Low-impedance Tetrodes using Carbon Nanotube-Polypyrrole Composite Deposition

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Abstract

A tetrode is one of the neural electrodes, and it is widely used to record neural signals in the brain of a freely moving animal. The impedance of a neural electrode is an important parameter because it determines the signal-to-noise ratio of the recorded neural signals. Here, we developed a modification technique using carbon nanotube-polypyrrole composite nanostructures to decrease the impedances of tetrodes. The synthesis of the carbon nanotube and polypyrrole nanostructures was performed in two steps. In the first step, randomly dispersed carbon nanotubes and pyrrole monomers were gathered and aligned on the tetrode electrode. Next, they were electro-polymerized on the electrode surface. As the applied time (step-1 and step-2) and the offset voltage increased, the impedances of the tetrodes decreased. The modification technique is, therefore, an important and useful of lowering the impedances of tetrodes.

Keywords: Tetrode, Carbon nanotube, Polypyrrole, Pyrrole monomer, Impedance

1. INTRODUCTION

The tetrode is a type of neural electrode that consists of four microwires with a width less than 30 μm, and it is widely used in neuroscientific research because it can isolate a single-unit from multiple neuronal signals in the brains of freely moving animals \([1,2]\). The recording performance of tetrodes is primarily determined by their impedances \([3,4]\) because high-impedance electrodes increase the thermal noise and signal loss in the noise \([5,6]\). In order to reduce the impedances of tetrodes, gold or platinum is typically electro-deposited onto the tetrodes.

Recently, many studies have introduced methods to reduce the impedances of electrodes using surface modification techniques. These surface modification techniques are primarily focused on increasing the electrochemical surface area (ESA) \([7]\) through micro/nano-structures, using conductive polymers \([8-10]\), iridium oxide films \([11,12]\), and carbon nanotubes (CNTs) \([13-17]\). Surface modification techniques are very effective in reducing the impedances of tetrodes because they increase the ESA while maintaining the original surface area of the electrode, and can exclude a shorting problem between adjacent electrodes.

Furthermore, CNTs are widely used as materials for surface modifications, owing to their many superior properties, such as mechanical stability, intrinsically large surface areas \((700 \text{ m}^2\text{g}^{-1}-1000 \text{ m}^2\text{g}^{-1})\), chemical durability, and extremely high conductance \([18]\). Polypyrrole (PPY) also represents a promising material for surface modification, because of its high conductivity, chemical stability, and biocompatibility \([19,20]\). When combined, the CNT/PPY composite could be a very promising material for surface modification because of its significant enhancement of capacitance \([21]\). However, lowering the impedances of tetrodes has not been attempted in a previous study.

In this paper, we report a surface modification technique to reduce the impedances of tetrodes, using the CNT/PPY composite. The impedances of CNT/PPY modified tetrodes were controlled by varying the applied time (step-1, step-2) and the magnitude of the offset voltage. The impedances of CNT/PPY modified tetrodes were described, and their morphologies were observed using a scanning electron microscope (SEM). The results showed that the surface modification using CNT/PPY is a promising technique to reduce the impedances of tetrodes.
2. EXPERIMENTAL

2.1 Preparation of CNTs and pyrrole solutions

A surfactant solution was prepared by mixing deionized water (40 mL) with 1.4 wt% of sodium dodecyl sulfate (SDS, Sigma-Aldrich, St. Louis, MO, USA), with stirring. Single-walled nanotubes (SWNTs) were produced by an arc discharge process (diameter: 1.0 nm-1.2 nm, length: 5 μm-20 μm, Hanwha Nanotech, South Korea). Moreover, 3 mg of SWNTs were dispersed in the surfactant solution by sonication for 4 h. A 5 μL solution of pyrrole monomers (reagent grade, purity 98%, Sigma-Aldrich, St. Louis, MO, USA) was added to 1 mL of the CNTs solution.

2.2 Mechanism diagram of synthesis process of CNT/PPY nanostructures

The electrochemical deposition of CNTs with conductive polymers has been widely used in electrode modification [21]. In this paper, the synthesis process of CNT/PPY nanostructures was comprised of two steps. The CNTs were encapsulated by an anionic surfactant and well dispersed in a solution. Figure 1(a) shows the pyrrole monomers placed between molecules of anionic surfactants and CNTs.

In the first step, randomly dispersed CNTs and pyrrole monomers were attracted and aligned to the tetrodes by the AC electric field, without the offset voltage (Fig. 1(b)). When an electric field was applied, micelle-encapsulated CNTs were gathered to the tetrodes by dielectrophoresis (DEP). In the second step, the CNT/PPY nanostructures were synthesized on the surfaces of tetrodes by the electro-polymerization of pyrrole monomers. The pyrrole monomers can be polymerized, and CNT/PPY nanostructures can also be synthesized on the surfaces of tetrodes, when the potential is sufficiently higher than a certain value.

2.3 Experimental set-up and process

Figure 2(a) shows a schematic of the surface modification process, which consisted of a tetrode, reference electrode (gold), a solution containing CNTs and pyrrole monomers, and a function generator. An aqueous solution (20 μL) containing CNTs and pyrrole monomers was placed on the reference electrode, and the tetrode was precisely controlled using a three-axis stage. The function generator applied an AC voltage between the reference electrode and the tetrode. The applied AC voltage (voltage: 4 Vpp, frequency: 800 kHz) was divided into two steps: without offset voltage (step-1) and with offset voltage (step-2), as shown in Fig. 2(b). The applied offset voltage changed from 0.4 V-1.2 V. The applied step-1 time was changed from 10 s-30 s, and the step-2 time was varied from 1 s-4 s.

Fig. 1. Mechanism diagram of synthesis process of CNT/PPY nanostructures. (a) Disordered micelle-encapsulated CNTs without electric field; (b) CNTs accumulated and aligned to tetrodes by dielectrophoretic force; (c) electroactive monomer polymerized at the surfaces of tetrodes in the presence of offset voltage.
3. RESULTS AND DISCUSSIONS

3.1 Synthesis of CNT/PPY nanostructures with and without DC offset voltage

The applied AC voltage was divided into two steps: without off-set voltage and with offset voltage. As mentioned above, the randomly dispersed CNTs and pyrrole monomers could be gathered on the surfaces of tetrodes by the applied AC voltage (step-1). Moreover, the CNT/PPY nanostructures could be synthesized on the tetrodes because of the electro-polymerization of pyrroles under the applied AC voltage with offset (step-2). Figure 3 shows the results obtained without and with the DC offset voltage. As expected, in Fig. 3(a), CNT/PPY nanostructures were not synthesized onto the tetrodes (without offset voltage). However, in Fig. 3(b), CNT/PPY nanostructures were synthesized on the tetrodes, due to the presence of the offset voltage.

3.2 Dependence of impedance on the applied time and offset voltage

The impedance of a neural electrode is an essential parameter for neural recording. This is because the impedance affects the signal-to-noise ratio (SNR) of the recorded neural signals. Thus, the impedance should be optimized to be less than hundreds of kΩ, for a low thermal noise and a high SNR of neural signals. In general, the initial impedances of tetrodes range from 2 MΩ to 3 MΩ, measured at 1 kHz. In this paper, the impedance was normalized to the ratio of decreased impedance to initial impedance (RDI) because the initial impedances were not same. Figure 4(a) shows the RDIs changing the applied step-1 time from
In the first step, randomly dispersed CNTs and pyrrole monomers in a solution were gathered and aligned to the tetrodes. Thus, as the applied step-1 time increases, more CNTs and pyrrole monomers can collect on the tetrodes. The results show that the RDIs were further increased with the increasing applied step-1 time, and the RDIs were 65% at 10 s, 68% at 20 s, and 79% at 30 s. Figure 5 shows the tetrode morphology after the surface modification using CNT/PPY composites, and Figs. 5(a), 5(b), 5(c) show the results obtained by varying the applied time of step-1. As the applied step-1 time increases, more CNT/PPY nanostructures can be synthesized on the electrode.

In the second step, the gathered CNTs and pyrrole monomers were synthesized on the electrode by electro-polymerization. The amounts of synthesized CNTs and pyrrole monomers may be affected by the applied offset voltage and time. Figure 4(b) shows the variation of RDIs with the applied step-2 time in the range of 1 s - 4 s. Thus, as the applied step-2 time increases, more CNTs and pyrrole monomers can be synthesized on the surfaces of tetrodes. The results show that the RDIs were further increased with the increasing applied step-2 time, and the RDIs were 68% at 1 s, 74% at 2 s, and 69% at 4 s. In practice, the RDI of the 4 s condition was slightly lower, when compared to that of 2 s condition. In Fig. 5(f) depicting the condition at 4 s), sizes of the CNT/PPY nanostructures were slightly larger than the sizes of those in other conditions. In the 4 s condition, although larger amounts of CNTs and pyrrole monomers were synthesized, synthesized amounts were not used to increase the numbers of CNT/PPY nanostructures, but to increase the size of the CNT/PPY nanostructures. Therefore, the RDI corresponding to the 4 s condition may be slightly lower than that in the 2 s condition.

Figure 4(c) shows the RDIs changing the applied offset voltage of step-2 from 0.4 V - 1.2 V. As the applied offset voltage increases, more CNTs and pyrrole monomers can be synthesized on the surfaces of tetrodes. The RDIs were further increased with the increase of the applied offset voltage, and the RDIs were 11% (0.4 V), 74% (0.8 V), and 85% (1.2 V). Figs. 5(g), 5(h), and 5(i) show the results obtained by varying the offset voltage of step-2. As the applied offset voltage increases, more CNT/PPY nanostructures can be synthesized on the tetrodes.

4. CONCLUSIONS

In summary, a novel surface modification technique, using CNT/PPY nanostructures, was developed to enhance the impedances of tetrodes. The process of CNT/PPY nanostructure
synthesis was comprised of two steps. In the first step, CNTs and pyrrole monomers were gathered without the DC offset voltage, and in the second step, the gathered CNTs and pyrrole monomers were synthesized on the surfaces of tetrodes with the DC offset voltage. The results showed that the CNT/PPY nanostructures were synthesized only under the condition that the offset voltage was applied. In the first step, as the applied time was increased, the impedance decreased. In the second step, as the applied time and the offset voltage increased, the impedance decreased. The SEM images showed that low impedance conditions correspond to high density CNT/PPY nanostructures. In this regard, we first investigated the surface modification using CNT/PPY nanostructures to lower the tetrode impedance. Thus, it can be confirmed that our novel modification techniques could be applied to lower the impedances of tetrodes.

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