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Short communication

Selective calcium ion detection with functionalized ZnO nanorods-extended gate MOSFET

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ABSTRACT

Zinc oxide nanorod-extended gate field effect transistor (MOSFET) is demonstrated for the detection of calcium (Ca^{2+}) ions. ZnO nanorods were grown on the surface of a silver wire to produce an electrochemical nanosensor for selectively detecting Ca^{2+}. The electrochemical response from the interaction between the ZnO nanorods and Ca^{2+} in an aqueous solution is coupled directly to the gate of a field effect transistor (MOSFET). The induced voltage change on the gate results in a measureable current response. In order to adapt the sensors for Ca^{2+} ions measurements in biological fluids with sufficient selectivity and stability, a plastic membrane coating containing ionophores was applied on the nanorods. The sensor exhibited a linear response within the range of interest from 1 μM to 1 mM. This work demonstrates a simple technique for sensitive detection of Ca^{2+} ions by efficient transfer of the chemical response directly to a standard electronic component producing a low impedance signal.

1. Introduction

In general the detection of biological and chemical species is central to many areas of healthcare and life sciences (Patolsky and Lieber, 2005). Calcium is essential in living cells; it has important functions such as regulation of enzyme activity, neuronal activity, muscle contraction and vesicle exocytosis. Hence it is important to know its concentration in different types of extra- and intracellular media. Electrochemical sensors respond to electron transfer, electron consumption, or electron generation during a chemical and biological interaction process. This class of sensors is of major importance in biomedical analysis and they are quite flexible to miniaturization. In potentiometric sensors the potential change due to the accumulation of charge (electrons) on the working electrode is measured relative to a reference electrode when no current is flowing (Gauglitz, 1996). The working electrode potential must depend on the concentration of the analyte in the solution. The reference electrode is needed to provide a defined reference potential. The key component of all potentiometric ion sensors is a membrane that can selectively transfer certain chemical species over others (Bakker et al., 1999, 1997, 1998). The vast majority of membranes used commercially are polymer-based. Most liquid membrane based ion-selective electrodes that are commercially available are PVC based. Other advantages were good sensitivity, fast response and excellent adhesion to solid-contact electrodes. Photo-cured membranes for ion sensitive electrodes (ISEs) have been developed for calcium (Moody et al., 1988; Cattrall et al., 1985; Cardwell et al., 1985). Analogous to the ion channels in cell membranes, these membranes contain the so-called ionophores and neutral carriers that can transfer specific ions for detection in complex samples.

Many electrochemical devices are also based on various forms of field effect transistor (FET) to measure pH changes, selective ion concentrations and the kinetics of biocatalytic reactions involving enzymes (Patolsky and Lieber, 2005). The first two pioneering chemical sensors based on transistors were the ion sensitive field effect transistor (ISFET) developed by Bergveld (1970) and the Pd-gate MOSFET invented by Lundström et al. (1975). The conversion of a FET into a sensing device normally involves the replacement of the metal gate electrode by a (bio) chemically sensitive interface (e.g. an analyte-selective membrane or an ion-conductive solution), which is brought in contact with the analyte solution (Errachid et al., 2004). Also present in or in conjunction with the analyte solution is a reference electrode, which completes the circuit via the gate voltage bias (Eggins, 2002; Schoning and Poghossian, 2002). Previously a ZnO nanorod array was selectively grown on the gate area of a HEMT for the detection of glucose (Kang et al., 2007).

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ZnO, on one hand is a popular material for gas-sensing applications. Point defects on ZnO surfaces are extremely important in gas sensing as they produce very large changes in the surface conductivity. ZnO nanostructures have also attracted considerable attention as a sensing material with great potential in various applications. ZnO nanorods specifically, have shown to be useful for electrical detection of biological species with high sensitivity (Wei et al., 2006; Kumar et al., 2006; Kim et al., 2006; Liu et al., 2006; Zhang et al., 2004; Huang and Choi, 2007). ZnO based nanosensors have previously been applied as pH sensors and for gas sensing (Tien et al., 2007; Al-Hilli et al., 2006; Kang et al., 2005; Gao and Wang, 2005; Wang et al., 2004; Fan et al., 2004). We have earlier investigated the potentiometric detection of calcium ions (Ca^{2+}) using ZnO nanorods (Asif et al., 2008).

Calcium ions are important for activating biological processes such as muscle contraction, protein secretion, cell death and development (Allan, 1966). Intracellular determination of Ca^{2+} is therefore of great interest and ZnO nanorod technology has potential for such measurements. An example of pH intracellular measurements has already been demonstrated (Al-Hilli et al., 2007).

The challenge here is to obtain acceptable signal quality with so small samples. In this article we therefore studied another approach to selectively detect Ca^{2+} ions by applying functionalized ZnO nanorods as an extended gate of a commercial MOSFET. In an extended gate field effect transistor (EGFET), as in other FETs, the amount of current flowing between the source and drain dependents on the gate potential. The potential generated at the surface of the reference electrode is added to the gate voltage and thus the current flowing between the source and drain will be directly related to the activity of the ion of interest in the sample solution.

The EGFET was introduced as an alternative for the fabrication of ISFETs (Batista and Mulato, 2005). The EGFET has several advantages when compared to the ISFET, mostly because metal oxide semiconductor field effect transistors (MOSFETs) are commercially available and easy way to connect the analyte to the gate of the FET. The fundamental characteristics of extended-gate FET sensors are described in Ishige et al. (2006).

Here we report the use of a ZnO nanorod-gated MOSFET for electrochemical detection of Ca^{2+} ions that gives a nearly linear current response to the concentration. In our previous work (Asif et al., 2008) we studied the potentiometric response of the same type of electrode and found a logarithmic change of the potential with 27 mV/decade of change of the Ca^{2+} concentration.

By using the extended gate sensing approach some advantages over potentiometric sensor can be obtained. In a potentiometric sensor some times the signal is relatively small and might need amplifications. Using the extended gate MOSFET we can easily amplify the signal and observe the detection through the modulation of the drain current. In our extended gate MOSFET with functionalized ZnO nanorods, the Ca^{2+} response was measured through the drain current of the MOSFET. The second advantage is the fact that the device is robust. The third advantage is related to the available size of the sample. As we sometimes have very small amounts of the analyte to be detected, it will not be practical to apply the small available sample volume directly on the gate. Instead a small part of the wire (with functionalized ZnO nanorods) can be inserted into the available analyte volume.

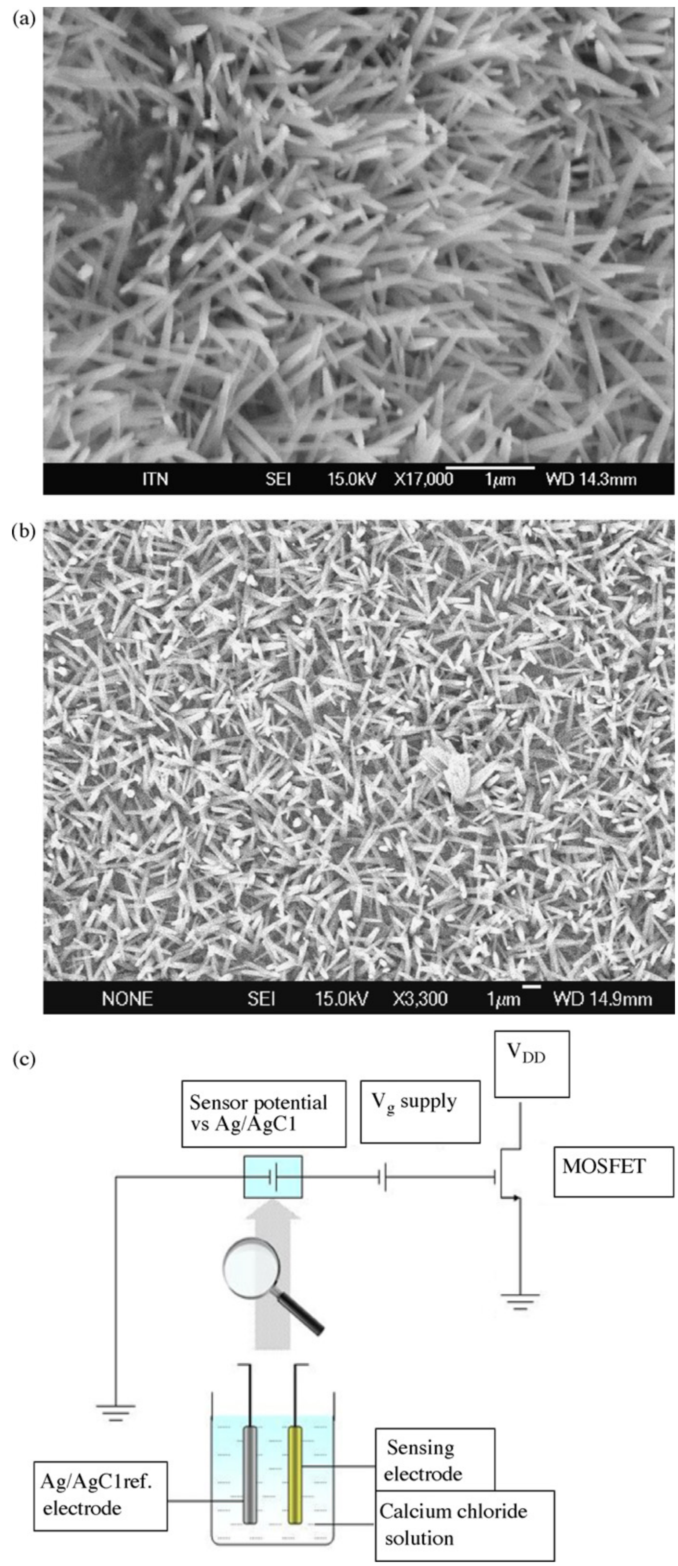

Fig. 1. A typical scanning electron microscope image (SEM) of the ZnO nanorods grown on a 0.25 mm diameter silver wire using low temperature chemical growth. (a) Pre-Ca^{2+} sensing measurements, (b) post Ca^{2+} sensing measurements, and (c) experimental setup for the Ca^{2+} detection used in the present study.

2. Materials and methods

ZnO nanorods were grown on the surface of a 0.25 mm thick silver wire by using the low temperature growth technique described previously (Asif et al., 2008). Images of the ZnO nanorod were taken with a Field Emission Scanning Electron Microscope (JEOL JSM-6335F SEM). They revealed that the diameter of the freshly grown ZnO nanorods was 100–150 nm and the length was 900–1000 nm (Fig. 1(a)). The ZnO nanorod array on the silver wire was coated with an 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+}