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Regular Article

Nonenzymatic flexible field-effect transistor based glucose sensor fabricated using NiO quantum dots modified ZnO nanorods

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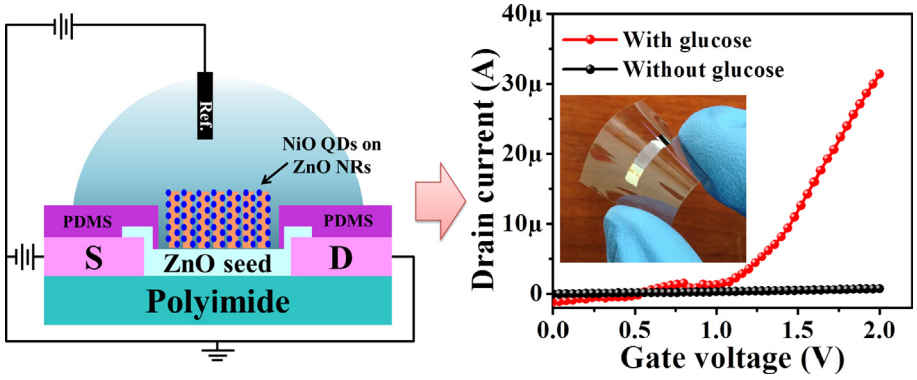
HIGHLIGHTS

- A non-enzymatic flexible FET based glucose biosensor was fabricated.
- Grown ZnO NRs between source-drain were modified with NiO QDs by sputtering.
- An enhanced electrocatalytic features were recorded for glucose detection.
- The proposed sensor showed wide-linear range, high sensitivity and a low detection limit.
- Successfully used for human whole blood sample and serum sample analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we fabricated nonenzymatic flexible field-effect transistor (f-FET) based glucose sensor using nickel oxide quantum dots (NiO QDs) modified zinc oxide nanorods (ZnO NRs). The ZnO NRs surfaces were coated with NiO QDs using radio frequency (RF) magnetron sputtering to enhance the electrocatalytic feature and the surface area of ZnO NRs. Under physiological conditions (pH 7.4), the nonenzymatic f-FET glucose sensor shows two linear ranges of 0.001–10 mM and 10–50 mM with the high sensitivity of 13.14 μA cm^{-2} mM^{-1} and 7.31 μA cm^{-2} mM^{-1}, respectively, along with good selectivity, stability and repeatability during glucose detection. The examination of human whole blood and serum samples reveal that the nonenzymatic f-FET based glucose sensor is capable of measuring glucose concentration efficiently in the presence of interfering species and thus can be offered as a promising device for further applications in clinical and non-clinical fields.

1. Introduction

Diabetes is one of the major health concerns with the worldwide prevalence and is predicted to be double to 300 million by 2025 [1]. Diabetic patients suffer from high blood glucose levels due to insulin deficiency that leads to the long-term damage and failure of various organs mainly heart, kidney, eyes, and blood vessels [2,3]. Among several approaches used for glucose

Abbreviations: Nf, Nafion; PET, polyethylene terephthalate; GOx, glucose oxidase; PANI, polyaniline; PAA, poly(acrylic acid); PDAB, poly(1,2-diaminobenzene); PMMA, poly methyl methacrylate; CPNTs, carboxylated polypyrrole nanotubes.

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concentration measurement, electrochemical based techniques have got enormous attention due to their high sensitivity, low production cost, simple instrumentation, and rapid response [4–8]. Recently, various attempts have been made for nonenzymatic detection of glucose with rapid response and accurate measurements using different electrochemical based methods [9–15]. The field-effect transistors (FETs) utilizing different nanostructures provide a robust and economically feasible platform in order to achieve high current amplification with sustainable and enhanced signal-to-noise ratio compared to other detection methodologies. Due to their excellent sensitivity and real-time measurement capability for bio- and chemical molecules, FET-based sensors are getting considerable interest.

A variety of metals and metal oxides (e.g. Au, Pd, Ag, Cu, Pt, Ni, CuO, Fe_2O_3, NiO, CoO, $CoWO_4$, MnO_2, TiO_2, etc.,) have been explored for direct glucose oxidation on the electrode surface (without using enzymes) [10–14,16–22]. Metal electrodes, especially Pt and Au are highly electroactive and can easily cause poisoning or fouling of the electrode surface and may result in low sensitivity and poor selectivity in glucose detection. Also, the cost of these metals needs to be considered. Ni-based materials have been extensively studied as electrode materials for nonenzymatic sensors because they can catalyze the electrocatalytic oxidation of glucose [23–29]. However, no work has been reported on nonenzymatic flexible FET based glucose sensor using NiO QDs modified ZnO NRs.

There is certainly room for the improvement in glucose sensing, probably the most frequent clinical measurement made by both clinicians and individuals needing to monitor blood glucose on a regular basis. Moreover, for measurements made outside the clinical laboratory, it is necessary to integrate the sampling and sample handling into the device. There is no interest in adjusting the pH or converting whole blood into serum unless the process is handled automatically. However, most of the nonenzymatic sensors require highly alkaline solutions (pH > 10). Therefore, considerable attentions are needed to develop the nonenzymatic electrodes that exhibit high electrocatalytic activity toward glucose oxidation under physiological conditions. This will help to make implantable sensing devices. Recently, Gao et al. fabricated electrochemical nonenzymatic glucose sensor using PtNi alloy NP-graphene composite that works under physiological conditions (pH 7.4) [29].

For the nonenzymatic sensors, sensitivity, selectivity, and stability are the three main issues that have to be solved. However, these analytical performances could be enhanced largely with the nanostructure material modification. A noble metal-semiconductor modification is the most popular system because of its wide application in sensors, where the metal in contact with the semiconductor greatly enhance the sensor performance [30–32]. Among the large group of semiconductors, ZnO has been used extensively for the development of sensors/biosensors due to their high specific surface area [33,34]. Recently, vertically-oriented ZnO nanostructures on electrode surfaces are getting more attention because they offer the larger surface area for modification and enzyme immobilization and thus enhance the sensing performance of fabricated sensors [14,35,36]. Therefore, modifying directly-grown ZnO nanostructures with NiO QDs will improve not only the detection performance of nonenzymatic glucose sensor but also improve the stability of electrode.

In this work, we have fabricated, for the first time, the nonenzymatic flexible FET (f-FET) glucose sensor using ZnO NRs modified with NiO QDs on polyimide. The fabricated f-FET glucose sensor showed a wide-linear range and high sensitivity with good stability and repeatability during glucose detection. Rivaling the state-of-the-art nanomaterial based sensors; our designed nonenzymatic f-FET glucose sensor presents exciting potential for practical applications in clinical and industrial sectors.

2. Experimental details

2.1. Reagents

Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%), glucose (D-(+)-99.5%), hexamethylenetetramine (HMTA, 99%), cholesterol, uric acid (UA), ascorbic acid (AA), dopamine (DA), human blood serum (H4522), and 1.0 M phosphate buffered saline (PBS, pH 7.4) were purchased from Sigma-Aldrich and used as-obtained without further purification. Ultrapure de-ionized (DI) water (purified with Milli-Q plus system, Millipore Co.) with resistivity of ~18 MΩ cm and freshly prepared solutions were exclusively used in all aqueous solutions and measurements, respectively.

2.2. ZnO NRs synthesis, surface modification with NiO QDs and Characterization

To synthesized ZnO NRs, 0.01 M of $Zn(NO_3)_2{\cdot}6H_2O$ and 0.01 M HMTA were first dissolved in 50 mL of DI water and then transferred into a Pyrex glass bottle. The Pyrex glass bottle was heated in a laboratory oven for 4 h at 85 °C after suspending the seeded substrates upside down. After completion of the reaction, ZnO NRs grown electrodes were rinsed with DI water to remove any impurity and dried in air for further processing. The synthesized ZnO NRs were modified with NiO QDs using radio frequency (RF) magnetron sputtering. To modify ZnO NRs with NiO QDs, NiO target with 99.99 % purity was sputtered onto the pre-defined area at 60 W RF power in argon (Ar) atmosphere. The operation pressure in the sputter chamber was 7.2 $\times 10^{-5}$ torr, while the sputtering time was varied 10–50 s.

The morphology of as-synthesized ZnO NRs and NiO QDs modified ZnO NRs were characterized by field-emission scanning electron microscopy (FESEM, Carl Zeiss SUPRA 40 VP) equipped with energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, JEOL-JEM-2010 equipped with CCD camera; operating voltage: 200 kV). The X-ray diffraction (XRD, Rigaku) patterns were measured with Cu-kα Radiation (λ = 1.54178 Å) at 40 kV.

2.3. Fabrication of nonenzymatic f-FET glucose sensor and electrical measurements

The fabrication process of the nonenzymatic f-FET glucose sensor is illustrated in Fig. 1. First, polyimide substrates were cleaned (i), followed by sputter deposition of Ag source-drain electrodes using Ag target (ii). Next, a thin ZnO seed layer was sputtered between source-drain using ZnO as a target (iii). Then, ZnO NRs were grown on the seeded layer (iv) by a low-temperature aqueous route (see Section 2.2 for details). Finally, the electrodes were insulated using PDMS leaving only active area, which reduces the leak current and prevents metal-nanorods contact (v). The NiO QDs were deposited on the grown ZnO NRs by RF sputter (vi).

The fabricated devices were measured using a data acquisition system (HP 4155A semiconductor parameter analyzer) for real-time data measurement. The direct current measurements were performed with two-terminal FET having a floating gate. The drain current (I_d) was recorded when the device was exposed to the different concentrations of glucose in the assigned gate voltage (V_g) range with a fixed drain-source voltage (V_{ds} = 0.0 V). The sensing tests were performed at room temperature using optimized 40 s deposited NiO QDs on ZnO NRs based nonenzymatic f-FET glucose sensor.