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**Published on:** 29 Nov 2011 - [Journal of Applied Physics](#) (American Institute of Physics (AIP))

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Original Publication:

Zafar Hussain Ibupoto, Syed Usman Ali, C O Chey, K Khun, Omer Nur and Magnus Willander, Selective zinc ion detection by functionalised ZnO nanorods with ionophore, 2011, Journal of Applied Physics, (110), 10, 104702.

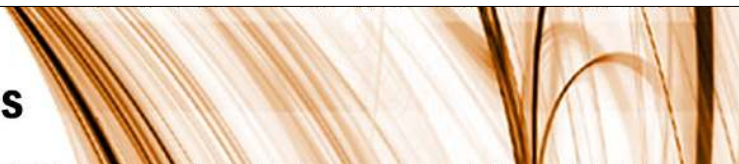
<http://dx.doi.org/10.1063/1.3662107>

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Citation: *J. Appl. Phys.* **110**, 104702 (2011); doi: 10.1063/1.3662107

View online: <http://dx.doi.org/10.1063/1.3662107>

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## ADVERTISEMENT



## Selective zinc ion detection by functionalised ZnO nanorods with ionophore

Z. H. Ibupoto,<sup>a)</sup> Syed M. Usman Ali, C. O. Chey, K. Khun, O. Nur, and Magnus Willander  
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(Received 2 September 2011; accepted 7 October 2011; published online 29 November 2011)

In this paper, highly dense and well aligned single-crystal zinc oxide nanorods were grown along the c-axis on a gold coated glass substrate using a low temperature aqueous chemical growth approach. The prepared ZnO nanorods were functionalized with plastic membrane coatings containing specific ionophore (12-crown-4) which is highly selective to zinc ions ( $\text{Zn}^{+2}$ ). The electrochemical response of the sensor was found to be linear over a relatively wide logarithmic concentration range from 1  $\mu\text{M}$  to 100 mM. The proposed sensor showed a good linearity with a high sensitivity of  $\sim 35$  mV/decade for sensing  $\text{Zn}^{+2}$  ions. A fast response time of less than 5 s with a good selectivity, repeatability, reproducibility, and negligible response to common interferents ions such as calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), or potassium ( $\text{K}^{+}$ ), and iron ( $\text{Fe}^{+3}$ ) and copper ( $\text{Cu}^{+2}$ ) was also demonstrated. Moreover, the proposed sensor showed good stoichiometric results for potentiometric titration. © 2011 American Institute of Physics. [doi:10.1063/1.3662107]

### I. INTRODUCTION

The zinc ion ( $\text{Zn}^{+2}$ ) is a very vital cation in the human body for the regulation of biological processes and other bodily functions which influence DNA synthesis, microtubule polymerization, gene expression, apoptosis, immune system function, and also the efficiency of enzymes such as carbonic anhydrase and matrix metalloproteinase.<sup>1</sup> Moreover, the zinc ion is also responsible for neurological disorders such as epilepsy and Alzheimer's diseases<sup>2</sup> and has less activity in a few biomedical and a good number of process streams, such as the wash streams. In addition, zinc is also found in food, e.g., proteins which are high in zinc content. The human body contains about 2 g on average. An excess of zinc above the normal level is dangerous to one's health to such an extent that death can occur. Therefore, the regulation and monitoring of  $\text{Zn}^{+2}$  is very important for patients who are suffering from an imbalanced level of Zn in the blood serum. There are various biosensors reported in the literature for the determination of zinc ion content using various analytical techniques like UV-*vis* spectroscopy,<sup>3</sup> flame atomic absorption spectrometry,<sup>4</sup> electrochemical (potentiometric methods),<sup>5</sup> etc. The determination of zinc is crucial due to its large presence in industry, medicine, environmental monitoring, etc., and waste products from different industries like paint, electroplating, pharmaceutical, and fine chemical manufacturing. Due to the broad and substantial use of zinc in the various sectors of industries, the demand for zinc ion selective sensors has increased. Especially for analytical measurements, ion selective sensors have provided more rapid, accurate, and non-destructive applications for low sample volumes at a low cost. Many attempts have been made to fabricate these ion selective sensors and based on these efforts, different ion selective sensors for alkali and

alkaline earth metals like halides, nitrate, etc., are reported in the present commercial market. But there are not many ion selective sensors of heavy metals, which are poisonous above some level of concentration and are not up to the commercial standard.

Recently, nanomaterials/nanostructures based electrochemical sensors have attracted the attention of researchers. Among the nanostructures, zinc oxide (ZnO) is of special interest for biological sensing due to many favorable properties like the wide direct bandgap (3.37 eV) and large exciton binding energy (60 meV). In addition, ZnO has high ionic bonding (60%), and it dissolves very slowly at biological pH values. ZnO nanomaterials can be used in a variety of electrochemical bio-sensing schemes due to their unique advantages combined with functionalization of selective membrane/enzymes. Due to these unique properties, these ZnO nanosensors offer some significant advantages owing to their small size and high surface area to volume ratios allowing for larger signals and better catalysis. Furthermore, the more rapid movement of analyte through the sensors shows higher sensitivity and a lower limit of detection as compared to those prepared from bulk ZnO devices. ZnO nanorods have large surface-to-volume ratios, so they are promising candidates for more sensitive nano-chemical sensors.<sup>6,7</sup> ZnO nanorods are n-type semiconductors and their electrical transport is dependent on the adsorption/desorption property of surface binding chemical species.<sup>8-13</sup> Many one-dimensional ZnO nanostructures like nanorods, nanowires, nanotubes, etc., have been synthesized by different methods and nano-devices based on these have been explored for electric field-effect switching,<sup>14</sup> single electron transistors,<sup>15</sup> biological and chemical sensing,<sup>16</sup> luminescence,<sup>17</sup> etc. The ZnO structure can be described as alternating planes made of tetrahedral coordinated  $\text{O}^{2-}$  and  $\text{Zn}^{2+}$  ions, well-endowed alternately along the c-axis,<sup>18</sup> and with two crystallographic planes having opposite polarity and different surface relaxation energies. Due to this, more growth rate along the c-axis

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is usually observed. The positively charged Zn-(0001) and negatively charged O-(000-1) ions give polar surfaces possessing a permanent dipole moment and polarization along the *c*-axis. These nanostructures have almost the same order of size of the biological and chemical species which are being sensed, and give good choices of basic transducers for generating electrical signals.

In the past few years, different research groups have successfully reported the use of Zn<sup>+2</sup> selective sensors using membrane coating on the surface which demonstrated different selectivity, sensitivities, and slow response times.<sup>19–28</sup> It has been found that, among different Zn<sup>+2</sup> ion selective membranes, the membranes based on macrocyclic compounds bind with metal cations selectively and are used in metal selective extraction, phase-transfer catalysis, membrane transport, and many other interrelated processes.<sup>29–34</sup> In addition, the complexation formed between the selective metal ions and macrocyclic coordinating atoms describe the sensitivity of the sensor prepared from it. Macrocyclic bases are new, cyclic, organic molecules having O, N, S, etc., which are electron rich in the inner sites for producing the complex through dipole-dipole or ion-dipole interactions with metal ions of suitable size. The crown ethers, sometimes known as cyclic ethers, are selective for metal ions.

In the present work, we have successfully demonstrated the determination of Zn<sup>+2</sup> ions using the zinc ion selective membrane (12-crown-4) in conjunction with poly vinyl chloride (PVC) onto the sensor surface based on ZnO nanorods grown on gold coated glassy electrodes with a good linearity, repeatability, reproducibility, and fast response time.

## II. EXPERIMENTAL DETAILS

Well aligned, vertically grown ZnO nanorods were grown on gold coated glass by employing a low cost, low temperature hydrothermal method. To grow the ZnO nanorod arrays on the gold coated glass substrate, first the substrate was washed and cleaned using acetone, isopropanol, and de-ionized water. After cleaning, an adhesive layer of titanium of 20 nm thickness was evaporated on the glass substrate. Next, 100 nm thickness of gold was evaporated on it. Then the gold coated glass was spin coated by using a seed solution of zinc acetate di hydrate and annealed at 115 °C for 20 min. Then the substrates were held in a teflon sample holder and the growth process of ZnO nanorods was carried out in an equimolar concentration (0.075 M) solution of zinc nitrate hex hydrate [Zn(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O] and hexamethylenetetramine [C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>], each with a purity of 99.9%. The solution of both reacting substances was prepared in deionized water and the solution was kept in a pre-heated oven at 95 °C for 5–7 h. During the growth process, the small area of gold coated glass was covered in order for use as a contact pad for an output response. When the growth was completed, the grown ZnO nanorods were cleaned with de-ionized water in order to remove the ZnO residue particles and dried at room temperature. The ionophore (12-crown-4) has been well known for its good selectivity for Zn<sup>+2</sup> ions.<sup>35</sup> To prepare the Zn<sup>+2</sup> ion selective membrane, we used the following chemical reagents, ionophore (12-crown-4), sodium tetra-

phenyl-borate (NaTPB), di-*n*-butyl-phthalate (DBP), and poly vinyl chloride (PVC). All chemicals were of analytical grade and bought from Sigma-Aldrich. The PVC based Zn<sup>+2</sup> selective electrode was prepared using the following composition: 40 mg 12-crown-4, 40 mg NaTPB, 125 mg PVC, and 100 mg DBP. The solution of all the above membrane components were made in 12 ml of tetra-hydro-furan (THF). After the preparation of the selective membrane, the prepared ZnO nanorods were functionalized using the direct adsorption method and dried for about one hour at room temperature and then all the electrodes were kept at 4 °C in the refrigerator for about 12 h before use. The electrochemical experiments were carried out by using a functionalized Zn<sup>+2</sup> selective sensor electrode in combination with an Ag/AgCl reference electrode. The electrochemical potential was measured using pH meter model (model 827, Metrohm). All functionalized sensor electrodes were kept in free water vapor moisture and at 4 °C when not in use.

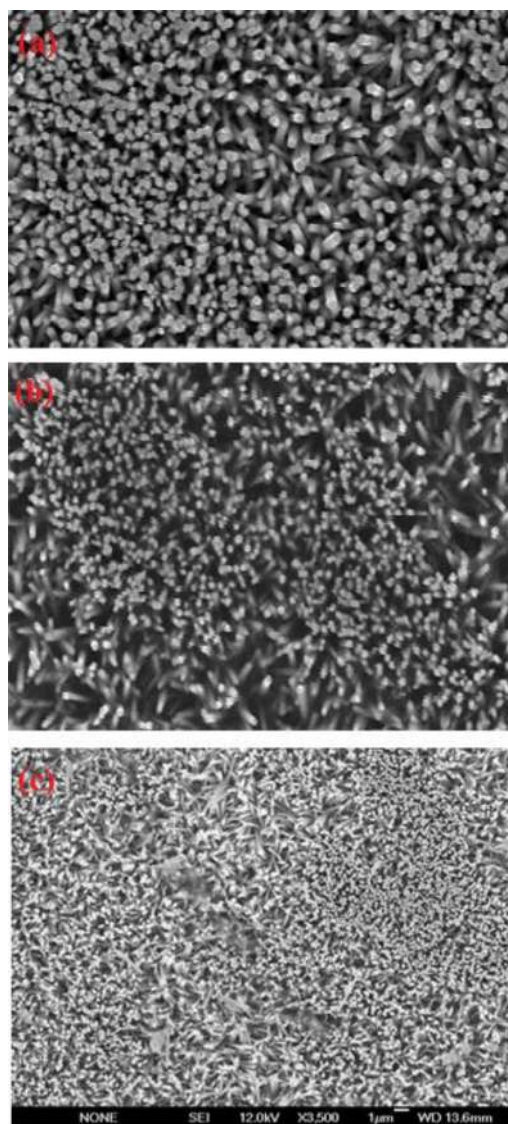


FIG. 1. (Color online) Typical scanning electron microscopy (SEM) images of ZnO nanorods grown on gold coated glass substrate using low temperature chemical growth. (a) The ZnO-nanorods as grown, (b) with ionophore coating, and (c) the same sensor after measurements.

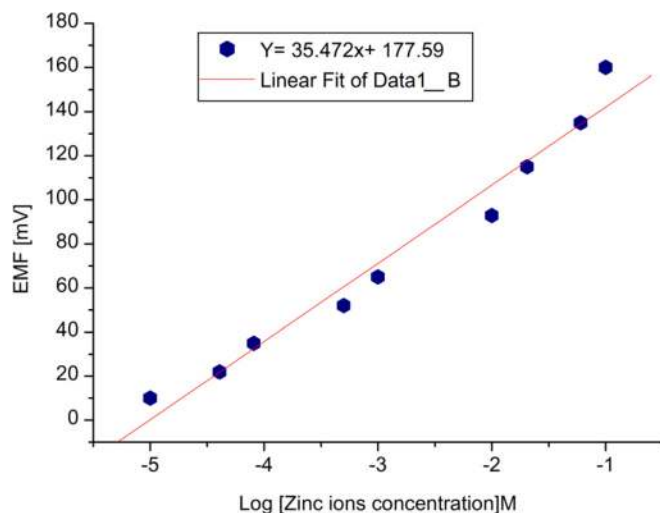


FIG. 2. (Color online) Calibration curve using ionophore coated ZnO-nanorods based sensor electrode showing the electrochemical response (EMF) at different zinc ions concentrations (10  $\mu$ M–100 mM) with Ag/AgCl reference electrode.

### III. RESULTS AND DISCUSSION

The morphological study of highly dense and well aligned grown ZnO nanorods was carried out using field emission scanning electron microscopy. In Fig. 1(a) it is quite clear that ZnO nanorods grown on the gold coated glass have good alignment along the surface and their shape looks like a rod with a hexagonal cross section. It can be clearly seen from the SEM image that the ZnO nanorods have diameters between 100 and 200 nm with 1  $\mu$  lengths as shown in Fig. 1(a). The SEM images of the functionalized ZnO nanorods prior to and after measurements has shown in Figs. 1(b) and 1(c). The selective determination of Zn<sup>+2</sup> ions was carried out in a test electrolyte solution prepared in a phosphate buffer of pH 7.4 by the potentiometric technique. The electro chemical response (EMF) was altered when the

concentration of the testing analytic periodically changed. The tested sensor configuration showed large dynamic ranges with an output response (EMF) that was linear versus the logarithmic concentration of zinc from 1  $\mu$ M to 100 mM as shown in Fig. 2.

The representation of electrochemical potential cell is given in the following way:



The potentiometric measurements with the functionalized ZnO nanorods based sensor was performed in a test electrolyte solution with the concentration range of zinc ions in the phosphate buffer from 1  $\mu$ M to 100 mM and the obtained results revealed that the proposed sensor possesses a good linearity and a sensitivity of 35 mV/decade at room temperature ( $23 \pm 2$ ) °C with a fast response time of less than 5 s as shown in Fig. 3. The biosensor performance was evaluated by different important parameters like the dynamic range, selectivity, detection limit, reproducibility, response time, etc. The reproducibility is a crucial property of the chemical sensor for knowing its working activity. In order to study the reproducibility and lifetime stability of the proposed sensor, we constructed 5 sensor electrodes independently at the same set of conditions and functionalized the membrane onto the ZnO nanorods. In order to check the reproducibility of the propose sensors, we checked the responses of all five prepared sensors in 5 mM Zn<sup>+2</sup> ion solution and a relative standard deviation of less than 3% was observed, as shown in Fig. 4. The presence of N, O, S, etc., in the crown ethers (ionophore) are responsible for providing a strong electrostatic attraction between Zn<sup>+2</sup> ions and ZnO nanorods and kept the sensor's functionality for a long duration so that the sensor could be reused several times. To investigate the working and long term stability of the proposed sensors, we periodically checked the sensors for more than eight weeks. These sensors exhibited good performance and gave good

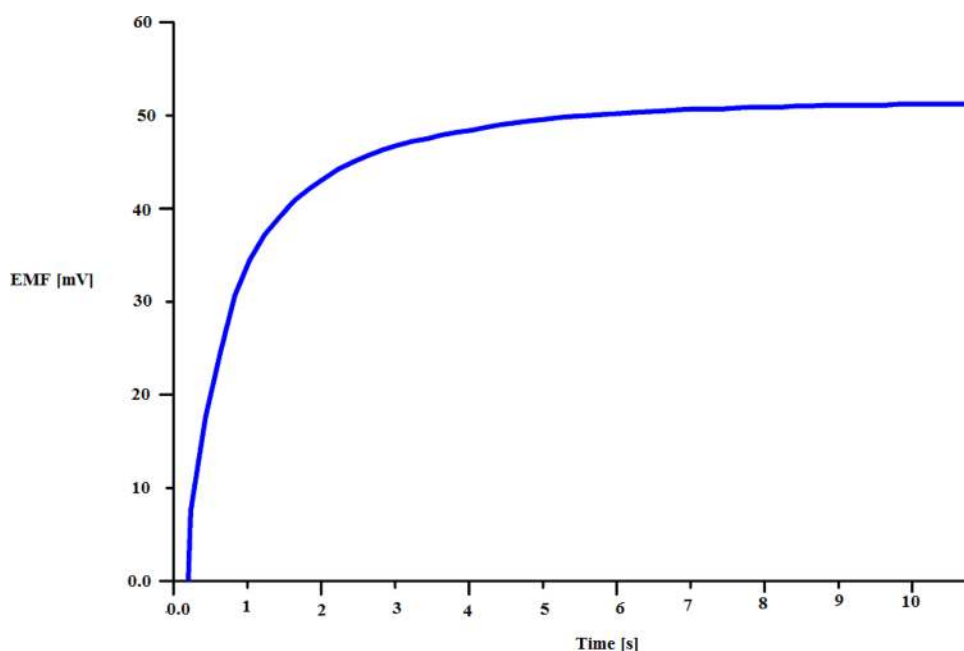


FIG. 3. (Color online) Calibration curve showing the time response of the proposed sensor in 500  $\mu$ M zinc ions test solution.

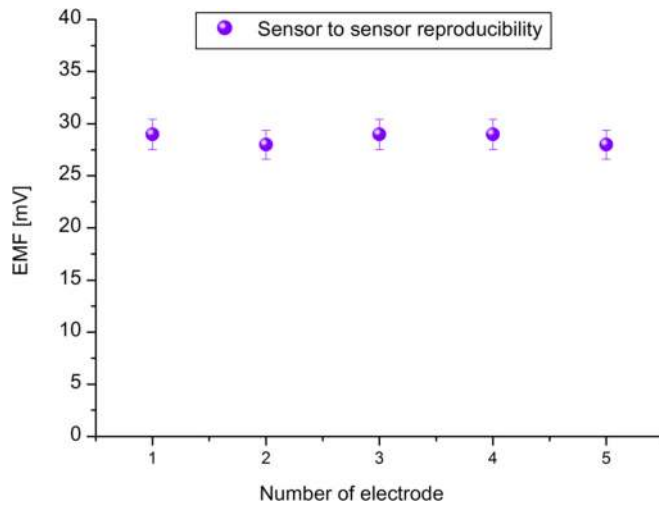


FIG. 4. (Color online) Calibration curve showing the sensor to sensor reproducibility in 60  $\mu\text{M}$  zinc ions test solution.

response to  $\text{Zn}^{+2}$  ions up to 90% of the original responses as shown in Fig. 5(a). Selectivity is the most important factor for biosensors, which gives the particular affinity for observing a single ion in a mixture of many ions. Various ways are used to measure the selectivity of potentiometric sensors.<sup>36</sup> These methods include solution method, the mixed solution method, the matched potential method, and the unbiased selective coefficients. Instead of using the above described methods, we tested the selectivity and stability of the sensor by output response curve. The selectivity was checked by adding 1  $\mu\text{M}$  each of calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), or potassium ( $\text{K}^+$ ), iron  $\text{Fe}^{+3}$ , and  $\text{Cu}^{+2}$  into the 1 mM zinc nitrate  $\text{Zn}(\text{NO}_3)_2$  solution. It was observed during the experiments that there was no substantial effect on the response of the sensor except that the addition of  $\text{Cu}^{+2}$  at high concentrations revealed that the sensor gave a minor distortion in output signal response, which was negligible. Thus, the sensors

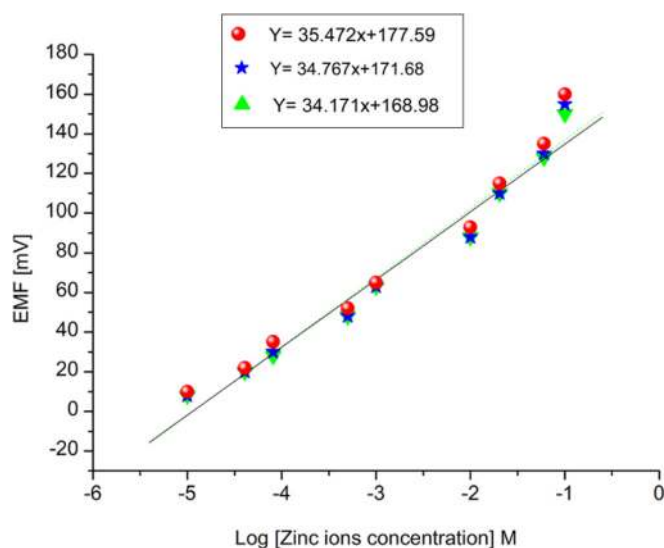


FIG. 5. (Color online) Calibration curves showing the proposed sensor reusability at room temperature after 2–3 h span in the zinc ions test solution from 10  $\mu\text{M}$  to 100 mM concentration range.

prepared with  $\text{Zn}^{+2}$  ions selective ionophore (12-crown-4) have demonstrated good selectivity toward the target ions in the presence of normal interfering species as shown in Fig. 5. All experiments were recapitulated using new fabricated sensors and insignificant interfering effects on the signal response were observed. These negligible changes for sensor the response can be ignored during the measuring setup. The aim of these studies is to investigate the stability in signal response at given pH and temperature for the  $\text{Zn}^{+2}$  ion selective membrane functionalized onto the ZnO nanorods. This is because both the temperature and the pH can affect the performance (EMF) of the proposed sensor electrode by bringing the difference in ionic mobility and ionic environment in the testing analytic solution. The effect of pH on sensor response was studied in 5 mM zinc nitrate  $\text{Zn}(\text{NO}_3)_2$  solution for the pH range 4–10 as shown in Fig. 6(a). During the experiments, it was observed that the proposed sensor exhibited a maximum stable signal at a pH around 7.4. However, at pH values greater than 8, the potential starts to decline due to the dissolution of ZnO at  $\text{pH} \geq 8$  (Ref. 37) and at pH concentrations lower than 6 the potential decreases substantially due to the solubility of the membrane in an acidic medium. Moreover, all experiments were carried out

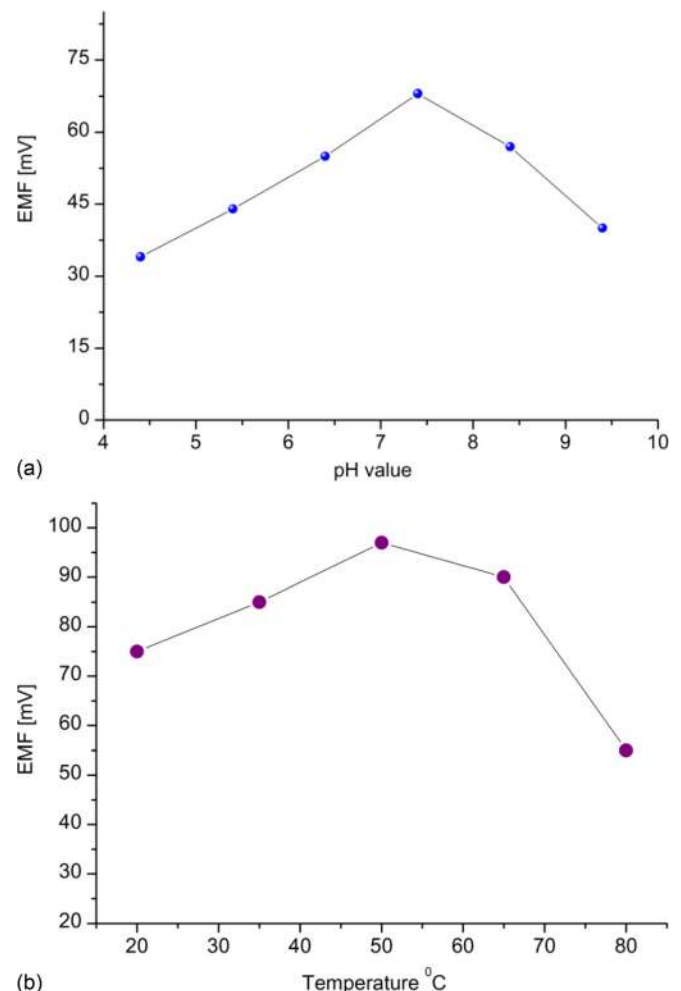


FIG. 6. (Color online) (a),(b) Calibration curves showing the study of EMF response with the influence of varying temperature and pH values.

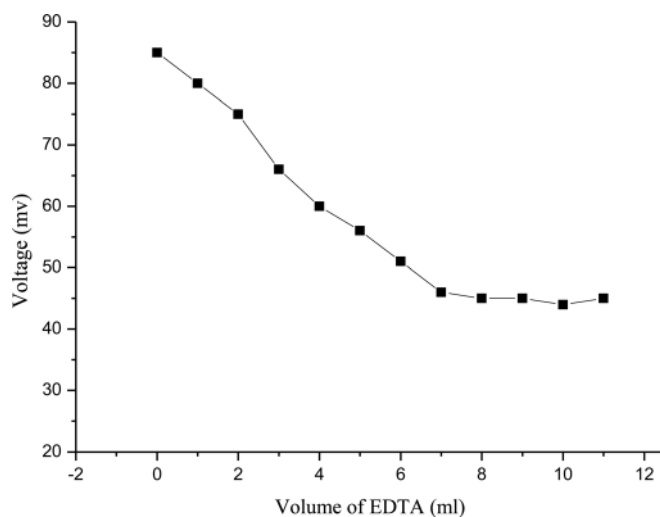


FIG. 7. Potentiometric titration curve of  $Zn^{+2}$  ions, 70 ml (10 mM) against EDTA (100 mM).

in zinc nitrate  $Zn(NO_3)$  solutions prepared in phosphate buffers at pH 7.4 because normally biological fluids also have a pH around 7.4. The sensor response is also affected by changing the temperature of the working environment so we also performed experiments to investigate the effect of temperature. In 20 mM zinc nitrate  $Zn(NO_3)$  solution, the effect of temperature was studied between 20–80 °C as shown in Fig. 6. It can be observed from Fig. 6 that the EMF gradually increases up to 45 °C, but at 50 °C and above the EMF lowered drastically. This is because of the weakening in the strength of the binding force of the membrane with ZnO nanorods as well as the fact that the ions in the solution possess higher mobility which offers high resistance to the  $Zn^{+2}$  ions moving toward the sensor electrode. Thus, the decline and instability in the response of the proposed sensor was observed at higher temperatures. Based on our obtained results, we have chosen room temperature because of the stable response and because it is easy to record experimental measurements at this temperature.

The proposed zinc ion sensor has been successfully employed in the potentiometric titration of  $Zn^{+2}$  with EDTA. We used 70 ml of  $Zn^{+2}$  solution of concentration 10 mM and titrated against the 100 mM solution of EDTA in a phosphate buffer solution of pH 7.4. The potentiometric titration curve is shown in Fig. 7. When we added the EDTA solution to a beaker containing the zinc ion solution, we observed that the output voltage decreased due to the decrease in concentration of zinc ions, which formed the complex compound when EDTA was added. It is quite clear from Fig. 7 that the potentiometric titration curve gave a sharp intersecting point, resulting in a good stoichiometry of  $Zn^{+2}$  ions with the EDTA complex compound. After this sharp intersecting point the potential became almost constant. This is because most of the zinc ions reacted with the EDTA and the small change in zinc ions was not detected by the zinc ion sensor. Thus, it is evident that this ZnO functionalised zinc ion sensor can be used for the determination of zinc ion by potentiometric titration with EDTA.

#### IV. CONCLUSION

In conclusion, we have explored using an easy fabrication method to demonstrate a highly selective zinc ion ( $Zn^{+2}$ ) sensor based on ZnO nanorods coated with specific ionophore (12-crown-4). These ZnO nanorods have revealed a strong electrostatic attraction between the crown ether (ionophore) and showed good performance in terms of the stability and functionality of the sensor. The proposed sensor has showed a fast response time of less than 5 s and a wide dynamic range in  $Zn^{+2}$  ion test electrolyte solution from 1  $\mu$ M to 100 mM. During the investigation, the sensor showed good selectivity, repeatability, sensitivity, stability, and negligible interference to other possible interfering metal ions. We have also successfully demonstrated the possible practical implication of the proposed sensor by performing potentiometric titration. Due to all of the above advantageous features of the proposed sensor, it can be applied for use in other biological and environmental areas.

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