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Dopamine wide range detection sensor based on modified Co₃O₄ nanowires electrode

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Abstract

Ultra-thin cobalt oxide (Co₃O₄) nanowires grown on gold coated glass substrates by the hydrothermal chemical deposition and have been used as a wide range dopamine potentiometric sensor. An anionic surfactant (sodium dodecylbenzenesulfonate) was used to achieve assisted growth procedure. Moreover, a polymeric membrane containing polyvinyl chloride as plasticized polymer, β -cyclodextrin as ionophore, and potassium tetrakis (4-chlorophenyl) borate as ionic additive were immobilized on the Co₃O₄ nanostructures through electrostatic adsorption method. X-ray diffraction, x-ray photoelectron spectroscopy, and scanning electron microscopy were used to characterize the electrodes while ultraviolet-visible absorption was used to investigate the band gap of the Co₃O₄ nanostructures. The structural characterization showed a cubic crystalline, pure phase, and nanowires morphology of the Co₃O₄. However, the morphology is altered when the surfactant concentration has been changed. The Co₃O₄ chemical modified electrodes were used in potentiometric measurements for dopamine in a 10⁻² M acetic acid/sodium acetate solution having a pH of 5.45. For dopamine range from 10⁻⁹ M to 10⁻² M, the potential response of the sensor electrode was linear with a slope of 52mV/decade. The wide range and high sensitivity of the modified Co₃O₄ nanowires based sensor for dopamine is attributed to the defects on the metal oxide that is dictated by the used surfactant along with the high surface area-to-volume ratio.

Key words: Potentiometric sensor, chemically modified electrode, surfactant, and dopamine chemical sensor.

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1. Introduction

To date, miniaturized chemical sensors sensitivity and limit of detection (LOD) are being intensely pursued in medical, environment, and chemical sciences [1-5]. Traditional potentiometric sensors usually employ an indicator electrode which can be an ion-selective electrode (ISE), redox electrode etc... and is used in sensing against a reference electrode [6,7]. On the other hand, the sensor electrode size requirement makes use of chemically modified electrodes (CMEs) desirable option [8, 9]. The fabrication of a thermodynamically stable electrochemical interface for a CME is a challenging task and it was suggested to use either an ISE membranes that contains an appropriate redox-active component, such as a lipophilic silver complex, or to contact the inner electrode via an intermediate polymer layer that is redox-active or has both electronic and ionic conductivity [10].

The biocompatibility, excellent electro-catalytic activities, and fast electron transfer kinetics accompanied with a high surface area to volume ratio; are properties of metal oxide nanostructures that gave a potential for their use in sensing [11-13]. Further, metal oxide nanostructures based sensor detection can effectively be improved by the physical or a chemical modification of electrode surface. Among these metal oxide nanostructures is cobalt oxide (Co_3O_4) also called tricobalt tetroxide and cobaltous oxide [14]. Co_3O_4 has been commonly used in energy storage [15] heterogeneous catalysts [16], sensor [17], and electrochromic devices [18]. Co_3O_4 is a p-type and is magnetic semiconductor material has both direct and indirect band gaps of 2.10 eV and 1.60 eV, respectively [19]. It has a cubic spinel structure with magnetic Co^{2+} ions distributed on tetrahedral sites and non-magnetic Co^{3+} ions on octahedral sites. Furthermore, Co_3O_4 is an ionic semiconductor with positively polar termination having two Co^{2+} , two Co^{3+} , and four O^{2-} ions and negatively polar termination with two Co^{3+} and four O^{2-} ions [20]. Thus, the diversity of these polar sites combined with the relatively large surface area to volume ratio of the Co_3O_4 nanostructures will not only help to easily detect the charges but also provide much electron transfer process on the electrode surface.

Recently, we have reported a simple potentiometric method for detecting dopamine (DA) molecules based on ZnO nanorods see [21]. DA is a potential neurotransmitter in the brain, and the abnormal dopamine receptor signaling and the dopaminergic nerve function are involved in several neurological disorders. In our previous sensor based on ZnO nanorods the DA concentrations range achieved were between 1×10^{-6} M and 1×10^{-1} M, with sensitivity

of 49 mV/decade. The focus of the present paper is the use of Co_3O_4 nanostructures based modified electrodes to further increase the sensitivity and obtain a lower LOD. We have used an anionic surfactant so called sodium dodecyl benzene sulfonate (SDBS). Surfactants are used to tune the morphology of the grown nanostructures [22, 23] and improve the performance of an electrode [24]. We have used different complementary techniques to characterize the grown material and fabricated a sensitive wide detection range dopamine sensor.

2. Materials and Methods

2.1. Synthesis of Co_3O_4 nanostructures

Glass substrates were sonicated in ultrasonic bath for about 10 min. in acetone, deionized water, and isopropanol respectively and were finally dried by flowing air gun. The substrates were then fixed into vacuum chamber of an evaporator instrument (Satis CR 725). After this an adhesive layer of 20 nm of titanium was evaporated on the substrates and followed by a 100 nm thickness layer of gold thin film. Then the metal coated substrates were seeded with cobalt acetate anhydrous layer via spin coating technique at 1000 rpm. This process was repeated three times and then the samples were annealed at a temperature of 120 °C for 5 min. The substrates were fixed upside down in a solution containing 100 mL deionized water solution, urea and cobalt chloride of equimolar (0.1 M) and in addition to SDBS of different concentrations. The SDBS concentrations used were 1.4, and 2.9 mM, respectively. These different SDBS concentrations were chosen to tune the morphology of the grown Co_3O_4 . After completion of the growth duration, the samples were washed with deionized water and dried at room temperature. The resulting cobalt hydroxide nanostructures were annealed at 450 °C for 3 hours for the conversion of the hydroxide phase of cobalt into crystalline oxide phase.

2.2. Membrane and indicator electrodes preparation

The membrane and the buffer solution were prepared using powdered polyvinyl chloride (PVC) (0.18 g) as plasticized polymer which was dissolved in tetrahydrofuran (6 mL), and mixed with β -cyclodextrin (β -CD) used as ionophore (0.04 g), potassium tetrakis (4-chlorophenyl) borate as ionic additive (0.01 g), and 2-fluoro-2'-nitrodiphenyl ether (0.4 g). All reagents were of analytical grade and were used without being submitted to any additional purification. All the chemicals were purchased from Sigma-Aldrich. The as grown Co_3O_4

nanostructures were dipped three times into the membrane solution. After that all the electrodes were left to dry in a fume hood at room temperature for one night. All the functionalized sensor electrodes were kept in a free water vapor moisture environment at room temperature when not in use.

2.3. Characterizations

The crystal quality of the cobalt oxide nanostructures was studied by x-ray powder diffraction (XRD) using a Phillips PW 1729 powder diffractometer equipped with CuK α radiation ($\lambda=1.5418$ Å) using a generator voltage of 40 kV and a current of 40 mA. The surface and chemical composition analyses were investigated by x-ray photoelectron spectroscopy (XPS) technique and were measured by vacuum generators ESCA200 using a monochromatic Al (K α) radiation. The morphology and structural properties of the Co₃O₄ nanostructures were examined by LEO 1550 Gemini field emission scanning electron microscope (SEM) operated at different voltages. The electrochemical potential have been measured by a functionalized Co₃O₄ nanostructures based indicator electrodes and were measured against a silver-silver chloride as reference electrode at room temperature using an electrical instrument (Keithley 2400). Optical absorption spectra were obtained by a PerkinElmer Lambda 900 UV–visible spectrophotometer. Co₃O₄ nanostructures grown on glass substrate were used for the measurements. A blank glass slide was used as reference.

3. Result and discussions

3.1. Morphology and structural characteristics

The XRD pattern of the annealed sample of Co₃O₄ nanostructures are shown in Figure 1. All of the five diffraction peaks could be indexed to cubic crystalline Co₃O₄, which are consistent with the values reported in the JCPDS card no. 42-1467. However, the peaks are less intense, as compared to the Au peak. In order to confirm the XRD results, surface and chemical composition analyses were investigated by XPS. A wide and short XPS scans are shown in Figure 2 (a-c). Co 2p XPS spectrum of the product is represented by Figure 2 (b) where the spin-orbital splitting peaks at ~ 780 and ~ 795 eV, are assigned to the Co 2p_{2/3} and Co 2p_{1/2} which is in agreements with the data reported for pure Co₃O₄ crystals with a spinel structure [17, 25]. The peak at ~ 770 eV is corresponded to the Auger peak of cobalt [25]. The peaks at ~ 789 eV, and ~ 803 eV are attributed to 2p_{2/3} and 2p_{1/2} shake-up satellite of Co³⁺, respectively [26]. The decomposition of the Co 2p spectrum of Co₃O₄ contains the

contribution of Co^{3+} octahedral and of Co^{2+} tetrahedral. The O 1s XPS peaks (Figure 2(c)) at ~ 530 eV, which corresponds to the oxygen species in the Co_3O_4 phase and at ~ 531 eV might be due to the hydroxyl group and adsorbed water [26, 27]. Figure 3 (a, and b). shows SEM images at low and high magnification for Co_3O_4 nanowires grown at relatively high concentration 2.8 mM of the SDBS and in Figure 3 (c and d) Co_3O_4 nanowires achieved with 1.4 mM of SDBS are shown. All the nanowires were having a diameter of around 50 nm. These results are also in agreement with other reports [22, and 28], where they investigated the effect of the surfactant on the growth of ZnO nanostructures. Although many researchers studied the effect of organic additives on the growth of metal oxide nanostructures, the full explanation has not been yet realized. We believe that the SDBS in the growth solution would initiate the growth by the formation of an electrical double layer [29] at the interface. Since the whole system have been subjected to $\sim 90^\circ\text{C}$ there would be an aggregation of the SDBS molecules on the substrate [31-32]. This aggregates which are form of micelles have a crucial effect into the thermodynamics of the system and hence controlling and forming template for the growth of Co_3O_4 nanostructures.

In general point defects include Frenkel type, Schottky type, and the impurity type [33] and the doping of metal oxide semiconductors may lead to all or one of them. Consequently, defects change the optical and electronic properties of the material and this may result in electronic energy states within the band gap of the metal oxide semiconductor [34]. In order to obtain information about the electronic structure and the transition from point defects UV-Vis. spectroscopy was used, as shown in Figure 4(a) absorption spectrum for three Co_3O_4 nanostructures grown with 0, 1.4, 2.8 mM of the SDBS on glass substrate. Two absorption peaks were observed at ~ 2.35 , and 1.57 eV. To determine the photon energy “optical bandgap”, we plot $(\alpha E)^2$ versus E in Figure 4(b) for all three Co_3O_4 nanostructures, where α , and E are the absorption coefficient and photon energy, respectively [35]. The linear extrapolation of $(\alpha E)^2$ give two band gap values of each Co_3O_4 nanostructure $\sim 3.65 - 2.05$ eV for the structure grown without SDBS, $\sim 3.95 - 2.09$ eV for Co_3O_4 grown using 1.4 mM SDBS, and finally $\sim 4 - 2.29$ eV for Co_3O_4 grown with a 2.8 mM SDBS. The first band gap can be attributed to charge transfer from $\text{O}^{2-} \rightarrow \text{Co}^{+2}$, and the second band gap from $\text{O}^{2-} \rightarrow \text{Co}^{+3}$ [36, 37]. At this point it's convenient to recall that, the band gap of bulk materials can be largely increased when compared with counterparts of the nanomaterial [38]. Furthermore, impurities as a direct influence of the SDBS may be dominant, and result in electronic energy states within the band gap of the Co_3O_4 nanostructure [34, 39].

3.2. Electrochemical measurements

Different properties of the present chemical sensors (slope, linear response range, response time, selectivity, and reproducibility) were studied by a potentiometric method where the system has employed the Co_3O_4 CMEs as the indicator electrodes (Figure 5 (a-d)) versus Ag/AgCl as a reference electrode. While changing the dopamine molecule concentration from 1 nM to 10 mM in the buffer solution, the electromotive force is changed; this is shown in Figure 6. Usually, the concentration of DA in biological systems is in the range of 10^{-8} to 10^{-6} M [40]. As a lower level 10^{-8} has not been achieved by using ZnO based sensor that was reported previously [21], it was appealing to seek a more sensitive sensor. The obtained results revealed that the proposed sensor possesses a lower LOD compared to previously reported sensor [21]. The lower LOD was found to be 0.06×10^{-9} M and below that concentration, there was deviation from linearity. Moreover, as it can be seen from Figure 6 the slope that addressed the sensitivity of the CME was found to be 52 mV/decade. The lower LOD, wide range of detection and a good sensitivity of the presented CMEs are attributed to the high surface-to-volume ratio of the Co_3O_4 nanowires and their better electro-catalytic properties [41]. On the other hand, these results might be connected to the presence of the surfactant as have been suggested in [24]. Where they described that, the addition of surfactant has a dual effect; one in modifying the morphology and the other is by enhancing the sensitivity. Moreover, as pointed out above after an aggregation, this adsorbed layer might give rise to the creation of the point defects upon dehydration of the cobalt hydroxide phase. Since it is known that defects have a significant impact on surfaces of metal oxides and would enhance the catalytic activity of the Co_3O_4 [34, 42]. The response time is plotted in Figure 7 where it shows that, a value less than 10 s is the time needed for the CME to reach the saturation mode which was measured in 0.1 mM of DA. Moreover, the selectivity has been examined (Figure 8). Upon the addition of 100 μl of 100 mM uric acid, urea, and ascorbic acid respectively to 0.1 mM DA solution. The results indicate that, such interference is not significantly affecting the DA signal intensity which is attributed to the pores size of ionophore β -CD that has a cage-like supramolecular structure, and hydrophobic cavity which could permit certain molecules to pass and prevents the others [43]. It is worth mentioning that, the pore diameter of the β -CD is ~ 0.7 nm and for the DA is around 0.5 nm *i.e.*, benzene ring size and possibly all the interfering compounds examined in this work were less than the β -CD diameter. However, a hydrophobic cavity of the β -CD can be affected to some extent. Finally, we measured reproducibility in 0.01 mM concentration of DA as is shown in Figure

9. Responses of five prepared CMEs (two 2.8 mM of SDBD, three with 1.4 mM) were examined. No observable deviations were recorded. Mostly the robustness may be attributed to the existence of PVC. We can infer that, the proposed CMEs works well under the normal conditions of blood serum.

4. Conclusion

We have developed a chemically modified electrode by synthesizing Co_3O_4 nanostructures with ultra-thin morphology. The morphologies of the Co_3O_4 nanostructures were readily tunable by changing the concentration of SDBS as an additive in the growth solution. The Co_3O_4 nanostructures were showed nanowires shape with a different density depending on the concentration of the SDBS. The ultra-thin morphology is due to the “directing agent” features of the SDBS. The selectivity for DA was achieved by combing a plasticizer PVC polymer and β -CD ionophore. A wide range of detection ranging from 10^{-9} M and up to 10^{-2} M was achieved. This range of detections is suitable for DA concentration in human body (10^{-8} M- 10^{-6} M). Moreover, the sensor selectivity was as high as 52 mV/decade and a response time of about 10 s. These sensing properties are attributed to the defects and high surface-to-volume ratio along with their electro-catalytic properties. The findings in this paper indicate the importance of the use of controlled nanostructures morphology for developing efficient functional materials.

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Figure captions

Figure 1: XRD pattern of the product, which is addressed Co_3O_4 nanostructures and Au.

Figure 2: XPS study of the as grown Co_3O_4 nanostructures on Au. (a) The wide scan, (b) Co 2p, and (c) O1s spectra.

Figure 3: Shows the morphology of the of Co_3O_4 nanostructures as grown with a different amounts of SDBS (a) 0.1, and (b) 0.05 g with high and low magnifications and both of them are dense with a high aspect ratio.

Figure 4: (a) UV. Vis. absorption spectra, the inset shows the adsorption peaks, and (b) plot of $(\alpha E)^2$ versus photon energy for the Co_3O_4 nanostructures.

Figure 5: Illustrate the fabrication of electrode modifications (a) spin coating of cobalt acetate on Au coated glass, (b) growth of Co_3O_4 nanostructures, (c) immobilization of polymeric membrane by deep coating, and (d) proposed mechanism of CME where a DA accumulated and β -CD controlled that selections.

Figure 6: Calibration curve is showing the sensitivity and the linear response range of our constructed CMEs.

Figure 7: Response time less than 10 s measured in 0.1 mM concentration of DA.

Figure 8: Shows that, a selectivity of constructed CMEs upon the addition of 100 μl of 100 mM uric acid, urea, and ascorbic acid respectively to 0.1 mM DA solution.

Figure 9: Reproducibility of five prepared CMEs (two with 2.8 mM of SDBD, and three with 1.4 mM).

Fig. 1:

Fig. 2 (a):

Fig. 2(b):

Fig. 2(c):

Fig. 3(a):

Fig. 3(b):

Fig 4 (a):

Fig 4 (b):

Fig. 5:

Fig. 6:

Fig. 7:

Fig. 8:

Fig. 9: