $(-a^*)$/red $(+a^*)$ and blue $(-b^*)$/yellow $(+b^*)$ colors.

The composition of PANI, PEDOT and PANI-PEDOT films was determined using Raman spectrometer Alpha 300R from WITec. This spectrometer was equipped with 532 nm laser excitation source. Diffusion coefficients were calculated from data gathered by performing cyclic voltammetry using a three electrode cell where glass/ITO slide modified with a polymer film was used as the working electrode. Cyclic voltammetry was performed in 0.1 M LiClO$_4$ and 0.2 M H$_2$SO$_4$ solution. The lower and upper vertex potentials were 0 and +1 V respectively, while the potential sweep rate was varied from 30 mV s^{-1} to 250 mV s^{-1}.

The conductivity of polymer films was investigated by electrochemical impedance spectroscopy (EIS). The potentiostat/galvanostat PGSTAT30-Autolab was used to record the EIS spectra of ITO electrodes electrochemically coated with the PEDOT, PANI and PEDOT-PANI polymers (area A is 0.8 cm^2). The solution of 0.2 M H$_2$SO$_4$ containing 0.1 M LiClO$_4$ was used as an electrolyte in a three-electrode cell configuration. The counter electrode was a titanium plate of 1 cm^2 geometric area and a reference electrode was Ag/AgCl$_{(3M\ KCl)}$. An AC sinusoidal perturbation with amplitude of 5 mV was applied to record the electrochemical impedance spectra in a frequency range from 50 mHz to 1 MHz. The EIS data was fitted by using corresponding equivalent circuit by EIS Spectrum Analyser software.

2.6. Evaluation of pH sensing abilities

pH sensing properties of PANI and PANI-PEDOT films were examined after incubation of glass/ITO electrode, which was modified with a polymer film, in the cuvette and varying solution pH. 0.1 M Britton-Robinson buffer was used in order to have a wide range of solutions with different pH values. Absorption spectra were recorded in the range from 400 to 1100 nm 5 min after changing the buffer.

3. Results and discussion

High quality polymer films were prepared on the glass/ITO electrode. The typical cyclic voltammograms of electrochemical deposition of PEDOT, PANI and their nanocomposite on a glass/ITO electrode are shown in figure 1. The formation of "nucleation loop" [37] of the first cycle was observed during the electrodeposition of all three (PANI, PEDOT and PANI-PEDOT) polymer films. Such loops are typical for the nucleation process of conducting polymers [38, 39] and can be related to the homogeneous reaction between starting monomers and oligomers of follow-up products [40]. The increase of current density with each cycle of electropolymerization confirms a gradual formation of conducting polymer film [41]. In the case of PEDOT film (Fig. 1A), oxidation peaks were not observed. The polymerization of PEDOT takes place in potential range from +1 to +1.1 V [42]. The potential range of up to +1.1 V was selected in order to prevent overoxidation of the film, which occurs at higher potentials. Furthermore, when the polymerization potential is lower than +1.15 V, the conductivity of PEDOT film synthesized using aqueous polymerization solution containing LiClO$_4$ as a supporting electrolyte is noticeably higher [42-44]. During the PEDOT film formation, the blue color intensity of

formed film has progressively increased (Fig. 1A). Synthesized PEDOT film was of blue color ($L^* = 18.7$, $a^* = -0.81$, $b^* = -16.3$).

Reversible changes of film color from light green at low potentials to violet at higher potentials were observed during the synthesis of PANI. As a result, the saturated green color ($L^* = 51.9$, $a^* = -13.1$, $b^* = 3.0$) PANI film was produced. During electrodeposition (Fig. 1B) the increase in current density of three oxidation peaks at +0.25, +0.55 and +0.75 V were registered, while fourth peak at +0.95 V decreased during polymerization. First and fourth peaks are related to the changes of PANI oxidation state. Leucoemeraldine form at +0.25 V is converted into emeraldine salt, another peak at +0.95 V is associated with the conversion of emeraldine salt to pernigraniline form. The formation of p-benzoquinone and hydroquinone as breakdown products, which are necessary to observe the conversion of PANI partially oxidized state to fully oxidized form, occurs at +0.55 V [45, 46]. The presence of oxidation peak at +0.75 V reveals the formation of the polymer chain. When potential is higher than +0.8 V, generated di-radical di-cations are acting as an electrophiles and interact with a neutral aniline molecules [47]. In the cyclic voltammograms, which are registered during the electrochemical deposition of PANI-PEDOT film (aniline and EDOT monomers ratio 20:1), two oxidation peaks at +0.57, +0.75 V were observed. These peaks are related to the polymerization of aniline, while the similarity of cyclic voltammograms of PEDOT and PANI-PEDOT in the region from +1.0 to +1.1 V confirms the electrodeposition of PEDOT. The color of electrodeposited PANI-PEDOT film was green-grey ($L^* = 33.8$, $a^* = -1.5$, $b^* = 4.2$).
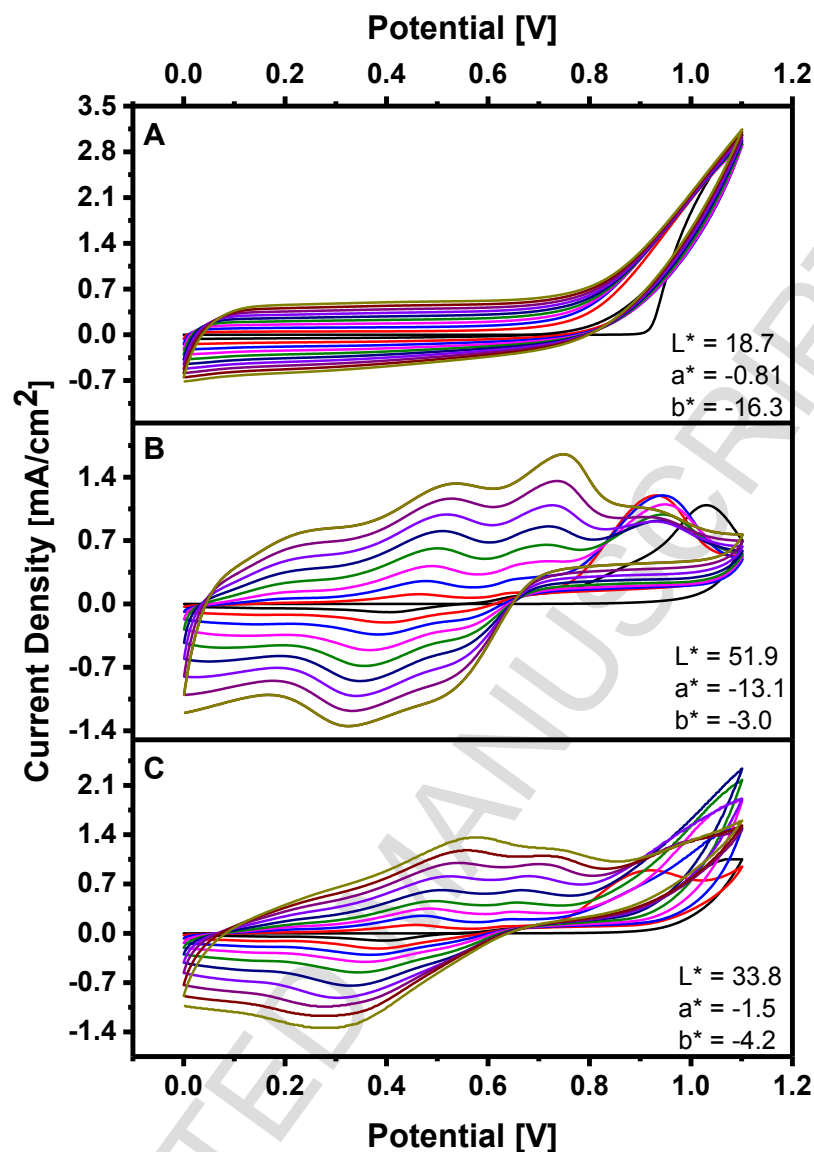
Fig. 1. Cyclic voltammograms obtained during the synthesis of PEDOT (**A**) PANI (**B**) and PANI-PEDOT (aniline and EDOT monomers ratio 20:1) (**C**) films. Electrochemical synthesis was performed in 0.2 M H_2SO_4 solution containing 0.1 M $LiClO_4$, the sweep rate of electrode potential was 50 mV s^{-1}.

The morphology of PANI, PEDOT, PANI-PEDOT films was studied using a SEM (Fig. 2). The surface of synthesized polymers film was rough. The surface of PANI-PEDOT film (Fig. 2C,D) was covered by different size globules with granules on it. A lump-like and fibrous clump structures were randomly distributed on the surface. Globular structures indicates the presence of PEDOT (Fig. 2B) [31], whereas lump-like and fibrous [48] clumps are related to formation of PANI (Fig. 2A).
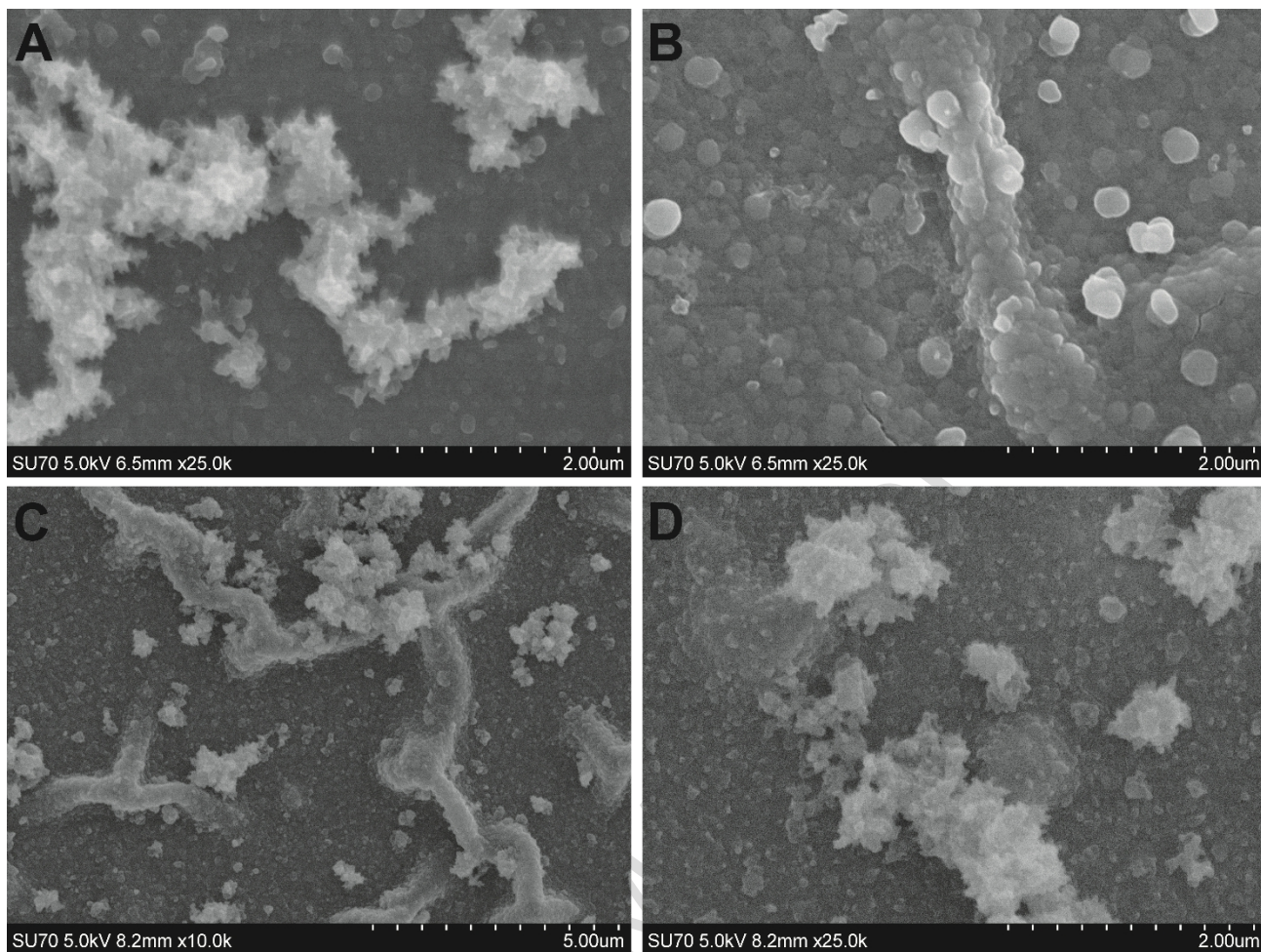
Fig. 2. SEM images of (**A**) PANI, (**B**) PEDOT and (**C, D**) PANI-PEDOT (aniline and EDOT monomers ratio 20:1) films.

AFM in contact mode was used for the evaluation of morphology and thickness of polymer films (Fig. 3). Surfaces of all films were quite rough with a large number of irregularities, which are typical for electrodeposited polymer films. PEDOT film was six times thicker in comparison to PANI film, 479 ± 3 and 75 ± 2 nm respectively. Surface irregularities of the PEDOT film reaching up to 600 nm were a few times higher than surface irregularities of PANI film. The root mean square (RMS) roughness of PEDOT and PANI films was of 296 ± 15 and 111 ± 21 nm on over the whole area, while on the smoother surface sites it was 64.6 ± 19.2 and 11.9 ± 5.3 nm respectively. The PANI-PEDOT film thickness (496 ± 14 nm) was similar to that of the PEDOT film, however, the surface structure was different. The PEDOT film was more homogeneous with randomly distributed round shape spheres (globules), while the PANI-PEDOT film roughness is considerably higher across all the surface area (RMS = 398 ± 28 nm).
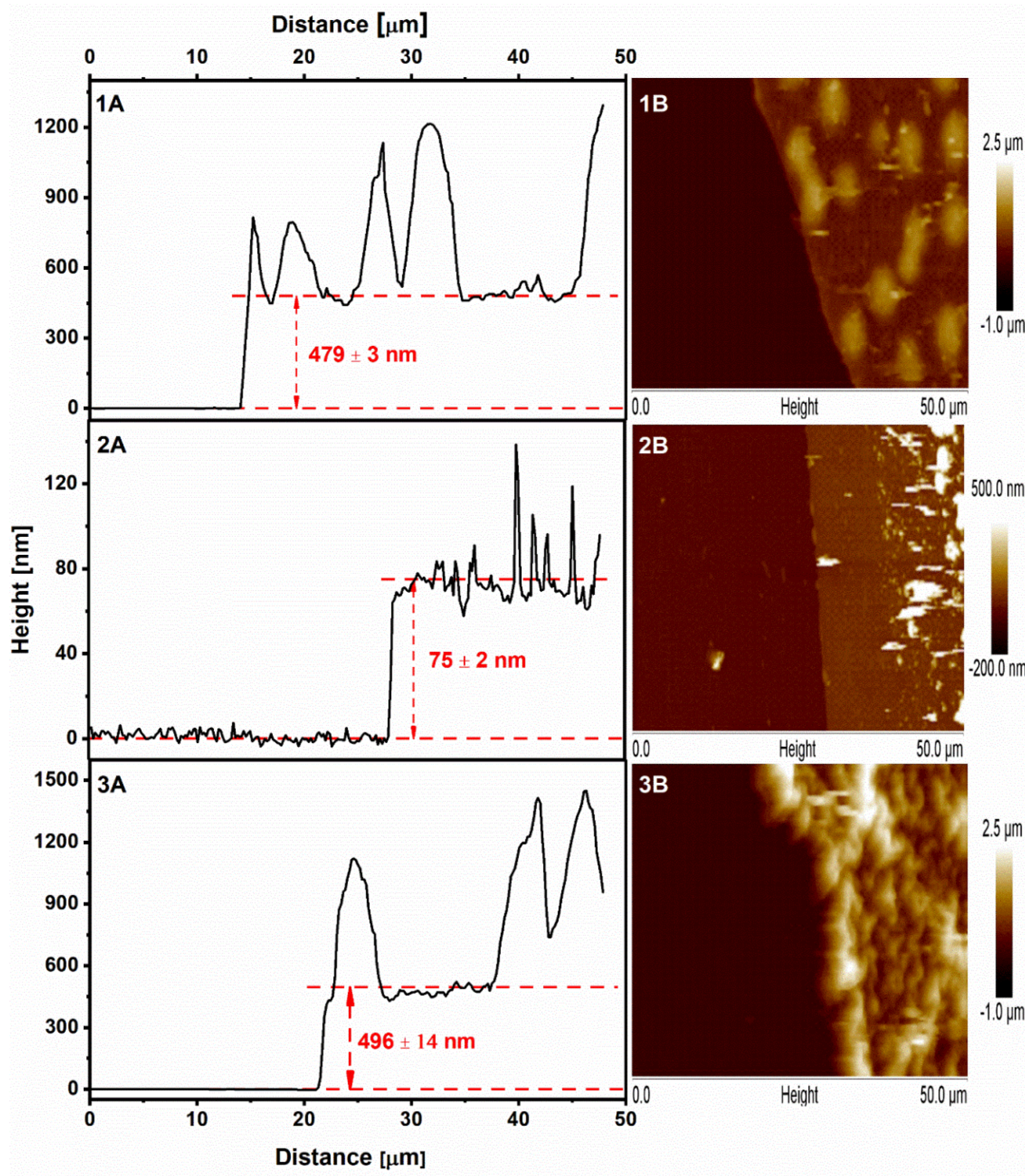
Fig. 3. The surface topography evaluation of PEDOT (**1**), PANI (**2**) and PANI-PEDOT (aniline and EDOT monomers ratio 20:1) (**3**) films on glass/ITO slides obtained by AFM. The surface section (**A**) and 2D AFM image (**B**).

In order to confirm successful polymerization, Raman spectra of PANI, PEDOT and PANI-PEDOT films were collected (Fig. 4). All typical characteristic vibrations were observed for PANI film. The bands at 1191 and 1258 cm^{-1} are attributed to a C-H bending of the quinoid and benzenoid rings. Moreover, a C-C stretching of the benzene ring was observed at 1623 cm^{-1}. The bands at 1342 and

10

1506 cm^{-1} are attributed to C-N$^+$ of the polaron radical cation and C=N of the quinoid protonated diimine units [49-51]. In the Raman spectra of PEDOT film, the most intense band at 1440 cm^{-1} corresponds to a symmetric C=C stretching. In addition, other characteristic peaks correspond to a C=C antisymmetric stretching (1575 cm^{-1}), C-C stretching of the quinoidal ring (1522 cm^{-1}) and C-S-C deformation (705 cm^{-1}). The peaks at 449, 582 and 1000 cm^{-1} are observed due to oxyethylene ring deformation [35, 52, 53]. Peaks, which are related to PANI, were not registered in PANI-PEDOT spectra or their intensity was low. However, all characteristics peaks of PEDOT were observed. It can be explained by a larger amount of PEDOT in comparison with PANI synthesized during electropolymerization of PANI-PEDOT film. A variance between thicknesses of PANI and PEDOT films determined by AFM can also denote a larger amount of PEDOT in PANI-PEDOT film.
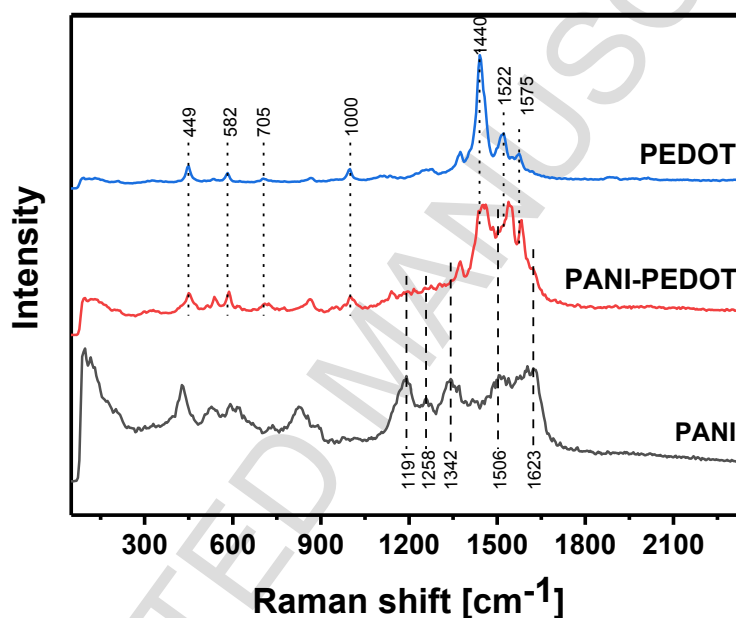
Fig. 4. Raman spectra of PANI, PEDOT and PANI-PEDOT (aniline and EDOT monomers ratio 20:1) films.

Characteristic PEDOT peaks at 1440, 1522 and 1575 cm^{-1} were shifted to higher frequencies in PANI-PEDOT spectra. It indicates a copolymerization of aniline and EDOT. For an assessment of EDOT and aniline copolymer structure, a Raman spectrum of a theoretical molecule, which has the EDOT and aniline quinoidal moieties, was computed using density functional theory (DFT). It was determined that a new medium intensity signals at around 1690 cm^{-1} and 1230 cm^{-1}, which correspond to the C-N (quinoidal) and C-N (aniline) stretching, should be observed in the Raman spectrum of the copolymer. However, no peaks were observed in the same region of the PANI-PEDOT spectra. In addition, production of ANI radical occurs at +0.75 V, wherein the polymerization of EDOT takes

place at the region from +1.0 to +1.1 V [42]. Therefore, it is unlikely that copolymer was formed during the electrochemical deposition. The shift of the peaks in Raman spectra can be explained by the interaction between formed PANI and PEDOT polymers.

We assume that the conductivity of the films has a decisive influence on the thickness of the formed films. To validate this approach, the polymer films were explored using CV by changing the sweep rate of electrode potential from 30 to 250 mV s^{-1} in 0.2 M H$_2$SO$_4$ aqueous solution containing 0.1 M LiClO$_4$ (Fig. 5). Firstly, a number of charge (i.e., electrons, holes or protons) transfers per molecule (*n*) were estimated from the oxidation and reduction peaks of cyclic voltammograms. The value of *n* represents the homogeneity of the film and can be evaluated by the full width at half of the peak maximum (FWHM) as described by equation 1 [54]:

$$n = \frac{3.53RT}{FWHM \times F} = \frac{90.6mV}{FWHM} \qquad (1)$$

where *R* is an ideal gas constant, *T* is an absolute temperature and *F* (96485 s A mol^{-1}) is a Faraday constant. The value of *n* is estimated to be around 2 for all the electroactive polymers. For the reversible electrochemical process, surface coverage degree (Γ) (surface activity), which in this particular system reflects the activity of the electroactive polymer electrodeposited on the electrode surface, was determined from the slope of oxidation or reduction peaks current (*I*) dependence *vs v*, by using Equation 2 [55]:

$$I = \frac{n^2 F^2 A \Gamma}{4RT} v \qquad (2)$$

where *A* (cm^2) is the electrode area, *F* (96485 s A mol^{-1}) is Faraday constant, Γ (mol cm^{-2}) is the coverage degree, *v* (V s^{-1}) is a potential sweep rate. From this experiment, very similar surface activities of around 10^{-9} mol cm^{-2} were measured for all prepared films. Charge density ρ (cm^{-3}) was calculated by using equation 3 knowing the surface activity value (Γ) and thickness (d) of the electroactive film:

$$\rho = \frac{\Gamma N_A}{d} \qquad (3)$$

where N_A is Avogadro number (6.022×10^{23} mol^{-1}). The calculated charge densities are summarized in table 1. In order to determine the effective diffusion coefficient *D* (cm^2 s^{-1}), the Randles-Sevcik equation (Eq. 4) was applied [56]:

$$I = 0.4463nAFN_A\rho\sqrt{\frac{nFvD}{RT}} \qquad (4)$$

The values of *D* were estimated from a slope of linear dependency of current density on potential sweep rate (from 30 to 250 mV s^{-1}). The effective diffusion coefficient of 4.7×10^{-10} cm^2 s^{-1} for the PANI

12

film is very similar to that obtained for proton diffusion [57]. Moreover, charge diffusion coefficients for the PEDOT and PANI-PEDOT films are almost 100 times higher than that of PANI film and they are around 10^{-8} cm^2 s^{-1}. Therefore, the PANI-PEDOT film should possess a similar conductivity to the PEDOT film.
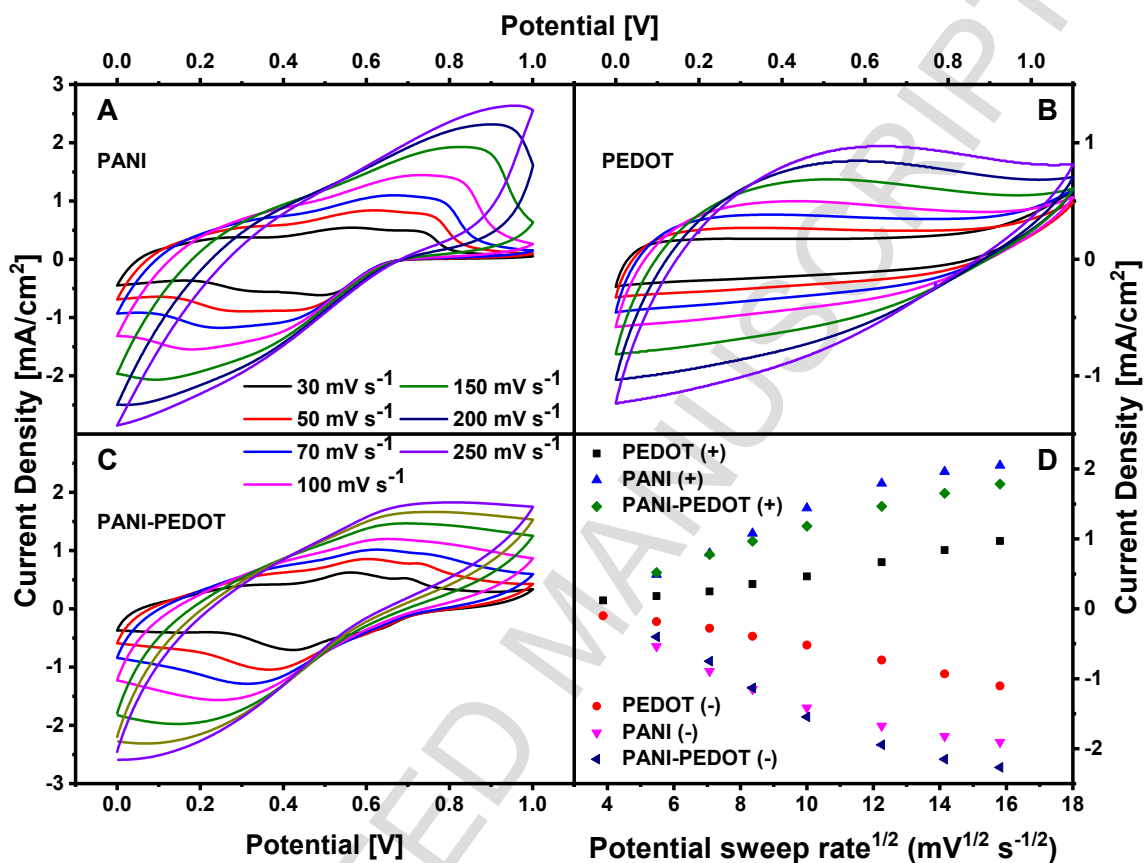
Fig. 5. The 5th cycle of cyclic voltammograms of (**A**) PANI, (**B**) PEDOT and (**C**) PANI-PEDOT (aniline and EDOT monomers ratio 20:1) films recorded at different electrode potential sweep rates (from 30 to 250 mV s^{-1}) in 0.2 M H_2SO_4 aqueous solution containing 0.1 M $LiClO_4$. (**D**) The relationships between oxidation and reduction peaks current density and a square root of the electrode potential sweep rate.

Additionally, electrochemical properties of the PANI, PEDOT and PANI-PEDOT films were investigated by performing the EIS measurements. EIS is a very powerful experimental technique for the characterization of electrodes modified with polymer-based films [58]. The electrochemically deposited polymer films have been tested by using EIS runs with bias potentials of 0 V. Figure 6 shows a typical Nyquist plot of the PANI, PEDOT and PANI-PEDOT recorded at open circuit potential.
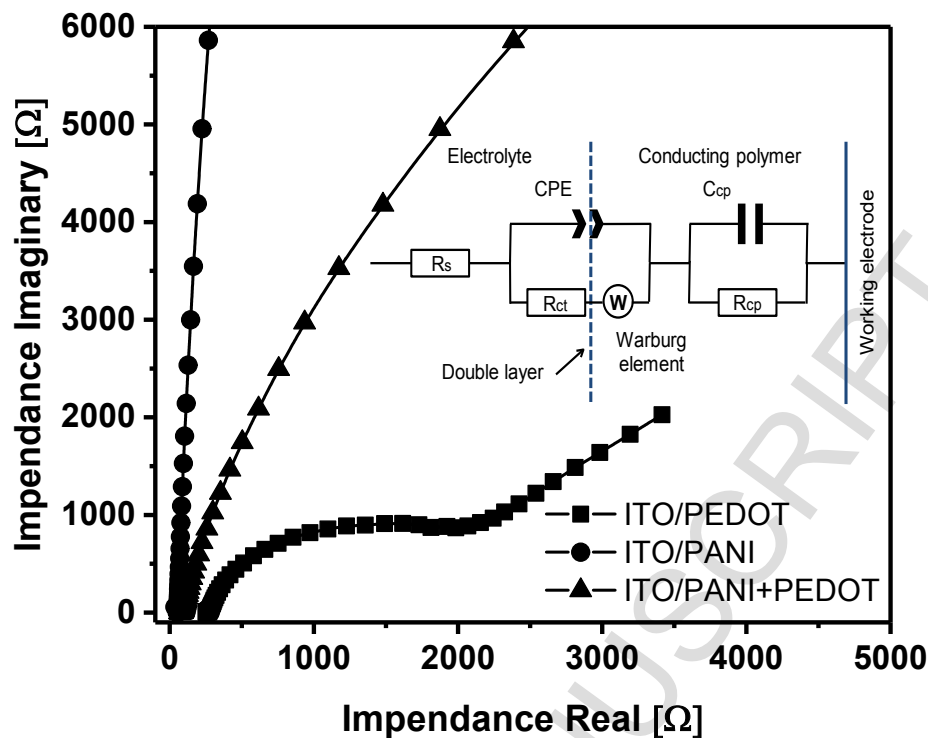
13

Fig. 6. Nyquist plots of PEDOT, PANI and PANI-PEDOT (aniline and EDOT monomers ratio 20:1) films deposited on the ITO glass in a solution of 0.2 M H_2SO_4 at 0 V *vs* Ag/AgCl$_{(3M\ KCl)}$. Inset: Equivalent circuit used for the fitting of the measured EIS data.

To analyse the EIS data, an equivalent circuit model was proposed (inset in Fig. 6). In this model, R_s is a resistivity of aqueous solution of electrolyte. R_{CT} is a charge-transfer resistivity, which is related to the potential gradient between ions in the aqueous electrolyte and the electrode surface, leading to the charge transfer phenomena. R_{CT} is resistivity controlled by the diffusion of charges through a double-layer between the electrolyte and electrode surface. Moreover, constant phase element (CPE) was used in this model instead of basic capacitors, as it is commonly done when the capacitive elements of a system are imperfect. To model the diffusion of charge through the double-layer the classical finite-length Warburg diffusion element (*W*) was used. Moreover, we have added the parallel-connected R_{CP} and C_{CP} elements as a second element of this equivalent circuit, which corresponds to the resistance and the charge capacity of the polymer film respectively, because PANI has shown a great potential towards application as a supercapacitor [59].

14

Table 1. The surface activity, charge density, diffusion coefficient, R_{CT}, R_{CP} and conductivity of PEDOT, PANI and PANI-PEDOT thin films deposited on the ITO electrode calculated from EIS experiment.

	PEDOT	PANI	PANI-PEDOT
Layer thickness d [nm]	479 ±3	75 ±2	496 ±14
Surface coverage degree Γ [mol cm^{-2}]	1.0×10^{-9}	2.6×10^{-9}	2.7×10^{-9}
Charge density ρ [cm^{-3}]	1.3×10^{19}	2.1×10^{20}	3.2×10^{19}
Diffusion coefficient D [cm^2 s^{-1}]	3.0×10^{-8}	4.7×10^{-10}	2.1×10^{-8}
Charge-transfer resistivity R_{CT} [kΩ]	1.9	3.5	5.0
Polymer film resistivity R_{CP} [kΩ]	3.4	400	19
Conductivity σ [S m^{-1}]	1.8×10^{-6}	2.3×10^{-9}	3.3×10^{-7}

The Nyquist plot of PEDOT shows two semi-circle arcs, one in the higher frequency range (or lower impedance) which later deviates to form another semicircle at the lower frequency range (or higher impendence). These two semicircles on EIS plot are expected due to two different process of charge transfer through the layer. The impedance at higher frequency corresponds to a charge transfer process through the double-layer between the electrolyte and the electrode surface. However, one semi-circle arc for the ITO/PANI and ITO/PANI-PEDOT samples was observed due to small contribution to the overall resistivity and capacity. By using the proposed equivalent circuit, the values of R_{CT} and the capacities of the double layer at a bias of 0 V vs Ag/AgCl$_{(3M\ KCl)}$ were calculated to be around 1.9, 3.5, 5.0 kΩ and 130, 83, 46 µF cm^{-2} for PEDOT, PANI and PEDOT-PANI respectively. Moreover, the resistivities (R_{CP}) of these conducting PEDOT, PANI and PEDOT-PANI polymers are around 3.4, 400 and 19 kΩ, respectively. From these R_{CP} resistivity, area and thickness of corresponding polymers on the electrode, the conductivities were calculated to be 1.8×10^{-6}, 2.3×10^{-9} and 3.3×10^{-7} S m^{-1} respectively, by using Equation (5):

$$\sigma = \frac{d}{R_{CP} A} \qquad (5)$$

EIS measurements confirmed that presence of PEDOT during electrochemical synthesis of PANI improved the conductivity of the formed PANI-PEDOT film. It was expected from CV measurements that the conductivity of PEDOT and PANI-PEDOT films should be on the same level, wherein EIS results showed that PANI-PEDOT film possesses about 6 times lower conductivity than PEDOT films.

This mismatch could appear due to the use of a different method for the evaluation of conductivity. In both cases, however, expected and calculated conductivity values of PANI-PEDOT film were comparable with PEDOT film and significantly different from PANI film.

The absorption spectra of PANI and PANI-PEDOT films on transparent glass/ITO electrode were registered from 400 to 1100 nm in pH range from 3.8 to 7.4 (Fig. 7). Such pH interval was chosen due to the possibility in the future to determine CO_2 with the developed sensor in aqueous solutions or in air. In the case of PANI film, two absorption maximums at 440 and 663 nm were observed. The absorption bands at 440 and 663 nm are related to $\pi \rightarrow \pi^*$ band transitions of the conjugated aromatic PANI system and excitation absorption of the quinoid rings, respectively [60]. The increase of absorbance at longer than 817 nm wavelengths, the formation of absorption peak at 663 nm and the decrease of absorption at 440 nm were monitored increasing pH value of buffer solution. A change of PANI film spectra can be explained by a variation in protonation degree of nitrogen atoms of the quinoid rings in PANI structure [16]. Isosbestic point was registered at 817 nm. It indicates the transition between two predominate forms (emeraldine and (per)nigraniline) of PANI [61]. In PANI-PEDOT spectra (Fig. 7C), three absorption maximums were observed and in comparison with PANI spectra a blue-shift of the peak at 663 nm to 602 nm and emergence of a peak at 895 nm, which likely also shifts from a region of longer wavelengths, were observed. However, for the absorption peak at 440 nm a small red-shift was registered. The position of isosbestic point changed from 817 to 801 nm, reflecting the change in the equilibrium between different oxidation states of PANI.

The deposition of polymer films from solutions containing different ratio of aniline and EDOT was performed in order to clarify the dependence of the absorption peak λ_{max} positions on the initial concentration ratio of monomers (Fig. 7B). For the formation of PEDOT-based film 0.01 M concentration of EDOT was used. Red-shifts of the absorption maximums at 602 and 895 nm were observed by increasing initial aniline concentration in the solution. It is possible to prepare PANI-PEDOT film with a desired color and position of the peaks by choosing aniline and EDOT ratio in the polymerization solution. The same effect for PANI and poly(acrylic acid) (PAA) deposited layer-by-layer was observed [61]. Red-shift of λ_{max} from 602 to 635 nm was monitored after the coating of PANI layer by PAA layer. It can be explained by the equilibrium shift of PANI oxidation states. In another report [62], blue shift of λ_{max} at 560 nm due to increasing of buffer solution pH value was observed after the addition of PEDOT to PANI and poly(4-styrenesulfonic acid) nanocomposite. A red-shift of a broad peak at 782 nm in the spectra of PANI film, which was triggered by a change of PANI oxidation level, has also been registered [63]. Additionally it was observed that PANI-PEDOT polymer film synthetized at aniline and EDOT ratio 20:1 exhibited the highest stability in water-based solutions.
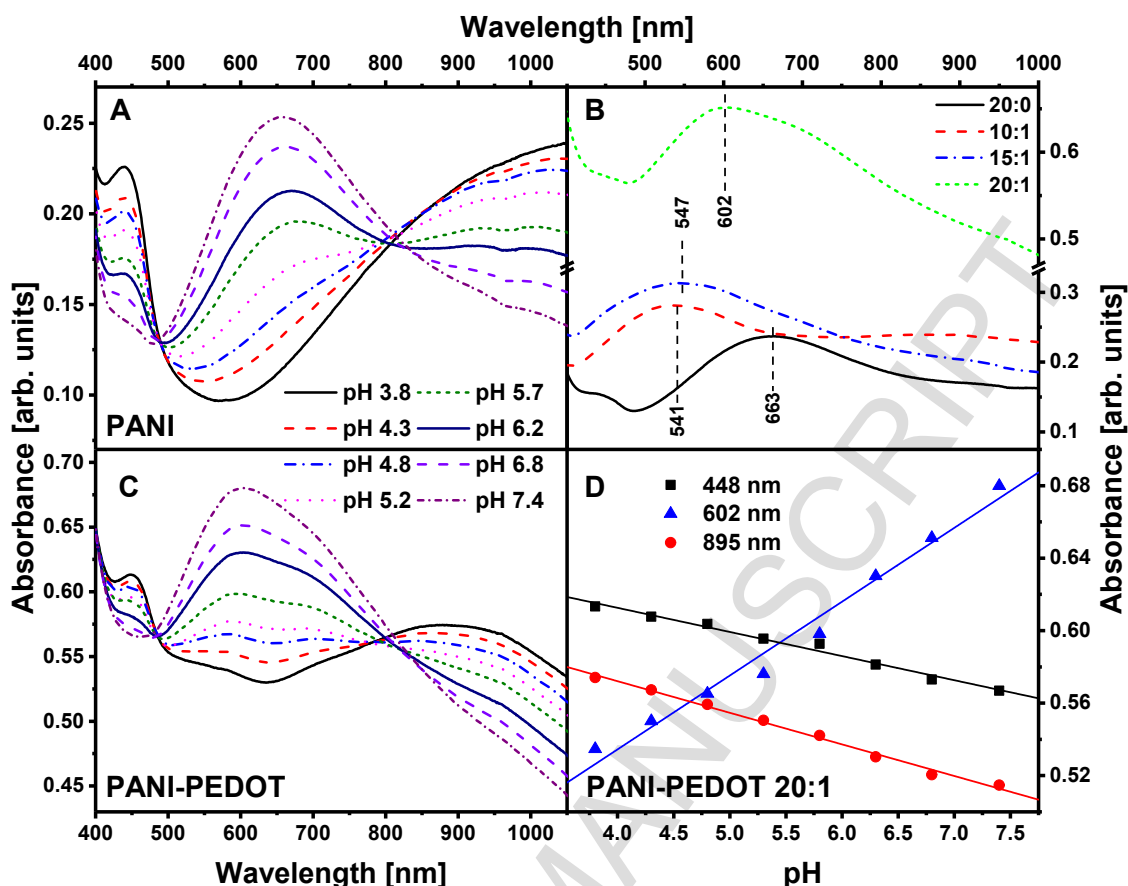
Fig. 7. A set of absorption spectra of (**A**) PANI and (**C**) PANI-PEDOT (aniline and EDOT monomers ratio 20:1) films recorded in a buffer of different pH. (**B**) absorption spectra of polymer films electrodeposited from a solution containing aniline and EDOT in various ratio: 20:0, 10:1, 15:1 and 20:1, recorded at pH 6.8. (**D**) Mean values of 20:1 PANI-PEDOT film absorption at 448, 602 and 895 nm in buffers of different pH.

The change of PANI-PEDOT film absorbance intensity at selected λ_{max} or the variation between ratios of absorbance of selected λ_{max} can be used as analytical signal for optical detection of pH in the range from pH 3.8 to 7.4 (Fig. 7D). The linear relationship between the absorbance at λ_{max} and solution pH were observed using the developed sensor. During the assessment of all three λ_{max}' (at 448, 602 and 895 nm) Pearson correlation coefficient was determined to be as 0.991 or higher. A number of groups have reported optical pH sensors based on PANI film [16, 18, 64, 65] formed on various substrates using different electrochemical synthesis methods. These optical pH sensors have shown reliable results in a wide pH range. However, the relationship between the analytical signal and solution pH value was not linear. It is related to PANI pKa value, which is equal to around 6.7 [16].

Table 2. Color coordinates in CIELAB system: L*, a* and b* for PANI and PANI-PEDOT (aniline and EDOT monomers ratio 20:1) films treated at different pH.

pH	PANI			PANI-PEDOT		
	L*	a*	b*	L*	a*	b*
3.8	38.5	-9.5	3.4	15.5	-2.8	5.7
4.3	38.1	-9.4	0.7	15.3	-2.1	3.4
4.8	37.4	-9.4	-0.6	14.2	-1.8	0.9
5.7	34.0	-8.8	-5.9	12.7	-1.7	-2.7
6.8	33.4	-8.3	-9.0	10.7	-1.2	-5.5
7.4	33.2	-8.1	-10.0	10.6	-0.9	-7.1

Additional reflectance measurements of PANI and PANI-PEDOT films in buffer solution of different pH were performed for evaluation of polymer films color changed. The CIE L^*, a^*, b^* parameters of polymer films are summarized in Table 2. In both cases the lightness (L^*) decreased, a^* moved to positive direction (less green) and b^* become more negative (more blue) when pH value was increased from 3.8 to 7.4, wherein L^* was 2-3 times higher for PANI film. In case of PANI film a^* and b^* values changed from -9.5 to -8.1 and from 3.4 to -10.0 respectively. a^* parameter was lower for PANI-PEDOT film and equal to -2.8 at pH 3.8 and -0.9 at pH 7.4, whereas b* value was higher and equal to 5.7 at pH 3.8 and -7.1 at pH 7.4. This difference can be associated with PEDOT influence on PANI-PEDOT film color.

Table 3. Response time of PANI and PANI-PEDOT (aniline and EDOT monomers ratio 20:1) films.

pH change	t_{95} [s]	
	PANI	PANI-PEDOT
3.6 → 4.7	558	88
4.7 → 6.0	522	78
6.0 → 7.0	466	94

The PANI-PEDOT film showed advancement in comparison with PANI film by improved response time towards pH changes (Table 3). Response time was calculated as a time required for reaching 95 % of the full optical signal of the film at a corresponding pH. The absorbance was monitored at 663 nm for PANI and at 602 nm for PANI-PEDOT films. Response time was evaluated by changing solution pH: (i) from 3.6 to 4.7, (ii) from 4.7 to 6.0, and (iii) from 6.0 to 7.0. For the three pH

intervals, the optical response of PANI-PEDOT film was up to 7 times faster (the response time was up to 7 times shorter) in comparison with that of PANI film. The response time depends on the thickness of the film and should be lower for thinner films [66]. Contrary to this statement, in our study the response time of PANI-PEDOT film was faster than that for PANI film although PANI-PEDOT film was 6.6 times thicker.

4. Conclusions

PANI-PEDOT film electrochemically deposited on a transparent glass/ITO electrode was characterized using different techniques. The presence of PEDOT during electrochemical synthesis of PANI improved the conductivity of the formed PANI-PEDOT film and shortened the response time of the developed sensor. It should be noted that the absorbance at λ_{maxs} (at 448, 602 and 895 nm) of electrodeposited PANI-PEDOT film depended linearly on pH value of solution in the pH range from 3.8 to 7.4. The position of λ_{maxs} can be controlled/tuned by changing initial concentrations of monomers (aniline and EDOT) allowing the development of pH sensors, which are less sensitive to the influence of interfering compounds that can be present in the analytical-matrix. Thus, the developed sensor can be used for the determination of pH in physiologically important pH interval, especially when the acidification of physiological fluids occurs during the course of diseases. In addition, synthesized PANI-PEDOT film can be used in the design of CO_2 sensors sensitive to the pH change of solution containing dissolved CO_2.

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Highlights

- PANI, PEDOT and PANI-PEDOT films were electrodeposited on glass/ITO electrode from aqueous solutions
- Thickness, surface activity, charge density, conductivity and diffusion coefficients of films were compared
- PANI-PEDOT film showed improved conductivity and shortened response time towards pH changes
- The position of λ_{maxs}, of PANI-PEDOT film can be tuned by the variation of polymerization solution composition
- Absorbance at λ_{maxs}, of PANI-PEDOT film depends linearly on the pH in the range from 3.8 to 7.4