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ZnO modified gold disc: A new route to efficient glucose sensing

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ABSTRACT

Surface of a gold disc was modified by depositing ZnO film electrochemically. AFM analysis of the film shows *c*-axis oriented pillar like structures grown normal to the surface. Sensor surface was prepared by immobilizing glucose oxidase (GOD) on the ZnO modified gold disc. Different concentrations of glucose (50–1000 ng/ml) were taken to monitor the sensor response. Sensor was found to be highly sensitive to low concentrations of glucose and sensitivity increases linearly in the range of 50–250 ng/ml. The high sensitivity of the ZnO modified gold disc may be attributed to the SPR induced electron transfer between the two systems (i.e. Au and ZnO). The work indicates promising application of the system as a tool for studying sensitive bio-specific interactions, with further development of highly sensitive and selective bio-molecular and chemical SPR based optical sensors.

1. Introduction

Recently we have witnessed an over whelming increase in the research and development activity aimed at realization of optical based sensors for the measurement of chemical and biological quantities. First optical based chemical sensor was developed based on the measurement of changes in the absorption spectrum for the measurement of the concentrations of CO_2 and O_2 [1]. Since then large number of optical methods have been exploited for applications in chemical and biological sensors including photoluminescence spectroscopy, Raman spectroscopy, ellipsometry, interferometry, optical waveguides and surface plasmon resonance [2–6]. Optical based sensors are advantageous over the other modes of sensing because of its non-destruction and highly sensitive nature. Out of the mentioned optical based sensors, SPR based sensors are found to be one of the most sensitive techniques.

Optical excitation of the surface plasmons (SP) at the resonance condition or surface plasmon resonance (SPR), by the method of attenuated total reflection (ATR) was first demonstrated in the late sixties by Kretschmann and Raether [7] and Otto [8]. Since then SPR have been investigated intensively and their properties have been assessed [9,10]. The phenomenon known as ATR-SPR is one of the most sensitive methods for sensor applications. In the ATR-SPR technique, the resonance occurs at the metal dielectric interface. For the SPR to occur, the real part of the dielectric function of the metal film (very thin as compared to the wavelength of the light) should exhibit a large negative value at the particular chosen wavelength. Surface plasmon resonance (SPR) occurs in the visible range of the electromagnetic spectrum for the free electron-like metals such as silver and gold. A fast decaying evanescent field is developed at the interface between the metal film and the dielectric. This evanescent field interacts with the materials at the close vicinity of the thin metal film. SPR based sensors are known to detect refractive index (RI) changes smaller than 10^{-5} at the close vicinity of the metal film which influence the surface plasmon resonance (SPR) absorption peak position [11]. In conventional prism coupled ATR-SPR experiments, the SPR is observed as a sharp decrease in the intensity of the reflected light at a certain angle of incidence.

The potential of SPR for characterization of thin films and monitoring processes at the metal interfaces were realized in seventies [12,13]. Use of SPR in gas detection and biosensing applications was demonstrated by Nylander and Liedberg thereafter [14–16]. Since then SPR sensing has been attracting lots of interest in the scientific community. Attempts have been made to immobilize biomolecules directly on the metal surface and its responses studied using a prism coupled home-made SPR set-up [17]. As SPR is a surface oriented method, it has shown great potential for affinity biosensors. It is useful mainly in studying the real time analysis of the biospecific interactions without the use of labeled molecules [2]. Now ATR-SPR based sensors has become a leading technology in the field of real-time analysis for bio-molecular interactions. The mechanism for detection is based on the change in the intensity and the angle depending on the dielectric interface. A choice of suitable dielectric layer in the form of polymers or metal oxides as an active layer for

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sensing chemicals and biomolecules, make this a very versatile tool for sensing applications.

Zinc oxide (ZnO), a wide band-gap semiconductor, has a hexagonal wurtzite crystal structure with high exciton binding energy (60 meV) [18]. It is one of the most versatile materials and exhibits a wide range of multifunctional properties and has been exploited for applications such as transparent electronics, UV-lasers, surface acoustic wave devices, acoustic sensors, gas sensors, varistors, etc. [19–22]. ZnO exhibit good electron transfer, excellent optical properties, biocompatibility, and antimicrobial behavior which led to its biomedical applications [23–25]. Shapes of the ZnO nanostructures are easily tunable and preparations of *c*-axis oriented ZnO films are required for realization of various functional devices [22,26].

In this report we used dual channel Autolab SPR set-up (ESPRIT) for detection of different concentrations of glucose. Our attempt here was to develop a highly selective and efficient glucose sensor which can detect very low concentrations. GOD was immobilized on *c*-axis oriented ZnO nanostructures deposited electrochemically on gold surface. GOD immobilized ZnO modified gold disc was used as the sensor surface for sensing different concentrations of glucose.

2. Experimental details

2.1. Reagents and chemicals

Extra pure enzyme glucose oxidase (GOD) and dextrose (D-Glucose) were used as the ligand and analyte respectively. 0.1 M HCl (AR grade, Sigma–Aldrich) and 0.01 M NaOH (AR grade, Sigma–Aldrich) were used as stock 1 and stock 2 solutions. 0.1 M HCOONa (sodium formate) (AR grade, CDH) with pH 3.7, adjusted using formic acid (AR grade, Merck) was used as the running buffer. All the above solutions were prepared in de-mineralized water. 1.5 ml of the formate buffer was taken for preparing 12.5 μg/ml solution of glucose oxidase. Solutions of 0.4 M EDC (Fluka, Sigma–Aldrich), 0.1 M NHS (Fluka, Sigma–Aldrich) were prepared in de-mineralized water.

Zinc nitrate ($Zn(NO_3)_2$) and potassium chloride (KCl) salts obtained from Sigma–Aldrich was used for electro-chemical deposition of ZnO film. Molar concentration between $Zn(NO_3)_2$ and KCl was fixed at 2:1 (20 mM:10 mM).

Different concentrations of glucose were prepared in de-mineralized water. For the glucose sensing measurements de-mineralized water was used as the running buffer. 10 mM HCl and NaOH solutions were used as stock 1 and stock 2 solutions.

2.2. Apparatus

Electrochemical workstation with platinum (Pt) counter electrode provided with the Autolab Electrochemical SPR (ESPR) set-up (ESPRIT) was used for electrochemical deposition of ZnO nanostructures on the gold surface. Cyclic voltammeter (Autolab) was used for the same for applying the required potential. Surface morphology of the gold disc and ZnO modified gold disc was characterized using atomic force microscopy (Vecco diCT-II). Immobilization of GOD and glucose sensing measurements were carried out using dual channel Auto-lab SPR (ESPRIT) set-up. The set-up is provided with a temperature controller (0–70 °C range) through water flow system (Julabo chiller).

2.3. Preparation of the active layer

A commercially available gold disc (Autolab) with Au(1 1 1) plane surface, was taken for these particular set of studies. Electrochemical deposition of ZnO on the gold surface was carried out using the electrochemical workstation set-up at 70 °C. After optimizing the number of cycles for an appropriate thickness, a cyclic voltage of −1 to 1 V was applied and allowed to run for two cycles to obtain the required thickness. Details of the preparation of thin films of ZnO by electrochemical deposition potentiostatically have already been reported [27]. In the present case, we used a cyclic voltammeter instead of a fixed potential. Fig. 1 shows the response curve for ZnO electrochemical deposition on gold surface using ESPR. After the deposition, film was washed several times with de-mineralized water and dried under N_2 atmosphere and kept for one

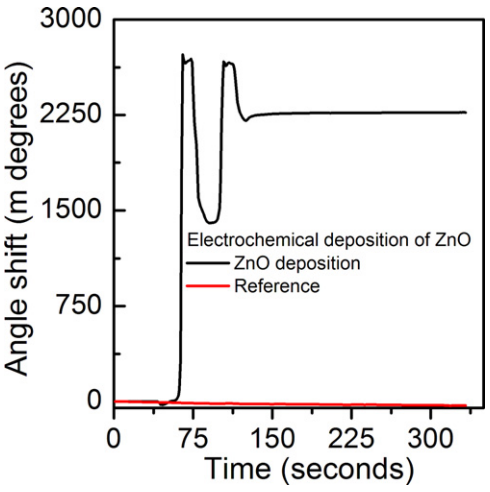

Fig. 1. ESPR response curve for electro-chemical deposition of ZnO.

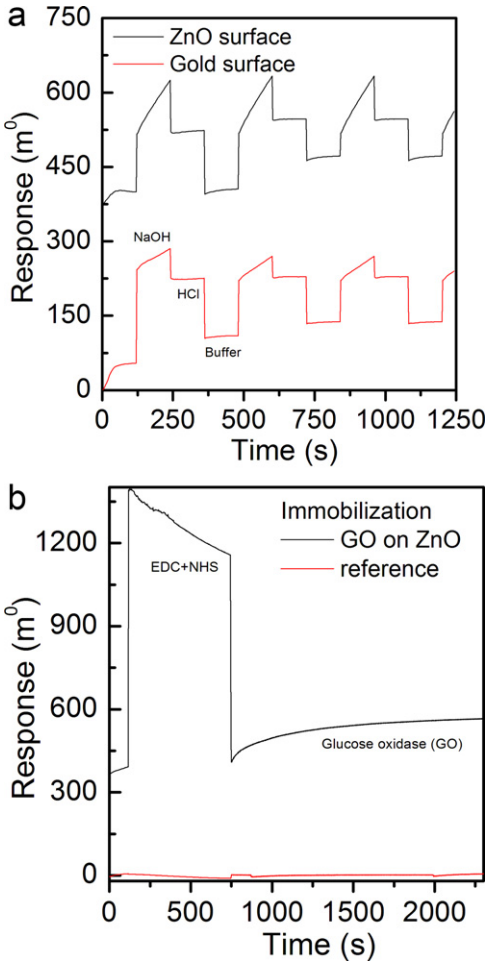

Fig. 2. Response curve for (a) surface stabilization of active layer (ZnO modified gold disc). (b) Immobilization of GOD on the active layer.