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

Sensitive 1,2-dichlorobenzene chemi-sensor development based on solvothermally prepared FeO/CdO nanocubes for environmental safety

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ARTICLE INFO

Article history:
Received 24 June 2017
Received in revised form 25 December 2017
Accepted 16 January 2018
Available online xxx

Keywords:
1,2-Dichlorobenzene chemi-sensor
FeO/CdO nanocubes
Solvothermal method
Electrochemical technique
Sensitivity
Environmental safety

ABSTRACT

In this approach, we report the assembly of a dynamic, high sensitive, selective and reproducible 1,2-dichlorobenzene (1,2-DCB) chemi-sensor development based on solvothermally prepared nanocubes (NCs) of FeO/CdO. The synthesized FeO/CdO NCs was exhibited as an excellent electron mediator during the sensing performance of 1,2-DCB in aqueous medium and this research work was executed by electrochemical method. The morphological, optical, elemental, and structural characterization of synthesized NCs were investigated by various conventional techniques such as FTIR, UV–vis, FESEM, XPS, EDS, and XRD. NCs were used to fabricate glassy carbon electrode (GCE) with nafion conducting binder. The sensitivity of proposed chemi-sensor was estimated from the slope of calibration curve attained as current versus concentration of 1,2-DCB relation. It was introduced a reliable future sensitive sensor development using FeO/CdO NCs by electrochemical approach for the probable detection of toxic 1,2-DCB and other environmental carcinogenic chemicals for the safety of environmental and health care fields.

Introduction

Now a days, the incineration is very popular and extensively implemented technology for hazardous wastes treatment from municipal, medical, and industry to produce energy or others useful chemicals [1]. Such units are widely used today as an "environmentally friendly" alternative to the traditional disposal of wastes [2]. Therefore, the modern incineration technology plays a significant role to reduce the emission of CO_2 in the atmosphere. Due to incomplete combustion, this process can produced many chlorinated organic and other chemicals [3]. Based on the high toxicity, bioaccumulation and environmental persistence of chlorinated volatile organic compounds from stationary sources have attracted significant attention [4]. Consequently, the chlorinated hydrocarbons are important contaminants for surface, ground, and marine water pollution. Therefore, 1,2-DCB is a great health and environmental concern due to its high toxicity and bioaccumulation capacity. If, the portable water sources are contaminated with chloro-organic compounds particularly 1,2-DCB, it may cause the thyroid cancer and soft tissue sarcoma in human body [5]. A considerable number of studies on the toxicity of chlorinated benzenes indicate that the liver and the kidneys are their principal target [6]. Therefore, it is urgently needed to the development of an easy and reliable method for detection and quantification of 1,2-DCB even at a trace amount. The analytical techniques, like gas/liquid chromatography, has been used to detect 1,2-DCB, but this process is very old and conventional with various disadvantages such as time consuming, expensive, and not portable.

Recently, the electrochemical method is becoming popular for its accurate detection of hazardous toxin due to great advantages including high selectivity, wide linear dynamic detection range, lower detection limit, rapid response, and portable with simple operating procedure [7]. To enhance the electron transfer rate on the surface of working electrode of electrochemical sensor, still it has a difficulty by electrochemical approaches for the detection of environmentally hazardous chemical. Therefore, the directly grown nanostructures of transition metal oxides on the anticipated working electrode of sensor should be promising for the reliable and operative identification of toxic chemical and biochemical species [8]. So it is the purpose to use the electron mediator (nanostructured transition metal oxides) for improving the

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https://doi.org/10.1016/j.jiec.2018.01.019
1226-086X/

functionalities and sensitivities of the sensors that helps fast electron transfer between the surface of anticipating working electrode and the analytes in the desire buffer medium [9]. Nanoparticle of iron oxide has been considered as a significant sensing material for environmental toxic and hazardous chemicals due to its large surface area, robustness, availability and simple to prepare, reliable performance at a very low concentration of target toxin [10]. According to Rahman et al., fabricated a chloroform sensor based on the β-Fe_2O_3 nanoparticles which exhibited the good sensitivity with a lower detection limit in short response time [11] and another chemical sensor constructed by using ZnO–Fe_2O_3 as electron mediator for sensing phenyl hydrazine which demonstrated the lower sensitivity with the higher detection range [12]. The CdO/Fe_2O_3 semiconducting nanomaterial has been extensively studied as an efficient electron mediator for methanol chemical sensor development in phosphate buffer medium [13]. The several reports claimed that the transition semiconductor nanostructured metal oxides as CdO can be applied as a efficient and proficient electron mediator for sensing chemicals and toxic chemicals [14–17].

Since, 1,2-DCB is an extremely toxic and usually causes serious problem to the health and environment. Therefore, it is urgently necessary for the development of a reliable method for successive detection of 1,2-DCB in aqueous medium by using electrochemical approaches. To evaluate of 1,2-DCB by FeO/CdO NCs, the prepared NCs were significantly used to coat on the flat GCE as very thin layer with conducting binder and the resulted FeO/CdO NCs/binder/GCE sensor probe was implemented to detect 1,2-DCB. The sensor analytical performances including with sensitivity, response time, repeatability, linear dynamic range and detection limit was investigated very carefully. Therefore, this research approach might be a reliable and efficient way to the development of electrochemical sensor using ultra-sensitive transition metal oxides in the field of health career and environmental sector in broad scales.

Experimental

Materials and methods

The part of this study, analytical grade chemicals such as ammonium hydroxide, ferrous chloride, cadmium chloride, nafion (5% nafion suspension in ethanol), 2-nitrophenol, 3-methoxyphenol, 4-aminophenol, 4-methoxyphenol, bisphenol A, ethanol, hydrazine, methanol, 1,2-dichlorobenzene, p-nitro-phenol, monosodium phosphate, and disodium phosphate were procured from the Sigma–Aldrich Company (USA), and used directly as received. FTIR and UV–vis spectra of FeO/CdO NCs were investigated on a Thermo scientific NICOLET iS50 FTIR spectrometer (Madison, WI, USA) and 300 UV-visible spectrophotometer (Thermo scientific) correspondingly. The XPS study was performed on FeO/CdO NCs to find out the binding energies (eV) of Fe, Cd, and O with corresponding oxidation states by using a K-α1 spectrometer (Thermo scientific, K-α1 1066) with an excitation radiation source (A1 Kα1, Beam spot size = 300.0 μm, pass energy = 200.0 eV, pressure ~ 10^{-8} Torr). The optical categorizations such as molecular arrangement, elemental analysis, morphology, and particle size of the synthesized FeO/CdO NCs were studied using FESEM (JEOL, JSM-7600F, Japan) equipped XEDS. The face crystallinity of FeO/CdO NCs was estimated by implementation of XRD assessment and this experiment was carried out under ambient conditions. The USA originated Keithley electrometer (6517A, USA) was used to detect 1,2-DCB by electrochemical approach.

Preparation of FeO/CdO NCs by solvothermal process

The analytical grade precursor's cadmium chloride ($CdCl_2$) and ferrous chloride ($FeCl_2$) were used to prepare the FeO/CdO NCs by facile solvothermal process. The solvothermal is widely implemented, efficient and reliable method to synthesis of nano-doped transition metal oxides. By using this technique, the resultant nano-doped metals oxides are smaller in grain size and high crystalline phase formation is achieved in short period of time. For execution of this study, the calculated amount of $CdCl_2$, and $FeCl_2$ were dissolved with deionized water (100.0 mL) in a conical flask (250.0 mL) under continuous magnetic stirring. Then, prepared 0.1 M NH_4OH was added dropwise in the resultant solution to adjust pH gradually up to 10.5 and all the metal ions are co-precipitated out as metal hydroxide form. At this condition, the whole solution was placed in autoclave at 150.0 °C. Finally, the Fe$(OH)_2$/Cd$(OH)_2$ sample was obtained as co-precipitate and separated from water. Consequently, the obtained Fe$(OH)_2$/Cd$(OH)_2$ was allowed to dry in an oven at 110.0 °C for overnight. At the end of sample preparation, the resultant dried sample was subjected to calcine at 500.0 °C in a high temperature muffle furnace around 6 h. In this process of calcination, Fe$(OH)_2$/Cd$(OH)_2$ was transformed to its oxides (FeO/CdO) form in the presence of atmospheric oxygen. To achieve the nano-size particles, the calcined sample was ground in a mortar. The proposed reaction scheme is given in below.

In aqueous medium:

$$NH_4OH_{(l)} \leftrightarrows NH^{4+}{}_{(aq)} + OH^{-}{}_{(aq)} \quad \text{(i)}$$

$$FeCl_{2(s)} \rightarrow Fe^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} \quad \text{(ii)}$$

$$CdCl_{2(s)} \rightarrow Cd^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} \quad \text{(iii)}$$

$$Fe^{2+}{}_{(aq)} + Cd^{2+}{}_{(aq)} + OH^{-}{}_{(aq)} + nH_2O \leftrightarrows Fe(OH)_2/Cd(OH)_{2(s)}{\cdot}nH_2O\downarrow \quad \text{(iv)}$$

In the muffle furnace:

$$Fe(OH)_2/Cd(OH)_{2(s)} + O_2 \rightarrow FeO/CdO + H_2O \quad \text{(v)}$$

Since, the K_s (solubility product constant) for the both metal hydroxides (K_s for Fe$(OH)_2$ is 4.87×10^{-17} and K_s for Cd$(OH)_2$ is 7.2×10^{-15}) [18] is very low at pH = 10.5. Thus, the metal ions are precipitated quantitatively in the form of metal hydroxides at pH of 10.5. Due to continuously addition of ammonium hydroxide as dropwise in the solution, the pH of the solution starts to rise and since Fe$(OH)_2$ has the lower value of K_s, it is beginning to precipitate first to form the nuclei of crystal formation. Then, the aggregations of Fe$(OH)_2$ crystallites starts with each other. As gradually increases the pH of solution, the cadmium metal ion will also start to precipitate and adsorb in the crystallites of Fe$(OH)_2$. The previous authors has been described the analogous growth pattern of nano-materials [19–23]. Therefore, the resulted nanocrystals are separated from water and successively washed with water and ethanol to dry in an oven for overnight at 110.0 °C. Finally, the calcination process is performed at 500.0 °C for 6 h in the furnace (Barnstead Thermolyne, 6000 Furnace, USA). In the calcination process, FeO/CdO nucleus growth is taken place by itself and mutual aggregation, and then re-aggregates and formed aggregated FeO/CdO nanocrystals. Nanocrystal crystallizes and re-aggregates with each other counter parts through Vander-Waals forces and reforms FeO/CdO NCs cubic morphology, which is presented in Scheme 1.

Fabrication of GCE with FeO/CdO NCs

The phosphate buffer (PBS-solution) at pH = 6.5 was prepared by mixing of equi-molar concentration of 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 solution in 100.0 mL de-ionize water at room

Please cite this article in press as: M.M. Rahman, et al., Sensitive 1,2-dichlorobenzene chemi-sensor development based on solvothermally prepared FeO/CdO nanocubes for environmental safety, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.01.019