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Layer-by-layer assembled nanorough iridium-oxide/platinum-black for low-voltage microscale electrode neurostimulation

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ABSTRACT

Electrical neural stimulating electrodes play an important role in medical applications and improving health/medical conditions. However, size reduction for low-invasive electrodes creates issues with high electrolyte/electrode interfacial impedance and low charge-injection characteristics, which makes it impossible to stimulate neurons/cells. To overcome these limitations, we propose an electrode material for low-voltage microscale electrode neurostimulation that combines the advantages of low impedance of iridium oxide (IrOx) with the enhanced surface area of platinum black (Pt-black). Based on a simple, rapid, low-temperature electroplating process, herein a low impedance and high charge-injection electrode is fabricated by a layer-by-layer assembly of IrOx/Pt-black with nanoscale roughness. The assembled nanorough-IrOx/Pt-black electrode has an impedance of 32 Ω cm^2 at 1 kHz and a charge-injection delivery capacity (Q_{CDC}) of 46.7 mC cm^{-2}, which are 0.5 and 2.4 times the values for the same-sized IrOx/flat-Pt electrode, respectively. The stimulation capability of the nanorough-IrOx/Pt-black plated microelectrode is confirmed by *in vivo* stimulations of the sciatic nerve of a mouse. The threshold voltages of 8-μm-diameter and 11-μm-diameter electrodes are 700 mV and 300 mV, respectively. However, increasing the diameter of high Q_{CDC} nanorough-IrOx/Pt-black can further reduce the stimulation voltage. Consequently, nanorough-IrOx/Pt-black is applicable to low-voltage microscale electrode neurostimulations for powerful *in vivo*/*in vitro* electrophysiological measurements.

1. Introduction

Electrical neural stimulating electrodes, which play an important role in medical applications, have been used to improve medical conditions, including epilepsy, Parkinson disease [1], blindness [2], and hearing loss [3]. Recent advances in brain–machine interface (BMI) technology, which enables direct communications between the brain and external actuators [4,5], have realized a powerful neural stimulation application where tactile feedback occurs through microscale stimulation of the somatosensory cortex, or the so called brain–machine–brain interface (BMBI) [6]. Conventional electrodes, which are composed of sharpened needle-like metal electrodes with diameters of several tens of microns or larger, are typically used in electrical stimulations of neurons/cells [7]. Although the needle-electrode diameter can be further reduced using recent microfabrication technology for low invasive electrodes and chronic device implantations [8–10], size reduction-induced issues such as high electrolyte/electrode interfacial impedance and low charge injection characteristics of the electrode remain problematic in high-performance microscale stimulations of neurons/cells [11]. Such size reduction-induced issues make it impossible for the electrode to stimulate the target neurons, as well as the recording [12]. Moreover, improving both the impedance and charge-injection characteristics of the electrode is important to reduce the stimulating voltages applied to the electrode in a biological sample such as a brain or nerve.

Candidate electrode materials to improve the electrode's electrical properties have been reported: Pt-black [13], titanium nitride (TiN) [14], IrOx [15], poly(3,4-ethylenedioxythiophene) (PEDOT) [11], and carbon nanotube (CNT) [16]. Pt-black can enhance the

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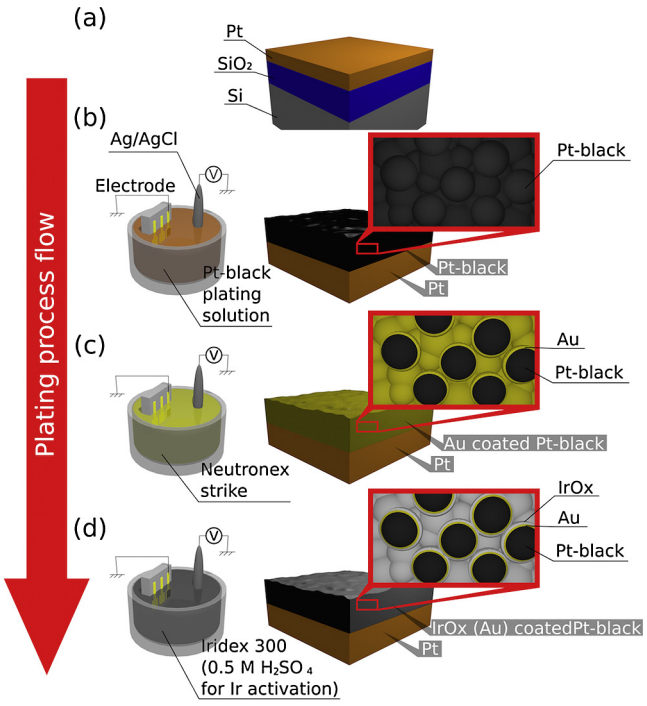

Fig. 1. Fabrication process steps for a nanorough-IrOx/Pt-black electrode: (a) initial flat-Pt platform electrode, (b) Pt-black plating over the Pt electrode, (c) Au plating as the adhesion layer, and (d) Ir plating and subsequent activation of the Ir for nanorough-IrOx/Pt-black.

effective surface area of Pt by creating nanoporous [13], and its mechanical stability has been demonstrated by penetrating the Pt-black tipped microneedle into a rat's cortex [9]. IrOx is a material with an excellent charge-injection delivery capacity (Q_{CDC}) (*e.g.*, 3.0 mC cm^{-2} for IrOx $\gg$ 0.075 mC cm^{-2} for Pt) [17]. Herein we combine these materials to develop low-impedance and high charge-injection electrodes *via* a layer-by-layer assembly of IrOx/Pt-black with nanoscale roughness based on electroplating, which is a simple, rapid, and low temperature (<60 °C) process. Hence, electrodes can be prepared on numerous device substrates, including silicon-microelectronics, flexible thin films, and three-dimensional micro/nanoelectromechanical systems (MEMS, NEMS) [8,9].

2. Methods

Nanorough-IrOx/Pt-black electrodes were fabricated by a layer-by-layer nanoscale assembly technique. Of the three layers, the first layer of Pt-black was used as a nanoporous template to enhance the effective electrode area [13], while the second gold (Au) layer improved the interfacial adhesion between Pt-black and the subsequent Ir layer. The third layer of IrOx was used to improve Q_{CDC} of the electrode [15].

Fabrication was based on a simple, rapid, low-temperature electroplating process. The first layer of Pt-black was electroplated with a Pt chloride solution (10 g $H_2PtCl_6{\cdot}6H_2O$, 0.1 g $Pb(CH_3COO)_2{\cdot}3H_2O$, and 300 ml deionized water (DIW) at room temperature) [13]. For a 100-nm thick Pt-black, the plating direct-current (DC) bias was 400 mV with a plating time of 10 s (Fig. 1b). After forming an Au adhesive layer at 32 °C (Neutronex Strike Au, Tanaka Holdings Co., Ltd.) (Fig. 1c), an ~10-nm-thick Ir layer was electroplated with an Ir solution (Iridex-300, Tanaka Holdings Co., Ltd.) at a 700-mV DC bias for 2 min and a plating temperature of 60 °C (Fig. 1d). Then Ir activation was achieved in a 0.5 M H_2SO_4 solution (room temperature). To avoid filling the nanoporous template of Pt-black with Au and Ir, thicknesses of the Au and Ir were limited to ~10 nm and ~10 nm, respectively. To activate Ir, we used triangle wave signals (+600 mV for high and −200 mV for low levels) at 100 mV s^{-1} for 2300 cycles. Fig. 2a shows a fabricated millimeter-scale nanorough-IrOx/Pt-black electrode array using platform 0.5-mm × 1.5-mm flat-Pt electrodes. Fig. 2b shows a microscale nanorough-IrOx/Pt-black electrode fabricated using an 8-μm-diameter flat-Pt electrode.

3. Results and discussion

Nanorough-IrOx/Pt-black electrodes can be assembled on Pt electrodes with numerous patterns (Fig. 2a and b). The atomic force microscope (AFM) image shows that the enhanced surface roughness of the IrOx/Pt-black electrode is due to the first layer of Pt-black (Fig. 2d). The roughness of IrOx/Pt-black is larger than other IrOx layers formed on a flat-Pt electrode using the same plating process without forming Pt-black (Fig. 2c). The transmission electron microscope (TEM) image of IrOx/Pt-black confirms that the observed roughness in the AFM image is consistent with the cross-sectional structure of the electrode with a similar roughness of ~100 nm (Fig. 2e).

The electrical properties of the fabricated nanorough-IrOx/Pt-black electrode were measured in saline. For microscale electrode measurements, size reduction-induced effects such as the spreading resistance of the electrode [18] and parasitic impedance of the device interconnection [12] should be eliminated in order to obtain size-independent properties of a nanorough-IrOx/Pt-black electrode. Thus, we investigated a millimeter-scaled electrode (0.5 mm × 1.5 mm, Fig. 2a).

To obtain the impedance shifts during the plating processes, herein step-by-step impedances for Pt, Pt-black, nanorough-Ir/Pt-black, and nanorough-IrOx/Pt-black were measured. Note that "nanorough-Ir/Pt-black" indicates a nanorough-Ir/Pt-black electrode before Ir activation. The electrode impedance was measured in a room temperature 0.9% NaCl saline solution bath with a sinusoidal wave (200 mV_{p-p} amplitude, 3×10^{-3} Hz–1 MHz) applied *via* a silver–silver chloride (Ag–AgCl) counter electrode. An impedance analyzer (Model 1260A Impedance/Gain-Phase Analyzer, AMETIC, Inc) was used in all impedance measurements. The step-by-step measurements clearly demonstrate a reduced electrode impedance. Compared to the initial Pt layer and the first layer of the Pt-black electrode, nanorough-IrOx/Pt-black has a 40-fold and 2-fold lower impedance at 1 kHz, respectively (Fig. 3a). The calculated impedance of nanorough-IrOx/Pt-black per unit area was 32 Ω cm^2 at 1 kHz. In the frequency range of 1–100 Hz, the electrode shifts from the capacitive phase to the resistive phase after Pt-black electroplating during the impedance measurements (Fig. 3b). The maximum resistive-phase angle in this electrode process occurs after IrOx formation by Ir activation. In a frequency range of 10^{-3}–1 Hz, nanorough-IrOx/Pt-black and flat-IrOx/Pt exhibit further capacitive phases compared to nanorough-Ir/Pt-black and Pt-black. This phase difference is due to the increased constant phase element (CPE) and the decreased interfacial resistance after IrOx formation by Ir activation [19].

To investigate the change in Q_{CDC} for different electrodes (Pt, Pt-black, nanorough-Ir/Pt-black, and nanorough-IrOx/Pt-black), we measured the step-by-step cyclic voltammogram (CV) responses. The electrodes were placed in the same saline bath, and swept from −0.85 to 0.9 V for Pt and Pt-black, and from −0.9 to 1 V for nanorough-Ir/Pt-black, nanorough-IrOx/Pt-black, and IrOx/flat-Pt at a constant sweep rate of 100 mV s^{-1} *versus* a Ag–AgCl reference electrode and a Pt counter electrode. Each CV response was