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Single step electrochemical fabrication of highly loaded palladium nanoparticles decorated chemically reduced graphene oxide and its electrocatalytic applications

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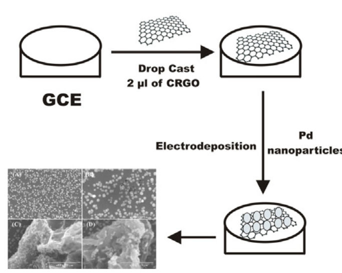
HIGHLIGHTS

- A highly loaded palladium nanoparticle on the chemically modified reduced graphene oxide (CRGO) has been prepared.
- Simultaneous determination of dopamine and diclofenac.
- Real sample application.
- Sufficient enough peak separation around 0.43 V for DA and diclofenac.
- The electrode possesses good stability, reproducibility, sensitivity and wide linear range.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile electrochemical approach has been developed for the synthesis of Palladium (Pd) nanoparticles decorated chemically reduced graphene oxide (CRGO) sheets on glassy carbon electrode (GCE) and indium tin oxide (ITO) electrodes by simple electrochemical deposition process. The electrochemical measurements and surface morphology of the as prepared nanocomposite electrode were studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) analysis. The amount of CRGO loading was optimized by EIS analysis. The presence of CRGO in the film enhances the surface coverage concentration and also increases the electron transfer rate constant of the Pd nanoparticles. The palladium nanoparticles successfully decorated on CRGO modified electrode (CRGO/Pd) and it exhibits a noticeable electrocatalytic activity towards the simultaneous detection of dopamine (DA) and diclofenac in pH 7 PBS solution. Exclusively, the proposed CRGO/Pd nanocomposite film modified GCE successfully and showed two well separated anodic oxidation peaks for the detection of DA and diclofenac in mixture solutions with a linear range of 2–63 µM. The film was also successfully used for the simultaneous detection of DA and diclofenac in real samples with a linear range of 2–50 µM. Furthermore, the proposed CRGO/Pd nanocomposite film modified electrode also retains the advantage of easy fabrication, high sensitivity, selectivity and good repeatability.

1. Introduction

Graphene, a rising star in material science, chemistry, physics and nanotechnology has attracted enormous research interest since its unprecedented discovery and characterizations by manual mechanical cleavage from graphite using Scotch tape [1,2]. In

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addition, graphene has unique electrochemical properties such as fast electron transfer and excellent conductivity and wide electrochemical potential window that have the ability to enhance the direct electron transfer at the bare glassy carbon electrodes to broadened their applications in the field of electrochemical biosensors [3]. Graphene sheets have the tendency to form graphite due to the van der Waals force of attraction [4]. Moreover, due to its hydrophobic nature dispersion of graphene in aqueous media is difficult. Until now, versatile strategies have been employed by several researchers to attain large yield and high quality of graphene [5,6]. Nowadays, the common methods to obtain graphene sheets include mechanical cleavage, chemical vapor deposition, and chemical reduction of graphene oxide (GO) [7]. Among these methods, the chemical reduction method is most commonly used, because it has advantages of low-cost and bulk-scale production. Reduced graphene oxide (RGO), characterized as incompletely reduced product of GO, is the intermediate state between graphene and GO. Owing to the incomplete reduction, RGO has several types of oxygen-containing functional groups and defects which can support chemically active sites for usage in catalytic reactions and interacting with metal nanoparticles [8,9]. Hence, RGO has great potential to be applied in biosensors [10], plastic electronics [11], photo catalysts and solar cells [12–16]. Recently, graphene and RGO are widely used as supports for active transition metals owing to their large surface area and outstanding electronic conductivity [17–19].

On the other hand, noble metal nanoparticles are known to be excellent catalysts, due to their high ratio of surface atoms with free valences to the cluster of total atoms. Palladium (Pd) nanoparticles are part of the platinum group of metals, which possess their own special properties for the electrode modification process. Previously, Pd nanoparticles modified electrodes have been used for various types of electrochemical sensors. For example, there have been reports of electrodeposited Pd nanoparticles on single-walled carbon nanotubes for flexible hydrogen sensors [20], Pd-modified carbon nanotubes synthesized in supercritical fluid for oxygen reduction [21], electrodeposited nano platinum-Pd alloy in nafion film-coated GCE [22], Pd nanoparticles supported multi-walled carbon nanotubes [23] for the electrocatalytic oxidation of formaldehyde, and GCE–nafion–polyaniline–Pd nanoparticles modified electrode [24] for the electrocatalytic oxidation of formic acid, Pd nanoparticles encapsulated channels for protein bio sensing and the reduction of H_2O_2 DNA-templated preparation of Pd nanoparticles on ITO for H_2O_2 reduction and ascorbic acid (AA) oxidation [25].

Next, there is a constant requirement to develop a sensor for the biologically important compounds. Dopamine (DA) plays a vital role for physiological processes in human metabolism. The first species plays an important role in the human brain and a loss of DA-containing neurons may result in some serious diseases such as Parkinson. The main difficulty with the electrochemical detection of DA in brain fluids is the coexistence of many interfering compounds. Diclofenac is known as a non-steroidal anti-inflammatory drug mainly utilized as an analgesic agent to reduce inflammation and pain under certain conditions. In most of the countries it has been utilized as a drug to cure minor aches, pains and fever associated with common infections. Therefore, detection and determination of diclofenac is an important criterion in the pharmaceutical analysis. Various types of analytical techniques have been found as suitable for the detection and determination of diclofenac. In this, employment of electrochemical methods by utilizing film-modified electrodes was found as easier, convenient and reliable for the detection and determination of diclofenac. Previously, various types of potentiometric, membrane and voltammetric sensors were reported for the detection of diclofenac.

Determination of diclofenac in pharmaceutical preparations using a potentiometric sensor immobilized in a graphite matrix [26], determination of diclofenac in pharmaceuticals and urine samples using a membrane sensor based on the ion associate of diclofenac with rhodamine B [27], and manganese (III) porphyrin-based potentiometric sensors for diclofenac assay in pharmaceutical preparations [28] were reported. Voltammetric sensors, various types of electrodes [29], molecularly imprinted film modified carbon electrodes [30], nano-structured electrochemical sensing film constructed by multi-wall carbon nanotubes–surfactant composite [31], an edge-plane pyrolytic graphite electrode with single-wall carbon nanotubes [32] and edge plane pyrolytic graphite electrode and its determination in human urine [33], for diclofenac detection were reported. Therefore detection and determination of DA and diclofenac combination is a vital and new one. In particular, developing a new type of sensor for the simultaneous detection and determination of DA and diclofenac will be more useful for the detection of these compounds in the real life. Hence, in this report we have a simple fabrication of Pd nanoparticles decorated chemically reduced graphene oxide (CRGO) modified electrode. This redox complex with the nano structure was employed for the selective electrocatalytic determination of DA and diclofenac by making CRGO/Pd nanocomposite. This composite was prepared on GCE and ITO electrodes by simple two steps process drop casting of CRGO followed by electrodeposition of Pd nanoparticles. Prepared electrode was characterized using surface analysis technique SEM along with electrochemical techniques CV and EIS. CRGO/Pd modified electrode successfully separated DA and diclofenac without any interference and was quantified in lab and real samples using differential pulse voltammetric (LSV) method.

2. Experimental

2.1. Apparatus

Electrochemical measurements like cyclic voltammetry (CV) and Linear sweep voltammetry were performed by a CHI 1205A electrochemical analyzer. A conventional three-electrode cell was used at room temperature with glassy carbon electrode (GCE) (surface area = 0.07 cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. The potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphology of the film was studied by SEM (Hitachi, Japan). Electrochemical impedance studies (EIS) were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik Gmbh & Co KG, Germany).

2.2. Materials

Potassium tetrachloropalladate (II) was obtained from Strem chemicals (USA). Graphite powder; dopamine (DA) and diclofenac sodium salt were purchased from Sigma–Aldrich. DA and diclofenac solutions were prepared every day. The other chemicals (Merck) were used in this investigation with analytical grade (99%). All the solutions were prepared using double distilled water. Electrocatalytic studies were carried out in 0.05 M pH 7 PBS solution. Pure nitrogen gas was purged through all the experimental solutions for removing dissolved oxygen.

2.3. Electrochemical fabrication of CRGO/Pd nanocomposite modified electrode

Graphite oxide was synthesized from graphite by the modified Hummer's method [34–36]. The as-obtained graphite oxide was