Journal of Industrial and Engineering Chemistry xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

4-Hexylresorcinol sensor development based on wet-chemically prepared Co_3O_4@Er_2O_3 nanorods: A practical approach

Tahir Ali Sheikh[a,b], Mohammed M. Rahman[a,b,*], Abdullah M. Asiri[a,b], Hadi M. Marwani[a,b], Md. Rabiul Awual[c]

[a] Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia
[b] Center of Excellence for Advanced Materials Research, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia
[c] Depertment of Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

ARTICLE INFO

Article history:
Received 26 September 2017
Received in revised form 29 May 2018
Accepted 13 June 2018
Available online xxx

Keywords:
Co_3O_4@Er_2O_3 nanorods
4-Hexyl resorcinol
Sensitivity
Glassy carbon electrode
Environmental safety

ABSTRACT

In this approach, Co_3O_4@Er_2O_3 nanorods (NRs) were prepared by a wet-chemical method using reducing agents in alkaline medium. The resulting nanoparticles were characterized in details by UV/Vis and FT-IR spectroscopy, X-ray powder diffraction, Elemental dispersive analysis (EDS) coupled with field-emission scanning electron microscopy (FESEM). Co_3O_4@Er_2O_3NRs were deposited on a glassy carbon electrode (GCE) to give a selective sensor with a fast response toward 4-hexyl resorcinol (4-HR) in phosphate buffer phase (PBS) by electrochemical approach. The 4-HR sensor also displays good sensitivity, large linear dynamic range, lowest detection limit, and long-term stability, and enhanced electrochemical response. The calibration plot is linear over the 0.1 nM–0.01 M 4-HR concentration range. The sensitivity is ~14.765 $\mu A \mu M^{-1} cm^{-2}$, and the detection limit is 64.29 pM (signal-to-noise ratio, at a SNR of 3). We also discuss possible future prospective uses of this doped metal oxide semiconductor nanomaterial in terms of chemical sensing.

Introduction

Nanoscience and nanotechnology have great impact not only on the growth of modern science but also living beings of this universe. These are the emerging field of this era with wealth of applications in various fields such as biological [1], pharmaceutical [2], food industry [3], energy storage & conversion devices [4], toxic chemicals sensing [5] and many other industries. The growth of these fields relies on the production and application of different morphologies. Semiconductor nanomaterials of metal oxides have very impressive physical and chemical properties than their bulk substances such as enhanced electrical conductivity, optical property, structural and magnetic properties, mechanical strength, catalytic activity and thermal stability [6–11]. Lately, advance researches on semiconductor nanomaterials have revealed that doped metal oxides have increased in popularity owing to their excellent physio-chemical propertiessuch as mechanical strength, heat tolerance, electrical conductance, electro-magnetic property, and photo-catalytic property etc. [12]. As we know that rare earth elements have the high electric conductivity and doping with semiconductor transition metals can further improve its electrical performance. So in this approach erbium in combination with cobalt was used to synthesized the doped semiconductor nanostructure material with improve electrical performance. Similarly, among the transition metal oxides, cobalt oxide (Co_3O_4) is found to be very important with respect of its distinctive commercial applications such as gas sensing [13–16], catalysis [17], energy storage [18], magnetic resonance imaging (MRI) and drug delivery [19]. Herein the synthesis of Co_3O_4@Er_2O_3 NRs reported by facile wet chemical method for electrochemical detection of toxic chemicals in aqueous solutions. These days, a vast and unwanted amount of hazard substances/chemicals are being released in our ecosystem due to rapid industrialization and urbanization. Among the hazards chemicals phenolic compounds and their derivative are ubiquitous contaminants in our environment and have very toxic effect in our ecosystem. The main sources of these ubiquitous contaminants are municipal, pharmaceutical, food and agriculture industries because of their wide range of uses in dyes, paint, polymers, drugs, and other organic substances [20]. 4-HR is well

* Corresponding author at: Center of Excellence for Advanced Materials Research & Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia.
E-mail addresses: mmrahman@kau.edu.sa, mmrahmanh@gmail.com (M.M. Rahman).

https://doi.org/10.1016/j.jiec.2018.06.012
1226-086X/

known derivative of phenol and has many commercial uses in food, pharmaceutical and cosmetic industries [21]. In some pharmaceutical preparations, it develops the bacteriocidal [22], antiseptic [23] and anesthetic [24] properties in addition to the vermifuges activity [25]. In food industries it is used as an additive/preservative in frozen foods to increase their shelf life. It act as an anti-browning agent during the storage of apple slices. In frozen sea food such as shrimps, crabs and prawns it is used as melanosis inhibitor in combination with EDTA and sodium pyrophosphate and also increase their shelf life [26–28]. In cosmetic industries, it is also used in anti-aging, skin whiting & lightening creams and hair dyes [29,30]. 4-HR is also known as cosmetic biocides because it reduces the lines and wrinkles on skin, protects it from ultraviolet A & B rays and also inhibits the growth of microbes on skin by killing them [31]. Due to the vast use of 4-HR in our daily life it is easily absorbed through skin and gastric tract, which causes the thyroid dysfunction, hematuria, hypothermia, dyspnea, CNS effects, altered relative adrenal gland weights, irritation in skin, eyes, nose, throat and upper respiratory system. The National Institute for Occupational Safety and Health (NIOSH), World Health Organization (WHO) and New Jersey Department of Health, USA, have declared it as hazardous substance [32–34].

Owing to its acute toxicity different analytical methods such as high performance liquid chromatography coupled with different detectors such as UV [35], fluorescence [28] and mass spectrometry [36], thin layer chromatography (TLC) [37], spectrophotometry [38], amperometric [39] and cyclic voltammetric [21,40] methods have been reported for the determination of 4-hexylresorcinol. Multi-walled carbon nanotubes (MWCNT) and activated carbon cloth (ACC) have been used as adsorbent material for the adsorption of 4-HR and resorcinol from aqueous solution [21,41,42]. These reported methods are not very effective because they are very expensive and complicated. So it has become our need to design the cheap and reliable method for the sensitive, selective and accurate determination of 4-HR. GCE modified with nanomaterials as chemical sensors have been reported for the detection of toxic chemicals [43,44]. In this study GCE, fabricated with Co_3O_4@Er_2O_3 NRs, was designed to develop the ultra-sensitive and selective sensor for the detection of 4-HR among the various toxic chemicals by electrochemical approach using electrochemical technique. This nanomaterial displays the very good structural and morphological metal oxide nanostructure in addition to the very sensitive transduction in liquid-surface interactions to modify the electrochemical properties which was investigated by reliable electrochemical method under normal condition. It offers an effective, cheap, reliable and rapid detection of 4-HR qualitatively and quantitatively. As per our knowledge, this is the first selective study report for the detection of 4-HR qualitatively and quantitatively using electrochemical technique in short response time based on Co_3O_4@Er_2O_3 NRs which were coated with conducting binder nafion onto GCE.

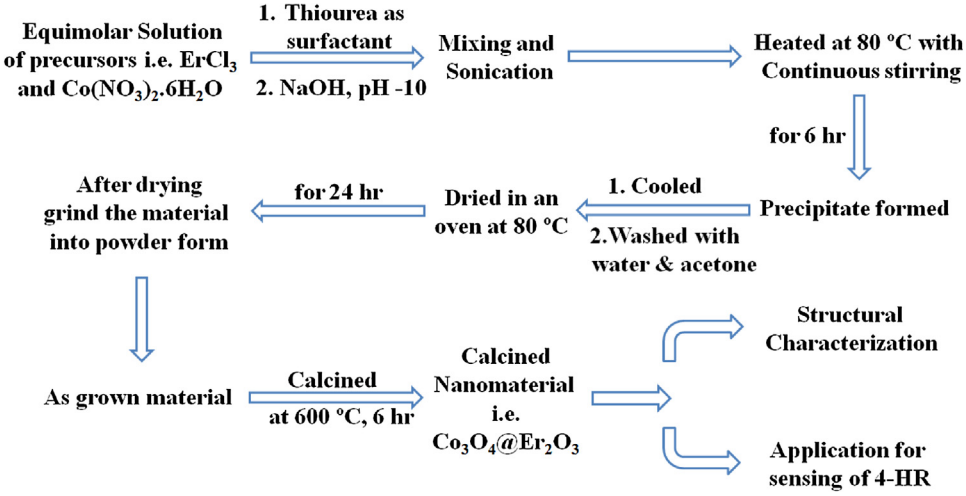
Experimental section

Materials and methods

The analytical grade chemicals such as erbium(III) chloride ($ErCl_3$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), sodium hydroxide, thiourea, nafion (5% ethanolic solution), 2, 4-dinitrophenol (2,4-DNP), 2-aminophenol (2-AP), 3-methoxy phenylhydrazine HCL (3-MP HDN), 3-methoxyphenol (3-MP), 4-hexylresorcinol (4-HR), 4-nitrophenyl hydrazine (4-NP HDN), bisphenol A (BPA), M-tolyl hydrazine (M-Tol HDN), phenylhydrazine (Ph-HDN) and *p*-nitrophenol (*p*-NP), monosodium phosphate and disodium phosphate were purchased from the Sigma-Aldrich company and used without any further modification and refinement. Spectroscopic characterization such as FTIR and UV/Vis spectra of the synthesized Co_3O_4@Er_2O_3 NRs were investigated on Thermo scientific NICOLET iS50 FTIR spectrometer (Madison, WI, USA), and 300 UV/Vis spectrophotometer (Thermo scientific), respectively. FESEM (JEOL, JSM-7600F, Japan) equipped EDS was also used to study the optical categorizations such as elemental analysis, molecular arrangement and morphology of the Co_3O_4@Er_2O_3 NRs. In addition to these above stipulated analytical tools crystallinity of the Co_3O_4@Er_2O_3 NRs were observed by the implementation of XRD analysis under ambient conditions. Trace detection of 4-HR was carried out by Keithley electrometer (6517A, USA) and the designed Co_3O_4@Er_2O_3 NRs/Nafion/GCE was used as a working electrode with conducting binder (ethanolic 5% nafion). A renowned electrochemical technique such as electrochemical method was applied at selective potential for probing the 4-HR qualitatively and quantitatively. De-ionized water was used in this whole study for the solutions preparation.

Synthesis of Co_3O_4@Er_2O_3 NRs by wet-chemical method

Co_3O_4@Er_2O_3 NRs were synthesized by wet-chemical method, Scheme 1. In this method Erbium(III)chloride ($ErCl_3$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and NaOH were used as reacting precursors. Equimolar solutions of $ErCl_3$ (50 ml) and (Co



Scheme 1. Schematic diagram of wet-chemical process for the preparation of Co_3O_4@Er_2O_3nanorods.

Please cite this article in press as: T.A. Sheikh, et al., 4-Hexylresorcinol sensor development based on wet-chemically prepared Co_3O_4@Er_2O_3 nanorods: A practical approach, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.06.012