Journal of Electroanalytical Chemistry 811 (2018) 78–83

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Black phosphorene modified glassy carbon electrode for the sensitive voltammetric detection of rutin

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ARTICLE INFO

Keywords:
Black phosphorene
Poly(3,4–ethylenedioxythiophene)–poly (styrenesulfonate)
Rutin
Electroanalysis

ABSTRACT

As a common flavonoid glycoside, rutin owns excellent physiologic activities and has been widely used in clinical chemistry and human health. Therefore the establishment of sensitive and reliable methods for rutin determination is highly important. Black phosphorene (BP) nanosheet modified glassy carbon electrode (GCE) was fabricated by using poly(3,4–ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) as the film and the stabilizer. The incorporation of BP with PEDOT:PSS resulted in a stable nanocomposite (BP–PEDOT:PSS) and its performance were characterized by SEM, EDS and Raman. BP–PEDOT:PSS/GCE showed excellent conductivity and stability, which was applied for the sensitive voltammetric determination of rutin, a commonly used electroactive drug. On cyclic voltammogram a pair of well–defined redox peak of rutin could be obviously observed with enhanced voltammetric response, which could be due to the presence of BP nanosheet that accelerated the electrode reaction. Electrochemical parameters were calculated with the electron transfer coefficient (α) as 0.55 and the apparent heterogeneous electron transfer rate constant (k_s) as 4.22 s^{-1}. Under the selected conditions differential pulse voltammetric oxidation peak current of rutin showed linear dependence on its concentration within two sections of 0.02–15.0 μmol/L and 15.0–80.0 μmol/L with a low detection limit of 0.007 μmol/L ($3S_0/S$). Rutin tablet samples were successfully examined by the as-proposed method with satisfactory results, showing the practical applications.

1. Introduction

As a new kind of inorganic two–dimensional nanosheet, black phosphorene (BP) has exhibited unusual structure and performances, which has become the research topics in recent years [1]. BP is a p–type semiconductor with layered structure, which can be produced by various methods such as micromechanical exfoliation, liquid–phase exfoliation, supercritical carbon dioxide–assisted synthesis, and so on [2]. BP exhibits excellent properties such as tunable direct band gap [3], good flexibility [4], high mobility [5] and anisotropic electrical conduction [6]. Recently the advances of synthesis, characterization and applications of BP–based devices have been reviewed in detail [7,8]. However BP is not stable in ambient conditions and gradually degraded due to the interaction with oxygen, water with light. Therefore the stability of BP had been studied and remained with different methods [9,10].

Poly(3,4–ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) is a conductive polymer with high conductivity, stability and process ability, which has been used in the field of electrochemistry such as solar cells [11], organic photovoltaics [12], thermoelectrics [13] and modified electrodes [14]. Lee et al. synthesized a paper–based graphene dots/PEDOT:PSS modified electrode as the counter electrode in a flexible dye–sensitized solar cell [15]. Li et al. constructed a PEDOT:PSS/AuNPs/1–methyl–4–mercaptopyridine modified screen–printed carbon electrode as a sensing platform for tyramine [16]. Lee et al. investigated the effect of incorporation of BP with PEDOT:PSS on conductivity and electro–phonon coupling [17]. Zhang et al. checked the environmental stability of BP–PEDOT:PSS hybrid semiconductor composite in water [18]. The introduction of PEDOT:PSS with BP results in a stable film with high electrical conductivity and excellent environmental stability.

Rutin is a common flavonoid glycoside, which has been widely used in clinical chemistry and human health due to the excellent physiologic activities such as anti–tumor, anti–inflammatory, anti–oxidant and anti–bacteria [19,20]. Therefore it is important to explore reliable

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https://doi.org/10.1016/j.jelechem.2018.01.038
Received 10 December 2017; Received in revised form 20 January 2018; Accepted 21 January 2018

methods for rutin analysis. So far many efforts have been paid on rutin detection such as HPLC [21], spectrophotometry [22], chemiluminescence [23], capillary electrophoresis [24] and electrochemistry [25]. However, some of them are suffered from disadvantages including expensive devices, time–consuming procedure, poor sensitivity or the usage of toxic organic reagents. Electrochemical approaches have roused many attentions in the analysis of electrochemical active molecules with the virtues of low–cost apparatus, high sensitivity, wide linear range and simplicity [26–28]. Due to the electroactivity of rutin, various electrochemical approaches for rutin analysis have been explored [29–32].

In this paper BP and PEDOT:PSS nanocomposite modified glassy carbon electrode (BP–PEDOT:PSS/GCE) was fabricated and its performances were investigated by SEM, EDS, Raman and voltammetry. Due to the enhanced electrochemical responses on the modified electrode, electroanalytical application was checked with rutin as the model target. Electrochemical data showed that the voltammetric response of rutin was greatly enhanced on BP–PEDOT:PSS/GCE. Therefore a novel sensitive voltammetric approach for rutin analysis was further explored. Moreover this electrochemical biosensor showed selective and reliable applications in rutin tablets samples with satisfactory results. The procedure for the construction of BP–PEDOT:PSS/GCE and rutin analysis were illustrated in the following Scheme 1.

2. Experimental

2.1. Reagents

BP nanosheet (0.8 mg/mL in ethanol, Nanjing XFNANO Mater. Tech. Co. Ltd., China), conductive grade PEDOT:PSS (1.5 wt% dispersion in water, Kuer Chem. Tech. Co. Ltd., China) and rutin (Sinopharm. Chem. Reagent Co. Ltd., China) were used as received. 0.1 mol/L phosphate buffer solutions (PBS) were used as the supporting electrolyte and all testing solutions were prepared with doubly distilled water.

2.2. Apparatus

Scanning electron microscopy (SEM) and energy dispersive spectra (EDS) were conducted on a Merlin Compact transmission electron microscope (Zeiss, Germany). Raman spectrum was obtained on a LabRAM HR system using 532 nm lasers (Horiba, France). A CHI 660D electrochemical workstation (Shanghai CH Instrument, China) was used for all voltammetric experiments with a typical three–electrode mode. BP–PEDOT:PSS/GCE, saturated calomel electrode (SCE) and platinum wire electrode were used as working, reference and counter electrode, respectively. A nitrogen-filled glovebox was used to keep a vacuum or nitrogen atmosphere for BP nanosheet dispersion and electrode modification.

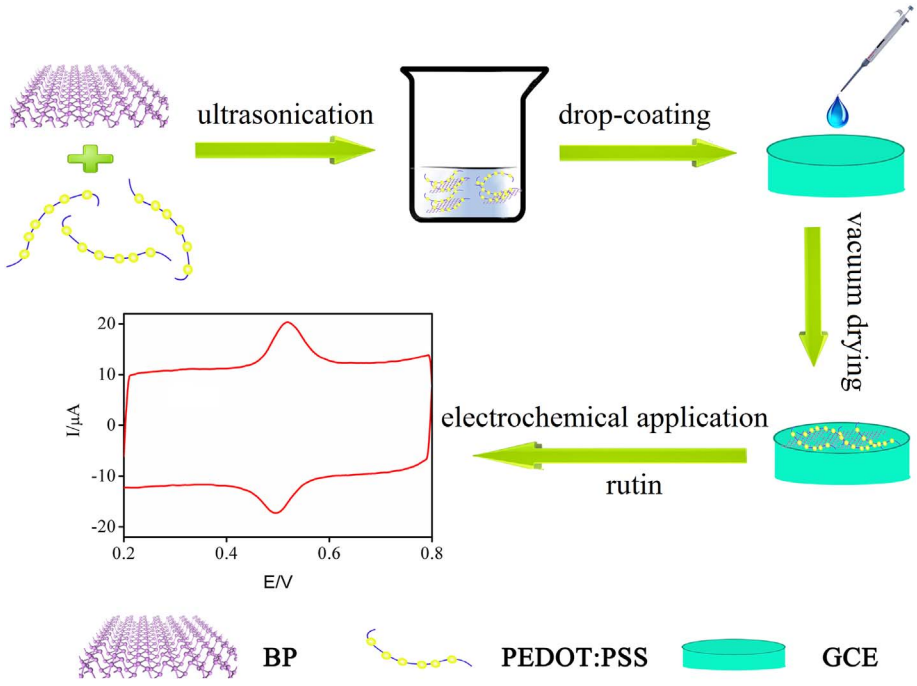
2.3. Electrode fabrication

GCE (ϕ = 3 mm) was pretreated according to a widely reported procedure [33]. In a highly pure nitrogen–filled glovebox, a 0.4 mg/mL BP–PEDOT:PSS nanocomposite was prepared by mixing PEDOT:PSS and BP nanosheet in absolute ethanol. After ultra–sonication for 3 h, 5.0 μL of the resulted homogeneous mixture was coasted on GCE surface to obtain BP–PEDOT:PSS/GCE, which was dried in vacuum before use and stored in 4 °C refrigerator.

3. Results and discussions

3.1. Characterization of BP–PEDOT:PSS nanocomposite

SEM experiment was performed to characterize the morphologic and structural features of BP–PEDOT:PSS nanocomposite with the images shown in Fig. 1. Flake–like structure of BP could be observed clearly (Fig. 1A), indicating the well dispersion of BP nanosheet in absolute ethanol without agglomeration. SEM image of PEDOT:PSS (Fig. 1B) gave a flat and compact structure with some aggregation, which might be caused by the evaporation of solvent. As for BP–PEDOT:PSS composite (Fig. 1C), a compact surface appeared with BP nanosheet covered, which indicated the formation of BP–PEDOT:PSS composite. The changes of SEM image indicated the interaction of BP and PEDOT:PSS resulted in a nanocomposite that could prevent the agglomeration and facilitate the stable presence of BP nanosheet [18]. The components of BP–PEDOT:PSS composite was further verified by EDS with the spectra shown in Fig. 1D–F. The EDS profile of BP–PEDOT:PSS (Fig. 1F) revealed the presence of chemical elements P, C, S



Scheme 1. Fabrication procedure of BP–PEDOT:PSS/GCE and rutin electroanalysis.