Electropolymerization and Properties of Poly (3-anilinethiophene) Thin Film
Saengrawee Sriwichai*[a,b], Paphawadee Netsuwan [c], Sukon Phanichphant [b] and Akira Baba [d]
[a] Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.
b] Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.
c] Nanoscience and Nanotechnology Program, Graduate School, Chiang Mai University, Chiang Mai 50200, Thailand.
d] Center for Transdisciplinary Research and Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan.
*Author for correspondence; e-mail: saengrawee.s@cmu.ac.th

ABSTRACT
The poly(3-anilinethiophene) (P3AT) thin film was prepared by electropolymerization of its monomer, 3-anilinethiophene, on indium tin oxide (ITO) and gold-coated high refractive index glass substrates which were also used as working electrodes in electrochemical measurements. The obtained film was characterized by UV-vis absorption, Fourier-transform infrared (FT-IR) and surface plasmon resonance (SPR) spectroscopy which indicating the formation of P3AT on the substrates. The UV-vis and FT-IR results confirmed the formation of this polythiophene homopolymer containing primary amine groups as substituent groups. The surface morphology of the films after applying various constant potentials (-0.2, 0.5 and 0.6 V) compared with open circuit potential in neutral phosphate buffered saline (pH 7.4) solution was studied by atomic force microscopy (AFM). The P3AT film at different applied potentials showed different surface morphologies and roughnesses. The obtained polymer film should be suitable for construction of immunosensors in the future.

Keywords: poly(3-anilinethiophene), electropolymerization, thin film, cyclic voltammetry, surface plasmon resonance (SPR)

1. INTRODUCTION
Conjugated or conducting polymers such as polythiophenes, polyfluorene, polyaniline, polypyrrole and their derivatives have become an interesting material in a wide range of applications including organic light-emitting diodes (OLEDs), electrochromic displays, organic solar cells and biosensors/immunosensors [1-6]. Polthiophenes, one of the interesting conducting polymers, have been synthesized via both chemical and electrochemical methods [7-10]. Introducing functional groups e.g. alkyl, alkoxyde or
sulfonate groups to the polythiophene backbone had made it soluble in organic solvents and thus suitable for most applications especially thin film electronic applications [11-12]. Recently, conducting polymers including polyanilines and polypyrroles containing functional groups e.g. carboxylic acid, sulfonic acid, sulfide or amine group in structures, had served as sensor modification molecules for detection of biomolecules including glucose, protein, and human antibodies [13-17]. The doping/dedoping and electrochromic properties of conducting polymer films had been the most interesting properties to study for such applications [18].

Fabrication of conducting polymer ultrathin films using an oxidative electrochemical method or electropolymerization is of great interest for depositing insoluble conducting polymer ultrathin film. The purification and isolation processes are not necessary for this polymer synthesis method. However, consideration of solvent for electropolymerization process is also important for film formation on working electrode substrate [1-2]. Electropolymerization allows both inter- and intramolecular crosslinking of electroactive monomer unit. This method is also practical for electro-optical application devices such as OLEDs, biosensors, and organic transistors [3-4,14-16]. Surface plasmon resonance (SPR) spectroscopy has become a powerful technique for characterization and both in-situ and ex-situ monitoring the changes of electrolyte/substrate interfaces and ultrathin films [17,19]. Many recent works had reported on using in situ electrochemical-surface plasmon resonance (EC-SPR) spectroscopy, which is a combination of electrochemical method and SPR spectroscopy, for monitoring the change of optical and electrochemical properties of conducting polymer ultrathin film and also studying an interaction between biomolecules and/or conducting polymers in biosensor and immunosensor applications [13,17,20-23]. The other well-known characterization methods including cyclic voltammetry, UV-vis absorption, Fourier-transform infrared (FT-IR), nuclear magnetic resonance (NMR) spectroscopy have also been recently employed for examining the polymer products from both chemical polymerization and electropolymerization [7-9,24].

The aims of the present work are to fabricate and study the optical/electrochemical property of poly(3-anilinethiophene) (P3AT) thin film. The electrochemical method was employed to fabricate the P3AT film from its monomer on indium tin oxide (ITO)-coated glass and gold-coated high refractive index glass substrates. The formation of the polymer film was confirmed by cyclic voltammetry, UV-vis absorption, FT-IR and SPR spectroscopy. For future application in immunosensor, the effect of various constant applied potentials to surface morphology of the P3AT film in neutral solution (pH 7.4) was studied by atomic force microscopy (AFM).

2. MATERIALS AND METHODS

2.1 Materials and Chemicals

All chemicals used in this experiment were purchased from Sigma-Aldrich and used as received. Phosphate-buffered saline (PBS) solution (pH 7.4) was prepared from PBS tablet dissolving in deionized water. The ITO-coated glass substrate (Sigma-Aldrich) and gold-coated high refractive index glass substrate were prepared following our previous works [22-23].

2.2 Instruments

UV-vis spectra were recorded using a
Hewlett Packard model 8452A. FT-IR spectra were obtained from FT-IR spectrometer (Bruker, Tenser 27). The setup of SPR spectroscopy was previously discussed in more details [19]. The excitation source is He-Ne laser with wavelength of 632 nm. For the electrochemical experiment, a 3-electrode system with computer-controlled model eDAQ ED410 e-corder 410 was employed for cyclic voltammetry. The working electrode was ITO-coated glass substrate and gold-coated high refractive index glass substrate. The gold substrate was obtained by vacuum evaporation of 2.5 nm Cr and 45 nm Au, respectively, on high refractive index glass. Ag/Ag+, Ag/AgCl and platinum wire were used as reference and counter electrodes, respectively. All potentials reported in this work are relative to these electrodes.

2.3 Electropolymerization of 3-anilinethiophene

The electropolymerization was performed using a solution of 10 mM of 3-anilinethiophene in anhydrous acetonitrile containing 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF₆) with a potential ranging from 0 V to 1.1 V at scan rate of 20 mV/s for 2 cycles. The Ag/Ag⁺ non-aqueous electrode was used as reference electrode for this experiment. The obtained P3AT film was characterized by UV-vis absorption, FT-IR and SPR spectroscopy. The UV-vis absorption and FT-IR spectra of monomer solution in anhydrous acetonitrile and the obtained polymer film on the ITO substrate were compared. The SPR angular scan curves were obtained in acetonitrile before and after electropolymerization on the gold substrate. Schematic diagram representing the electropolymerization of 3-anilinethiophene to P3AT was shown in Figure 1.

Figure 1. Schematic diagram showing electropolymerization of 3-anilinethiophene to P3AT.

2.4 Morphology Study of the P3AT Film at Various Constant Applied Potentials

For further morphology study, constant potentials of -0.2, 0.5, 0.6 V and open circuit were applied to the prepared P3AT films on ITO substrate in neutral PBS solution (pH 7.4) for 5 min. The Ag/AgCl aqueous electrode was used as reference electrode for this experiment. The obtained films were studied by AFM (Veeco, NanoscopeIII).

3. RESULTS AND DISCUSSION

3.1 Electropolymerization of 3-anilinethiophene

Figure 2 shows the cyclic voltammogram (CV) during electropolymerization of 10 mM 3-anilinethiophene containing 0.1 M TBAPF₆ in anhydrous acetonitrile with a potential ranging from 0 V to 1.1 V at scan rate of 20 mV/s for 2 cycles on ITO substrate. The CV trace showed the oxidation onset at about 0.4 V, indicating the formation of P3AT film on the substrate. The peak current at about 0.8 V corresponded to the formation of P3AT film on the substrate. This peak current decreased with potential cycling indicating the growth of P3AT film. The P3AT film showed the doping peak at about 0.2 V during anodic scan in second cycle as shown in the inset of Figure 2. An unclear dedoping peak was observed during cathodic scan. After electropolymerization, a pale-yellow P3AT
film on the ITO substrate was obtained. In addition, the oxidation and reduction peaks of polyaniline which can be easily occurred [21] could not be observed in this study. This can confirm that the amine group of the monomer could not be undergone electropolymerization to polyaniline.

3.2 Characterization of the P3AT Thin Film

The UV-vis absorption spectra of 3-anilinethiophene monomer solution in acetonitrile and the P3AT film on ITO substrate were shown in Figure 3. The maximum absorption wavelength (λ_{max}) of the monomer solution appears at about 307 nm which originate from π-π* transition of the monomer unit [22]. This peak was also observed for P3AT film. The UV-vis absorption spectrum of the P3AT film showed a new red shift peak at about 435 nm which contributes to the formation of more conjugation linkage of the polymer on the substrate [26]. This new peak attributed to π-π* interband transition of polythiophene homopolymers as previously reported [7-8, 24-25]. This could confirm polymerization of the thiophene monomer units to the P3AT polymer film.

Figure 3. UV-vis absorption spectra of monomer solution compared with P3AT film on ITO substrate.

FT-IR spectroscopy was employed for further confirmation the formation of this polythiophene homopolymer and the presence of primary amine group with para-substitution aromatic structure. FT-IR spectra of the 3-anilinethiophene monomer and P3AT showed distinct different characteristic peaks as shown in Figure 4. From the FT-IR spectra, the peaks at about 3300 cm\(^{-1}\) are attributed to N-H stretching of primary amine in both monomer and P3AT polymer unit. The C-N stretching peaks of primary amine also appeared at about 1200 cm\(^{-1}\) and 1030 cm\(^{-1}\) for the monomer and P3AT polymer, respectively. In addition, FT-IR spectrum of P3AT showed the two peaks which attributed to para-substituted aromatic structure at about 1700 and 1500 cm\(^{-1}\). The C-H out-of-plane bending of 1,4-substituted aromatic ring is also observed at about 850 cm\(^{-1}\) [27]. This result is consistent with the CV and UV-vis absorption results, confirming the formation of polythiophene homopolymer film on the substrate.
For further confirmation of the P3AT polymer film formation, the SPR angular scan measurements were performed in acetonitrile before and after electropolymerization on gold-coated high refractive index glass substrate. As shown in Figure 5, the dip incident angle was shifted to higher angle after electropolymerization indicating the formation of the polymer film. The film thickness was calculated by fitting the experimental SPR curve with a Fresnel equation algorithm (Winspall software version 2.20). The obtained P3AT film thickness was about 20 nm.

3.3 Morphology Study of The P3AT Film at Various Constant Applied Potentials

The surface morphology of the P3AT film on the ITO substrate at constant applied potentials of -0.2 V, 0.5 V, and 0.6 V compared with an open circuit potential in PBS solution was studied by AFM. Figure 6 shows AFM images of the films after applying constant potentials for 5 min comparing with the film without applying potential (open circuit potential). The polymer film fabricated by electropolymerization method normally showed rough surface morphology [10]. The AFM images represented the effect of potentials on surface morphology of P3AT film. The film at an applied potential of -0.2 V shows the lowest average roughness of 10.3 nm compared with the films at the potentials of 0.5 V (average roughness = 95.6 nm), 0.6 V (average roughness = 48.5 nm) and the P3AT film at open circuit potential (average roughness = 46.5 nm). Since the roughness of the film is related to the disordering of the film [23], this indicates that the P3AT film shows the highest disordering with an applied potential of 0.5 V. This is probably due to the applied positive potential affected positively aminated-surface of the P3AT film. Our previous work [21] in immunosensor application showed that the most disordered poly(3-aminobenzoic acid) film at an applied potential of -0.2 V resulted in enhancing the binding process of antibody and antigen. These results would be useful for further on-going work in immunosensor application.
4. CONCLUSIONS

The electropolymerized poly (3-anilinethiophene) (P3AT) thin film was prepared on ITO and gold-coated glass substrates. The optical property of the obtained P3AT film was studied by UV-vis absorption spectroscopy and surface plasmon resonance (SPR) spectroscopy. The UV-vis absorption spectrum of the polymer film showed a new red shift peak compared with its monomer indicating the formation of polythiophene homopolymer. Moreover, the FT-IR spectra of monomer and P3AT solutions showed the remaining of para-substitution aromatic peaks indicating that electropolymerization occurred at a thiophene unit. The SPR dip angle was shifted to higher angle after electropolymerization. This also confirms the formation of the P3AT film on the substrates. For future application in immunosensor, various constant applied potentials were applied to the P3AT film in neutral PBS solution to study the morphology of the films at different applied potentials. The films showed different morphologies at different applied potentials.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Chiang Mai University for young staff research funding and the Research Grant for New Scholar (MRG5580133) from the Thailand Research Fund (TRF), the Thailand’s Office of the Higher Education Commission (CHE). The partial funding support from the National Research University Project under Thailand’s Office of the Higher Education Commission is also acknowledged.

Figure 6. AFM images of P3AT film (a) before applying constant potential and after applying constant potential of (b) -0.2 V, (c) 0.5 V and (d) 0.6 V in PBS solution.
REFERENCES


