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Research Letter

Studies on Calcium Ion Selectivity of ZnO Nanowire Sensors Using Ionophore Membrane Coatings

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Zinc oxide nanorods with 100 nm diameter and 900 nm length were grown on the surface of a silver wire (0.25 mm in diameter) with the aim to produce electrochemical nanosensors. It is shown that the ZnO nanorods exhibit a Ca^{2+}-dependent electrochemical potentiometric behavior in an aqueous solution. The potential difference was found to be linear over a large logarithmic concentration range (1 μM to 0.1 M) using Ag/AgCl as a reference electrode and the response time was less than one minute. In order to adapt the sensors for calcium ion measurements in biological fluids with sufficient selectivity and stability, plastic membrane coatings containing ionophores were applied. These functionalized ZnO nanorods sensors showed a high sensitivity (26.55 mV/decade) and good stability.

1. INTRODUCTION

Calcium is essential in the living cells; it has important functions such as regulation of enzyme activity, neuronal activity, muscle contraction, and vesicle exocytosis. In this letter, we present measurements showing potentiometric sensitivity of functionalized ZnO nanorods of Ca^{2+} in water solution. The advantages of ZnO nanorod sensors are their small size, being biosafe, possesses polar surface, and many other properties that facilitate chemical sensing. The detection of biological and chemical species is central to many areas of healthcare and life sciences [1]. Of major importance to detection is the signal transduction associated with selective recognition of a biological or chemical species of interest. Nanostructures, such as nanowires [2–7] and nanocrystals [7–12], offer new and sometimes unique opportunities in this rich and interdisciplinary area of science and technology. The diameters of these nanostructures are comparable to the size of the biological and chemical species being sensed, which intuitively makes them represent excellent primary transducers for producing electrical signals.

ZnO nanorods, nanowires, and nanotubes have recently attracted considerable attention for the detection of chemical and biological species [13–18]. Among a variety of nanosensor systems, the nanostructured electrochemical wire approach employed in this study is one which offers high sensitivity and real-time detection [19]. ZnO nanostructures have unique advantages including high surface to volume ratio, nontoxicity, chemical stability, electrochemical activity, and high electron communication features, which make them one of the most promising materials for chemical and biological applications [20].

The focus of the current study is the fabrication and demonstration of ZnO nanorods on a relatively thin silver wire suitable for the sensing of calcium ions in aqueous chemical solutions. Silver wire with grown ZnO nanorods has proven to be a convenient and practical choice as we have demonstrated before in our intracellular pH nanosensor developed earlier [19]. Our main efforts have been directed toward the construction of a sensor having potentiometric properties. These ZnO nanorods are highly sensitive to detect and monitor calcium ions with potential applicability to in vivo measurements during biological processes in which Ca^{2+} is important for activating biological processes such as muscle contraction, protein secretion, as well as cell death and development [21].

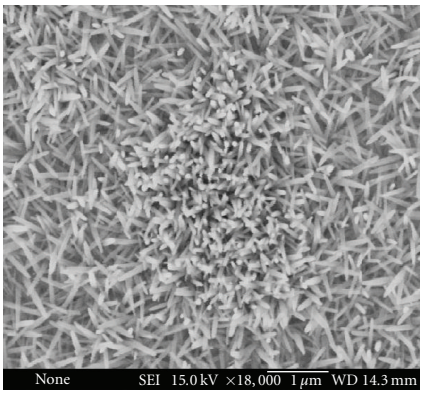


Figure 1: SEM images of ZnO nanorods on silver wire that is 0.25 mm in diameter. The nanorods are 100 to 150 nm in diameter and 900–1000 nm long.

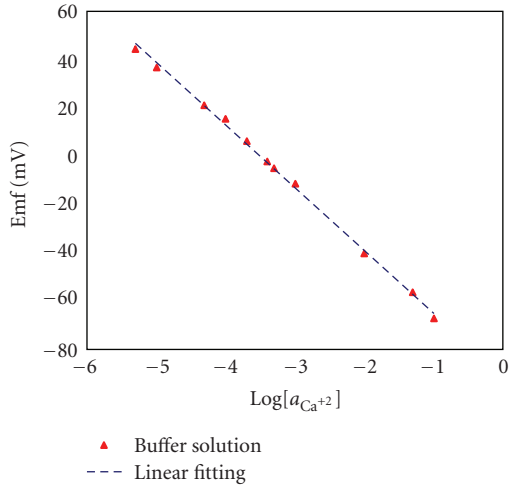


Figure 2: Calibration curve showing the electrochemical potential difference, for the ZnO nanorod as potentiometric electrode with Ag/AgCl reference electrode versus logarithmic concentration range for Ca^{2+} change for buffer solution.

2. EXPERIMENTAL DETAILS

ZnO nanorods were grown on the surface of 0.25 mm thick silver wire by using a low-temperature growth technique as described below. For the optimization steps the silver wire (0.25 mm in diameter) was cut into small pieces of 5 cm in length. The wires were dipped into the seed solution to facilitate aligned growth. The wires were then dried in air for one minute. ZnO nanorods were grown in 150 mL of aqueous solution of 0.025 M zinc nitrate ($Zn(NO_3)_2$) and 0.025 M hexamethylenetetramine (HMT, $C_6H_{12}N_4$) in a conventional flask. The reaction temperature was kept at 95°C.

SEM images of the ZnO nanowires grown on the silver wires were made with a field emission scanning electron microscope (JEOL JSM-6335F Scanning Electron Microscope) revealed that the diameter of the nanowires was 100–150 nm and the length was 900–1000 nm as shown in Figure 1. The nanorods were rather uniform in size.

The ZnO layer on the silver wires was coated with ionophore membrane by a manual procedure. Powdered PVC, 120 mg was dissolved in 5 mL tetrahydrofuran together with 10 mg of a plasticizer (dibutyl phthalate, DBP) and 10 mg of Ca^{2+}-specific ionophore (DB18C6). All chemicals were from Sigma-Aldrich-Fluka. The ZnO-coated wires were dipped two times into and in between the ionophore solution, and the solvent was allowed to evaporate. After this the probes were conditioned in 10 mM $CaCl_2$ solution.

The electrochemical potential of the Ca^{2+}-probe was measured with an Orion model 420 A+ pH-meter (Thermo Electron Corporation) versus an Ag/AgCl reference electrode. The ZnO-coated silver wire was mounted in a three-way junction for chromatography (Upchurch) using a tubing coupling screw and a small O-ring to make a fluid-tight seal around the wire. One of the remaining ports of the T-coupling was connected to a peristaltic pump and the other port served as outlet and was connected with the reference electrode. Thus a flow cell was formed with low dead volume allowing easy and quick change of sample solution. The response of the Ca^{2+}-probe was checked with $CaCl_2$ solutions with pH around 7 of all concentrations.

3. RESULTS AND DISCUSSION

The potentiometric response of the Ca^{2+}-electrode was studied in aqueous solutions of $CaCl_2$ with concentration ranging from 1 μM to 0.1 M. The construction of a two-electrode electrochemical potential cell is as follows:

Reference electrode | reference electrolyte solution || test electrolyte solution | indicator electrode.

The electrochemical cell voltage (electromotive force) changes when the composition of the test electrolyte is changed. These changes can be related to the concentration of ions in the test solution via a calibration procedure. The actual electrochemical potential cell can be described by the following diagram:

$$Ag|ZnO|CaCl_2||Cl^-|AgCl|Ag. \quad (1)$$

Figure 2 shows a typical induced voltage of our potentiometric sensor for different concentrations of Ca^{2+} ions. As clearly seen it presents a linear dependence, which implies that such sensor configuration can provide a large dynamic range.

Polymeric membranes are mainly made of polymer, which can selectively transfer certain chemical species over others. Therefore, membranes are the key component of all potentiometric ion sensors [22–24]. In fact, the vast majority of membranes used commercially are polymer-based. Analogous to biological ion channels, in analytical technology there are the so called ionophores and neutral carriers incorporated into synthetic membranes or biomolecule membranes in order to achieve the desired selectivity or detection of ionic species in complex samples.

DB18C6 is a coplanar, symmetrical, and polyether with a highly charged cavity [25] with diameter of 4 Å and can accommodate only the nonsolvated metal cation.

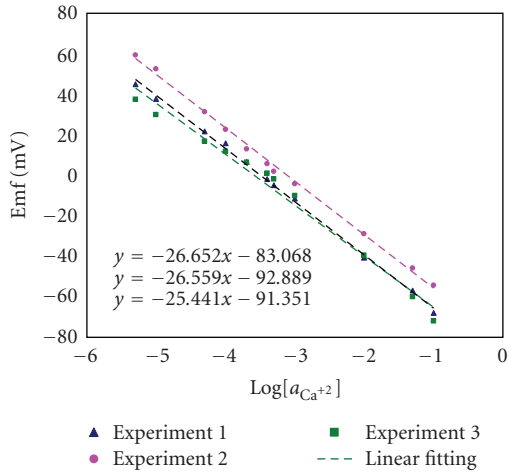


Figure 3: Calibration curves from three different experiments using the same sensor electrode showing the electrochemical potential difference at different Ca^{2+} ion concentrations for the ZnO nanorod electrode with an Ag/AgCl reference electrode.

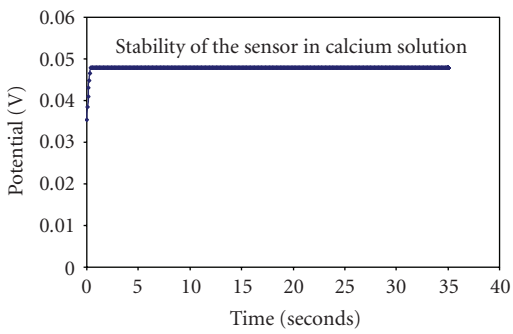
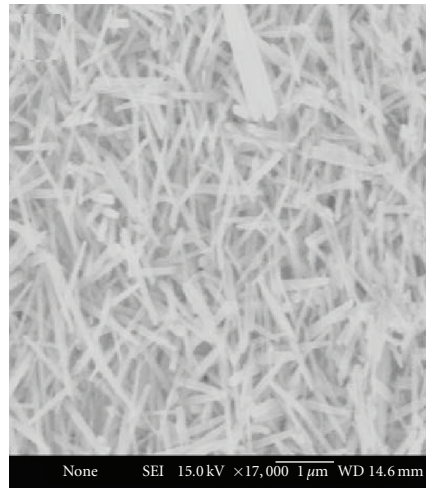
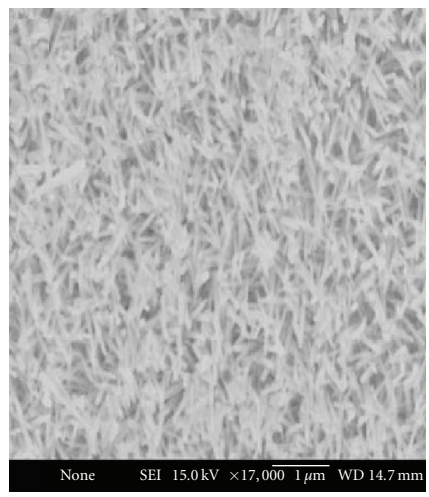


Figure 4: Stability curve for ZnO nanorod sensor at a Ca^{2+} concentration of 0.001 mM.



(a)



(b)

Figure 5: Scanning electron microscopy images of the ZnO nanorods grown on silver wire using low temperature growth. (a) Nanorods on silver wire coated with membrane before measurement. (b) SEM of the same sensor after measurements.

The calcium ion being solvated in aqueous medium has a diameter of 7 Å, which is too large to be accommodated in the cavity. High charge on the oxygen atoms of DB18C6 turns the oxygen atoms into strong donors [26]. Calcium ions are also strong acids. Consequently there should be reasonably good interaction between oxygen atoms and calcium ions.

It is expected that the covalent functionalization is a chemical process in which a strong bond is formed between the nanostructured material and the biological and chemical species. In most cases, some previous chemical modification of the surface is necessary to create active groups that are necessary for the binding of biological and chemical species [27].

The emf values of the Ca^{2+}-electrode system obtained with $CaCl_2$ solutions in water ranging from 1 μM to 0.1 M are plotted against the logarithmic concentration of Ca^{2+} as shown in Figure 3. The diagram includes three experiments showing good reproducibility and linearity. Here, the same ZnO sensor electrode was used for the three experiments to check the reproducibility. The ZnO sensor electrode was carefully washed with 18 MΩ water after each reading to remove the Ca^{2+} ions from the surface of the electrode. These calibration curves are for PVC membrane-coated ZnO electrodes with DB18C6 as ionophore. The coating increases the stability considerably as well as the selectivity. The results show that the electrode is highly sensitive to calcium ions with a slope around 26.5 mV/decade. The response time is fast. It takes less than one minute to obtain a stable signal as shown in Figure 4. The morphology of the functionalized ZnO sensor electrode was investigated after measurements. The results are shown in Figure 5. The ZnO nanorods were not dissolved but affected after measurements. As clearly seen in Figure 5(b), it shows shorter and thinner nanorods as compared to Figure 5(a). This was important to investigate as it is known that ZnO nanostructures can dissolve in many different aqueous solutions of different pH values. This result was expected because the functionalization provided protection for the surface of the nanowires.

4. CONCLUSION

We have studied the use of ZnO nanorods as electrochemical nanosensor for Ca^{2+} in water solutions. A convenient sensor design was realized by growing the ZnO nanorods on a thin silver wire that could be readily inserted into a low-volume flow cell. Good performance in stability and selectivity was achieved by coating the sensor surface with a plastic ionophore membrane. The potential difference was linear over a wide logarithmic concentration range (1 μM to 0.1 M). These results demonstrated the capability of performing biologically relevant measurements inside a solution of $CaCl_2$ using functionalized ZnO nanorods.

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