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A comparative study on 4-aminophenol sensor development with various CdO nanocomposites

Mohammed M. Rahman [a,b,*,1], Faisal K. Algethami [b], Abdullah M. Asiri [a,b], Hadi M. Marwani [a,b,*], Basma Alhogbi [b]

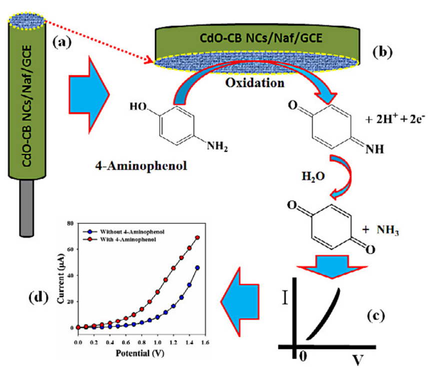
[a] Center of Excellence for Advanced Materials Research (CEAMR), Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

[b] Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

HIGHLIGHTS

- Facile CdO–CB, GO, CNTs nanocomposites prepared by wet-chemical method.
- Sensitive and Selective 4-aminophenol chemical sensor.
- Lowest detection limit (0.14 nM) ever found.
- Chemical sensor development with nanotechnology.
- Environmental safety and protection.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanocomposites of carbon black (CB), carbon nanotubes (CNT), graphene oxide (GO) with CdO were prepared by the wet-chemical method in alkaline medium (pH > 10) and were applied to the 4-aminophenol (4-AP) electrochemical sensor. The NCs were characterized by using different conventional methods, such as UV/vis. spectroscopy, FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM) and X-ray diffraction pattern (XRD). CdO–NCs were then immobilized onto the flat of a glassy carbon electrode (GCE) by using binders (5% nafion) to fabricate CdO–CB NCs/Nafion/GCE. 4-AP was a target analyte. It exhibits a fast response towards CdO–CB NCs/Nafion/GCE sensor by a simple and reliable *I–V* electrochemical approach compared to other electrode assembly (CdO–CNTs, CdO–GO, and CdO alone). The 4-AP sensor was exhibited higher sensitivity, lower detection limit, large dynamic concentration range and fast response. The calibration curve plot was linear within the concentration range of 4-AP from 1.0 nM to 0.1 mM with the correlation coefficient (r^2) of 0.954. The sensitivity and detection limit were ∼6.67 $\mu A cm^{-2} \mu M^{-1}$ and ∼0.14 ± 0.02 nM (signal-to-noise ratio at an SNR of 3) respectively. Furthermore, CdO–CB NCs/Nafion/GCE is exhibited the highest selectivity for toxic 4-AP

* Corresponding authors at: Center of Excellence for Advanced Materials Research (CEAMR), Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia.

E-mail addresses: mmrahman@kau.edu.sa (M.M. Rahman), hmarwani@kau.edu.sa (H.M. Marwani).

1 Fax: +966 026952292.

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chemicals compared to only CdO–CNT, CdO–GO and CdO nanocomposites. Finally, this approach was successfully applied for the detection of 4-AP in water samples.

1. Introduction

Phenol and its derivatives including 1-naphthol, cresol, and 4-AP are important substances in a widely range of industrial processes. They are broad applied in production of dyes, plastics, chemical inhibitor, and antioxidants [1]. 4-AP is a substance of high toxicity and has nephrotoxicity and teratogenic effect in humans [2,3]. Therefore, there is an essential demand to develop of simple and reliable analytical methods for the detection and determination of 4-AP for the environmental control. There are many analytical methods for the detection and determination of 4-AP, such as high performance liquid chromatography (HPLC) [4], spectrophotometry [5–7], colorimetry [8,9], and electrochemical methods [10–15]. However, most of these methods have some disadvantages such as expensive equipment, difficult sample preparation and requiring special reagents. Hence, there is an increasing demand for new and simple analytical methods to detect of 4-AP that can provide accurate and quick results without complicated analysis.

Development of reliable and sensitive methods were used for the detection of phenolic compounds for environmental safety, protection, food quality control, and health [16–19]. There are several phenolic compounds have been classified as "priority pollutants" by both the United States Environmental Protection Agency and the European Commission. Phenolic compounds are comparatively general in waste streams of diverse large-scale processing and manufacturing where they serve as precursor materials in various industries such as coal mining, crude oil refining, paper bleaching, and production of dyes, resins, plastics, explosives, detergents, pharmaceuticals, pesticides, and herbicides [20–24]. In difference, few phenols of plant origin have been originated to display a broad range of attractive physiological characteristics as antioxidants, anti-inflammatories, and cardiovascular prophylactics, promoting their use as additives in some alcoholic beverages and food products [25–29]. Recent determination methods such as spectro-photometry, fluorimetry, gas or liquid chromatography, mass spectrometry and capillary electrophoresis are usually perceptive and consistent but possess limitations, such as being expensive, time-consuming and requiring pre-concentration and extraction steps that increase the risk of sample loss and generation of other hazardous byproducts [30–34]. Electrochemical sensing of phenolic compounds represents a promising approach that can be utilized to complement already existing methods owing to collective characteristics such as high sensitivity and selectivity, low cost, simple instrumentation and potential for miniaturization [35–38]. Simple and reliable *I–V* electrochemical methods with the chemical sensors exhibit the higher response, higher sensitivity, large dynamic range, lower detection limits and stable signals compared to classical methods for 4-AP detection. The chemical sensors that based on the metal oxide nanostructures are usually used for the detection of different toxic chemicals because of their many advantages such as large surface area, electrical conductivity, higher response and thermal stability [39,40]. Furthermore, there are many uses for transition metal oxide nanomaterials (semiconductor), such as UV photo-detectors [41,42], field-emission electron sources [43], field consequence transistors [44], gas sensors [45], doped nanomaterials [46,47], and different other functional devices [48].

The aim of this study is the detection of 4-AP by using simple, reliable and highly sensitive electrochemical method for the first time. We used a simple wet chemical method to prepare CdO–CB nanocomposites. This CdO–CB NCs were used as a thin nanocomposite films on the glassy carbon electrode with binders (5% nafion) to fabricate CdO–CB NCs/Nafion/GCE sensor. The CdO–CB NCs/Nafion/GCE sensor depicts high sensitivity and high selectivity for detection of 4-AP by using electrochemical *I–V* techniques at room conditions.

2. Experimental sections

2.1. Materials and method

Cadmium chloride hemi(pentahydrate) ($CdCl_2 \cdot 2.5\ H_2O$), sodium hydroxide (NaOH), trisodium citrate dehydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$), disodium phosphate, monosodium phosphate, Melamine, Ethanol, methanol, 4-AP, Bisphenol A, p-Nitrophenol, ammonium hydroxide, Carbon Black (CB), Hydrazine, M-Tolyl hydrazine hydrochloride, nafion (5% ethanolic solution), and all other chemicals in this study were of analytical grade and were acquired from Sigma–Aldrich Company.

The CdO–CB NCs was examined by using many different devices. UV/visible spectroscopy studies were done with Lambda-950, Perkin Elmer, Germany (http://www.perkinelmer.com). FTIR spectra for the CdO–CB NCs were obtained using a spectrophotometer (Spectrum-100 FT-IR, Perkin Elmer, Germany) in the range of 400–4000 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) measurement for the CdO–CB NCs sample was performed on a Thermo Scientific K-Alpha KA1066 spectrometer with a monochromatic Al$K\alpha 1$ X-ray radiation source as the excitation source. Transmission Electron Microscopes (TEM) was performed with a JEM-1011 microscope (JEOL, Tokyo, Japan) at 100 kV accelerated voltage. The X-ray diffraction (XRD) studies were measured by an X-ray diffractometer (XRD, Thermo scientific, ARL Extra) using a Cu$K\alpha 1$ radiation ($\lambda = 1.5406$ nm) at 40.0 kV and current of 35.0 mA applied for the measurements.

The electrochemical measurements were carried out on an Electrometer (Keithley, 6517A, Electrometer, USA) using *I–V* method. In *I–V* system, two electrodes were used, where the bare glassy carbon electrode (GCE, surface area: 0.0316 cm^2) or modified GC electrode was used as the working electrode and a platinum wire as the counter electrode. The working electrode and the counter electrode connected directly in the electrometer. In room temperature, the current was measured against the potential of fabricated The CdO–CB NCs electrode for selective 4-AP detection.

2.2. Preparation of nanocomposites by wet-chemical method

CdO–CB NCs were synthesized by a simple wet-chemical method at room conditions by using Cadmium chloride hemi(pentahydrate) ($CdCl_2 \cdot 2.5H_2O$), trisodium citrate dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$), sodium hydroxide (NaOH), and carbon black