Research Article

Selective Thallium (I) Ion Sensor Based on Functionalised ZnO Nanorods

Z. H. Ibupoto, Syed M. Usman Ali, K. Khun, and Magnus Willander

Department of Science and Technology, Linköping University, Campus Norrköping, 60174 Norrköping, Sweden

Correspondence should be addressed to Z. H. Ibupoto, zafar.hussain.ibupoto@liu.se

Received 14 February 2012; Accepted 5 August 2012

Academic Editor: Jinhui Song

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Well controlled in length and highly aligned ZnO nanorods were grown on the gold-coated glass substrate by hydrothermal growth method. ZnO nanorods were functionalised with selective thallium (I) ion ionophore dibenzylidiaz-18-crown-6 (DBzDA18C6). The thallium ion sensor showed wide linear potentiometric response to thallium (I) ion concentrations (1×10^{-7} M to 5×10^{-2} M) with high sensitivity of 36.87 ± 1.49 mV/decade. Moreover, thallium (I) ion demonstrated fast response time of less than 5 s, high selectivity, reproducibility, storage stability, and negligible response to common interferents. The proposed thallium (I) ion-sensor electrode was also used as an indicator electrode in the potentiometric titration, and it has shown good stoichiometric response for the determination of thallium (I) ion.

1. Introduction

When zinc, cadmium, and lead metals are produced by the burning of coal, during this thallium (Tl^{+1}) a poisonous metal ion penetrates into the atmosphere as a major waste product [1]. Thallium are dangerous to all people when they come in contact for very short time with the environment where amount of thallium ions is too much, and due to this they can suffer from the gastrointestinal aggravation as well as nerve problems [2]. The compounds of thallium in which two atoms of thallium (I) are present are very toxic such as thallium sulphate (Tl_2SO_4), even the compounds containing single atom of thallium as thallium acetate (CH_3COOTl) and thallium carbonate (Tl_2CO_3). Furthermore, thallium (I) ion has the ability to replace K^{+1} in energizing the few vital enzymes such as ATPase and pyruvate kinase [3]. Thallium (I) is atoxic, when its concentration is very low as about 0.5 mg/100 g of tissue [4]. If thallium (I) ion concentration in the human body is present in excess for long time, this in result brings a change in the blood composition, harms liver, kidney, intestinal, testicular tissue, and causes hair loss [5]. Because of the poisonous effects of thallium (I) ion and its different chemical compounds, it is highly needed to measure the concentration of thallium (I) ion in real biological and

environmental samples. There are many methods which have been used for the determination of thallium (I) ion such as spectrophotometric measurement, graphite-furnace atomic absorption spectrometric, flame atomic absorption spectrometric (FAAS) afterwards the extraction [6, 7], respectively, inductive-coupled plasma mass spectrometric (ICP-MS), voltammetry, and potentiometric methods. There are many advantageous of potentiometric technique such as cheap, simple, accurate, and easy to handle with the biological samples. The highness of this technique is lying on the fact that it uses the ion-selective electrodes, which are largely used for the determination of metal cations [8]. There is not so much work reported in the literature for the determination of thallium (I) ion, with the membrane electrodes due to lack in the selectivity in the presence of 1A group metal cations, linearity, and resistance to the change in the pH of testing solution. However, different crown ethers were used as selective thallium (I) ionophore in the development of ion-selective electrodes, but many of them had low range of detection of thallium ion concentrations (1×10^{-5} – 1×10^{-1} M). These ion-selective electrodes based on these crown ethers had also faced big problems during the construction and rarely detected the trace quantity of thallium (I) ions [9].

Today, the researchers are paying more attention to the nanomaterial-/nanostructure-based electrochemical sensors. Zinc oxide (ZnO) nanomaterial is well known among other nanomaterials for its valuable applications in the field of biosensors and chemical sensors due to their high surface area to volume ratio.

Moreover, ZnO has strong ionic bonding characteristics about (60%) and offered more resistance to dissolve at biological pH value. There are many ways to utilize the ZnO nanostructures in the field of electrochemical biosensing processes because of its ease in functionalization with selective membranes/enzymes. ZnO-nanostructure-based nanosensors have many unique properties, these nanosensors possess a small size and high surface area to volume ratios which results in strong signals, and higher catalytic property and allows the fast flow of to be tested electrolytically via sensor and thus show good sensitivity and a lower limit of detection (LOD) as compared to the sensors based on the bulk ZnO.

Due to the high surface area to volume ratio of ZnO nanorods, these are the potential candidates for more sensitive nanochemical sensors [10, 11]. ZnO nanorods are n-type semiconductors and their electrical transport depends on the adsorption/desorption phenomenon of chemical substances which attach to the surface [12–17]. There are many one-dimensional (1D) ZnO nanostructures such as nanorods, nanowires, nanobelts, nanowalls, and nanotubes, among others, which have been synthesised through different growth methods and based on these nanorods nanodevices like electric field-effect switching [18], single electron transistors [19], biological and chemical sensing [20], and luminescence [21], among others, which have been reported. The crystalline structure of ZnO is tetrahedral in which zinc (Zn^{2+}) and oxide (O^{2-}) ions are periodically arranged along the c -axis [18] and having two opposite crystallographic polar planes with different surface relaxation energies. It is the reason that mostly the growth of ZnO nanostructures increases along the c -axis. The positively charged Zn-(0001) and negatively charged O-(0001 $^{-}$) ions together possess polar surfaces, permanent dipole moment, and high polarization along the c -axis. The size of biological and chemical substances, which are being sensed, is almost the same to the diameter of ZnO nanorods, that is, ZnO nanorods are good transducers in generating the strong electrical signals.

In this study, we have fabricated the ZnO nanorods on the gold-coated glass substrate and functionalised with dibenzylidiaz-18-crown-6 (DBzDA18C6) which is highly selective an ionophore for the detection of thallium (I) ions. The proposed thallium (I) ion sensor based on the functionalised ZnO nanorods showed good linear behaviour over the wide range of thallium ion concentrations (1×10^{-7} to 5×10^{-2} M) and offered negligible response towards the alkali metal ions and other common heavy metal interferents.

2. Experimental Section

2.1. Materials. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), ethylenedi-

FIGURE 1: A typical FESEM image of ZnO nanorods grown on the gold coated glass substrate using hydrothermal growth method.

aminetetraacetic acid (EDTA), dibutyl phthalate (DBP), o-nitrophenyl octyl ether (o-NPOE), benzyl acetate (BA), tetrahydrofuran (THF), high molecular weight poly vinyl chloride (PVC), a selective thallium (I) ion ionophore dibenzylidiaz-18-crown-6 (DBzDA18C6), thallium nitrate (TlNO_3), sodium tetra phenyl borate (NaTPB), and all other interfering metal cations salts were purchased from Sigma Aldrich Sweden. The pH of testing solution was controlled by using the 1×10^{-1} M hydrochloric acid and 1×10^{-1} M sodium hydroxide. All other chemicals were used of analytical grade.

2.2. The Fabrication and Synthesis of the ZnO Nanorods. The procedure of fabrication of glass substrates and growth of ZnO nanorods are as described: The glass substrates were washed with isopropanol and sonicated in the ultrasonic bath for 10 minutes. Then, these were washed with deionized water and dried by nitrogen gas. Afterwards, these glass substrates were affixed in the vacuum chamber of evaporator Satis (CR 725) and 10 nm thin film of chromium (Cr) was evaporated then followed by the 100 nm thickness layer of gold (Au). The growth of ZnO nanorods is as follows: firstly, these gold-coated glass substrates were cleaned with water and dried by nitrogen gas, and then a simple hydrothermal growth method was used for the growth of ZnO nanorods [22]. A homogeneous seed layer of zinc acetate dihydrate was produced on these glass substrates by using spin-coating technique at 2500 r.p.m. for 25 seconds, and then substrates were annealed in the preheated oven for 20 minutes at 120°C . Finally, these substrates were stuck on the Teflon sample holder and placed into an equimolar aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$, then, kept into the oven for 6 to 8 hours at 96°C . When the growth time was completed, the substrates were washed with deionized water in order to remove the solid residual particles and dried by the nitrogen gas. After that, the morphology of grown ZnO nanostructures was studied by the field emission scanning electron microscopy (FESEM) and we observed that the grown ZnO nanorods were highly aligned and well controlled in length as shown in Figure 1.

2.3. The Functionalization of ZnO Nanorods with Selective Thallium (I) Ion Ionophore. For the functionalization of ZnO nanorods, we used different amounts of ionophore, PVC, various plasticizers, such as DBP, o-NPOE, BA, and additive NaTPB into 3 mL of THF. After optimization, we found that 8 mg of DBzDA18C6, 170 mg of PVC, 60 mg of o-NPOE, and 1 mg NaTPB have shown the best results regarding to sensitivity, selectivity, detection range of thallium (I) ion concentrations, and so forth. The ZnO nanorods grown on gold-coated glass substrate were functionalised with this ionophore solution for 3–5 minutes and dried for 12 hours and kept at 4°C when not in use. The thallium (I) ion sensor was used as a working electrode in conjunction with Ag/AgCl as a reference electrode for the potentiometric

measurement of thallium (I) ion for the concentration range of 1×10^{-7} M to 5×10^{-2} M. The output response of each thallium (I) concentration solution was measured using pH meter (model 744 Metrohm). The time response of the thallium (I) ion-sensor electrode was measured using electrical instrument Keithley 2400.

3. Result and Discussion

3.1. The Output Response of the Thallium (I) Ion-Sensor Electrode Based on Functionalized ZnO Nanorods. The electrochemical representation of thallium (I) ion-sensor electrode is given by following way:

The response time of ion-sensor electrode mainly depends on the concentration of being tested an electrolyte and as the number of ions of tested analyte changes into the solution during the measurements, then the output response of ion-sensor electrode also alters. During the experiment, when thallium (I) ion sensor electrode was employed into the 1×10^{-7} to 1×10^{-1} M thallium nitrate solution, we have observed that the ion sensor responded very well up to 5×10^{-2} M, but after 5×10^{-2} M concentration, the ion sensor was sensing the thallium (I) with low output voltage due to the saturation limit of proposed ion-sensor electrode. The output response of thallium ion sensor for 1×10^{-7} to 5×10^{-2} M concentration of thallium (I) ion is shown in the calibration curve of the logarithm concentration of thallium (I) ion versus the output voltage response in Figure 2. From Figure 2, it can be observed that the proposed ion sensor has responded according to the Nernst's equation for whole concentration range.

Thallium (I) ion sensor has shown good linearity for a large dynamic concentration 1×10^{-7} to 5×10^{-2} M of thallium ion and better sensitivity about 36.87 ± 1.49 mV/decade with a regression coefficient $R^2 = 0.98$. The advantages of the proposed thallium ion sensor based on the functionalised ZnO nanorods with DBzDA18C6 are the lower detection limit 1×10^{-7} M concentration of thallium ion and fast response time of less than 5 seconds, which is better than the previous work based on the same ionophore used for the detection of thallium ion [23]. These obtained results of linearity, lower limit of detection, sensitivity, and fast response time of the present selective thallium ion sensor favour to use it for the detection of trace amount of thallium ion from the biological and environmental samples.

3.2. The Effect of Thallium Ion Concentration on the Response Time of Thallium (I) Ion-Sensor Electrode. In this study, we investigated that the response time of thallium ion sensor depends on the ionic concentration of thallium ion into

testing solution. We tested the ion-sensor electrode into each concentration and found that the sensor showed about 15 s response time for 1×10^{-7} M concentration of thallium ion and for 1×10^{-2} M thallium ion concentration the response time was less than 5 s as shown in Figure 3. However, for higher concentration, the response time was also observed less than 5 s. This is most probably due to fast kinetic complex reaction of thallium ion with the ionophore on functionalised ZnO nanorods [9].

3.3. The Effect of pH and the Interfering Ions on the Output Response of the Thallium Ion Sensor. The pH of analyte solution has also an influence on the response of ion-sensor electrode and we have examined this effect on the 1×10^{-3} M thallium ion solution for the pH range 3 to 12 as shown in Figure 4. It can be inferred from the pH calibration curve that response of thallium ion sensor was found almost the same from pH range 4 to 10, but above pH 10, the output voltage response was lowered because of the result of hydroxyl (OH^{-1}) ion. Below pH 4, the output response was also observed in decreasing order due to the two reasons, firstly that ZnO nanorods are very sensitive to higher acidic medium and start to dissolve into the testing solution [24] and another possible reason may be that the crown ether may act as base, accept the proton and make less chances for the complexation with thallium ion [25]. For evaluating the performance of a sensor, selectivity is the basic parameter and we observed selectivity in two different experiments. In the first experiment, we followed the mixed method and tested the thallium ion-sensor electrode in the thallium ion 1×10^{-4} M solution in the presence of interfering ions for concentration range 1×10^{-7} to 5×10^{-1} M with addition of one mL of each interfering ion. We found that there was no significant effect of interfering ions on the output response of thallium ion sensor as shown in Figure 5. For confirming the either effect of higher volume of interfering ions, we increased the volume of interfering ions from 1 mL to 3 mL but we found that the sensor electrode responded the same

FIGURE 2: Calibration curve for thallium ion sensor.

FIGURE 3: Time response of thallium (I) ion sensor in 1×10^{-2} M solution of thallium nitrate.

as with 1 mL of interfering ions. On another experiment, we used the separation method for determination of selectivity coefficient and we tested the thallium ion-sensor electrode into the 1×10^{-4} M thallium ion solution and separately to 1×10^{-4} M solution of each interfering ion. The calculated selectivity coefficient for each interfering ion is given in Table 1. It was observed during the experiment that the proposed thallium ion-sensor electrode showed good selectivity in the presence of interfering ions.

3.4. Study of Reproducibility and Durability of Proposed Thallium (I) Ion Sensor. The aim of this study was to examine the output response of one sensor to another sensor. We functionalised the five independent sensor electrodes based on ZnO nanorods and tested into the 1×10^{-4} M solution of thallium (I) ion, it was observed that each thallium ion-sensor electrode has shown good output response of reproducibility with relative standard deviation less than 3% as shown in Figure 6. In order to investigate the life time of thallium (I) ion-sensor electrode, we regularly tested

FIGURE 4: The effect of pH on the output response of thallium (I) ion sensor.

FIGURE 5: The behaviour of thallium ion sensor in the presence 1×10^{-4} M of interfering ions.

the thallium ion-sensor electrode for about four weeks. We found that thallium ion-sensor electrode maintained its detection range, sensitivity, repeatability, and we followed the Nernst's behaviour for four weeks except that in the fourth week, the detection range was changed from 1×10^{-7} to 1×10^{-6} M as shown in Table 2. This decrease in the detection range might be due to slight detachment of ionophore from the surface of functionalised ZnO nanorods with passage of time.

3.5. The Proposed Application of the Thallium Ion Sensor. The aim of this study was to find out the practical application of the present ion sensor and for this reason we used the ion-sensor electrode as an indicator electrode for the potentiometric titration of thallium (I) ion under the room

TABLE 1: The logarithm of the selectivity coefficient of the thallium ion sensor for different interferences in 1×10^{-4} M.

Interference (B)	$-\log K_{\text{TL}, B}^{\text{pot}}$
K^{1+}	4.65
Ca^{2+}	4.63
Na^{1+}	4.66
Mg^{2+}	4.40
Li^{1+}	4.55
Cu^{2+}	4.11
Cs^{1+}	4.33
Fe^{3+}	3.50

FIGURE 6: The sensor to sensor response in the 1×10^{-5} M.

TABLE 2: Representing the durability of thallium (I) ion sensor.

Number of days	Slope (mV/decade)	Linear range (M)
1 day	36.87 ± 1.49	1×10^{-7} – 5×10^{-2}
1 week	37.10 ± 2.20	1×10^{-7} – 5×10^{-2}
2 weeks	36.62 ± 2.44	1×10^{-7} – 5×10^{-2}
3 weeks	36.69 ± 2.56	1×10^{-7} – 5×10^{-2}
4 weeks	35.53 ± 1.12	1×10^{-6} – 5×10^{-2}

temperature conditions. We assayed the ion sensor electrode in titration of 18 mL of 2×10^{-3} M solution of thallium ion against the 5×10^{-2} M EDTA solution as shown in Figure 7. The titration curve revealed a good stoichiometric relation for the determination of thallium ion from unknown samples, due to this evidence thallium ion-sensor electrode based on functionalised ZnO nanorods can be used as an indicator electrode. The pH and ionic strength were not adjusted during the experiments.

4. Conclusion

In the present work, we have built up a thallium (I) ion selective electrode based on the functionalized ZnO nanorods with DBzDA18C6. The proposed ion sensor has demonstrated excellent linearity for 1×10^{-7} M to 5×10^{-2} M

FIGURE 7: The potentiometric titration curve of thallium (I) ion sensor for 18 mL of 2×10^{-3} M thallium nitrate solution with 5×10^{-2} M solution of EDTA.

thallium ion concentration, high selectivity against the common interfering ions, good sensitivity about 36.87 ± 1.49 mV/decade, reproducibility, and stability for more than three weeks, and fast response time less than 5 s. For practical application, the thallium ion sensor electrode was used as an indicator electrode in the potentiometric titration and the sensor electrode showed better stoichiometric relation for the determination of thallium ion. All the obtained results indicate that the present thallium ion sensor can be used for the determination of trace quantities of thallium ion from environmental and biological samples.

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