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Short communication

Enhanced catalytic and dopamine sensing properties of electrochemically reduced conducting polymer nanocomposite doped with pure graphene oxide

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ABSTRACT

Significantly enhanced catalytic activity of a nanocomposite composed of conducting polymer poly (3,4-ethylenedioxythiophene) (PEDOT) doped with graphene oxide (GO) was achieved through a simple electrochemical reduction process. The nanocomposite (PEDOT/GO) was electrodeposited on an electrode and followed by electrochemical reduction, and the obtained reduced nanocomposite (PEDOT/RGO) modified electrode exhibited lowered electrochemical impedance and excellent electrocatalytic activity towards the oxidation of dopamine. Based on the excellent catalytic property of PEDOT/RGO, an electrochemical sensor capable of sensitive and selective detection of DA was developed. The fabricated sensor can detect DA in a wide linear range from 0.1 to 175 μM, with a detection limit of 39 nM, and it is free from common interferences such as uric acid and ascorbic acid.

1. Introduction

Dopamine (DA) plays an important physiological role as an extracellular chemical messenger in cardiovascular, renal, hormonal, and central nervous systems. DA levels are found to be correlated with the severity and progression of neurological disorders such as Parkinson's and Alzheimer's diseases (Lunardi et al., 2009; Mohadesi et al., 2011; Rand et al., 2013; Zhang et al., 2012). Therefore, sensitive and selective detection of dopamine is of great importance for the understanding and diagnostics of neurological diseases. In the past years, various methods, such as liquid chromatography (Sasa and Blank, 1977), spectroscopy (Moghadam et al., 2011), fluorescence (Seckin and Volkan, 2005) and electrochemical analysis (Tong et al., 2013) have been used for the assay of DA. Among them, electrochemical analysis has received much attention due to its considerably high sensitivity, rapid response, low cost and ease of operation. Many attempts have been made to develop chemically modified electrodes with a variety of materials for the selective determination of DA, and the most popularly used materials are carbon nanomaterials, such as carbon nanotubes (Li et al., 2012, 2011), graphene (Li et al., 2010; Sun et al., 2011; Wang et al., 2013) and graphene oxide (GO) (Liu et al., 2012; Yuan et al., 2013).

In recent years, GO has attracted great interest because of its unique physical and chemical properties (Chen et al., 2012; Lee et al., 2012). As GO possesses many oxygen containing functional groups, such as hydroxyl, epoxide and carboxyl groups, it can be easily dispersed in aqueous solution. Moreover, owing to the abundance of carboxyl groups that are negatively charged in aqueous solution, GO can act as an excellent dopant for the chemical and electrochemical polymerization of conducting polymers. For example, polyaniline doped with GO sheets was chemically synthesized via the in-situ polymerization process (Wang et al., 2009), polypyrrole nanocomposite with GO was prepared through liquid/liquid interfacial polymerization (Bora and Dolui, 2012). Generally, electrochemical polymerization can form composite films on the electrode surfaces, and they are suitable for sensing applications. Overoxidized polypyrrole/graphene modified electrode has been reported to be able to detect dopamine in the presence of ascorbic acid (Zhuang et al., 2011), while the molecularly imprinted polymer based on polypyrrole incorporated with GO has been fabricated for the determination of quercetin (Sun et al., 2013).

Our group and others have prepared GO doped conducting polymer poly (3,4-ethylenedioxythiophene) (PEDOT) nanocomposite through electrodeposition (Luo et al., 2013; Zhu et al., 2012). However, as GO is the oxidized form of graphene, and its

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conductivity is decreased along with the level of oxidation (Inhwa et al., 2008), the commonly used form GO without reduction normally has poor conductivity. More recently, Ambrosi and Pumera (2013) have reported that GO can be electrochemically reduced to precisely adjust its electrochemical property. In light of this result, here, we aim to electrochemically prepare a GO doped PEDOT (PEDOT/GO) nanocomposite, and then reduce the GO in the nanocomposite electrochemically so as to improve electrochemical catalytic property of the resulting nanocomposite. That is, using a facile all-electrochemical process to obtain electrodeposited PEDOT nanocomposite doped with reduced GO. Interestingly, significantly enhanced catalytic property of the PEDOT/GO nanocomposite was observed after electrochemical reduction, and a sensitive and selective DA sensor was further developed based on this novel yet simply obtained nanocomposite.

2. Experimental

2.1. Reagents

GO was purchased from Nanjing Xian Feng Nanomaterials Technology Co., Ltd. (Nanjing, China). 3,4-ethylenedioxythiophene (EDOT) was obtained from Aladdin Reagents (Shanghai, China). All other reagents were of analytical grade. Millipore water from a Milli-Q water purifying system was used throughout all experiments.

2.2. Preparation and electrochemical reduction of PEDOT/GO nanocomposite

GCE was polished, cleaned and electrochemically pretreated in phosphate buffered saline (PBS) according to a previous report (Luo et al., 2007). For the preparation of the PEDOT/GO nanocomposite, GCE was immersed in a solution containing 2 mg mL^{-1} GO and 0.02 M EDOT, followed by electrochemical polymerization using cyclic voltammetry (CV) with potential scanning between −0.2 and 1.2 V at a scan rate of 100 mV s^{-1} for 13 cycles. The electrochemical reduction of the PEDOT/GO nanocomposite was carried out in PBS (0.2 M, pH 7.4) by applying a potential of −0.9 V for 600 s. GCEs modified with the nanocomposite before and after electrochemical reduction were denoted as PEDOT/GO/GCE and PEDOT/RGO/GCE, respectively.

2.3. Electrochemical measurements and physical characterization

Electrochemical experiments were performed with a CHI760D electrochemical workstation (Shanghai CH Instruments Co., China) coupled with a three-electrode system. A bare or modified glassy carbon electrode (GCE, diameter 3.0 mm) was used as the working electrode, and an Ag/AgCl (3 M KCl) electrode and a platinum wire electrode were used as reference and auxiliary electrodes, respectively.

Electrochemical impedance spectroscopy (EIS) measurements were recorded in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl within a frequency range of 1–100,000 Hz. The amplitude of the applied sine wave was 5 mV with the direct current potential set at 0.20 V. DA detection was performed using amperometry in stirring PBS, with the potential set at 0.2 V. All experiments were conducted at ambient temperature.

Field emission scanning electron microscope (SEM) was performed with a JEOL JSM-7500 F SEM instrument (Hitachi High-Technology Co., Ltd., Japan).

3. Results and discussion

3.1. Characterization of nanocomposite films

SEM images of the PEDOT/GO and PEDOT/RGO nanocomposite films are shown in Fig. 1A and B. It is clear that the electrodeposited PEDOT/GO film is generally uniform, and it shows a wrinkled surface morphology. After electrochemical reduction, the obtained PEDOT/RGO film became rougher and more wrinkled (Fig. 1B). This morphology change is clearly resulted from the electrochemical reduction of GO in the nanocomposite, as at the potential of −0.9 V, GO can be reduced (Ambrosi and Pumera, 2013) while PEDOT is still stable (Kiya et al., 2007).

Electrochemical properties of electrodes modified with the PEDOT/GO and PEDOT/RGO films were characterized with Faradaic EIS in the presence of a redox probe. Fig. 2A shows the Nyquist plots of electrodes with different modifications. The semicircle portion of the plot corresponds to the charge transfer process, with the diameter of the semicircle equivalent to the charge transfer resistance (R_{ct}) (Xu et al., 2013), while the linear portion reflects the diffusion limited process at the electrode interface. It is clear that with the electrochemical deposition of PEDOT/GO on the GCE, the obtained PEDOT/GO/GCE shows a much lower R_{ct} than that of the bare GCE. This is consistent with the fact that the electrodeposited nanocomposite film is conductive, and it can

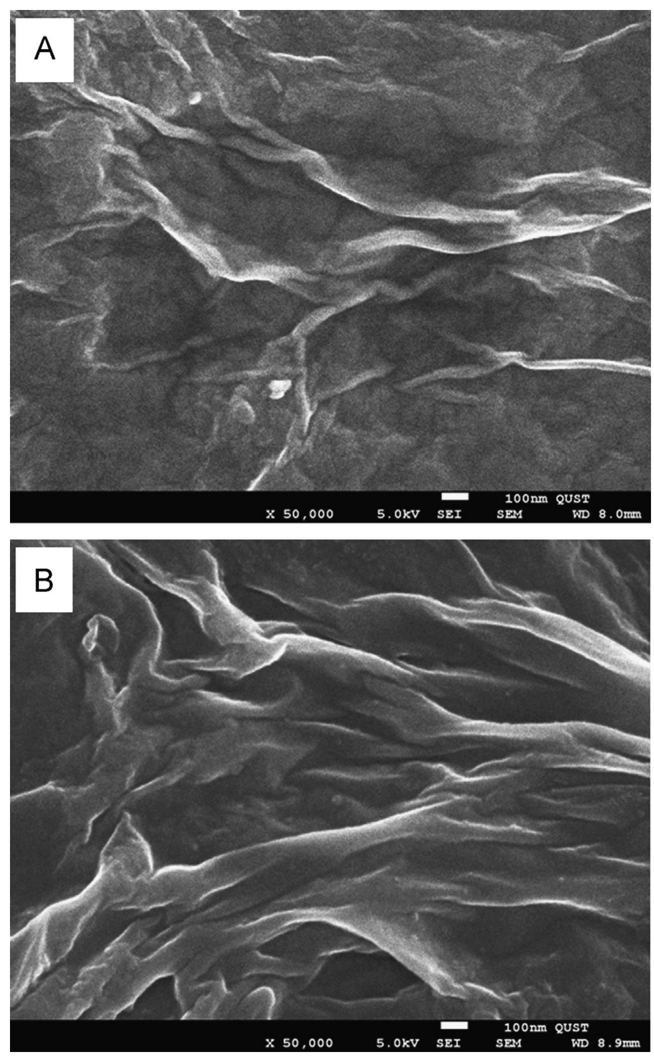

Fig. 1. SEM images of the PEDOT/GO (A) and the PEDOT/RGO (B) nanocomposite films.