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Electrochemical sensor for hydroquinone and catechol based on electrochemically reduced GO–terthiophene–CNT

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ABSTRACT

The GO–TT–CNT hybrid material was prepared by the in-situ polymerization of graphene oxide (GO), multi-walled carbon nanotube (CNT), and terthiophene (TT). The GO–TT–CNT hybrid material was characterized via Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and field emission–scanning electron microscope (FE–SEM). The electrochemical detections of hydroquinone (HQ) and catechol (CC) were verified via cyclic voltammetry (CV), differential pulse voltammetry (DPV), and amperometric response. Electrochemically reduced GO–TT–CNT [ER(GO–TT–CNT)] was obtained through the electrochemical reduction of GO–TT–CNT in a PBS solution (pH 5). The ER(GO–TT–CNT) was employed to detect HQ and CC. The effects of ER(GO–TT–CNT) in various pH (pH 4.04–9.01) in the PBS solution were investigated for the detection of HQ and CC. The detection limits of HQ and CC were 3.5×10^{-2} and 4.9×10^{-3} μM, respectively. Resorcinol (RS), H_2O_2, and ascorbic acid (AA) as interference materials showed negligible effects on the HQ and CC responses, demonstrating the high selectivity of the proposed biosensor.

1. Introduction

In human medicine, hydroquinone (HQ) is used as a topical application for skin whitening for reducing the color of the skin. It does not have the same predisposition to cause dermatitis as metal does. Numerous studies have revealed, however, that HQ can cause exogenous ochronosis, a disfiguring disease in which blue-black pigments are deposited onto the skin, if taken orally, but skin preparations containing the ingredient are administered topically. While using HQ as a lightening agent can be effective with proper use, it can also cause skin sensitivity. HQ is sometimes combined with alpha hydroxy acids that exfoliate the skin to quicken the lightening process. HQ undergoes oxidation under mild conditions to give benzoquinone. This process can be reversed. Some naturally occurring HQ derivatives exhibit this sort of reactivity. Industrially, this reaction is exploited both with HQ itself but more often with its derivatives, where one OH has been replaced by an amine. Small amounts of catechol occur naturally in fruits and vegetables, along with the enzyme polyphenol oxidase (also known as *catecholase* or *catechol oxidase*). Upon mixing the enzyme with the substrate and exposure to oxygen (as when a potato or apple is cut and left out), the colorless catechol oxidizes to reddish-brown melanoid pigments, derivatives of benzoquinone. Benzoquinone is said to be antimicrobial, which slows the spoilage of wounded fruits and other plant parts. Catechol is produced by the reversible two-electron, two-proton reduction of 1,2-benzoquinone (Scheme 1)[13].

GO-CNT was manufactured from water-dispersible GO and CNT [10–12], and was used as supercapacitors [7,8,29]. This method has the following advantages: (1) it is a simple and efficient method; (2) the strong π–π stacking interactions between the t-CNTs and r-GO in the hybrid favor efficient load transfer between the fillers themselves compared to the simple mixture of the two kinds of fillers without interactions; and (3) the 3D nano-structured hybrids show a much stronger interfacial interaction between the matrix and hybrid fillers than that with r-GO or t-CNTs alone [28]. There are few reports in the literature about the detection of HQ and CC through the use of various electrochemical methods and electrodes. The determination of HQ involves the use of various electrodes (carbon nanomaterials, ionic-liquid-composite-film-modified electrode [6,14], metal-modified electrodes [17,21,36], immobilized selectively on the CNT/PEDOT/CPE [32]). Meanwhile, a major obstacle in the simultaneous determination of HQ and CC is the overlapping voltammetric responses. For example, HQ and CC have been determined simultaneously using a graphene-modified electrode [19], metal/carbon nanomaterials [12,16,20,22,26], and polymer and carbon nanomaterials [27].

In this work, we prepared a GO–TT–CNT hybrid material by the *in-situ* polymerization of GO, CNT, and TT in between. The hybrid materials were characterized via Raman spectroscopy, XPS, and

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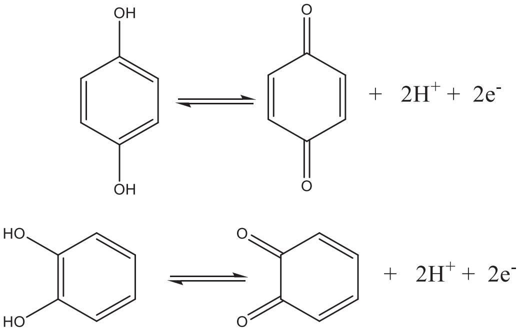


Scheme 1. Mechanism of the electrochemical oxidations of HQ and CC.

FE–SEM. ER(GO–TT–CNT) can be employed for the electrochemical detection of HQ and CC. The detection potentials and currents of HQ and CC were verified *via* CV, DPV, and amperometric response. The pH influence was investigated on various pH values (pH 4.04–9.01) in the PBS solution of various. The concentrations of HQ and CC, various scan rates, and interference experiments on interfering substances were also investigated.

2. Experiment

2.1. Materials and chemicals

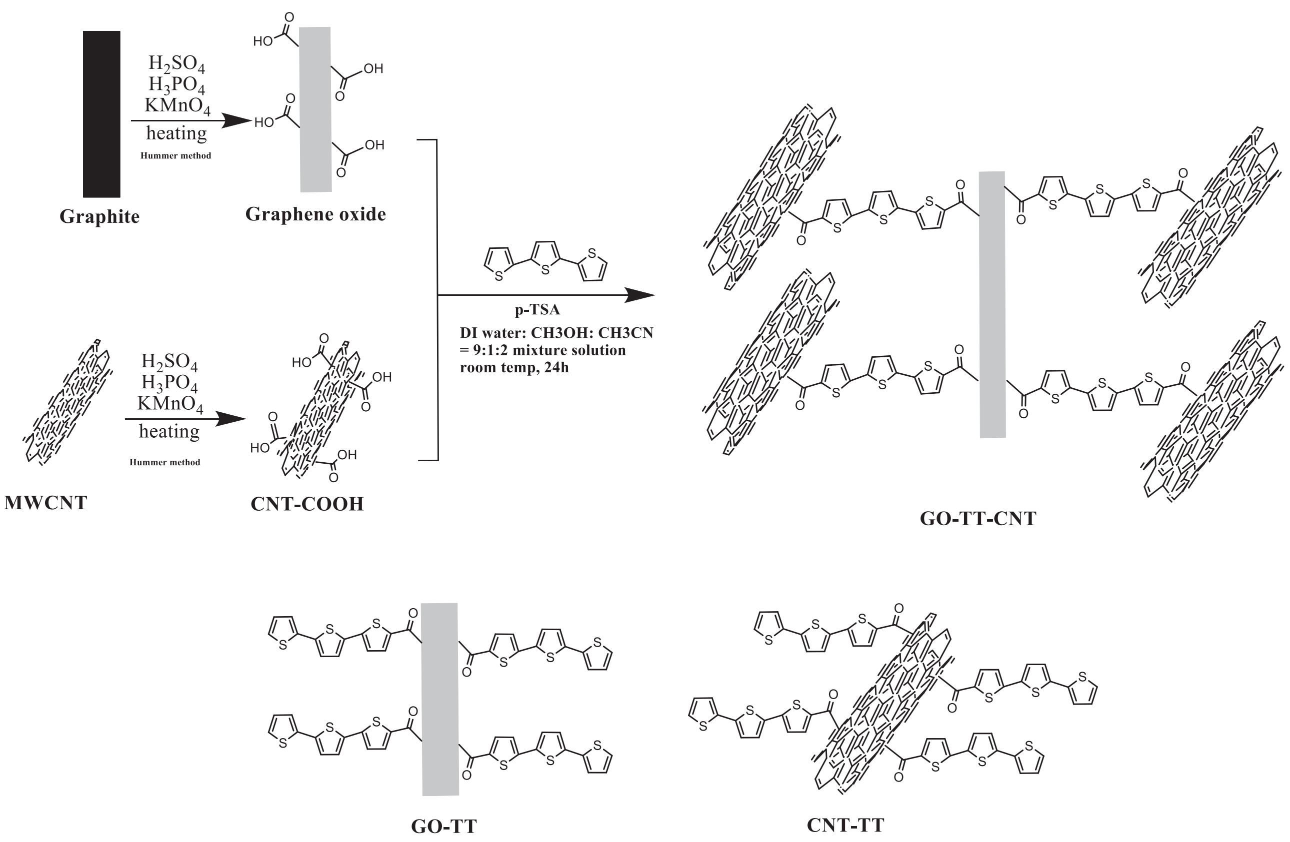
The graphite powder (~325 mesh, 99.999%), HQ, CC, RS, and TT were purchased from Aldrich. The MWCNT was manufactured by Carbon Nano Tech Co., Ltd. (Pohang, South Korea). Their diameter and length were 20–30 nm and 1.0–2.0 μm, respectively. CH_3OH and CH_3CN were purchased from OCI Co., Ltd. All the other reagents were of analytical grade, and were used without further purification. A PBS buffer solution was prepared with 0.1 M NaH_2PO_4, and its pH was adjusted with 0.1 M NaOH and 0.1 M H_3PO_4. Doubly distilled water was used in the preparation of the aqueous electrolyte solutions.

2.2. Characterization

The Raman spectra were recorded on a Lab Ram HR800 UV Raman microscope (Horiba Jobin-Yvon, France), KBSI, Gwangju Center. The XPS data analysis program Advantage ver.4.54 (Thermo Electron Corp., England) was used. This system uses an unmonochromatized Mg K (1253.6 eV) source and a spherical section analyzer. Survey scan data were collected using 50 eV pass energy. The surface morphologies of the materials were measured via FE–SEM with a MIRA 3 LMU (TESCAN, Czech Republic). A three-electrode assembly cell consisting of a modified glassy carbon electrode (GCE, 3.0 mm diameter) as the working electrode was used, and a platinum-wire electrode was used as the auxiliary electrode. An Ag/AgCl (3.0 M NaCl) electrode supplied by BAS (Model MF-2052) was used as the reference electrode. All the potentials were reported with respect to that of the Ag/AgCl electrode at room temperature under an argon atmosphere. The electrochemical techniques, including CV, DPV, and amperometric response, were carried out using a BAS 100B/W voltammetric analyzer (Bioanalytical Systems, West Lafayette, IN, USA) and a CHI electrochemical workstation (CH Instruments Inc., USA) in a grounded Faraday cage. The pH was measured using a pH glass electrode with a JENCO meter.

2.3. Synthesis of GO–TT–CNT

The synthesis procedure of GO–TT–CNT is shown in Scheme 2. GO was obtained by oxidizing graphite using the improved



Scheme 2. Synthesis of GO–TT, CNT–TT and GO–TT–CNT.