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Electrocatalysis and simultaneous determination of catechol and quinol by poly(malachite green) coated multiwalled carbon nanotube film

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ABSTRACT

Electrochemically active composite film that contains multiwalled carbon nanotubes (MWCNTs), Nafion (NF), and poly(malachite green) (PMG) has been synthesized on glassy carbon electrode (GCE), gold, and indium tin oxide (ITO) electrodes by potentiodynamic method. The presence of MWCNTs in the composite film (MWCNT–NF–PMG) enhances the surface coverage concentration (Γ) of PMG by fivefold. Similarly, an electrochemical quartz crystal microbalance study revealed enhancement in the deposition of PMG at MWCNT–NF film when compared with bare and only NF modified electrodes. The surface morphology of the composite film was studied using atomic force microscopy, which revealed that the PMG incorporated on MWCNT–NF film. The composite film exhibited enhanced electrocatalytic activity toward the mixture of biochemical compounds catechol and quinol. The electrocatalytic responses of analytes at MWCNT–NF–PMG composite film were measured using both cyclic voltammetry (CV) and differential pulse voltammetry (DPV). From electrocatalysis studies, well-separated voltammetric peaks were obtained at the composite film for catechol and quinol with a peak separation of 147 mV. The sensitivity values of the composite film toward catechol and quinol by the DPV technique were 0.4 and 3.2 mA mM^{-1} cm^{-2}, respectively, which are higher than the values obtained by the CV technique. Similarly, the above-mentioned values are better than the previously reported electroanalytical values for the same analytes.

Catechol and quinol are phenolic compounds and often coexist as isomers in environmental samples. Their crucial role in industrial applications causes their coexistence as environmental pollutants with high toxicity; therefore, several traditional and electrochemical methods have been developed for their determination [1–4]. When compared with several methods, the electrochemical method reduces the operating complexity, time, and reagents used for the determination of isomers. However, electrochemical analysis on unmodified electrodes, such as glassy carbon electrode (GCE)[1], has limitations because of the overlapping of oxidation potentials of catechol and quinol; hence, it often suffers from a pronounced fouling effect along with poor selectivity and reproducibility. Ghanem and others have overcome the above-mentioned problem by using chemically modified electrodes for the electrocatalysis and simultaneous determination of catechol and quinol [4–8].

Among the various preparation methods of chemically modified electrodes, electropolymerization is a simple but powerful method in targeting selective modification of different types of electrodes with desired matrices. The important advantages of electropolymerization are the easy synthesis and deposition of desired electroactive polymers onto the conductive surface from monomer solutions and the precise electrochemical control of their formation rate and thickness. These electroactive polymers have useful properties such as electronic conductivity and ionic conductivity [9]. As a consequence of all these above-mentioned advantages, the electropolymerization of electroactive polymers along with carbon nanotube (CNT) matrices has received considerable attraction during recent years. Numerous conjugated polymers have been electrochemically synthesized for their application in the fabrication of chemical and biochemical sensor devices [10–14]. These conjugated polymers used in sensor devices exhibit enhancement in the electrocatalytic activity toward the oxidation or reduction of several chemical and biochemical compounds [15] where some of the functional groups in polymers act as a catalyst [16,17]. In the current article, the term *enhanced electrocatalytic activity* is described as both an increase in peak current and lower overpotential [18]. The wide variety of applications of matrices made of CNTs for the detection of chemical and

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[1] *Abbreviations used:* GCE, glassy carbon electrode; CNT, carbon nanotube; MG, malachite green; PMG, poly(malachite green); FT-IR, Fourier transform infrared; UV–vis, ultraviolet–visible; MWCNT, multiwalled carbon nanotube; NF, Nafion; CV, cyclic voltammetry; EQCM, electrochemical quartz crystal microbalance; DPV, differential pulse voltammetry; AFM, atomic force microscopy; ITO, indium tin oxide; LOD, limit of detection; LOQ, limit of quantification.

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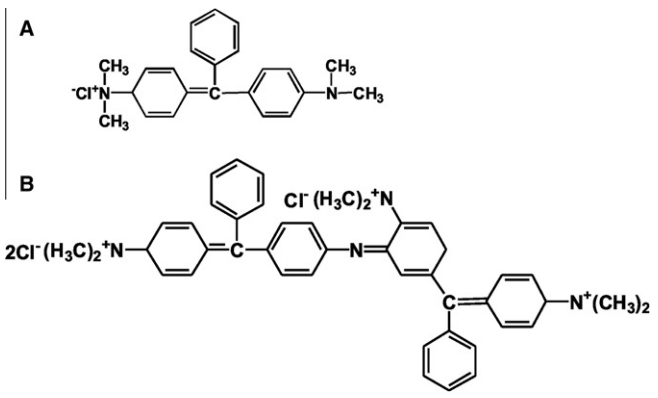
biochemical compounds has already been reported in the literature [19–22].

Even though the electrocatalytic activity of conjugated polymers and CNT matrices individually shows good results, new studies have been developed during the past decade for the preparation of composite films composed of both CNTs and conjugated polymers to improve matrix properties such as high sensitivity and good stability [23–25]. The incorporation of CNTs in conjugated polymers leads to the formation of new composite materials having the properties of each component with a synergistic effect that would be useful in particular applications [26]. These electroactive polymer/CNT composite matrices possess good solubility in organic solvents compared with unmodified CNTs. Moreover, polymer matrices exhibit high compatibility in the presence of CNTs [27]. There have been past attempts for the preparation of composite and sandwiched films made of polymer adsorbed on CNTs, and these were used for electrocatalysis studies such as selective detection of dopamine in the presence of ascorbic acid [28]. The sandwiched films were also used in the designing of nanodevices with the help of noncovalent adsorption, electrodeposition, and so forth [29].

Among the conjugated polymers, a group of them representing azines, such as phenazines, phenothiazines, and phenoxazines, have been widely used in bioelectrochemistry as redox indicators and mediators [30]. The electropolymerization of azine group compounds is usually performed by anodic oxidation in acidic medium [31,32]. Similar to these azine dyes, malachite green (MG) is also a dye compound that has an open but ionized structure; hence, the resulting polymer is promising in exhibiting interesting features such as fast rate of charge transfer and ion transport and good catalytic ability toward small biomolecules [33]. Previous studies have reported that poly(malachite green) (PMG) can be synthesized by electrochemical polymerization of MG. These studies also reported the growth mechanism of PMG along with electrochemical, Fourier transform infrared (FT-IR), and ultraviolet–visible (UV–vis) studies [33–35]. The chemical structures of MG and PMG are shown in Scheme 1.

In this article, we report a novel composite film, MWCNT–NF–PMG, made of multiwalled carbon nanotubes (MWCNTs) that were dispersed using Nafion (NF) and then incorporated with PMG. MWCNT–NF–PMG composite film's characterization, enhancement in functional properties, peak current, and electrocatalytic activity are also reported along with its application in the simultaneous determination of catechol and quinol. When compared with previously reported analytical values, MWCNT–NF–PMG composite film modified electrode has enhanced electrocatalysis of catechol and quinol [4,6–8]. The MWCNT–NF–PMG film preparation involves two steps: (i) electrodes are modified with uniformly well-dispersed MWCNT–NF, (ii) which is then modified with PMG.



Scheme 1. Chemical structures of MG (A) and PMG (B).

Materials and methods

Materials

MG, NF, MWCNTs (outer diameter = 10–20 nm, inner diameter = 2–10 nm, length = 0.5–200 μm), catechol, and quinol obtained from Aldrich and Sigma–Aldrich were used as received. All other used chemicals were of analytical grade. The preparation of aqueous solution was done with double distilled deionized water. Solutions used for the experiments were deoxygenated by purging with prepurified nitrogen gas. The pH 1.5 aqueous solution was prepared from H_2SO_4.

Apparatus

Cyclic voltammetry (CV), electrochemical quartz crystal microbalance (EQCM), and differential pulse voltammetry (DPV) studies were performed using analytical system models CHI-405, CHI-400, and CHI-750 potentiostats, respectively. A conventional three-electrode cell assembly consisting of an Ag/AgCl reference electrode and a platinum wire counter electrode were used for the electrochemical measurements. The working electrode was GCE modified with PMG, NF–PMG, or MWCNT–NF–PMG composite films. In these experiments, all of the potentials are reported versus Ag/AgCl reference electrode. The working electrode for EQCM measurements was an 8-MHz AT-cut quartz crystal coated with a gold electrode. The diameter of the quartz crystal was 13.7 mm, and that of the gold electrode was 5 mm. The morphological characterizations of the films were examined by means of atomic force microscopy (AFM) (Being Nano-Instruments CSPM-4000). All of the measurements were carried out at 25 ± 2 °C.

Preparation of MWCNT–NF–PMG composite electrodes

The important challenge in the dispersion of MWCNTs was preparation of a homogeneous solution. In general, the dispersion of CNTs has been carried out by physical (milling) and chemical methods (covalent and noncovalent functionalization). These methods cause damage to CNTs and add impurities to them [36,37]. To overcome these drawbacks, hydrophobic interaction between NF and MWCNTs was used for our experiments [38,39]. Briefly, the dispersion of MWCNTs was done by using 5% NF (2 ml of NF in 10 ml of water) with 10 mg of MWCNTs (MWCNT–NF). The uniform dispersion of MWCNTs was obtained by 6 h of ultrasonication of MWCNT–NF mixture.

Before starting each experiment, GCEs were polished using a BAS polishing kit with 0.05 μm alumina slurry and then rinsed and ultrasonicated in double distilled deionized water. The GCEs studied were uniformly coated with 10 μl of MWCNT–NF mixture (0.13 mg cm^{-2} MWCNTs) and dried at room temperature. Then MG was electropolymerized on the MWCNT–NF modified GCE from 5 mM MG present in pH 1.5 H_2SO_4 aqueous solution. The electropolymerization was performed by consecutive cyclic voltammograms (25 cycles) over an optimized potential range of 0–1.2 V at a scan rate of 100 mV s^{-1}. After that, the modified MWCNT–NF–PMG electrode was carefully washed with double distilled deionized water.

Results and discussion

Electropolymerization of MG at various electrodes and their characterizations

The electropolymerization of MG (from 5 mM MG solution) using electrochemical oxidation on unmodified, MWCNT–NF