Sensors and Actuators A 193 (2013) 141–148

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

PEDOT/MWCNT composite film coated microelectrode arrays for neural interface improvement

Sanyuan Chen, Weihua Pei*, Qiang Gui, Rongyu Tang, Yuanfang Chen, Shanshan Zhao, Huan Wang, Hongda Chen

State Key Laboratory of Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

ARTICLE INFO

Article history:
Received 24 October 2012
Received in revised form
21 December 2012
Accepted 14 January 2013
Available online 23 January 2013

Keywords:
Microelectrode arrays
PEDOT/MWCNT
Electrodeposition
Charge injection limit
Neural interface

ABSTRACT

High-performance electrode materials play a crucial role at the interface of implantable neural electrode. To realize bidirectional transduction between neural tissue and neural microelectrodes, the electrode material must satisfy the function of stimulating and recording. As the number and density of electrode increase, tiny electrodes with high performance are needed in future bioengineering study. In this study, a method of electrochemically co-deposited poly(3,4-ethylenedioxythiophene)/multi-walled carbon nanotube (PEDOT/MWCNT) onto microelectrode arrays with 8 channels was investigated. After modification, the impedance, charge transfer ability and frequency response characteristic were improved simultaneously. Compared with bare golden electrode, the coated microelectrodes with a surface area of 615 μm^2 exhibited a particularly high safe charge injection limit of 7.74 mC/cm^2 and low impedance of 12 kΩ at 1 kHz. In vivo inferior colliculus implantation of rats revealed that the composite film coated microelectrodes showed higher signal to noise ratio recordings >15 dB compared to 6 dB SNR of bare gold microelectrodes.

1. Introduction

Microelectrodes for neural stimulation and recording play an important role in the study of neural prosthesis [1,2], information decoding of in vivo neural network [3], brain computer interface [4] and so on. The size of individual electrode sites has become a key parameter in microelectrode design for a number of reasons. First, smaller electrode sites facilitate the development of more densely microelectrode arrays with higher spatial resolution. When the electrode size shrinks to the same scale of neurons, researchers can sample from a particular neuron out of billions of neurons to precisely study how neural network interact to produce biologically relevant behaviors. Second, smaller electrode sites shrink the volume of the total microelectrode, which in turn cause less damage during implantation.

However, decreasing the size of an electrode site increases the impedance, which seriously impacts high-resolution stimulation and recording [5]. Impedance degrades recording properties by two mechanisms: noise and shunt loss [6], which both increase in proportion to impedance. Neural signals will be overwhelmed when the impedance exceeds 5 MΩ [7]. Besides, high electrode impedance means high potential at the neural-electrode interface and cause irreversible chemical reactions or heat accumulation, which can lead to electrode corrosion and damage of surrounding tissue [8].

Since the electrochemical properties of an electrode are mainly dependent on the materials present on the interface, a common approach to bring down the impedance of electrodes with small sites is to coat them with suitable materials. Conductive polymers (CPs) coatings have been widely used to be an enabling technology for smaller electrode designs [9]. The reason of high conductivity of conductive polymer lies in a conjugated backbone with a high degree of π-orbital overlap that can be subjected to oxidation or reduction by electron acceptors or donors, resulting in p-type or n-type doped materials, respectively [10]. By changing dopant concentrations, electrical conductivity can be enhanced by as much as 15 orders of magnitude.

In recent years, poly(3,4-ethylenedioxythiophene) (PEDOT) has exhibited promising adhesion and biocompatibility among the known CPs [11]. PEDOT doped with different counterions such as ClO_4 [12] and dodecyl sulfate [13] and poly(styrene sulfate) (PSS) [14] has been electrochemically polymerized from aqueous solutions and electrochemical deposited on neural microelectrode arrays to form soft, low impedance and biologically active coatings.

Among all the nano materials, carbon nanotubes have attracted much attention due to its intriguing physicochemical properties [15,16]. The extraordinary strength, electrical conductivity and chemical stability have made CNT attractive for interfacing

* Corresponding author. Tel.: +86 10 8230 4345x803.
E-mail address: peiwh@semi.ac.cn (W. Pei).

0924-4247/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.sna.2013.01.033

with neural systems to develop biocompatible and neuroprosthetic electrodes [17]. However, the poor adhesion between CNT and substrate was a major obstacle to form an ideal neural interface [18–20], and the biocompatibility was influenced by different selected dispersants [21].

In this paper, we developed a simple method to deposit PEDOT and MWCNT simultaneously to build a composite film with better adhesion, electrical and biocompatibility performance. We adopt carbon nanotubes into PEDOT polymerization to electrodeposite MWCNT doped PEDOT on neural microelectrode arrays. Neural microelectrode arrays were fabricated in wafer scale on SOI substrate. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry and potential transient method were used to characterize the electrode–electrolyte interface of the modified neural microelectrodes. Based on the results of the characterization, the electrical parameters of the deposition process are optimized. Acute implantation in inferior colliculus using PEDOT/MWCNT coated microelectrodes was carried out and high quality neural activity was recorded and exhibited a markedly lower noise floor than controls.

2. Materials and methods

2.1. Materials

3,4-Ethylenedioxythiophene (EDOT) monomer (>98%) and poly(styrene sulfate) (PSS) were purchased from Yacoo Corp (Suzhou, China). Carboxyl modified multi-walled CNT with the length of 0.5–2 μm and diameter of 10–20 nm was a commercial product purchased from Chengdu Organic Chemicals Co. Ltd. (China). All other chemicals were of analytical grade. Deionized (DI) water was used in all experiments.

2.2. Neural microelectrode arrays fabrication

The neural microelectrode arrays comprise a slender needle-like probe, which is slightly tapered with a total length of 6 mm. 8 recording sites are aligned along the probe spacing 200 μm apart, with a diameter of 30 μm. The process to produce neural microelectrodes is a standard photolithography process, which was reported in another paper [22]. The microelectrodes are realized on a 4 in. SOI wafer, which consist of four structure layers: substrate layer, lower dielectric layer, metal layer and upper dielectric layer. Substrate layer supplies mechanical strength for the insertion of microelectrode implantation while lower and upper dielectric layers sandwich the metal layer to form an insulation enclosure. The thickness of microelectrodes is 15 μm thick, much thinner than a full wafer thickness. Openings in the upper dielectric layer along the probe define vertical connections to underlying gold traces for interfacing to the tissues. At the rear of the probe, gold wire bond pads facilitate connections with signal processing instrument by customized printed circuit boards.

2.3. Electrochemical deposition process

An aqueous solution containing 0.1 wt% EDOT, 0.2 wt% PSS and 2 mg/mL MWCNT in deionized water were dispersed under ultrasonic irradiation for 1 h to form a fully electropolymerization of PEDOT [23]. Electrochemical deposition of PEDOT/MWCNT was accomplished on the microelectrode sites using electrochemical workstation (CHI 660D). In the galvanostatic experiments, various current densities were applied to optimize electrodeposition condition, while the total amount of transferred charge was kept constant for all current densities. For a microelectrode with a surface area of 2.8×10^{-3} cm^2, the charge applied for the electrodeposition is 0.7 μC, while the current is changed from 2 nA to 100 nA and with it changes the time. The film thickness was controlled by adjusting electrochemical deposition time.

In all electrochemical experiments of this study, electrodes were mounted in a three-electrode cell with an Ag/AgCl electrode acting as a reference electrode and a large-area Pt electrode as a counter electrode.

2.4. Electrochemical measurements

Electrochemical workstation was used to evaluate electrochemical characterization of electrode sites for 10 probes in vitro. A solution of 0.1 M phosphate buffer solution (PBS, pH = 7.2) at 25 °C was used as an electrolyte in a three-electrode cell configuration. A 10 mV RMS sine wave was used to record the impedance over a frequency range of 1–10^5 Hz. Cyclic voltammetric measurements were performed between potentials of −0.6 V and 0.8 V (vs. Ag/AgCl) with a scan rate of 500 mV/s. Before each CV curve was recorded, several cycles were swept to insure that the modified film had reached a stable state. ZSimpWin software was used for the measurement and curve fitting analyses. Potential transient measurements were used to determine safe charge injection (Qinj) limits. Current pulsing was performed with CHI instrument (Chenhua, China) that provides biphasic current pulses of desired amplitudes and precise width. All potential transient responses were measured in a three-electrode cell comprised with an Ag/AgCl electrode acting as a reference electrode and a large-area Pt electrode as a counter electrode. The electrode potential excursion was recorded against an Ag/AgCl reference electrode.

2.5. Morphology

Information about the surface morphology and microstructure of the coatings were obtained using Optical microscopy and scanning electron microscope. SEM images were taken with a typical voltage of 5 kV.

2.6. Animal preparation

All procedures were conducted in accordance with protocols approved by the institutional animal ethical committee, and the regulations for the care and use of laboratory animals Adult male Sprague-Dawley rats weighting about 250 g were used for the implantation experiment. After being anesthetized with urethane (1.4 g/kg, 20% solution) the rats were immobilized in a standard stereotaxic frame. A stainless steel bone-screw was inserted into the skull. The electrode connector was grounded to the bone-screw using a surface insulated stainless steel wire. Microelectrode arrays were advanced by a hydraulic microdrive (FHC, Bowdoin, ME, USA). Anesthesia level was monitored by breathing patterns and eye blink reflex during recording. Craniotomy was performed according to the rat brain atlas [24].

2.7. Electrophysiological recording

Recorded neural signals were acquired using Tucker Davis Technologies (TDT) multichannel neural acquisition processor. Acoustic stimuli with different amplitude and frequency were delivered through an electrostatic speaker 25 cm far away from the animal's ear. All stimuli were delivered in an open field in an anechoic chamber. Neural signals recorded were amplified (5000×), filtered (0.3–5 kHz) and digitized at 25 kHz [25].