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Direct electrodeposition of Graphene enhanced conductive polymer on microelectrode for biosensing application

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ABSTRACT

Engineering of neural interface with nanomaterials for high spatial resolution neural recording and stimulation is still hindered by materials properties and modification methods. Recently, poly(3,4-ethylene-dioxythiophene) (PEDOT) has been widely used as an electrode-tissue interface material for its good electrochemical property. However, cracks and delamination of PEDOT film under pulse stimulation are found which restrict its long-term applications. This paper develops a flexible electrochemical method about the co-deposition of graphene with PEDOT on microelectrode sites to enhance the long-term stability and improve the electrochemical properties of microelectrode. This method is unique and profound because it co-deposits graphene with PEDOT on microelectrode sites directly and avoids the harmful post reduction process. And, most importantly, significantly improved electrochemical performances of the modified microelectrodes (compared to PEDOT-GO) are demonstrated due to the large effective surface area, good conductivity and excellent mechanical property of graphene. Furthermore, the good mechanical stability of the composites is verified by ultrasonication and CV scanning tests. *In-vivo* acute implantation of the microelectrodes reveals the modified microelectrodes show higher recording performance than the unmodified ones. These findings suggest the composites are excellent candidates for the applications of neural interface.

1. Introduction

Neural microelectrode is being developed as a technique to investigate the brain functions (Nicolelis, 2001) and treat many diseases by electrophysiological recording and functional electrical stimulation (Green and Abidian, 2015). Advances in silicon micromachining, biomaterials and system integration technologies have made progressive development in neural microelectrodes that can stimulate and record from a population of neurons for an extended period of time (Wise et al., 2008). The Michigan type microelectrode is one example of such neural prostheses. Currently, one of the main challenges in developing Michigan microelectrodes is how to fabricate a high-density microelectrode array (MEA), which can improve the sensitivity and spatial selectivity of the stimulation and recording functions (Winter et al., 2007). However, as electrode size drops to microscale (higher spatial resolution), the impedance of electrode site increases and the quality of signal recordings decreases (lower sensitivity). Thus, there is a tradeoff between the size (spatial selectivity) and the quality of signal recordings (sensitivity) in neural microelectrodes (Cogan, 2008). Therefore, it is urgent to realize a low impedance neural interface for improving signal quality without compromising its spatial selectivity.

So far, the most widely used electrode materials are noble metals such as gold, platinum, iridium, titanium and their alloys due to their biocompatibility and long-term stability during chronic implantation (Merrill et al., 2005). However, these materials are not suitable for microelectrodes with small-area sites due to their low charge injection limits (0.05–0.3 mC/cm^2) (Weiland et al., 2002) and few options for dramatic impedance improvement (Polikov et al., 2005). Therefore, some novel electrode materials are being explored to increase the charge injection capacity and decrease the interface impedance such as iridium oxide (IrO_x), titanium nitride (TiN), and PEDOT (Venkatraman et al., 2011). Among these materials, PEDOT is an electrically conducting polymer which has been utilized for improving the long-

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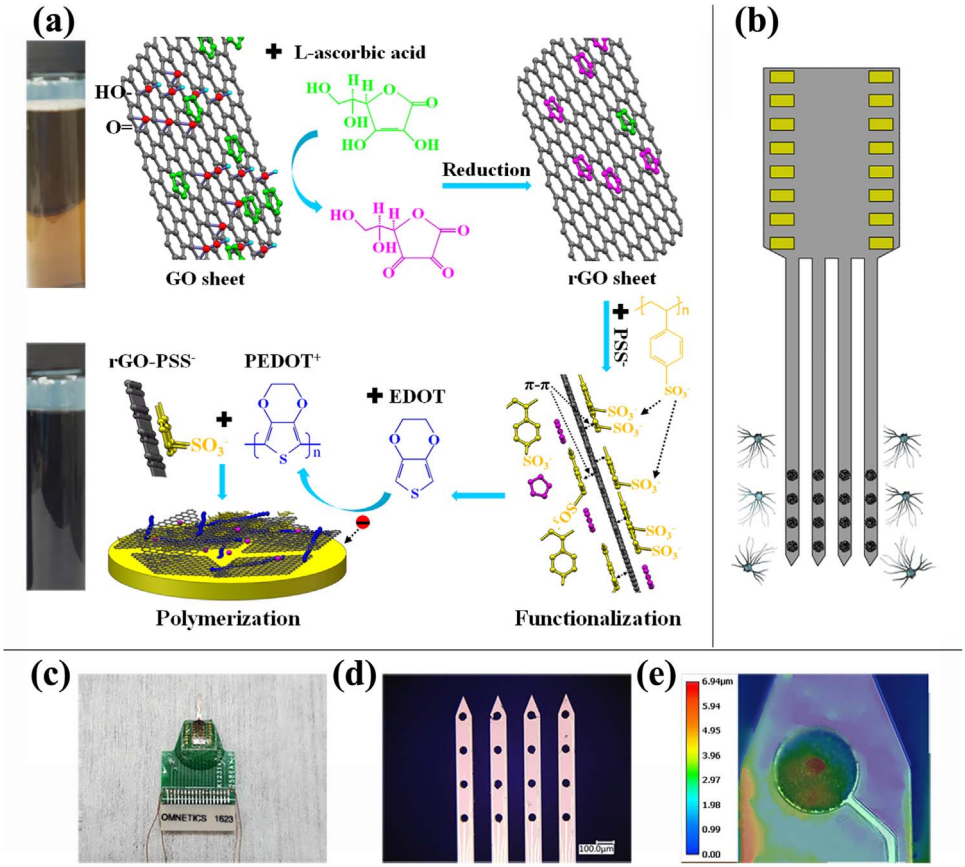

Fig. 1. Schematic illustration of PP-rGO20 fabrication on neural microelectrodes. (a) The reduction process of GO dispersions and the co-deposition of EDOT monomer with PSS functionalized rGO sheets on microelectrode site. (b) The schematic of the PP-rGO20 modified microelectrode recording from several neurons. (c) Photograph of the 16-channel microelectrode assembled with a customized PCB. The 2-D (d) and 3-D (e) micrograph of PP-rGO20 modified microelectrode with a deposition time of 10 min. The overall thickness of the as-deposited PP-rGO20 was between 1.78 μm and 3.56 μm.

term stability of microelectrode (Green et al., 2008). PEDOT coating on microelectrode sites can reduce impedance and increase charge injection limit dramatically (Cui and Martin, 2003). Besides, the structure and property of PEDOT can be modified by doping counter ions such as polymers (poly(4-styrenesulfonate), tosylate, dodecyl benzene sulphonic acid) (Asplund et al., 2010; Hsiao et al., 2011; Ghasemi-Mobarakeh et al., 2011; Martin et al., 2010) and carbon nano materials (carbon nanotubes, graphene) (Zhou et al., 2013; Tian et al., 2014; Hui et al., 2015; Österholm et al., 2012; Lindfors et al., 2013), which further improve the performance of PEDOT. Among these doping ions, the single atom layer structural graphene is very promising for its excellent optical, electrical, thermal and mechanical properties (Zhu et al., 2010). Besides, it has been reported has good biocompatibility and can promote the neurite sprouting and outgrowth of mouse hippocampal cells (Li et al., 2011; Park et al., 2011). Composites incorporating both PEDOT and graphene/graphene oxide (GO) can be fabricated to obtain multi-functions. Therefore, a flexible method for preparing graphene doped PEDOT composites on microelectrode sites is urgent to realize an ideal neural interface device.

In recent years, PEDOT/graphene composites have been investigated for their potential applications in biosensors (Hui et al., 2015; Lu et al., 2013;), super capacitors (Damlin et al., 2015), electrocatalysts (Foronda et al., 2013), energy harvesters (Yoo et al., 2014) and dye-sensitized solar cells (Wan et al., 2015; Hong et al., 2008) due to their excellent electrochemical and mechanical properties. In these applications, PEDOT/graphene composites are mainly fabricated using GO or reduced graphene oxide (rGO) via simple mix and in-situ polymerization. For PEDOT-GO composites, a post reduction process of GO is necessary to exhibit the conductivity of graphene (Damlin et al., 2015; Wang et al., 2012). However, the post reduction is always undesirable because of the toxic reductants and harmful side reactions. A more preferable method would be to use rGO directly. But, direct coating of PEDOT on rGO sheets is difficult because of the poor dispersion of rGO sheets in aqueous. To prevent the irreversible aggregation of rGO sheets, non-covalent and covalent functionalization of rGO with various molecules has been adopted (Hong et al., 2008; Xu et al., 2009). Here, we prepared a well dispersed rGO solution by reducing GO with the biocompatible L-ascorbic acid (L-AA) as reductant. After adding poly(4-styrenesulfonate) (PSS) as counter ions and ethylenedioxythiophene (EDOT) as monomer, a flexible electrochemical method was adopt to realize the co-deposition of PEDOT:PSS-rGO (PP-rGO) composites on microelectrode sites. To the best of our knowledge, electrochemical co-deposition of PP-rGO composites on microelectrode sites without post reduction has rarely been reported.

2. Materials and methods

2.1. Reagents and materials

GO solution (0.1 mg/ml) was purchased from Nanjing XFNANO Materials Tech Co., Ltd (China). L-ascorbic acid (LAA), ammonia solution (25–28%) and phosphate buffered saline (PBS, pH 7.4) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). PSS and EDOT were purchased from Sigma Aldrich Chemicals Co. (USA). SOI wafers were purchased from RDMICRO Co., Ltd (China).

2.2. Microelectrodes fabrication

Fig. S1 showed the fabrication process of the Michigan type microelectrodes. At first, a silicon-on-insulator (SOI) wafer was chosen