Polypyrrole (PPy) Conductive Polymer Coating of Dry Patterned Vertical CNT (pvCNT) Electrode to Improve Mechanical Stability

Mohammad Abu-Saude, Student Member, IEEE, and Bashir I. Morshed, Member, IEEE, EMBS

Electrical and Computer Engineering, The University of Memphis, TN, 38152, USA

***Abstract* — Traditional wet or gel electrodes are not suitable for long duration neuro-physiological monitoring. Dry electrodes for impedimetric sensing of physiological parameters (such as ECG, EEG, and GSR) promise the ability for long duration monitoring. We have previously demonstrated a novel nanotechnology based dry electrode configuration fabricated with patterned vertically-aligned carbon nanotube (pvCNT) for neuro-physiological impedimetric measurements. However, the fabricated sensors were mechanically weakly adhered to the substrate. This paper describes a coating mechanism of pvCNT with a thin layer of conductive polymer, Polypyrrole (PPy), to increase mechanical stability, while preserving superior impedance properties of pvCNT. The electrodes were fabricated on circular stainless-steel (SS) foil substrate (ϕ = 10 mm, and thickness = 2 mils). Electrically conductive multi-walled CNT were grown in pattered pillar formation with a square base of 100 µm each side, and an inter-pillar spacing of 200 µm. The heights of the pillars were between 1 to 1.5 mm. The coating procedure involved applying 10 µL of PPy after preparing the pvCNT with 70% ethyl alcohol solution, and flash drying at 300°C. A comparative test with commercial ECG electrodes and non-coated version show that coated pvCNT has lower electrical impedance compared to commercial electrode whereas higher impedance compared to non-coated version. The signal capture were comparable for all electrodes in vitro. The peel test reveal much stronger mechanical adhesion of the pvCNT with the SS substrate when coated with PPy. The results demonstrate the feasibility of coating pvCNT dry electrodes with PPy for robustness.**

Keywords— Dry impedimetric electrode, Carbon Nanotube (CNT), pvCNT electrode, Nano-electrode, PPy coating, EEG electrode, ECG electrode.

I. Introduction

Physiological and neurological signals require impedimetric interfacing with the skin to capture bio-signals, such as electroencephalography (EEG), electrocardiography (ECG/EKG), electromyography (EMG), and Galvanic Skin Response (GSR), for diagnostics, monitoring and therapy [1,2]. The traditional impedimetric interfacing Ag/AgCl electrodes with wet or gel interfacing medium operate well for a short duration, but degrades very quickly, as the evaporation of fluids effects the performance of the electrodes. This performance deterioration leads to unreliable signal capture quality after short time [3-6]. Even though gel electrodes operates for longer than wet electrode, in addition to environment noise, gel interfacing suffers from severe contact noise [7-9].

The dry electrodes might have the potential for long duration sensing without degrading of impedances [2]. However, there are a number of significant issues that need to be resolved including the impedance, the contact surface, interfacial potential, and noise. The low impedance electrode has the potential to reduce the noise during recording the physiological and neurological signals. We have previously shown that pvCNT have lower contact impedance than the traditional wet electrodes [10,11], however pvCNT electrodes suffered from the weakness of mechanically stable adherence to the substrate. Furthermore, even though small amount of CNT on dermis is not considered hazard, there is still risk of toxicity or skin reaction to CNT exposure. In this paper, we propose to resolve these issues of pvCNT dry electrode by improving the mechanical adherence strength of the pvCNT with stainless steel (SS) substrate using an electrically conductive polymer (Polypyrrole, PPy) coating. Conductive PPy polymer thin film has been used in other work [12]. The PPy was also preferred due to its easy preparation process, high electrical conductivity, and environment safety.

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II. PvCNT Faprication

Multi-walled carbon nanotube (MWCNT) can be an excellent electrical conductive nano-material [13]. Some studies have shown that CNT based electrodes can be stable and reliable to neuronal signals [13], and not toxic at low concentration to the epidermis [14,15]. CNT based impedimetric electrodes, however, had a limited success [9] due to two prime limitations: (1) the CNTs were uniformly grown on the substrate without any gap leading to poor electrode-skin contact, and (2) the CNTs did not have enough height to penetrate through the epidermal ridges.

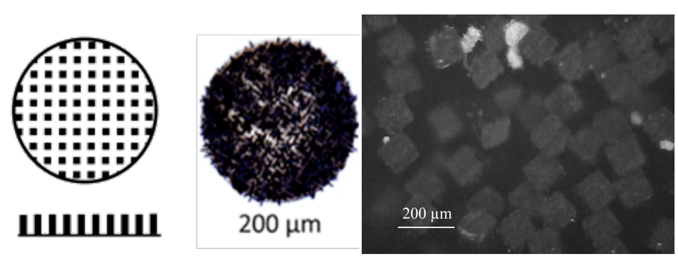

Fig. 1. **Left:** Schematic design of the pattern for pvCNT growith on SS substrate. **Middle:** An Optecal micoscope image of a pvCNT (200 µm spacing) showing many tightly ensembled vertical pillars in an organized fashion. **Right:** Optical microscope image of a pvCNT sensor top surface (100 µm spacing) showing the bristle arrangement of the pillars.

In our previous work we have fabricated many of pvCNT electrodes for dry impedimetric sensing [10,11]. The CNTs were grown in squared pillar patterns with a sufficient height to penetrate through the pores and the ridges of the Stratum Corneum of epidermis. We have used MWCNT due to its electrical conductivity and mechanical properties [9]. The fabricated pvCNT electrode is an ensemble of an array of MWCNT in pillar formation. Each pillar was grown vertically on a square base of 100 µm in each side over a circular stainless steel (SS) foil substrate (ϕ = 10 mm, 2 mils thick). The CNTs were grown up to heights of 1 to 1.5 mm, and three different spacing between the pillars (50, 100 and 200 µm). In this work, only 200 µm spacing electrodes were tested for coating and characterization. Electrode with other spacings are expected to behave similarly. A representative mask pattern and photographs of a pvCNT electrode are shown in Fig. 1.

III. Experimental Setup

A. *Coating Procedure*

The main goal of this procedure is to add extra strength and adhesiveness to the pvCNT pillars to attach them firmly on the SS substrate. PPy was used for coating of sensors and electrodes in many applications [16]. Using chemical or electrochemical procedures the conductivity of the PPy can be changed from insulating to metallic [17]. A liquid PPy from Sigma Aldrich (product number 482552) was utilized in this study. The pvCNT electrode used had 200 µm spacing between pillars. Other components in the protocol were 70% Ethyl Alcohol, a petri dish of heat tampered glass, a hot-air heat gun (reflow type), and an air displacement micropipette. The pvCNT coating procedure was developed with the following protocol:

(1) Prepare a dry pvCNT electrode and place it inside the petri dish.

(2) Apply 10 µL of 70% ethyl alcohol to the top of the electrode, and wait until all of the substrate is covered.

(3) Thereafter, add 10 µL of the PPy to the top of the electrode such that it covers all the substrate.

(4) Immediately flash dry the PPy using a preheated heat gun at 300°C at 10 cm distance from the top of the electrode for 30 seconds to 1 minute.

B. *Impedance measurments*

The impedance of the uncoated pvCNT electrodes and the coated electrodes were analyzed by Agilent 4294A Precision Impedance Analyzer (Agilent Technologies Inc., Santa Clara, CA, USA) using the Dielectric Fixture 16451B at room temperature (~23ºC). The fixture was compensated and calibrated as per manufacture instruction to ensure accurate measurements. A VBA macro for Microsoft Excel (Microsoft Corp, Redmond, WA, USA) was used to transfer the data from the analyzer to the PC through a LAN cable, and Matalab scripts (MathWorks, Natick, MA, USA) were used to analyze and plot the data.

C. *Signal Capturing in Bench Test*

We have shown that the half-cell potential for the pvCNT electrode interfaced with Al foils is very small (~15 mv). Same experiments were repeated for the PPy coated pvCNT electrodes to measure the half-cell potential. The signal was applied to the Al-foil and captured using the coated pvCNT.

D. *Compression and peel test*

A small pressure was applied with the dielectric fixture 16451B by twisting the torque knop. Microscopy pictures were taken before and after the experiments. The peel test was used to measure the adhesion strength of the pvCNT pillars with the SS substrate by holding the substrate with a double sided tape, while a drafting tape was attached to the top surface of the pvCNT electrode, and then peeled off slowly at ~45° angle. A mini-digital microscope camera (Vividia 2.0MP Handheld USB Digital Microscope, Oasis Scientific Inc., Taylors, SC) was used to inspect the samples prior and after these experiments.

IV. Experimental Results

The impedance results are presented in terms of amplitude (|Z|) and the phase angle (θ).

A. *PPy coating.*

The results of the coating process are depicted in Fig. 2, where the left image shows the pvCNT before coating, and the right image shows the pvCNT after coating. The images show that the cross-sections of the pvCNT pillars have shrunk after coating. This is possibly due to the high surface tension and viscosity of PPy.

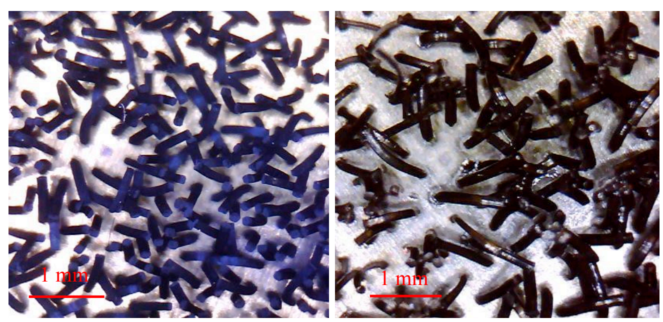

Fig. 2. A pvCNT electrode (left) before coating and (right) after coating.

B. *Impedance*

1. *Sensors Impedance measurement with dielectric fixture*

Measurement of the impedance of pvCNT electrode was collected using Agilent Fixture 16451B, where it was assured that the two plates were barely in contact with the substrate and the CNTs tips (stopping at a single click of the torque knob). Fig. 3 top plot shows the absolute impedance (|Z|) for the 200 µm gap with and without PPy coating, and the bottom plot shows the phase angle of the impedance for the same electrodes.

After coating with thin film PPy over the pvCNT electrodes, we can expect the total impedance to increase by the impedance of PPy thin film layer from the value of uncoated pvCNT electrode. As per expectation, the impedance of non-coated pvCNT electrode was 8.15 Ω at 40 Hz, whereas the impedance increased to 18.76 Ω after PPy coating. Thus, it indicates 10.61 Ω resistance increase due to the PPy coating, which is a function of the thickness of the PPy layer. The phase without coating is almost constant and close to zero, whereas in the coated version slightly changes the phase which increased up to 5º.

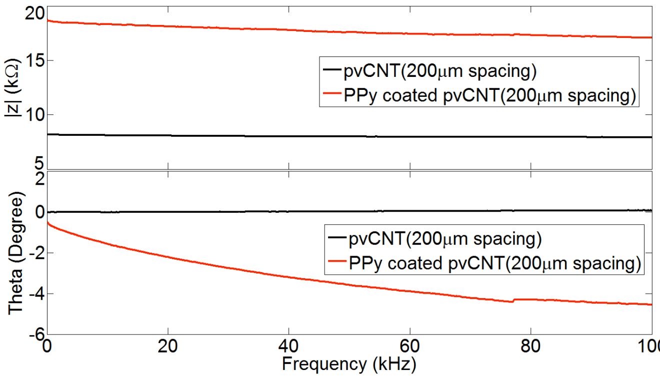

Fig. 3. The amplitude (top) and phase (bottom) of the impedance of non-coated pvCNT electrode and PPy coated pvCNT electrode.

C. *Signal Capture in Bench Test*

As we have shown in our previous papers, the potential drops on the electrodes using Al foil are 809.4 mV and 15 mV for GS-26 electrode and pvCNT electrode, respectively. Using the same experiment, the potential drop of the coated pvCNT electrode was measured to be ~0.13 mV as shown in Fig. 4.

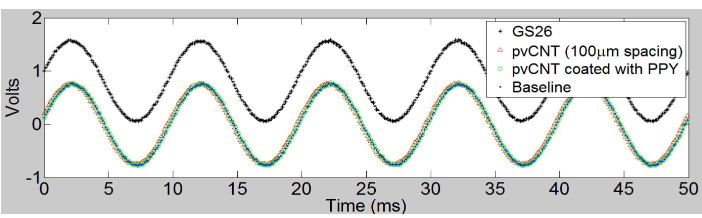

Fig. 4. Test results of pvCNT and GS26 with Al foil.

D. *Compression and peel test*

Mechanical stability is a very important factor for pvCNT electrode to ensure that all the CNT pillars are strongly attached to the substrate. Compression and peel test were used to conduct the mechanical stability. Fig. 5(a) shows the microscopy images of the coated pvCNT electrode after the compression test experiments. The pvCNT pillars were bent with the compression force.

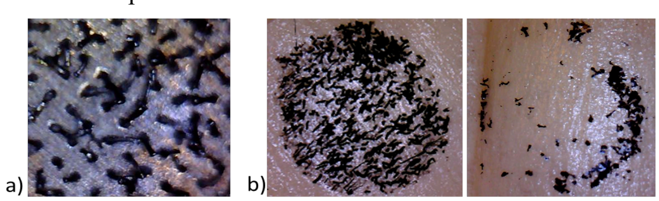

Fig. 5. (a) Microscopy images of the coated electrdoes after the compression experiments. (b) The peel test results show the peeled pillars on the drafting tape. (Left) the non-coated pvCNT electrode, and (Right) the coated pvCNT electrode.

Fig. 5b shows the peel test results for the coated and non-coated pvCNT electrodes. The amount of CNT pillars that were dislodged with the drafting tape for the non-coated electrode was significantly higher than the coated electrode, as clearly depicted in Fig. 5b. The lesser number of pvCNT pillars on drafting tape indicates that the pillars are strongly attached to the SS substrate.

V. Conclusions

Previously, we demonstrated a novel dry electrode of pvCNT fabricated using patterned and vertically aligned MWCNT pillars on SS circular disks (ϕ = 10 mm). The results showed stable and low impedance of electrode over short and long duration compared to commercial electrodes. The issue of pvCNT was weak mechanical adhesion strength with the substrate. In this work, we demonstrate an improvement by coating the pvCNT with an electrically conductive polymer (PPy). The results clearly demonstrate that the PPy coating provides the pvCNT electrode with higher mechanical strength, as well as minimizes the possibility of contamination or exposure of skin to CNT, although the impedance of the electrode has slightly increased. The developed coating method renders the pvCNT electrode for practical testing. One future direction is to collect EEG and ECG signals from animal model and study skin response to this novel dry electrode.

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