Sensors & Actuators: B. Chemical 271 (2018) 280–288

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Single walled carbon nanohorns composite for neural sensing and stimulation

Stefano Carli[a,*], Linda Lambertini[a], Elena Zucchini[a,b], Francesca Ciarpella[a,b], Alice Scarpellini[c], Mirko Prato[d], Elisa Castagnola[a], Luciano Fadiga[a,b], Davide Ricci[a]

[a] Center for Translational Neurophysiology of Speech and Communication, Istituto Italiano di Tecnologia, Via Fossato di Mortara 17/19, 44121 Ferrara, Italy
[b] Section of Human Physiology, University of Ferrara, Via Fossato di Mortara 17/19, 44121, Ferrara, Italy
[c] Electron Microscopy Facility, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
[d] Materials Characterization Facility, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

ARTICLE INFO

Keywords:
PEDOT
Electrodeposition
Single walled carbon nanohorns
Neural sensing and stimulation
Multielectrode arrays
Neural implants

ABSTRACT

Oxidized single walled carbon nanohorns (ox-SWCNH) were electrodeposited onto gold microelectrode arrays in conjunction with poly(3,4-ethylenedioxythiophene) (PEDOT) and polystirenesulfonate (PSS), and the properties of the new composite material for neural recording and stimulation were assessed. PEDOT/ox-SWCNH composites were compared with films prepared with one of the most notorious carbonaceous material in this field, the oxidized multi-walled Carbon Nanotubes (ox-MWCNT). The PEDOT/ox-SWCNH exhibited superior charge transfer capability, reflecting greater electroactive surface, as confirmed by SEM and EIS characterizations. As a consequence, a charge injection limit of 11.6 mC/cm^2 was observed for the new composite, which is higher than the one of PEDOT/ox-MWCNT (8.7 mC/cm^2). Having confirmed comparable neural recording performance, the PEDOT/ox-SWCNH composite results very promising for improving therapeutic electrical stimulation in the central and peripheral nervous systems.

1. Introduction

An ideal cortical microelectrode array for neural recording and stimulation needs to be minimally invasive, flexible and robust while providing low impedance and high charge transfer capability. Typical neural electrodes are made using noble metals and alloys but recently glassy carbon based microelectrodes have emerged [1,2]. Moreover, for neural stimulation, electrodes should be capable of injecting relatively large currents while minimizing electrode degradation due to faradaic effects, requirements generally satisfied by increasing the electrode size and, therefore, negatively affecting biocompatibility. In order to allow long-term use, the surface of the microelectrodes should be able to facilitate charge transport and minimize inflammatory reaction and gliosis.

To improve electrochemical properties and stability of microelectrode arrays, conductive polymers (CPs), such as polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT), are commonly electrodeposited onto the metal underlayer in order to significantly reduce the total impedance as well as to increase the total charge that can be accumulated. This leads to higher S/N ratios, higher charge injection limits, smaller voltage excursions and less heat generated at the interface during stimulation [3,4]. It has been demonstrated that PEDOT exhibits higher electrochemical stability than PPy [5], and is very promising in terms of biocompatibility as well [6,7].

Carbon nanotubes (CNT) have also been widely explored as co-dopant and dopant for PEDOT composites, enabling improved neural signals recording as well as chronic neural stimulation [8–13]. Among carbon based nanomaterials, high purity grade Single Walled Carbon Nanohorns (SWCNH) are produced by direct vaporization of pure graphite without the use of metal catalysts, originally by laser ablation [14], and later by arc discharge [15] or by induction of very intense, high frequency, eddy currents [16]. Having a basic structure similar to tiny carbon nanotubes, SWCNH maintain most of the typical properties of nanotubes including high electrical conductivity, high thermal conductivity and they are easy to be functionalized [17]. Pristine SWCNH are extremely hydrophobic but they can be readily functionalized with abundant oxygenated groups, such as carboxylic acid groups, by oxidative treatment in water-acidic media, to obtain hydrophilic oxidized SWCNH (ox-SWCNH). This treatment promotes the opening of the horn tip while preserving the conductivity and electrochemical properties. Here we report, for the first time, the use of ox-SWCNH as co-dopant for the electrodeposition of PEDOT/PSS onto microelectrode arrays for

* Corresponding author.
E-mail address: stefano.carli@iit.it (S. Carli).

https://doi.org/10.1016/j.snb.2018.05.083
Received 24 January 2018; Received in revised form 14 May 2018; Accepted 15 May 2018
Available online 19 May 2018

neural applications comparing their behavior with the similar composite based on oxidized multi walled carbon nanotubes (ox-MWCNT) [6–11].

2. Experimental

2.1. Materials and equipment

Pristine SWCNH were obtained from Carbonium s.r.l., Padova (Italy) [16]. ox-MWCNT were from Nanocyl S.A., Belgium (NC 3151, < 4% of COOH). All chemicals were from Sigma Aldrich except otherwise specified.

2.2. Electrochemical characterization

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and coating electrodepositions were carried out using a Reference 600 potentiostat (Gamry Instruments, USA) connected to a three-electrode electrochemical cell with a Pt wire as a counter electrode and a Ag/saturated AgCl reference electrode (+0.197 V *vs* NHE [18]). The charge storage capability (CSC) was calculated as the time integral of an entire CV cycle between +0.5 and −0.6 V. EIS were performed in three electrodes cell configuration by superimposing a voltage sine wave modulation (10 mV RMS amplitude, 0 V potential applied) within the frequency interval of 10^5–1 Hz. The software ZSimpWin V 3.2 (EChem Software) was used for equivalent circuit modeling of EIS data and χ^2 values in the range of 10^{-4}–10^{-6} were used to estimate the goodness of the fit. Voltage transients were collected with a Parstat 2273 potentiostat (Princeton Applied Research) in a two electrode configuration by applying cathodic-first balanced current pulses (1 ms single pulse, charge density 2 mC/cm^2). Electrical stimulation consisted of a series of cathodic-first charge balanced biphasic pulses with 6.37 mC/cm^2 charge density, 500 µs cathodic half-phase period and a frequency of 500 Hz. The electrochemical characterizations were collected in a 0.9% w/w sodium chloride aqueous solution.

2.3. Gold microelectrode arrays [19]

16-electrode arrays with (1.2 × 1.2) mm total recording area and 60 µm diameter recording sites (Fig. 1a) were used for electrochemical, morphological and X-ray photoemission spectroscopy (XPS) characterizations, as well as for neural activity recording. For stability tests under stimulation electrical pulses, similar arrays have been used, with microelectrode diameter of 100 µm.

2.4. PEDOT/ox-SWCNH and PEDOT/ox-MWCNT electrodeposition

A nanostructured gold layer was electrodeposited following our previously published work [19]. The composite electrodeposition solution was prepared by suspending ox-SWCNH [20] or ox-MWCNT in ultrapure water at the concentration of 1 mg/ml (Milli-Q, Millipore, USA) by horn sonication (Vibra-Cell VCX130, Sonics and Materials, USA) for thirty minutes (6 s at 66% duty cycle pulses, 4 W/ml). Poly (sodium 4-styrene sulfonate) (NaPSS, 0.1 M) and 3,4-ethylenedioxythiophene (EDOT, 0.05 M) were added to the suspension immediately after, and the mixture was stirred at room temperature for thirty minutes. The electrochemical deposition was carried out in potentiodynamic mode, in the potential range of 0 V–0.95 V, with a scan rate of 100 mV/s, for a total of 100 cycles. For sake of clarity, PEDOT composites electrodeposited by a deposition mixture containing ox-SWCNH or ox-MWCNT will be abbreviated with **NHs** or **NTs**, respectively. The deposition followed the detailed scheme reported in Fig. 1b. The same conditions were used to deposit PEDOT:PSS from a solution of EDOT (0.05 M) and NaPSS (0.1 M) in water. A schematic representation of the coated microelectrode is reported in Fig. 1c.

2.5. Optical and surface characterization

High-resolution scanning electron microscopy (SEM) imaging was carried out using a JEOL JSM 7500FA (Jeol, Tokyo, Japan) equipped with a cold FEG (field emission gun), operating at 5 kV acceleration voltage. When needed, the sample was carbon coated with a 10 nm thick film using an Emitech K950X high vacuum turbo system (Quorum Technologies Ltd, East Sussex – UK). XPS analyses were carried out using a Kratos Axis Ultra^{DLD} spectrometer (Kratos Analytical Ltd., UK) on 100 µm microelectrodes. XPS spectra were acquired using a monochromatic Al Kα source operated at 20 mA and 15 kV. High resolution spectra were collected at pass energy of 20 eV and energy step of 0.1 eV, and the Kratos charge neutralizer system was used on all specimens. Spectra have been charge corrected to the main line of the C 1 s spectrum set to 284.8 eV and analyzed with CasaXPS software (Casa Software, Ltd., version 2.3.17). Each sulfur species is represented by a S 2p doublet, due to spin-orbit coupling. In the fitting procedure, each doublet was fitted to a pair of peaks with the constraints of having the same full width at half maximum (fwhm), the standard spin–orbit splitting of 1.2 eV, and a statistical branching ratio of 1/2. The position of the S 2p doublet was identified by the position of the most intense component (*i.e.* S $2p_{3/2}$ component).

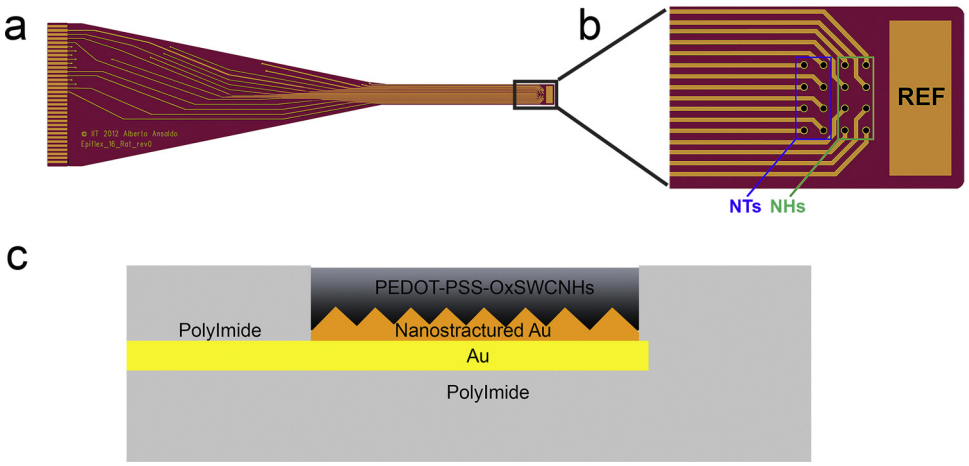

Fig. 1. a) Representative scheme of the whole µEcoG array used for neural signal recording, b) details on the position of NTs and NHs coatings on electrodes and c) scheme of the NHs modified microelectrode.