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Tunable Nanostructured Conducting Polymers for Neural Interface Applications

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Abstract

Advancement in the development of traditional metallic-based implantable electrodes for neural interfacing has reached a plateau in recent years in terms of their ability to provide safe, long-term, and high resolution stimulation and/or recording. The reduction of electrode size enables higher selectivity through increased electrodes per implant device; however, it also results in lower sensitivity at electrode-tissue interfaces. This limitation can be addressed through the utilization of conducting polymer (CP) coatings, which increase the effective surface area. In this work, we investigate the surface roughness of two common conducting polymers; poly(pyrrole) (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) in the form of films deposited using both potentiostatic (PSTAT) and galvanostatic (GSTAT) methods. We found that the surface roughness of both CP films can be increased by over 90% through control of both deposition time and applied electrical deposition (current for GSTAT and voltage for PSTAT). The impedance of PPy-modified electrodes was found to decrease by up to 88%. This study shows that the surface roughness of CPs can be modulated to control electrical properties of neural electrodes and may improve the cellular response of neurons.

I. Introduction

The development of neural interfaces holds considerable promise for creating bioelectronics that interface with the nervous system, potentially assisting patients with neurological disabilities or allowing for control of prostheses. [1] In order to realize this potential, neural interface devices must communicate with large numbers of neurons with a high signal-to-noise ratio for selectable time durations ranging from days to years. [2] Current electrodes constructed with conventional metallic materials are generally hard, dry, and static in nature and interact electronically. [3] These characteristics are mismatched with those of biological tissue that interacts ionically and is soft, wet, and dynamic, often resulting in reactive tissue responses and electrode encapsulation. [4] Furthermore, attempts to increase electrode sites per implant device in an effort to increase selectivity will reduce the surface area, resulting in higher impedance or lower sensitivity at electrode-tissue interface. [5] To overcome this limitation, one strategy is to utilize organic conducting polymers (CP) to the surface of neural electrodes. [6] CP's including poly(pyrrole) PPy and poly(3,4-

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ethylenedioxythiophene) (PEDOT) are able to conduct both electronic and ionic signals, and have thus attracted considerable attention for applications in biosensors and bioelectronics. [7] Applying CPs to neural electrodes is promising because biological signals are transported in the form of ionic currents in the environment of neurons. In addition, these materials have electrical conductivities similar to semiconductors and metals, but are mechanically soft, highly biocompatible, and have been shown to reduce electrode impedance when compared to metal-based electrodes of similar geometric area [8]. Many studies have focused on improving electrical performance of neural electrodes by creating unique micro and nano-structured CP's including microbowls [9] and nanofibers [10]. Despite advancement in application of CPs, the precise effect of surface roughness of CP films for further electrical improvements needs to be investigated. In this study, we have systematically investigated the surface roughness of both PPy and PEDOT using versatile electrochemical deposition in galvanostatic (GSTAT) and potentiostatic (PSTAT) modes. The fabricated films exhibit tunable surface roughness as a function of both deposition time and the magnitude of the appropriate electrical stimulus. We specifically demonstrated that the increase in surface roughness reduces the electrode impedance for PPy-modified electrodes produced using GSTAT deposition.

II. Materials and Methods

A. Materials

Pyrrole (Py, MW 67.09g/mol) and dopant poly (sodium-p-styrenesulfonate) (PSS, MW 70kg/mol) was purchased from Acros-Organics. 3,4-Ethylenedioxythiophene (EDOT) was purchased from Alfa Aesar. N-type Si wafers coated with SiO₂ were purchased from University Wafer Company. Stainless Steel wafer masks were designed in house and purchased after fabrication by PhotoEtch Company. All other materials and reagents were used as purchased.

B. Fabrication of Conductive Substrates

Gold electrodes were fabricated on Si wafers (two rectangles, 3x5 and 5x7mm, connected with a 1x3mm rectangle) using electron beam evaporative deposition and stainless steel masks. A thin (20nm) layer of chromium was deposited first to facilitate adhesion of the (100nm) Au layer to the Si wafers.

C. Fabrication of CP Films

Electrochemical polymerization was performed from a solution of 0.2M Py and 0.2M PSS, and 0.02M EDOT and 0.2M PSS in DI water on the 5x7mm rectangle of the shaped electrodes using an Autolab PGSTAT 128N (USA METROHM Company). Deposition in galvanostatic (GSTAT, two-electrode configuration) and potentiostatic (PSTAT, three-electrode configuration with Ag/AgCl reference) mode was carried out at room temperature for both PPy and PEDOT films. Deposition time was consistent for all experiment groups at 1, 2, 5, and 10min. For PPy, the GSTAT applied current density was 0.1, 0.5, 1.0, and 1.5mA/cm² and PSTAT applied voltage was 0.5, 0.55, 0.6, and 0.65V. For PEDOT, the GSTAT applied current density was 0.1, 0.2, 0.5, 1.0mA/cm² and PSTAT the applied voltage

was 0.8, 0.85, 0.9, and 0.95V. Once completed, electrodes were rinsed with ultrapure water (Millipore Milli-Q 8, 18.2M Ω .cm).

D. Electrical Characterization

Impedance spectroscopy (IS) was used to determine the conductivity of the PPy and PEDOT films fabricated in both GSTAT and PSTAT modes. Measurements were performed using a Metrohm Autolab PGSTAT 128N and Nova frequency response analyzer software in potentiostatic mode. A solution of 0.1M phosphate-buffered saline (PBS, pH=7.4) was used as the electrolyte in a three-electrode configuration. The Ag/AgCl reference electrode, Pt-foil counter electrode, and the shaped electrodes were immersed in the electrolyte solution. A sinusoidal AC signal (10mV rms amplitude) was imposed to measure the impedance magnitude over a frequency range of 1–10⁴Hz.

E. CP Film Roughness Analysis

The CP film roughness as a function of deposition time and applied stimulus was analyzed with an FEI 235 field-emission scanning electron microscope. Quantitative evaluation was performed using a Veeco Dimensions 3000 atomic force microscope in tapping mode using Si tips (force constant 0.4N/m). The same 25 μ m² section of each electrode was analyzed to determine the root-mean-square (Rq) surface roughness.

III. Results and Discussion

A. Fabrication of CP films

Fig. 1a shows a schematic of the CP film fabrication process. The workflow includes (1) immersion of the 5x7mm rectangle electrode in the monomer/dopant solution, (2) application of constant voltage or constant current density for a specific time duration, and (3) rinse of electrode surface in DI water and drying with N₂ gas.

Fig. 1b shows optical micrographs of PPy-modified electrodes fabricated in GSTAT mode at 0.1mA/cm² for 1, 2, 5, and 10min deposition times. The deposition of stable films was observed to only occur in a narrow window of time and applied electrical stimulus. Fig. 1c shows a delaminated PPy electrode produced using PSTAT deposition for 10min at 0.7V, demonstrating that for the same deposition time, a 0.05V outside the deposition window results in PPy film delamination. Presumably, the difference in surface energy between the rough surface of the film and the smooth PPy/Au interface is a cause of this delamination. Thus, the deposition settings in this study were carefully chosen to investigate only stable films.

B. Analysis of CP Surface Roughness

The surfaces morphology of all CP films was assessed using scanning electron microscopy (SEM). Fig. 2 shows a representative set of PPy modified electrodes deposited in GSTAT mode. At current density 0.1mA/cm² and 1min deposition time (Fig. 2b), PPy was slowly deposited as evidenced by the visible grain structure of the underlying Au surface (Fig. 2a). Fig. 2b–e indicates that as the current density and deposition time were increased to 1.5mA/cm² and 10min respectively, the PPy granular surface became distinctly visible and

continues to become rough. Similar observations were recorded for PPy and PEDOT depositions in both GSTAT and PSTAT modes, suggesting a dual dependence of film surface roughness on both applied stimuli (i.e. current density and voltage) and deposition time.

The surface roughness of CP films was quantified by atomic force microscopy (AFM). Fig. 2f shows a micrograph of an unmodified bare gold electrode as compared to PPy-modified electrodes coated at $0.1\text{mA}/\text{cm}^2$ for 1min (Fig. 2g), $0.5\text{mA}/\text{cm}^2$ for 2min (Fig. 2h), $1.0\text{mA}/\text{cm}^2$ for 5 min (Fig. 2i), and $1.5\text{mA}/\text{cm}^2$ for 10 min (Fig. 2j). As shown in Table 1, the Rq of PPy-modified electrodes fabricated using GSTAT deposition method increased as both deposition time and current density increased. At the shortest deposition time (1min) and the lowest current density ($0.1\text{mA}/\text{cm}^2$), Rq was found to increase from 1.62nm for bare gold to 4.01nm (~60% increase). At the longest deposition time (10min) and highest current density ($1.5\text{mA}/\text{cm}^2$), Rq increased to 26.1nm (~94% increase vs. bare gold). AFM results suggest that both current density and deposition time parameters have significant influence on the surface roughness of PPy.

For PPy deposited via PSTAT at 0.5 V for 1min, a lower initial Rq increase was recorded from 1.62nm (for bare gold) to 1.63nm (~0.5% increase). However, when the applied voltage increased to 0.55V, Rq increased to 15.3nm (~60% increase vs. bare gold). The slow initial increase is likely due to the low voltage, which was at the bottom edge of the observed narrow potential window for PPy PSTAT deposition in this study. At the longest deposition time (10min) and highest deposition voltage (0.65V), Rq increased to 25.6nm, (~93% vs. bare gold). Compared to GSTAT electrodeposition method, the PSTAT fabricated PPy films showed a greater increase in Rq when the applied potential increased at a specified deposition time.

In Table 2, the Rq of electrodeposited PEDOT films using GSTAT method initially showed a similar trend compared with PPy films electrodeposited using GSTAT method, with an initial increase from 1.62nm to 3.46nm (~50% vs. bare gold) at current density $0.1\text{mA}/\text{cm}^2$ and 1min deposition time. However, Rq decreased from 15.5nm to 11.1nm when the current density increased from $0.5\text{mA}/\text{cm}^2$ to $1.0\text{mA}/\text{cm}^2$ at 5min deposition time, and from 18.9nm to 13.9nm as the current density increased from $0.2\text{mA}/\text{cm}^2$ to $1.0\text{mA}/\text{cm}^2$ at 10min deposition time, respectively. Furthermore, for $1.0\text{mA}/\text{cm}^2$, Rq was observed to fluctuate between 11nm and 13nm as deposition time increased from 1min to 10min.

The origin of this behavior was not analyzed in this study. At all other settings, Rq was found to be dependent on the deposition time and the current density, with a maximum Rq increase from 1.62nm to 18.9nm at 10 min and $0.2\text{mA}/\text{cm}^2$ (90% vs. bare gold).

When, PEDOT was deposited in PSTAT mode, the CP film had a slow initial Rq increase from 1.62nm to 5.15nm at 1min and 0.8V (68% vs. bare gold) (Table 2), similar to PPy films fabricated in PSTAT mode. However, the Rq of PEDOT did not increase at higher voltage and deposition times. For deposition voltage 0.9V, Rq decreased from 18.3nm for 10min deposition time to 13.1nm for 5min deposition time. Additionally, for 0.95V at 2–10min deposition times, Rq increased slowly from 1.62nm to 13.5nm, then plateaued at 13.1nm. It is plausible that 0.95V could electrolyze water at the PEDOT-Au interface, especially in the

presence of the ionic dopant PSS. This may explain the similar behavior of PEDOT in both GSTAT and PSTAT modes.

C. Electrical Characterization

IS was used to assess the impact of surface roughness on the electrical conductivity of the PPy films. Fig. 3 shows the impedance spectra of these electrodes bearing films fabricated in GSTAT mode at different deposition times.

As the deposition current density increased, the impedance decreased over a large frequency range. For example at 10Hz, bare gold had an impedance of 558Ω. Over a 1min deposition time, the impedance decreased from 322Ω at deposition current density 0.1mA/cm² to 105Ω at deposition current density 1.5mA/cm² (81% decrease vs. bare gold) (Fig.3a). Similarly, at 2min deposition time, impedance decreased from 249Ω at 0.1mA/cm² to 93Ω at 1.5mA/cm² (83% decrease vs bare gold) (Fig. 3b). Likewise, at 5min deposition time, the impedance decreased from 191Ω at 0.1mA/cm² to 80Ω at 1.5mA/cm² (86% decrease vs. the bare) (Fig 3c.). Finally, the 10min deposition time impedance decreased from 147Ω at 0.1mA/cm² to 69Ω at 1.5mA/cm², yielding the greatest decrease in impedance (88% vs. the bare gold) (Fig. 3d). The impedance of the electrodes is highly dependent on the effective surface area [11]. For the PPy-modified electrode shown here, the surface roughness increase (Table 1) is directly correlated with the impedance decrease (Fig.3), indicating that the fabrication of nanostructured PPy and PEDOT films can be modulated in order to decrease the impedance of neural electrodes.

IV. Conclusion

We successfully demonstrated (1) electrochemical deposition of PPy and PEDOT polymer films on custom shaped Au electrodes, (2) control of CP film roughness through variation of both deposition time, and deposition current density for GSTAT and voltage for PSTAT, and (3) reduction of impedance of PPy-modified electrodes produced in GSTAT mode. This study demonstrates the potential of PPy and PEDOT to improve the electrical properties of bioelectronics for biomedical applications including neural interfaces and neural regeneration without the need for chemical modification or templating. Future studies will focus on more in-depth analysis of PPy and PEDOT fabrication techniques, their resulting surface topography, and their impact on the outgrowth of neuronal processes such as hippocampus neurons or dorsal root ganglion.

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References

1. Nicolelis MAL. Brain-machine interfaces to restore motor function and probe neural circuits. *Nature Rev Neurosci.* May.2003 4:417–422. [PubMed: 12728268]
2. Buzsaki G. Large-scale recording of neuronal ensembles. *Nat Neurosci.* May.2004 7:446–451. [PubMed: 15114356]
3. Fattahi P, Yang G, Kim G, Abidian MR. A Review of Organic and Inorganic Biomaterials for Neural Interfaces. *Adv Mat.* Mar.2014 26:1846–1885.

4. Nicolelis MAL, Dimitrov D, Carmena JM, Crist R, Lehew G, Kralik JD, et al. Chronic, multisite, multielectrode recordings in macaque monkeys. *Proc Nat Acad of Sci USA*. Sep.2003 100:11041–11046. [PubMed: 12960378]
5. Wallace GG, Spinks GM. Conducting polymers - A bridge across the bionic interface. *Chem Eng Prog*. Dec.2007 103:S18–S24.
6. Polikov VS, Tresco PA, Reichert WM. Response of brain tissue to chronically implanted neural electrodes. *J Neuro Method*. Oct.2005 148:1–18.
7. Smela E. Conjugated polymer actuators for biomedical applications. *Adv Mat*. Mar.2003 15:481–494.
8. Heeger AJ. Semiconducting and metallic polymers: The fourth generation of polymeric materials (Nobel lecture). *Angew ChemInt Ed*. 2001; 40:2591–2611.
9. Qu LT, Shi GQ, Yuan JY, Han GY, Chen F. Preparation of polypyrrole microstructures by direct electrochemical oxidation of pyrrole in an aqueous solution of camphorsulfonic acid. *J of Eanalyt Chem*. Jan.2004 561:149–156.
10. Abidian MR, Martin DC. Experimental and theoretical characterization of implantable neural microelectrodes modified with conducting polymer nanotubes. *Biomaterials*. Mar.2008 29:1273–1283. [PubMed: 18093644]
11. Barsoukov, E., Macdonald, JR. *Impedance spectroscopy : theory, experiment, and applications*. 2. Hoboken, N.J: Wiley-Interscience; 2005.

Figure 1.

Fabrication of CP modified electrodes. A) Schematic of electrochemical deposition of CP on electrodes. B) Optical micrograph of PPy samples prepared using GSTAT mode for $1.0\text{mA}/\text{cm}^2$ at 1, 2, 5, and 10 min deposition time respectively. C) Delamination of PPy film from Au surface when deposited at 0.7V for 10min. Scale bars = 5mm.

Figure 2.

Scanning electron micrographs of a) bare gold, and PPy-modified electrodes fabricated in GSTAT mode at b) $0.1\text{mA}/\text{cm}^2$ for 1min, c) $0.5\text{mA}/\text{cm}^2$ for 2min, d) $1.0\text{mA}/\text{cm}^2$ for 5min, and e) $1.5\text{mA}/\text{cm}^2$ for 10 min. Scale bars = $1\mu\text{m}$. Atomic force micrographs of the same f) bare gold electrode and PPy film at g) $0.1\text{mA}/\text{cm}^2$ for 1min, h) $0.5\text{mA}/\text{cm}^2$ for 2min, i) $1.0\text{mA}/\text{cm}^2$ for 5 min, and j) $1.5\text{mA}/\text{cm}^2$ for 10 min. Roughness increases with both deposition time and current density.

Figure 3.

Impedance spectroscopy of PPY-coated electrodes deposited in GSTAT mode at A) 1min B) 2min, C) 5min, and D) 10min. Bare gold electrodes (black upsidedown triangles) are compared to 0.1mA/cm² (red squares), 0.5mA/cm² (blue circles), 1.0mA/cm² (magenta diamonds), and 1.5mA/cm² (green triangles) at each depositions time.

TABLE I
Summary of the Root-Mean-Square Surface Roughness (nm) of PPy modified Electrodes

	PPy (GSTAT)					PPy (PSTAT)				
	0.1 mA/cm ²	0.5 mA/cm ²	1.0 mA/cm ²	1.5 mA/cm ²	1 mA/cm ²	0.5V	0.55V	0.6V	0.65V	
1 min	4.01	7.99	10.2	12.0	1.63	4.15	4.15	9.22	15.3	
2 min	5.21	10.3	13.6	15.4	1.82	7.93	7.93	12.6	19.2	
5 min	7.76	14.3	17.7	20.9	6.10	12.6	12.6	18.5	25.6	
10 min	9.82	18.3	21.6	26.1	10.1	19.2	19.2	20.2	25.6	

Summary of the Root-Mean-Square Surface Roughness (nm) of PEDOT modified Electrodes

TABLE II

	PEDOT (GSTAT)				PEDOT (PSTAT)			
	0.1 mA/cm ²	0.2 mA/cm ²	0.5 mA/cm ²	1.0 mA/cm ²	0.8V	0.85V	0.9V	0.95V
1 min	3.46	5.17	8.81	11.8	5.15	5.82	10.1	11.0
2 min	5.27	8.00	11.8	13.5	5.49	7.27	12.8	12.1
5 min	9.67	13.1	15.5	11.1	6.55	11.5	14.8	13.5
10 min	14.6	18.9	16.8	13.9	12.3	18.9	18.3	13.1