Available online at www.sciencedirect.com

ScienceDirect

Procedia Materials Science 11 (2015) 147 – 151

Procedia Materials Science

www.elsevier.com/locate/procedia

5th International Biennial Conference on Ultrafine Grained and Nanostructured Materials, UFGNSM15

Chemical Synthesis of Polypyrrole Nanotubes for Neural Microelectrodes

Z. Deljoo Kojabad[a], S. A. Shojaosadati[b,*]

[a]*Nanomaterials Group, Department of Materials Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran*
[b]*Biotechnology Group, Chemical Engineering Department, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran*

Abstract

A low impedance electrode/tissue interface is critically important for neural microelectrodes recording to maintain signal quality. In this study, polypyrrole (PPy) nanotubes used to decrease the interface impedance. PPy nanotubes were chemically synthesized inside the alumina template. SEM analysis showed 70 nm inside diameter of nanotubes. Electrochemical impedance spectroscopy (EIS) tests were performed for impedance measurement of PPy nanotubes coated microelectrode surface. The results showed that the impedance of the microelectrodes with PPy nanotubes coatings was four order of magnitude lower than the electrodes without coating in the neural frequency. EIS results also showed significant decrease in impedance of PPy nanotubes rather than PPy thin films.

Peer-review under responsibility of the organizing committee of UFGNSM15

Keywords: polypyrrole; nanotubes; chemical synthesis; neural microelectrodes.

1. Introduction

Polypyrrole and its derivatives are the most widely used conducting polymers in biomedical applications due to its biocompatibility and customizability Wadhwa et al. (2006). PPy nanostructures conductivity are an order of magnitude higher than in the bulk form of the polymer prepared by the same method Demoustier-Champagne et al. (1999). Among the various methods of fabricating nanowires and nanotubes, the template synthesis approach is a very simple, general and common method Hariri et al. (2013). Polypyrrole can be synthesized by various routes such as electrochemical and chemical methods. Electrochemical fabrication of polypyrrole nanowires through the nanopores

* Corresponding author. Tel.: +98-82883341; fax: +98-82883341.
E-mail address: shoja_sa@modares.ac.ir

Peer-review under responsibility of the organizing committee of UFGNSM15
doi:10.1016/j.mspro.2015.11.014

of AAO, or polycarbonate membranes and also chemical polymerization of pyrrole in the nanochannels of polycarbonate membranes have been reported, Hassanzadeh et al. (2012). Neural electrodes are used to recognize and treatment of disorders of neural network disturbances, Cogan (2008), Grill et al. (2009). In the physiologic environment, bioelectric signals are carried out in the form of ionic currents. The purpose of a neural electrode is to transduce these biological signals to and from electronic signals, Abidian and Martin (2010). A low impedance electrode/tissue interface is critically important for neural microelectrodes recording to maintain signal quality, Rui et al. (2011), Luo et al. (2011), Lu et al. (2012). Although several approaches are used to decrease the electrode/tissue interface impedance, Bellamkonda et al. (2005) but to the best of our knowledge this is the first study on the use of chemically synthesized PPy nanotubes to modify the neural interfaces. Use of conductive polymers due to their high ionic conductivity could result in reduction of interface impedance, Liu et al. (2011).

In this study PPy nanotubes array are synthesized chemically in the nanopores of AAO template and the PPy nanotubes coated microelectrode impedance is determined by electrochemical impedance spectroscopy and compare with bare microelectrode.

2. Experimental Procedure

AAO with pore diameter of 100 nm and thickness of 60 μm were purchased from Whatman (UK) and used as templates for the synthesis of PPy nanostructures. Pyrrole and Ferric chloride were obtained from Merck (Germany). Pyrrole was distilled prior to utilization. All other reagents were analytically graded and all aqueous solutions were prepared in deionized water.

A home-made two-compartment reaction chamber similar to the apparatus used by, Hassanzadeh et al. (2012), was used to prepare the PPy nanotubes. The two reaction chambers with 2.5cm diameter and 2cm height were constructed to hold the same volume of an oxidizing and pyrrole monomer solutions. Cylinders were fitted to each other by screw and a plastic washer used to seal the two-compartment chamber. Solutions were separated by the AAO template (Fig. 1.). 0.4 M Pyrrole monomer and 0.5 M $FeCl_3$ solutions were filled into each cell from the small holes on top of the compartment and polymerization occurred within the pores of the template. The monomer and oxidant reagents diffused toward each other through the nanopores of the template for 30 minutes and reacted to produce PPy nanotubes. The important point in PPy nanotube synthesis is that Pyrrole concentration and Time of the reaction should be controlled to achieve nanotube morphology.

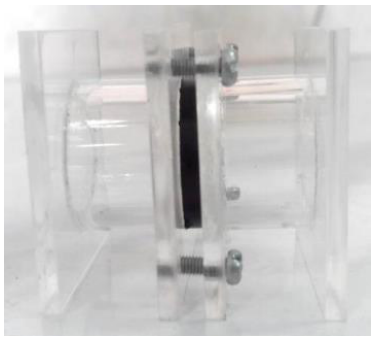

Fig. 1. The two-compartment chamber used for chemical polymerization of pyrrole inside the nanopores of AAO template.

3. Results and discussion

3.1. Scanning electron microscopy

After PPy nanotubes synthesis, the template was removed from the reaction chamber and rinsed two times with distilled water. To analyze the morphology of the obtained nanotubes, template was broken and a thin film of Au was sputtered on a cross section and SEM analysis was performed on the sample. Fig. 2 shows the SEM image of PPy nanotube.

As shown in Fig. 2 PPy nanotubes with diameter of 250 nm and inside diameter of 110 nm and thickness of 70 nm were obtained.

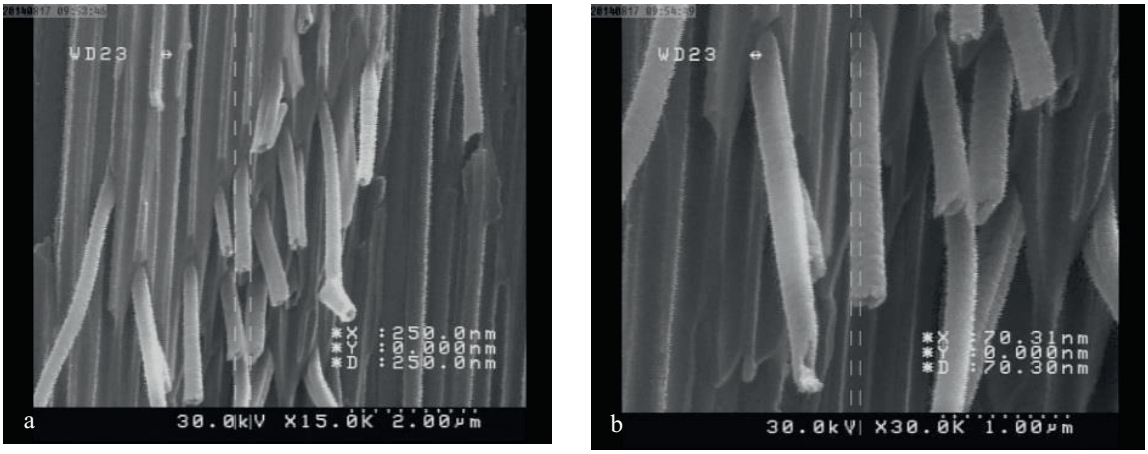

Fig. 2. SEM image of chemically synthesized PPy nanotubes with (a) diameter of 250nm; (b) thickness of 70nm.

Because the nucleation occurs at the walls of the template nanopores and growth starts from the wall to the center, more reaction time will lead to complete filling of the pores. Higher concentration of monomer and FeCl3 solutions lead to formation of a bulk layer of PPy on two sides of the template and prevent complete filling of nanopores so that even in high reaction times nanotubes will be synthesized. Fig. 3 shows the nanotube with small inner diameter and a bulk layer of PPy on the template surface.

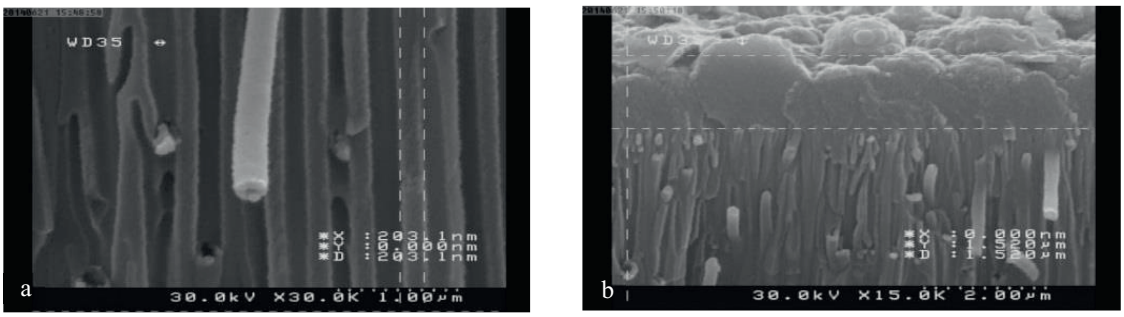

Fig. 3. SEM image of (a) PPy nanotube with a smaller inner dimeter; (b) bulk layer of PPy on the template surface.

3.2. Electrochemical Impedance spectroscopy

Figure 4 shows Bode diagram of neural array of PPy nanotubes coated microelectrode and the single bare stainless steel sheet. Results show that the four order of magnitude decreases in the impedance of PPy nanotubes rather than bare stainless steel in the whole range of frequency.

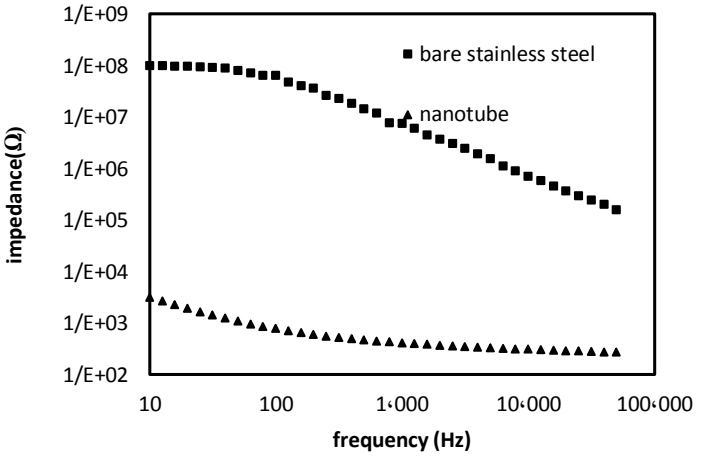

Fig. 4. Bode diagram of PPy nanowires, PPy nanotubes and bare stainless steel.

Decrease in the impedance of PPy nanotubes rather than bare stainless steel in the whole range of frequency is because of the high ion conductivity and high surface area of PPy nanotubes.

4. Conclusion

In this study PPy nanotubes array were synthesized chemically in the nanopores of AAO template. SEM analysis confirmed nanotube morphology and higher reaction time and monomer concentration resulted in nanowire morphology. The PPy nanotubes coated microelectrode impedance determined by electrochemical impedance spectroscopy showed four order of magnitude decrease rather than bare stainless steel in the whole range of frequency.

Acknowledgements

The authors would like to thank Tarbiat Modares University and Iran Nanotechnology Initiative Council (INIC) for the financial support of this work.

References

Abidian, M.R., Martin, D.C., 2010. Conducting-Polymer Nanotubes Improve Electrical Properties, Mechanical Adhesion, Neural Attachment, and Neurite Outgrowth of Neural Electrodes. NIH Public Access 6, 421–429.

Cogan, S.F., 2008. Neural stimulation and recording electrodes. Annual Review of Biomedical Engineering 10, 275–309.

Demoustier-Champagne, S., Duchet, J., Legra, R., 1999. Chemical and electrochemical synthesis of polypyrrole nanotubules. Synthetic Metals 101, 20-21.

Grill, W.M., Norman, S.E., Bellamkonda, R.V., 2009. Implanted neural interfaces: biochallenges and engineered solutions. Annual Review of Biomedical Engineering 11, 1-24.

Hariri, M.B., Dolati, A., Moakhar, R.S., 2013. The Potentiostatic Electrodeposition of Gold Nanowire/Nanotube in HAuCl4 Solutions Based on the Model of Recessed Cylindrical Ultramicroelectrode Array. Journal of the Electrochemical Society 160, D279–D288.

Hassanzadeh, N., Omidvar, H., Tabaian, S.H., 2012. Chemical synthesis of high density and long polypyrrole nanowire arrays using alumina membrane and their hydrogen sensing properties. Superlattices and Microstructures 51, 314–323.

He, W., Bellamkonda, R.V., 2005. Nanoscale neuro-integrative coatings for neural implants, Biomaterials 26, 2983–2990.

Liu, X., Yue, Z., Higgins, M.J., Wallace, G.G., 2011. Conducting polymers with immobilised fibrillar collagen for enhanced neural interfacing. Biomaterials 32, 7309-7317.

Lu, Y., Li, Y., Pan, J., Wei, P., Liu, N., Wu, B., 2012. Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate)-poly(vinyl alcohol)/poly(acrylic acid) interpenetrating polymer networks for improving optrode neural tissue interface in optogenetics. Biomaterials 33, 378-394.

Luo, X., Weaver, C.L., Zhou, D., Greenberg, R., Cui, X.T., 2011. Highly stable carbon nanotube doped poly(3,4 -ethylenedioxythiophene) for chronic neural stimulation. Biomaterials 32, 5551-5557.

Rui, Y., Liu, J., Wang, Y., Yang, C., 2011. Parylene-based implantable Pt-black coated flexible 3-D hemispherical microelectrode arrays for improved neural interfaces. Microsystem Technologies 17, 437–442.

Wadhwa, R., Lagenaur, C.F., Cui, X.T., 2006. Electrochemically controlled release of dexamethasone from conducting polymer polypyrrole coated electrode. Journal of Controlled Release 110, 531 – 541.