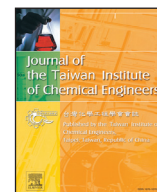




Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Development of selective chloroform sensor with transition metal oxide nanoparticle/multi-walled carbon nanotube nanocomposites by modified glassy carbon electrode

Mohammed M. Rahman^{a,b,*}, Hasan B. Balkhoyor^a, Abdullah M. Asiri^{a,b}, Tariq R. Sobahi^a

^a Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

^b Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:

Received 3 February 2016

Revised 27 May 2016

Accepted 4 June 2016

Available online xxx

Keywords:

NiO/MWCNT nanocomposites

Optical properties

Glassy carbon electrode

Structural properties

Chloroform detection

I–V method

ABSTRACT

Transition metal oxide (NiO) nanoparticles decorated multi-walled carbon nanotubes (NiO/MWCNT nanocomposites, NCs) were prepared by a facile solution method using reducing agents in alkaline medium. The NiO/MWCNT NCs were characterized by UV/vis, FT-IR, energy-dispersive X-ray spectroscopy (XEDS), powder X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and scanning electron microscopy (TEM). The NiO NPs or NiO/MWCNTs were deposited separately on flat glassy carbon electrode (GCE) with conducting binders (5% nafion) to result in a sensor that has a fast response towards selective chloroform (CHCl₃). Features including high-sensitivity, lower-detection limit, reliability, reproducibility, ease of integration, long-term stability, selective, and enhanced electrochemical performances are investigated in details. It is detailed studied the sensor performances with NiO NPs/GCE and NiO/MWCNT/GCE electrodes separately and found that NiO/MWCNT/GCE exhibits the higher sensitivity and lower detection limit compared to NiO/GCE assembly. The calibration plot is linear ($r^2 = 0.9763$) over concentration range (3.5 nM to 35.0 mM) with NiO/MWCNT/GCE. The sensitivity and detection limit was calculated for NiO/MWCNT/GCE as $\sim 917.7 \text{ nA/cm}^2 \mu\text{M}$ and $0.1034 \pm 0.0002 \text{ nM}$ (at a signal-to-noise-ratio, SNR of 3) respectively. Finally, the efficiency of the proposed chemi-sensors can be applied and effectively utilized for the detection of toxic chloroform compound in environmental and healthcare fields in broad scales.

© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Chloroform (trichloro-methane) CHCl₃ is an organic compound, colorless, sweet-smelling, dense liquid, and is considered somewhat carcinogenic, toxic, and hazardous, several million tons are produced annually as a precursor to industry as poly-tetrafluoroethylene and refrigerants, but its use for refrigerants is being phased out, it was once a widely used anesthetic, and used as a solvent in the pharmaceutical industry and for producing dyes and pesticides [1–3]. Chloroform vapors depress the central nervous system of human beings and animal. It is immediately treacherous and perfidious to life and health. Breathing about 1000 ppm for a short time can cause dizziness, fatigue, eyesight disturbance, headache, lung congestion, kidney damage, cancer, and even death.

Chronic chloroform exposure can damage the liver and the kidneys (where chloroform is metabolized to phosgene), and some people develop sores when the skin is immersed in chloroform [4]. The National Institute for Occupational Safety and Health set two limits for chloroform, recommended exposure limit of 2 ppm [for 60 min] based on risk evaluations using human or animal health effects data, and permissible exposure limit of 50 ppm as carcinogen substance with targeted organs such liver, kidneys, and central nervous system [5,6]. Detecting very low concentration environment polluted contaminations in fast and efficient way become essential; nanomaterials have superior properties as compared to their bulk substances, such as mechanical strength, thermal stability, catalytic activity, electrical conductivity, magnetic properties, and optical properties. Development of chemical sensors based semiconductor metal oxides and composites takes a major study for detection of various toxic elements and chemicals considering of its unique large surface areas properties. So, it is urgently required to develop cheap sensors with high sensing performance at low power consumption for detecting toxic chlorinated aliphatic hydrocarbon chloroform compound [7–13].

* Corresponding author at: Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia. Tel.: +966 59 6421830; fax: +966 026952292.

E-mail address: mmrahman@kau.edu.sa, mmrahmanh@gmail.com (M.M. Rahman).

Nickel oxide (NiO) semiconductor chemically stable has numerous chemical and physical applications, in solar and fuel cells, catalytic agents, gas sensing, electrochemical capacitance, antioxidant in bio-systems, and magnetic materials, NiO nanoparticles due to larger active surface area enhance its sensitivity and reactions [14–18]. Multi-walled carbon nanotubes (MWCNTs) have become one of the most attractive nanomaterials in nanotechnology revolution. With the continuous research of nanotechnology in material science, carbon nanomaterials have remarkable mechanical, electrical, and chemical properties with a high surface-to-volume ratio. Because of its exceptional properties, enhanced electron transfer, high thermal conductivity, better electrocatalytic activity, high interfacial adsorption properties, high biocompatibility, and can work as a catalyst support to control the size and the dispersion of the catalyst in use, MWCNTs semiconductor used as electrochemical sensors [19–22]. Utilizing nickel oxide with carbon nanotubes as (NiO/MWCNT) nanocomposites under significant studied for different applications like insulin and glucose sensors, electrochemical energy storage, electromagnetic wave absorbing, and water oxidation [23–28]. Metal oxide semiconductor materials such as SnO₂, ZnO, TiO₂, WO₃, Ga₂O₃ and In₂O₃ were widely used for chloroform sensor applications [29–31]. Every semiconductor based sensor not only has merits but also has some demerits, such as long response time, less sensitivity, poor selectivity, not economic, and the high requirement of operating temperature. Among the various reported methods to improve the performances of chemical sensors, the conjugation of metal oxides with different composites shows great potential in improving chemical response on sensitivity and selectivity, which is attributed to the synergistic effects that produced by different chloroform sensing components. So far there are many reports about compounds containing catalyst that have been applied to the chemical sensitive fields [32–34]. There is a high demand on introduced a portable, cheaper chemical detectors at work place for real time monitoring the levels of chloroform so that precautions can be taken in the presence of this toxic substance. One of the key features of these nanostructures is the large relationship surface/volume that makes them attractive for use as sensitive films chemical sensors, which possibly is a requisite for chloroform sensing at room temperature.

Therefore, in this study, NiO/MWCNT nanocomposites synthesized by solution process, which displayed a continuous structural and morphological improvement in transition-metal decorated onto carbon nanotubes. The NiO/MWCNT NCs allows very sensitive recognition and transduction in the chemical interaction to change the electrochemical properties. Finally, NiO/MWCNT NCs were fabricated to make a simple, reliable and efficient chemical sensor onto side-polished GCE surfaces and executed the chemical sensing performances with chloroform chemical at room conditions. To best of our knowledge, this is the first report for highly sensitive detection of chloroform with NiO/MWCNT NCs using simple and reliable *I*-*V* method in short response time.

2. Experimental sections

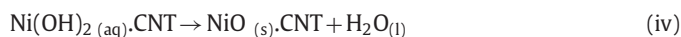
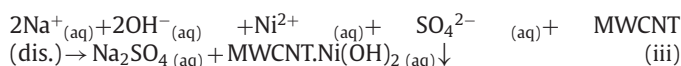
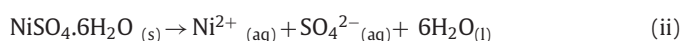
2.1. Materials and method

Nickel(II)sulfate hexahydrate (NiSO₄·6H₂O), sodium hydroxide (NaOH), disodium phosphate, monosodium phosphate, multi-walled carbon nanotubes, and all other chemicals used were of analytical grade and purchased from Sigma-Aldrich Company. The dried nickel(II)oxide-MWCNTs nanocomposite was investigated with UV/visible spectroscopy (Lambda-950, PerkinElmer, Germany). FT-IR spectra measured for the sample NiO/MWCNT NCs with a spectrophotometer (Spectrum-100, FT-IR) in the mid-IR range, which obtained from PerkinElmer, Germany. The XPS measurement of NiO/MWCNT NCs measured on a Thermo Scientific

K-Alpha KA1066 spectrometer (<http://www.thermoscientific.com>). A monochromatic AlK α x-ray radiation source used as excitation sources, and the beam-spot size kept in 300.0 μ m. The spectra recorded in the fixed analyzer transmission mode, where pass energy kept at 200.0 eV. The scanning of the spectra performed at pressures less 10⁻⁸ Torr. The powder X-ray diffraction (XRD) prototypes evaluated with an X-ray diffractometer (XRD, X'Pert Explorer, PANalytical diffractometer) prepared with CuK α ₁ radiation (λ :1.5406 nm) using a generator voltage of 40.0 kV and current of 35.0 mA applied for the measurement. The morphology of NiO/MWCNT NCs examined on FE-SEM instrument (FESEM, JSM-7600F, Japan). Elemental analysis investigated using EDS from JEOL, Japan. TEM sample was prepared as follows: the synthesized NiO/MWCNT NCs were dispersed into ethanol under ultrasonic vibration for 2 min, and then the TEM film was dipped in the solution and dried for investigation. *I*-*V* technique employed with an Electrometer (Keithley, 6517A, Electrometer, USA). In *I*-*V* system, two electrodes used working and counter electrodes connected directly in the electrometer. The current measured against the applied potential of fabricated NiO/MWCNT NCs sensor for selective chloroform detection.

2.2. Preparation of nanocomposite with NiO nanoparticles decorated MWCNTs

The two reactions carried out in two 250.0 ml Erlenmeyer flasks separately. For the first reaction, to 100.0 ml of 0.1 M NiSO₄·6H₂O solution and while stirring a 0.25 μ g of MWCNTs (1 wt%) added. The solution pH slowly was adjusted using sodium hydroxide 2.0 M solution dropwise to approximately pH = 10.0. The solution in the flask was kept under stirring and heating at around 80.0 °C for 6 h. It washed thoroughly with acetone and water then kept for drying at room condition. The as-grown products dried in the furnace at 60.0 °C for 24 h. The final product characterized in detail in terms of their morphological, structural, optical, and chemical properties. The second preparation was completed for NiO nanoparticles from 0.1 M NiSO₄·6H₂O solution in the flask without MWCNTs in same procedure. The following reactions (i)–(iv) summarized the formation of NiO nanoparticles,



2.3. Fabrication of glassy carbon electrode with NiO/MWCNT NCs

Phosphate buffer solution (PBS, 0.1 M, pH 7.0) prepared by mixing 0.2 M Na₂HPO₄ and 0.2 M NaH₂PO₄ solution in 100.0 mL of deionized water.

The glassy carbon electrode (GCE) fabricated by using NiO/MWCNT NCs with conducting binding. In briefly, the loading weight of NiO/MWCNTs onto GCE electrode and the method to fabricate electrode as follows: The GCE electrode (surface area 0.0316 cm²) was coated for thin-film preparation (thickness: 0.5 mm). 3.0 mg of NiO/MWCNT nanocomposite sample was mixed with ethanol to make it dispersed slurry. Then this solution is put onto the top of GCE and kept for drying. After drying the GCE-surface completely, 100.0 μ L of 5% nafion solution was dropped onto the fabricated surface for chemical gluing the nanocomposite onto GCE and then it was kept for drying again at 50.0 °C for 12 h. After complete drying of the film onto GCE, electrode is ready for the electrochemical measurement. An electrochemical cell constructed with NiO/MWCNT NCs coated GCE as a working

Download English Version:

<https://daneshyari.com/en/article/690185>

Download Persian Version:

<https://daneshyari.com/article/690185>

[Daneshyari.com](https://daneshyari.com)