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Carbon black co-adsorbed ZnO nanocomposites for selective benzaldehyde sensor development by electrochemical approach for environmental safety

Mohammed M. Rahman[a,b,*], M.M. Alam[c], Abdullah M. Asiri[a,b]

[a] Chemistry Department, King Abdulaziz University, Faculty of Science, Jeddah 21589, P.O. Box 80203, Saudi Arabia
[b] Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia
[c] Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Sylhet 3100, Bangladesh

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ABSTRACT

The nanocomposites (NCs) of carbon black (CB) co-adsorbed ZnO nanomaterials were synthesized by facile wet-chemical process at low temperature. The prepared NCs were characterized by UV/vis, EDS, TEM, FTIR, EIS, XPS, and powder XRD. In this research approach, a newly developed benzaldehyde (BZH) chemical sensor with active ZnO/CB is studied by electrochemical method. A uniform thin layer of ZnO/CB NCs was deposited on a glassy carbon electrode (GCE) with conducting binder to result the working electrode for BZH chemical sensor. The proposed chemical sensor is displays good selectivity with lower detection limit, long-term stability and enhanced electrochemical responses. The calibration plot is found to be linear over the concentration (LDR) range of 0.1 nM–0.1 mM. The sensitivity (5.0633 $\mu A\,\mu M^{-1}\,cm^{-2}$) and detection limit ($18.75 \pm 0.94$ pM) of projected BZH chemical sensor were estimated from the slope of calibration plot. Based on sensing performance of ZnO/CB NCs/binder/GCE, this chemical sensor is introduced a well-organized route of efficient detection of hazardous and carcinogenic chemicals to safe the environmental and healthcare sectors in broad scales.

Introduction

Due to the increase of the application areas of chemical sensor such as control of intelligent, diagnosis of medical and biomedical, detection of leakages of inflammable toxic gases and monitoring the environmental contamination, the sensor technology is an important issue in this decade [1–5]. The benzaldehyde is a volatile organic compound (VOC) and it has industrial importance to produce pharmaceuticals, flavors, perfume, foods, plastic additives and fragrances [6]. In United Sate of America (USA) and European Union (EU), the benzaldehyde is used as safe food additive and flavoring ingredients [7]. Recently, some researchers claimed that the benzaldehyde is carcinogenic and mutagenic substance [8]. The exposure of benzaldehyde at very low concentration level is a potential risk to human and animal health [9]. Therefore, it is urgently needed to detect benzaldehyde, particularly at ppm level concentration to attentive the people. There are some old and traditional methods such as high performance liquid chromatography (HPLC), gas chromatography (GC) and electroanalytical methods to detect BZH [10–12]. But the existing methods have difficulties such as expensive, time consuming, uneasy to portable and complicated detection system. Presently, the chemical sensors based on electrochemical approach is widely adopted due to its attractive facilities such as low cost, easy to handle, possess high sensitivity with lower detection limit, long time stability in chemical environment [13,14].

The oxides of transition metal (doped/undoped/composited) such as SnO_2 [15,16] ZnO [17,18], In_2O_3 [19,20], Fe_2O_3 [21], Co_3O_4 [22], TiO_2 [23], WO_3 [24] have been investigated as active nanomaterial in sensor applications. Among these metal oxides, ZnO is an important semi-conductive oxide with 3.3 eV band gap energy, 60 meV exciton binding energy, high range of resistivity (10^{-3}–10^5 W cm) and transparency in visible wave region [25–32]. Thus, ZnO exhibits outstanding Optical, electrical and piezo-electrical properties, which make the ZnO as an efficient active material in sensor application [33,34]. As sensing element, ZnO has been found potential candidate to detect bisphenol A [35], acetone [36], 4-aminophenol [37], and ethanol [38] in phosphate buffer medium successively. The carbonaceous nanostructured carbon

* Corresponding author at: Chemistry Department, King Abdulaziz University, Faculty of Science, Jeddah 21589, P.O. Box 80203, Saudi Arabia.
E-mail address: mmrahman@kau.edu.sa (M.M. Rahman).

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black (CB) processes very attractive electrochemical properties such as high chemical stability, large surface area, and excellent conductivity. Therefore, CB has been applied as sensing material to detect amoxicillin, nimesulide [39], estradiol [40], acetaminophen, folic acid, propranolol, caffeine [41], and hydrazine [42]. Therefore, this research approach is to development of a chemical sensor based on nanocomposite of ZnO-CB.

Herein, the desire electrochemical sensor based on electrochemical method was prepared using wet-chemically synthesized ZnO/CB NCs. The working electrode of proposed chemical sensor was fabricated by a GCE coated with ZnO/CB NCs as uniform very thin layer with conducting nafion (5% nafion suspension in ethanol) binder and applied to detect BZH in phosphate buffer medium successively. As an outcome of this research, the projected BZH chemical sensor has been showed good sensitivity with lower detection limit, a broad linear dynamic range, and precious reproducibility performance with short response time. Therefore, it can be concluded that this noble research approach might be simple and reliable way to development of electrochemical sensor using electrochemcial method in the field of environmental sector in broad scale.

Experimental sections

Materials ***and methods***

The laboratory grade chemicals such as 3-chlorophenol (3-CP), 3-methylaniline (3-MA), ammonium hydroxide (AH), tetrahydrofuran (THF), chloroform (Chl), benzaldehyde (BZH), methanol (MeOH), 2,4-dinitrophenol (2,4-DNP), melamine (MEL), pyridine, nafion (5% ethanolic solution), monosodium phosphate and disodium phosphate were purchased from the Sigma-Aldrich company and used directly without any purification. FTIR (Madison, WI, USA) and UV–vis (thermo scientific) analysis were implemented on prepared nanomaterials to result FTIR and UV–vis. spectrums. To quantify binding energy with corresponding oxidation states of species exiting, the synthesized nanomaterials were investigated by XPS analysis, on a K-α1 spectrometer (thermo scientific, K-α1 1066) with an excitation radiation source (A1 Kα1, Beam spot size = 300.0 mm, pass energy = 200.0 eV, pressure = 10–8 Torr). The structural morphology, molecular arrangement and particles size of ZnO/CB NCs were examined by TEM (JEOL, Japan) analysis. The crystallinity of prepared nanocomposites were identified by execution of XRD (powder x-ray diffraction) investigation. The electrochemical (I–V) measurement was carried out using USA originated Keithley electrometer (6517A, USA).

Preparation of ZnO/CB NCs by wet-chemical process

To synthesis of ZnO/CB NCs, zinc chloride ($ZnCl_2$), carbon black (CB) and ammonium hydroxide (NH_4OH) were used. The reliable and simple wet-chemical process (co-precipitation) was executed to prepare this NCs. The co-precipitation process is an efficient and easy system to the preparation of nanomaterials and the resultant nanomaterials (doped/undoped/composited) using hydrothermal process are smaller in grain size and phase. Following this method, the prepared 100.0 mL of 0.1 M $ZnCl_2$ solution in di-ionized water was taken in 250.0 mL conical flask and the measured amount of CB was added in this conical flask. Then, the whole mixture was kept on a hot plat at 80 °C temperature with contentious magnetic string system. To precipitate the metal ion in form of metal hydroxide, 0.1 M NH_4OH was added dropwise to increase the pH of solution gradually up to 10.5. At pH 10.5, all the metal ions were precipitated out quantitatively with CB in the form of Zn $(OH)_2{\cdot}CB{\cdot}nH_2O$ crystal. At this conditions, the process was kept for 6 h and after that, the precipitate was separated from the aqueous medium and washed with acetone and de-ionized water. Thus, the resulted mass was kept inside a low temperature oven at 110 °C temperature for overnight. This analogous system of formation of nanocrystal has been reported earlier [43,44]. The proposed reactions in conical flask are supposed as in below.

$$NH_4OH_{(l)} \leftrightarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \quad (1)$$

$$ZnCl_{2(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \quad (2)$$

$$Zn^{2+}{}_{(aq)} + CB_{(dis)} + OH^- + nH_2O \leftrightarrows Zn(OH)_2{\cdot}CB{\cdot}nH_2O \downarrow \quad (3)$$

Finally, the dehydrated $Zn(OH)_2{\cdot}CB{\cdot}nH_2O$ sample was subjected to calcine at 300 °C temperature for 6 h into a high temperature muffle furnace and due to the presence of atmospheric oxygen, the metal hydroxides were converted to metal oxides of ZnO·CB. But at this temperature, CB was not oxidized (thermal stability of CB is above 500 °C and oxidation of $Zn(OH)_2$ is below 300 °C temperature) [45,46]. The proposed reactions inside the muffle furnace are as follows.

$$Zn(OH)_2{\cdot}CB + O_2 \rightarrow ZnO{\cdot}CB + H_2O_{(v)} \quad (4)$$

Fabrication of GCE with ZnO/CB NCs

To fabricate the working electrode of desire chemical sensor, the commercial GCE with 0.0316 cm^2 surface area was used. A slurry of ZnO/CB NCs was prepared in ethanol and used to coat on the GCE as uniform thin layer. Then, the modified GCE was dried at room condition. To enhance the binding properties between NCs and GCE, a drop of nafion (5% ethanolic solution of nafion) was added onto dried GCE. Finally, the assembled working electrode (ZnO/CB NCs/binder/GCE) was dried inside an oven at 35 °C for a time adequate enough to dry the conducting film entirely. An electrochemical cell was assembled with Keithley electrometer, where ZnO/CB NCs/binders/GCE was acted as working and Pt-wire as counter electrode. The BZH solutions based on concentration ranging from 0.1 M to 0.1 nM were prepared and used as analyte to electrochemical investigate in the desire phosphate buffer system. A calibration plot as current vs. concentration of BZH was prepared. Considering the maximum linearity (r^2) of calibration curve, the linear dynamic range (LDR) was identified. The sensitivity and detection limit of desired chemical sensor were estimated from the slope of calibration curve. The used electrometer (Keithley electrometer, 6517A, USA) is simple two electrodes system. Amount of 0.1 M PBS (phosphate buffer solution) was kept constant as 10.0 mL throughout the electrochemical investigation.

Results and discussions

Binding energy ***analysis***

The synthesized NCs of ZnO/CB were investigated by the XPS analysis and the core level XPS spectrum of ZnO/CB NCs is represented in Fig. 1. As it is illustrated in Fig. 1(a), the observed spin orbitals of $Zn2p_{3/2}$ and $Zn2p_{1/2}$ are centered at 1022.0 and 1045.0 eV respectively. The spin energy separation between the two peaks of Zn2p level is 23.0 eV, and indicated to existence of Zn^{2+} in ZnO/CB NCs [47–51]. The core level orbit of O1s is shown an intense peak at 532.0 eV as demonstrated in Fig. 1(b). Therefore, it can be ascribed as existence of O^{2-} in lattice position of sample ZnO/CB NCs [52–54]. From this observation, it is confirmed that ZnO existed into the nanocomposite of ZnO/CB. The high relational of XPS spectrum of C1s is illustrated in Fig. 1(c) and as it is observed

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