Electrochemical enzyme-less urea sensor based on nano-tin oxide synthesized by hydrothermal technique

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ABSTRACT

Nano-Tin oxide was synthesized using hydrothermal method at 150 °C for 6 h and then thin films were deposited by electrophoretic method at an optimized voltage of 100 V for 5 min on electropolished aluminum substrate. Spherical particles of about 30–50 nm diameters are observed with partial agglomeration when observed under electron microscope, which are tetragonal rutile structure. XPS results showed peaks related to Sn 4d, Sn 3d, O 1s & C 1s with spin–orbit splitting of 8.4 eV for Sn 3d. Feasibility studies of enzyme less urea sensing characteristics of nano-tin oxide thin films are exhibited herein. The deposited films have been used for enzyme less urea sensing from 1 to 20 mM concentration in buffer solution. The sensors were characterized electrochemically to obtain cyclic voltammogram as a function of urea concentration and scan rate. The sensitivity is estimated as 18.9 μA/mM below 5 mM and 2.31 μA/mM above 5 mM with a limit of detection of 0.6 mM.

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1. Introduction

It is well known that the specialized neural sensors are considered as an exemplary tool reflecting the human senses that inspired scientist to find equivalent sensors using advance materials and technologies. Research on various types of biosensor development is a scientific achievements of researchers and technologists. A well-known example of such development is a commercial glucometer that utilizes enzyme to breakdown the blood glucose and corresponding electric signal is generated [1–7]. Much research has been done on enzyme based biosensors construction of urea, glucose, cholesterol and others. Though these sensors give specific signals related to particular molecule, but poses problem to re-usability and shelf-life etc. To address such problem, researchers are putting extensive efforts to find an alternate and reliable materials and methods that can provide a solution.

The matrix of the material for biosensor construction is most critical in such research with a critical role of transducer. With the advent of nanomaterials, such matrices have gained much more attention for adsorption based sensor due to increased surface to volume ratio. Metal oxides and their composites have been researched for such applications in addition to known applications as such combination results in unique physical/chemical properties for tailored applications. Therefore, the sensors fabricated with these materials can deliver better results than the conventional spectroscopic techniques. In addition, it is considered an integral part of the on-line monitoring panels which are characterized by low power for operation and its economic feasibility.

Most of the organisms' excrete nitrogen as waste and converts toxic ammonia to uric acid or urea. The normal urea level in serum is 3 mM–7 mM (equivalent to 15–40 mg/dl). Those patients suffer from the renal deficiency, serum urea concentration increases from 30 mM to 80 mM requiring patients to go for hemodialysis. Therefore, excess urea concentration in the blood can cause damage to body organs making it a critical molecule to be detected with considerable importance in agro-food chemistry and environmental monitoring.

Tin oxide; a known material for gas sensors, heating, solar cells with known chemical stability and useful electrical properties is also being explored for biosensing, as a new class of material [8–20]. Tiyagi et al. deposited NiO nanoparticles on conducting

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glass substrate and immobilized with urease for urea detection and studied the sensing characteristics using cyclic voltammetry and UV—visible spectroscopy [12]. In another publication, Solanki et al. used ZnO, ZnO-chitosan and immobilized urease and glutamate dehydrogenase for urea detection [13]. Kaushik et al. used iron oxide-chitosan composite with urease and glutamate dehydrogenase for urea detection [14]. In one of our earlier publications, we used nanostructured zinc oxide thin film where urease was covalently attached with ZnO to detect urea in solution [15]. However, all these reports are based on urease immobilized material resulting in urea sensing. Efforts are needed to find a suitable material that can detect urea without immobilizing urease in order to be a re-usable and reproducible sensor.

In this paper, we present an enzyme less detection of urea using nano tin oxide synthesized by hydrothermal method. SnO_2 films were deposited on electropolished Al-substrate by electrophoretic deposition method. Effect of urea on the electrochemical properties of the deposited tin oxide films have been investigated by obtaining cyclic voltammogram in different urea concentrations and at different scan rates.

2. Experimental details

2.1. Material synthesis

Tin powder (14509, Aldrich), Urea (ACS reagent, 99.0—100.5%) have been obtained from Sigma—Aldrich. Deionized water (DI, 18 MΩ, Milli-Q, Millipore Inc.) has been employed for preparing all aqueous solutions and rinsing of beakers. High-purity (99.999%) aluminum (Al) sheets were purchased from Hanaro trading corporation, Korea and were cut in rectangular form (size 10 mm × 20 mm × 2 mm thick) to be employed as substrate. These were degreased and cleaned using standard procedures and then electropolished using method reported elsewhere [19]. In a typical reaction, 5 gm of Sn-powder was dispersed in a mixture of 75 ml of H_2SO_4 (1 M, 97% pure) and 5 ml H_2O_2 (30% pure). The solution was stirred for 30 min on a magnetic stirrer and then loaded in a Teflon lined autoclave. This has been then sealed and heated to 150 °C for 6 h to complete the hydrothermal reaction. The resultant precipitates were decanted and washed on recurrent basis with DI water to neutral pH.

2.2. Film deposition and characterization

The electrophoretic method was used to deposit the films on electropolished Al-sheet at an optimized voltage of 100 V (current density of 25 mA/cm^2) for 5 min. The bath solution was prepared by using 2 mL of precipitate, 20 mL of H_2O (DI) and 30 mL of methanol (AR grade) and stirred for 10 min before using for electrodeposition. Deposition at 100 V resulted in uniform and adherent film with thickness of about 800 nm. The deposited films were then dried and used for Urea Sensing.

Field emission scanning electron microscope (FESEM, Hitachi S4700) has been employed for investigating the morphology of the deposited films. Structural, elemental and compositional analysis have been done with X-ray diffractometer (XRD, Rigaku, CuKα), Bruker's FTIR (Tensor 37, ATR) and S-Probe's ESCA model 2803 (Fision Instrument, 10 kV, 20 mA) with Al Kα as X-rays source.
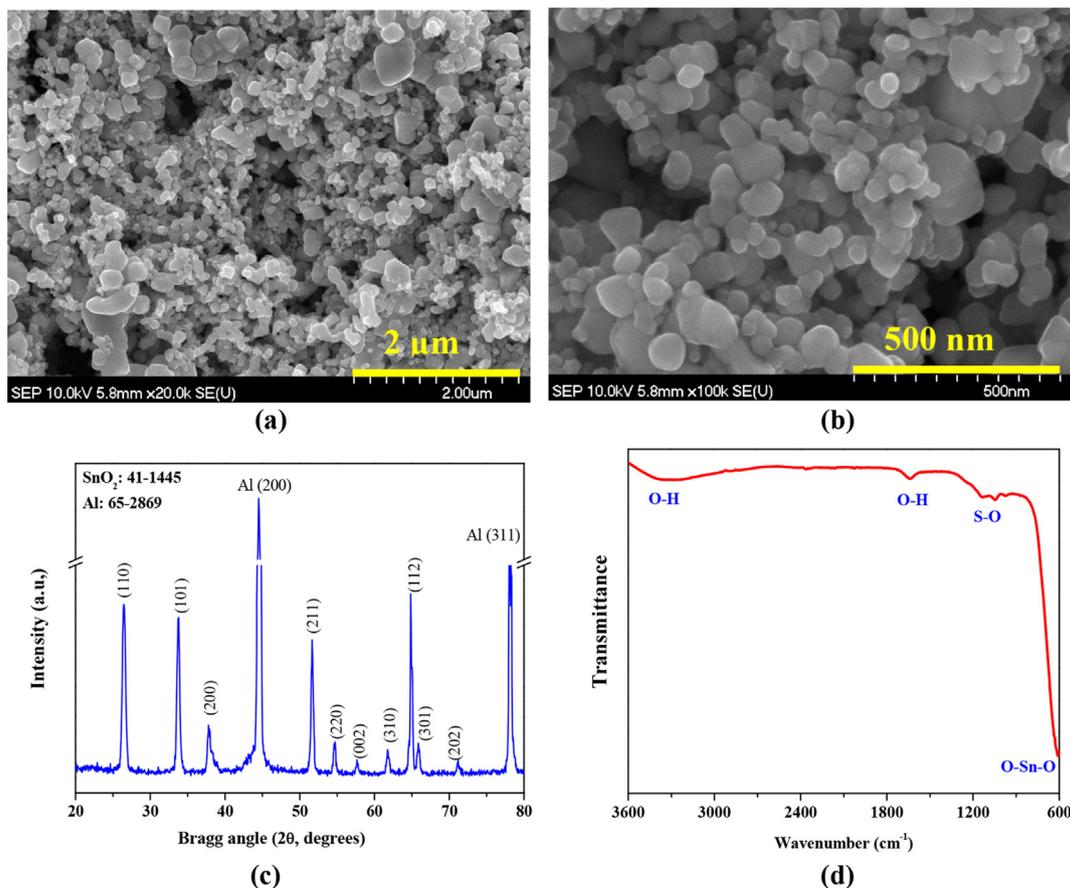

Fig. 1. (a) Low and (b) high resolution FESEM images of SnO_2 films deposited on Al-substrate, (c) X-ray diffraction spectrum of SnO_2 films and (d) FTIR spectrum of SnO_2 films.