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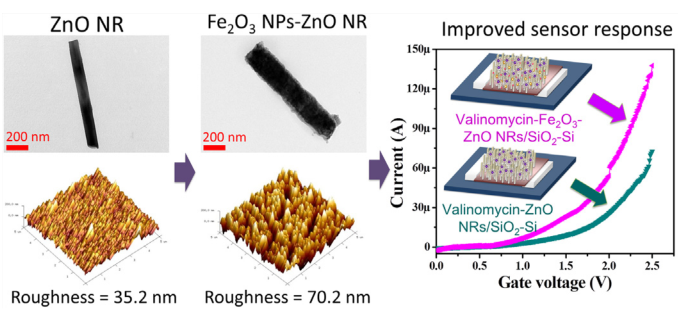
Regular Article

Fabrication of a solution-gated transistor based on valinomycin modified iron oxide nanoparticles decorated zinc oxide nanorods for potassium detection

Min-Sang Ahn [1], Rafiq Ahmad [1,*], Kiesar Sideeq Bhat, Jin-Young Yoo, Tahmineh Mahmoudi, Yoon-Bong Hahn [*]

School of Semiconductor and Chemical Engineering, Nanomaterials Processing, Research Center, Chonbuk National University, 567 Baekjedaero, Deokjin-gu, Jeonju-si, Jeollabuk-do 54896, Republic of Korea

GRAPHICAL ABSTRACT



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ABSTRACT

There are considerable interests to detect and monitor the abnormal level of minerals in water for avoiding/preventing any toxic effects after consumption. Herein, we report the fabrication of solution-gated field-effect-transistor (FET) based potassium sensor using iron oxide nanoparticles (Fe_2O_3 NPs) modified directly grown zinc oxide nanorods (ZnO NRs). The Fe_2O_3 NPs modification of ZnO NRs provided stability to nanorods surface and improved surface area for valinomycin immobilization. As-fabricated potassium sensor (valinomycin-Fe_2O_3 NPs-ZnO NRs/SiO_2/Si) provided enhanced current response with increasing potassium concentration. During sensing measurements, FET sensor showed high sensitivity (4.65 $\mu A/\mu M/cm^2$) in the linear range of 0.1 μM to 125 μM, low limit of detection (~0.04 μM), good stability, excellent reproducibility, and favorable selectivity. Thus, good sensing performance of the FET based potassium sensor presents it as simple, low-cost, and convenient device for selective detection of potassium in solution.

1. Introduction

Among minerals, potassium (K^+) ions are the important element for living beings including human life, as K^+ ions are easily absorbed in the gastrointestinal tract after consumption in drinking water [1–4]. Various attempts have been made to detect minerals concentration using different techniques i.e. ionic and

* Corresponding authors.
E-mail addresses: rahmad38@jbnu.ac.kr (R. Ahmad), ybhahn@chonbuk.ac.kr (Y.-B. Hahn).

[1] M.S.A. and R.A. contributed equally to this work.

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high-performance liquid chromatography, spectroscopic, electrochemical, photometry, potentiometric, and fluorescent based techniques [5–12]. These techniques are time-consuming and also require sampling, costly process, bulky size, and complicated instrumentation, which limit their usability.

Recently, potentiometric FET based sensors have attracted the interest of researchers due to their advantageous features i.e. small size, easy to operate, cost-effective, and successful utilization of semiconducting channel between source-drain (S-D) electrodes during sensor fabrication. Such channel is very sensitive to the external fields and gets easily affected by potential variation. Additionally, a selective membrane/enzyme in potentiometric ion sensors can easily or selectively detect specific species [13–15]. In addition, nanostructured materials are offering the excellent surface area for enzyme immobilizations and thereby improve the sensors performance. Among other metal oxides, zinc oxide (ZnO) is preferred due to easy synthesis method at low-temperature, easy tuning of its nanostructured morphology, and its excellent properties [16–24]. Also, the surface of ZnO nanostructured can be easily modified with metal and metal oxides to enhance the properties and surface area of materials [25–27].

In this paper, we report the fabrication of solution-gated FETs device using vertically grown ZnO NRs. The ZnO NRs surfaces were modified with Fe_2O_3 NPs to enhance the surface area, catalytic feature, and valinomycin immobilization efficacy. As a result, the fabricated FET based potassium sensor showed enhanced sensing performance towards increasing concentration of potassium. Moreover, the selectivity of as-fabricated FET sensor was evaluated in the presence of interfering species.

2. Experimental and methods

2.1. Chemicals

All the chemicals were used as obtained. Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%), iron(III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, ≥98%), hexamethylenetetramine (HMTA, 99%), Tris(hydroxymethyl)aminomethane (Tris), and valinomycin ($C_{54}H_{90}N_6O_{18}$) were purchased from Sigma-Aldrich.

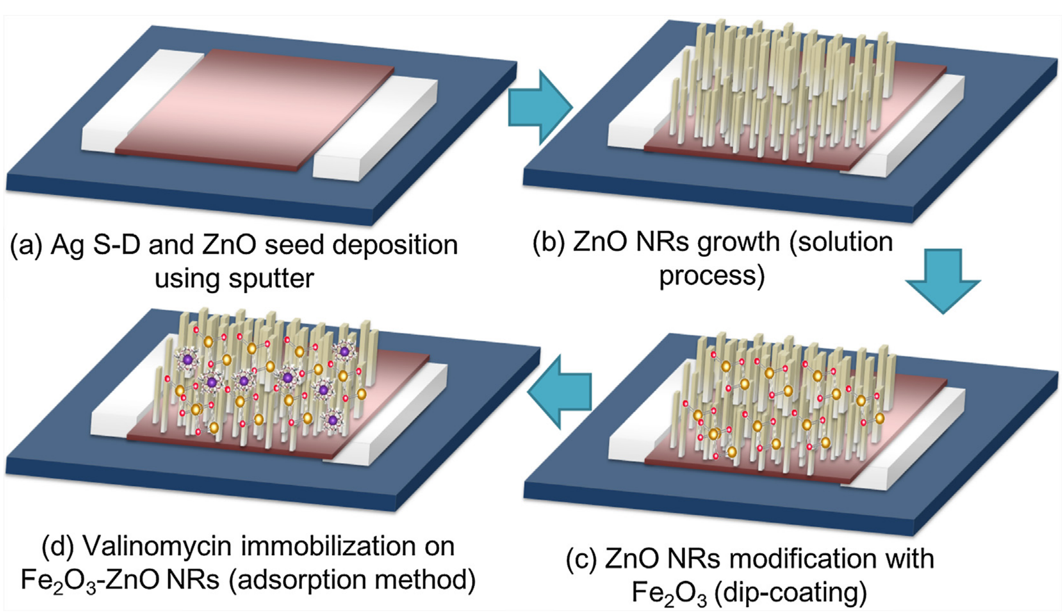
2.2. Fabrication of FET based potassium sensor

The fabrication illustration of FET based potassium sensor is shown in Scheme 1. First, silicon (Si, 100) with thermally formed silicon dioxide (SiO_2, 200 nm) was taken and cleaned using sonication. The radio frequency (RF) sputtering was used to sputter titanium (Ti, ~5 nm), silver (Ag, ~100 nm), and ZnO seed layer (~60 nm) for improving adhesion between Ag and Si/SiO_2 surface, as source-drain, and to grow ZnO NRs, respectively (a). After heating seeded substrate at 150 °C for 30 min on a hot plate, the ZnO NRs were grown using low-temperature solution method (b). In brief, $Zn(NO_3)_2{\cdot}6H_2O$ and HMTA (each 0.05 M) were added in a round-bottom three-neck Pyrex glass bottle containing 50 mL deionized water and dissolved followed by suspension of seeded substrate upside down and heating in the reaction mixture for 6 h at 80 °C. Then, after completion of the reaction, ZnO NRs grown substrates were removed, washed and dried at room temperature.

In the next step, as-grown ZnO NRs were functionalized with Fe_2O_3 NPs using dip-coating of ZnO $NRs/SiO_2/Si$ substrate for 2 min in the precursor solution of $Fe(NO_3)_3{\cdot}9H_2O$ (0.06 g) dissolved in 20 mL deionized water [25]. The samples were dried at room temperature and annealed at 400 °C for 2 h (c). Finally, valinomycin prepared in Tris buffer in the ratio of 1:4 (valinomycin as obtained from Sigma-Aldrich: Tris buffer) was immobilized on Fe_2O_3 NPs-ZnO NRs surface using adsorption method (d) and kept at 4 °C for further characterizations.

2.3. Characterizations

The surface morphology of as-grown ZnO NRs and Fe_2O_3 NPs modified ZnO NRs were characterized using field emission scanning electron microscopy (FESEM, Carl Zeiss SUPRA 40VP) with energy-dispersive X-ray spectroscopy (EDS) and JEOLJEM-2010 transmission electron microscopy (TEM). The crystallinity of bare ZnO NRs and Fe_2O_3 NPs modified ZnO NRs were examined using X-ray diffractometer (XRD, Rigaku) measured with Cu-Kα radiations of λ = 1.54178 Å in the range of 10–60° with 8°/min scanning speed. The surface roughness of as-synthesized ZnO NRs and Fe_2O_3 NPs modified ZnO NRs were analyzed in 5 μm × 5 μm scan area using tapping mode AFM (atomic force microscopy, Multimode-8,



Scheme 1. Schematic illustration of FET based potassium sensor fabrication process.