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Research article

Phenolic sensor development based on chromium oxide-decorated carbon nanotubes for environmental safety

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ABSTRACT

A nanocomposite (NC) composed of chromium(III)oxide nanomaterials decorated carbon nanotubes (Cr_2O_3–CNT NC) was prepared via a simple solution method with reducing agents in an alkaline medium. The Cr_2O_3–CNT NC was characterized using ultraviolet–visible (UV/Vs.) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, energy-dispersive X-ray spectroscopy (XEDS), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and field-emission scanning electron microscopy (FESEM). The Cr_2O_3–CNT composite was deposited on a flat glassy carbon electrode (GCE) with conducting nafion (5%) binders to produce a sensor that exhibited fast response and high selectivity toward 4-methoxyphenol (4MP) in phosphate buffer phase at pH 7. Furthermore, the sensor performance parameters, including the sensitivity, lower detection range, reliability, and reproducibility, ease of integration, long-term stability, and selectivity were investigated in detail. The calibration plot was found to be linear in the concentration range of 0.01 nM–0.1 μM. The sensitivity and detection limit were calculated as 1.4768 μA cm^{-2} μM^{-1} and 0.06428 ± 0.0002 nM (at a signal-to-noise ratio of 3), respectively. Thus, it was concluded that the proposed selective and efficient sensor represents a promising approach to effectively detect toxic phenolic compounds in the environment with acceptable and reliable results.

1. Introduction

Effective detection of toxic organic small molecules is an important step in the prevention of environmental and human health issues. The chemical 4-methoxyphenol ($CH_3OC_6H_4OH$; *p*-methoxyphenol) is typically utilized to produce lauryl aldehyde and lauric acid. Furthermore, it can also be utilized as a common solvent; a plasticizer; a low-temperature lubricant; a flavoring and fragrance agent in food, cosmetics, pharmaceutical products, and soap; a tobacco flavoring agent; an inhibitor; an antioxidant; a stabilizer; and an intermediate to manufacture other stabilizers, dyes, and pharmaceutical products (Zhang and Tay, 2016; Miao et al., 2015; Cui et al., 2010; Uğurlu et al., 2008; Liu et al., 2015). Since 4MP has a critical effect on human health and can cause serious environmental pollution (Shi et al., 2015), it is one of the most controlled toxic chemicals in many countries (Koshy et al., 1995). Moreover, industrial contamination associated with 4MP is of grave concern, not just because of the corresponding threat to human health and marine life, but also because of the steady increase in aquatic environmental pollution and the evolution of antibiotic-resistant microbial strains (Pino et al., 2007; Kita et al., 2009; Tanaka et al., 2010; Hinwood et al., 2008). Different physico-chemical methods have been proposed to treat and reduce the impact of 4MP and to study it as a model in comparison to natural metabolites such as dopamine, norepinephrine, and epinephrine (Hawley and Adams, 1964; Petek et al., 1973; Bredenberg et al., 1989; Shiau and Zeng, 2012).

Detecting very low concentrations of environmental pollutants via a fast and efficient method is essential, and the use of nanomaterials is being explored because their properties are superior to those of bulk substances in terms of mechanical strength, thermal stability, catalytic activity, electrical conductivity, and magnetic and optical properties. In particular, improvements in 4MP-detection techniques are critical for environmental protection and human safety. To date, the analytical techniques developed to detect 4MP

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quantities have been based on the use of gravimetric, ultraviolet spectroscopic, and polarographic analysis (Wang and Chen, 1996; Sanz, 2002). However, luminescence-quenching-based chemical detection through the use of luminescent materials is a much simpler, highly sensitive, and convenient alternative (Pramanik et al., 2011; Chen et al., 2013; Balamurugan et al., 2014; Gole et al., 2011). This technique involves the monitoring of transmission signals formed by the structural or electronic interactions between sensing nanomaterials and nanocomposite (NC) substrates.

Chemical sensors based on semiconducting metal oxides and composite nanomaterials are promising for the detection of various toxic elements and chemicals because of the uniquely large surface areas of such sensors (Wongchoosuk et al., 2010; Wang and Hu, 2009; Shi et al., 2015). A sensor signal is significantly enhanced in the presence of NCs or functional materials with or without doping on the sensor surfaces in chemical or biological systems. Semiconducting carbon nanotubes (CNTs) are currently utilized in the fabrication of electrochemical sensors (Lawal, 2015; Yang et al., 2015; Farhana et al., 2014; Wang and Arash, 2014), and the transition-metal oxide Cr_2O_3 has a variety of applications in optical and electronic devices, catalysis, wear-resistant materials, and advanced colorants. In particular, Cr_2O_3 nanoparticles are attracting attention because their larger active surface area yields both high sensitivity and enhanced reaction rates (Gupta et al., 2014; Gibot et al., 2015; Wang et al., 2015; Inturi et al., 2015; Wagh et al., 2006; Yang et al., 2009; Rahman et al., 2013; Ma et al., 2012). In this study, a Cr_2O_3–CNT NC was synthesized via a wet-chemical process, and structural and morphological improvements were realized by decorating CNTs with transition-metal-oxide nanoparticles. The Cr_2O_3–CNT NC allowed very sensitive detection through chemical interactions that changed their electrochemical properties. A simple, reliable, and efficient chemical sensor was then fabricated by depositing the Cr_2O_3–CNT NC on the surface of a polished GCE, and the effectiveness of its detection of 4MP under room-temperature (i.e., 25 °C) conditions was evaluated via a simple and reliable current–voltage (*I–V*) method with a short response time.

2. Experimental sections

2.1. Materials and methods

Chromium(III)chloride ($CrCl_3 \cdot 6H_2O$), sodium hydroxide (NaOH), disodium phosphate, monosodium phosphate, CNTs, and all other chemicals were of analytical grade and purchased from Sigma-Aldrich Company, USA. The Cr_2O–CNT NC was characterized via ultraviolet–visible (UV–vis) spectroscopy (Evolution 300 UV/visible spectrophotometer, Thermo Scientific, USA) and Fourier-transform infrared (FT-IR) spectroscopy (NICOLET iS50 FTIR spectrometer, Thermo Scientific, USA) in the range of 400–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS; K-Alpha KA1066 spectrometer, Thermo Scientific, USA) was conducted using a monochromatic Al K_α X-ray radiation source as the excitation source, and the beam-spot size was maintained at 300.0 μm. The spectra were recorded in the fixed analyzer transmission mode, where the pass energy was maintained at 200.0 eV and pressures less than 10^{-8} Torr were employed. In addition, X-ray diffractometry (XRD; ARL X'TRA diffractometer, Thermo Scientific, USA) was conducted using Cu $K_{\alpha 1}$ radiation (λ = 1.5406 nm) with a 40-kV generator voltage and a 35-mA current. The Cr_2O_3–CNT NC morphology was examined using a field-emission scanning electron microscope (FESEM; JSM-7600F, JEOL, Japan). Elemental analysis was performed using energy-dispersive X-ray spectroscopy (XEDS; JEOL, Japan), and *I–V* measurements were performed using an electrometer (6517A Electrometer, Keithley, USA). In the *I–V* system, the working and counter electrodes were connected directly to the electrometer; the electrode current was measured against the applied potential of the fabricated sensor to facilitate selective 4MP detection.

2.2. Preparation of Cr_2O_3 nanoparticles decorated CNTs in solution method

Two reactions were conducted separately in two 250.0-mL Erlenmeyer flasks: For the first reaction, 100.0 mL of a 0.1 M $CrCl_3 \cdot 6H_2O$ solution was prepared and stirred, and 0.25 μg of CNTs (1.0 wt%) was added to the mixture. The solution pH was slowly adjusted using a 2.0 M sodium hydroxide solution, which was added drop-wise to obtain a pH of >10.0 and allow complete reduction of the chromium ions. The solution was kept in the flask and constantly stirred while being heated to approximately 80.0 °C for 6 h. The resulting precipitate was washed thoroughly with acetone and water, and then dried at room temperature. The product was then dried in a furnace at 60.0 °C for 24 h, and its morphological, structural, optical, and chemical properties were investigated. Next, the same method was used to prepare chromium(III)oxide nanomaterial without CNTs in a 0.1 M $CrCl_3 \cdot 6H_2O$ solution in the second flask. The following reactions [Eqs. (1)–(4)] summarize the formation of the Cr_2O_3–CNT nanocomposite:

$$NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)} \quad (1)$$

$$CrCl_3 \cdot 6H_2O_{(s)} \rightarrow Cr^{3+}_{(aq)} + 3Cl^-_{(aq)} + 6H_2O_{(l)} \quad (2)$$

$$3Na^+_{(aq)} + 3OH^-_{(aq)} + Cr^{3+}_{(aq)} + 3Cl^-_{(aq)} + CNT(dis) \rightarrow 3NaCl_{(aq)} + Cr(OH)_{3(aq)} \cdot CNT\downarrow \quad (3)$$

$$2Cr(OH)_{3(aq)} \cdot CNT \rightarrow Cr_2O_{3(s)} \cdot CNT + 3H_2O_{(g)} \quad (4)$$

As obtained Cr_2O_3–CNTs NCs was characterized in detail in terms of their crystallinity, morphology, structure, and optical properties, and finally applied for 4MP sensing using GCE by I-V method. During Cr_2O_3–CNT NC growth, Cr_2O_3 nuclei initially formed. Aggregated Cr_2O_3 nanocrystals were then formed via Ostwald ripening around the dispersed CNTs under the influence of van der Waals forces. Thus, porous Cr_2O_3–CNT NCs were obtained, as shown in Scheme 1.

2.3. Fabrication and evaluation of GCE coated with Cr_2O_3–CNT NC

A phosphate buffer solution (PBS; 0.1 M, pH 7.0) was prepared by mixing 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 solutions in 100.0 mL of deionized (DI) water. A GCE (surface area: ~0.0316 cm^2) was fabricated, and a spatula was used to brush the Cr_2O_3/CNT NC together with a conducting binder on the electrode surface (5.0% Nafion solution in ethanol; NCs: Binders = 1: 1); the coated electrode was then placed in an air atmosphere for 12 h until a dried film with uniform thickness was obtained. An electrochemical cell was constructed, with the NC-coated GCE serving as the working electrode and a Pd wire serving as the counter electrode. Next, 4MP (0.1 M, stock solution) was diluted to different concentrations in DI water and used as the target chemical for detection. Throughout the chemical analysis, 10.0 mL of 0.1 M PBS was placed in a beaker and the analyte solution (25.0 μL) was added drop-wise systematically, yielding 4MP solutions with low to high concentration (0.01 nM–0.1 mM). The sensitivity was calculated from the slope of the *I–V* calibration plot.