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Poly(basic red 9) doped functionalized multi-walled carbon nanotubes as composite films for neurotransmitters biosensors

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ABSTRACT

This paper discusses the electrochemical polymerization of basic dye films, which are composed of basic red 9 (BR9), on various electrodes and the enhancement of the electropolymerization by functionalized multiwall carbon nanotubes (*f*-MWCNTs) modification of the electrode surface. The presence of *f*-MWCNTs enhances the surface coverage (Γ) and stability. Poly(BR9) films were electrocatalytically active for epinephrine and serotonin oxidation. The electrocatalytic oxidation current developed from the anodic peak of the redox couple. Electrochemical impedance spectroscopy (EIS) was applied to monitor the whole process of the electrode modification. EIS can provide useful information regarding the impedance changes on the electrode surface between each step. We studied the surface morphology of the composite film using scanning electron microscopy (SEM) and atomic force microscopy (AFM), which revealed that BR9 is doped on *f*-MWCNTs. Cyclic voltammetry (CV) was used for the measurement of the electroanalytical properties of the analytes. The sensitivity values for the *f*-MWCNTs/BR9 composite film were higher than the poly(BR9) and *f*-MWCNTs composite film. Finally, differential pulse voltammetry (DPV) was used for the detection of a mixture of analytes at the *f*-MWCNTs/BR9 composite film. We simulated a more complex system with both serotonin and epinephrine present simultaneously. This system also exhibited oxidation peaks for serotonin in bovine calf serum (BCS) and epinephrine injection for real samples determination at pH 7.0 at the *f*-MWCNTs/BR9 composite film.

1. Introduction

C.I. basic red 9 (BR9), a triarylmethane dye, was selected as the model compound to determine the interactions between dye and surfactant molecules. Other triamino derivatives of triphenylmethane dyes are produced by connecting the various functional compounds to the amino groups on the triphenylmethane. BR9 is also commonly used in the textile, leather, paper and ink industries [1]. Azo dyes, such as BR9 (contain —N=N— bonds), are resistant to biodegradation under aerobic conditions, whereas anaerobic treatment is applied successfully [2].

Electropolymerization of anilines linked with triarylamines causes polymerization of the three branches [3]. Several reports reveal that the polymerization a triphenylmethane derivative, fuchsin acid, a molecule that has three branched monomers, leads to a dendritic polymer [4]. Varieties of applications of carbon nanotubes (CNT) with dye were previously reported [5–7]. Although the electrocatalytic activity of the conjugated polymers and CNTs matrices individually exhibit excellent results, certain properties, such as the mechanical stability, sensitivity for different techniques and electrocatalysis of multiple compounds, are found to be poor.

Epinephrine (EP) is an important catecholamine neurotransmitter in the mammalian central nervous system and exists in the nervous tissue and body fluids as large organic cations [8]. EP plays an important role in the function of the central nervous, renal, hormonal, and cardiovascular systems [9]. The catecholamine drugs are used to treat hypertension, bronchial asthma, and organic heart

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disease and are used in cardiac surgery and myocardial infarction [10–12]. This compound controls the nervous system performance for a series of biological reactions and nervous chemical processes. Many diseases are related to changes of the EP concentration in living systems.

Serotonin (5-hydroxytryptamine, 5-HT) is a biogenic monoamine neurotransmitter that is synthesized both in the enteric nervous system and the central nervous system [13,14]. Serotonin is of enormous biological importance and is widely distributed in the central nervous system. A deficiency leads to mental disorders, such as Alzheimer's disease, infantile autism, mental retardation, sleep disorders and depression [15–17]. Electrochemical analysis at unmodified electrodes has limitations because of the overlapping of the oxidation potentials of biochemical compounds, and hence, often suffers from a pronounced fouling effect along with poor selectivity and reproducibility [18,19]. In the past, several modified electrodes were used for the simultaneous determination of neurotransmitters [20,21].

The quantitative determination of EP and serotonin concentrations is also helpful for developing nerve physiology, clinical diagnosis of some diseases and controlling medicine in pharmacological research [22]. The oxidation of these compounds is interesting because this process occurs in the human body. Due to their crucial role in neurochemistry and industrial applications, several traditional methods have been used for their determination. Therefore, it is important to examine the electrochemical behavior and to develop a quantitative method for studying the concentrations in body fluids [23]. Among these methods, electrochemical methods have more advantages over the others in sensing neurotransmitters present in living organisms [24].

This paper discusses the electrochemical polymerization of basic dye films composed of BR9 on various electrodes and the enhancement of the electropolymerization by functionalized multiwall carbon nanotubes *f*-MWCNTs modification of the electrode surface. Two-layer modified electrodes were prepared from poly(BR9) and *f*-MWCNTs composite films. Poly(BR9) films were electrocatalytically active for epinephrine and serotonin oxidation. The electrocatalytic oxidation current was observed to develop from the anodic peak of the redox couple.

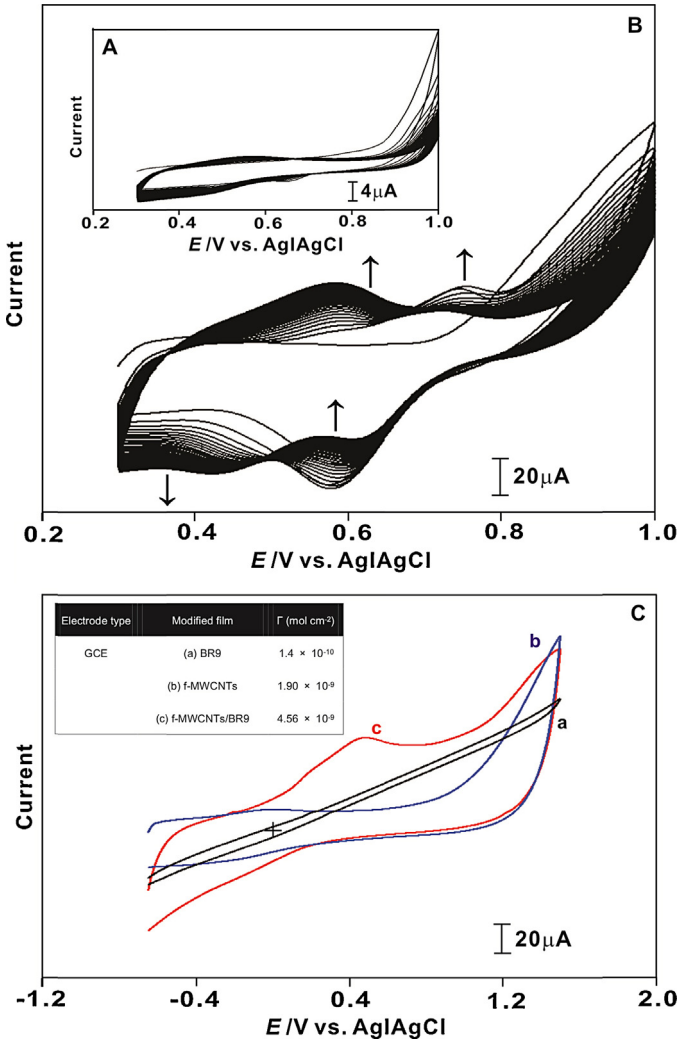

Fig. 1. Repetitive CVs of (A) BR9 and (B) *f*-MWCNTs/BR9 films from 5 mM BR9 in pH 1.0 H_2SO_4 buffer, scan rate at 100 mV s^{-1}. (C) Comparison of CVs of (a) BR9, (b) *f*-MWCNTs and (c) *f*-MWCNTs/BR9 films on GCE in pH 7.0 PBS buffer, scan rate at 100 mV s^{-1}.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (Aldrich) were used as received. C.I. BR9 (parafuchsin) was obtained from Fluka. EP, serotonin (5-HT), ascorbic acid (AA), uric acid (UA) and bovine calf serum (BCS) were obtained from Sigma. The EP injection was from Adrenalin®. All other chemicals were of analytical grade and were used without further purification Phosphate buffered saline (PBS, 0.1 M) and pH 1.0 H_2SO_4 solutions were used as the supporting electrolyte. Aqueous solutions were prepared using double-distilled deionized water and were de-aerated by purging with high purity nitrogen gas for approximately 20 min prior to performing the electrochemical experiments. In addition, a continuous flow of nitrogen over the aqueous solution was maintained during the measurements. Indium tin oxide (ITO) (7 Ω cm^{-2}) was purchased from Merck Display Technologies (MDT) Ltd. (Taiwan).

2.2. Apparatus

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed using a CHI-1205B, and differential pulse voltammetry (DPV) was conducted using a CHI-900 and CHI-410

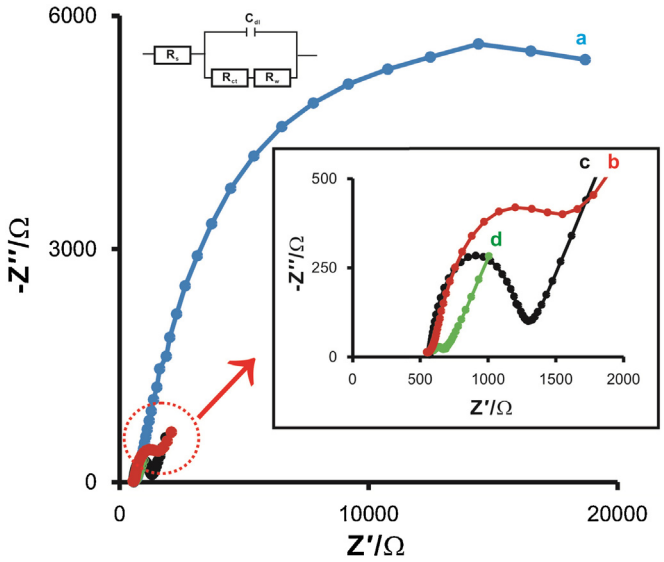

Fig. 2. Electrochemical impedance spectra (EIS) of (a) only BR9, (b) *f*-MWCNTs/BR9, (c) bare GCE and (d) *f*-MWCNTs in pH 7.0 PBS containing 5×10^{-3} M $[Fe(CN)_6]^{-3/-4}$ (Amplitude: 5 mV).