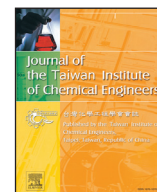




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Low energy nitrogen ion beam implanted tungsten trioxide thin films modified indium tin oxide electrode based acetylcholine sensor

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ABSTRACT

This paper reports the fabrication of non-enzymatic acetylcholine (ACh) electrochemical sensor based on low energy nitrogen ion (100 keV) implanted tungsten trioxide (WO₃) thin films modified indium tin oxide (ITO) electrode. The WO₃ thin films deposited on ITO by spin coating technique was subjected to nitrogen ion implantation with the optimum fluence of 1×10^{15} ions/cm². The implanted electrode was characterized by X-ray diffraction, field emission scanning electron microscopy (FESEM), photoluminescence spectra, Hall Effect measurements, cyclic voltammetry and amperometry. The implanted WO₃ modified ITO electrode induces desirable changes in the crystal structure, surface morphology and electron mobility. Compared with pristine WO₃/ITO, nitrogen ion implanted WO₃/ITO displayed improved electrical conductivity and electrocatalytic activity towards ACh oxidation in 0.1 M potassium hydroxide solution (KOH). Amperometric measurements showed that the fabricated electrode had a wide linear response range of 0.1–8000 μ M, higher sensitivity of 140.57 ± 0.62 mA/M/cm² and the lowest detection limit of 28 nM, which are superior among the non-enzymatic ACh electrochemical sensors. The proposed sensor exhibits an excellent anti-interferential ability, good stability and reproducibility and successfully applied for the determination of ACh levels in human serum samples.

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1. Introduction

Acetylcholine (ACh) was the first discovered neurotransmitter which can be found in the central nervous system, neuromuscular junctions, spinal cord and preganglionic and motor neurons [1]. It acts as a key link in the communication between neurons in the spinal cord and nerve skeletal junctions in vertebrates, and also plays an important role in transmitting signals in the brain. In peripheral nervous system, ACh binds to acetylcholine receptors (AChR) and regulates muscle contraction whereas in the central nervous system, it plays a crucial role in the processes related to behavioural activities such as arousal, attention, learning and memory [2]. Abnormal levels of ACh are associated with nerve disorders including Parkinson's disease, Alzheimer's disease, progressive dementia, Schizophrenia and motor dysfunction [3]. Therefore, in vitro and in vivo determination of ACh in biological samples is of considerable interest in neuronal cholinergic system research.

Various methods had been reported for ACh detection which includes matrix-assisted laser desorption ionization time-of-flight

mass spectrometry [4], high performance liquid chromatography coupled to post-column chemiluminescence detection [5], gas chromatography mass spectrometry [6], capillary zone electrophoresis [7] and enzymatic electrochemical biosensors [8]. Over the past decade, development of electrochemical non-enzymatic ACh biosensors has risen at considerable rate for ACh detection. The advantages include simple design, cost effectiveness, good stability and effective enzyme-like catalysis against temperature and pH [9]. Nanostructured metal oxides have recently aroused tremendous interests in a broad range of technological applications because of their significant size and shape-dependent properties, attractive nanomorphologies, functional biocompatibility, superior electron-transfer kinetics, non-toxic properties and high biological activity leading to enhanced sensing characteristics [10]. Among various nanostructured oxides of metals, tungsten trioxide (WO₃), an n-type indirect semiconductor with wide band gap ($E_g \sim 2.5 - 3.6$ eV), possesses distinctive features of polymorphic structural flexibility, high specific capacitance, high surface-to-volume ratio, high chemical stability, environmental compatibility and high reactivity [11,12]. Here, we propose a new strategy of using low energy nitrogen ion implantation on surfactant assisted WO₃ thin films modified indium tin oxide (ITO) for an efficient electrocatalytic oxidation towards ACh.

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Ion implantation has been employed to modify the surface chemistry and to regulate the depth of penetration by enhancing the physic-chemical properties of semiconducting nanostructures [13]. Several approaches for physic-chemical properties have been exploited using microwave irradiation, gamma rays, ultraviolet (UV) light, visible light, electron beams and ion beams. We have previously studied the effects of microwave, gamma ray and swift heavy ion irradiation on WO_3 NPs and investigated their sensing performances by fabricating electrochemical sensors for the detection of L-dopa, dopamine, serotonin, epinephrine, xanthine and guanine, respectively [14–18]. Low energy ion beam (LEIB) implantation is found to be an effective tool to incorporate foreign ions intrinsically into the host lattice which modifies the surface composition and consequently the properties of host counterparts [19]. Zhang et al., observed the effect of nitrogen ion implantation on tungsten surfaces leading to the formation of the $\text{W}_x(\text{O},\text{N})$ and WN which are not thermodynamically favoured. Meanwhile, stable WO_3 is also formed at the near-surface region of the chamber [20]. As reported by Livraghi et al., ion doping is an attractive approach to heal the oxygen vacant sites in a TiO_2 lattice and N-ion carriers are of particular interest for DSSC applications [21]. Sudhagar et al. examined the nitrogen ion implanted TiO_2 photoanodes to fabricate quantum-dot sensitized electrochemical cells [22]. Diwald et al. investigated the influence of nitrogen ion implantation on the photoactivity of the rutile TiO_2 single crystal surface [23]. Accordingly, we expect ion-doped metal oxides band bending due to modification in the electron concentration, morphology and favourable for efficient charge separation at interfacial electron transfer sites. Nevertheless, to the best of our knowledge, nitrogen ion implanted on WO_3/ITO electrode has not been used for sensor applications.

In the present study, WO_3 thin films were deposited on ITO substrate by spin coating method and were implanted with 100 keV nitrogen ions under optimum fluence of 1×10^{15} ions/ cm^2 . The effect of LEIB on the morphological, optical, electrical and electrochemical behaviour of implanted WO_3 thin films has been investigated. The electrochemical kinetics of the fabricated electrode was studied and finally applied to the determination of ACh by voltammetric and amperometric methods.

2. Experimental

2.1. Reagents

Acetylcholine chloride was purchased from Alfa Aesar, and the stock solution was prepared by dissolving 9.08 mg of acetylcholine chloride in 50 mL of de-ionized water (18 $\text{M}\Omega/\text{cm}$). Tungstic acid, ethylene diamine tetra acetic acid and sodium hydroxide solutions were purchased from Fischer Scientific. ITO plates were purchased from Technistro Technologies Limited. The solution of phosphate buffer (PBS, 0.1 M) was prepared by mixing Na_2HPO_4 and NaH_2PO_4 .

2.2. Apparatus

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker AXS D8 advanced diffractometer in the range of 20–80°. FESEM image and EDAX spectra were recorded using FEG QUANTA 250. Photoluminescence studies of the films were done by Optistat Oxford Instruments (Varian Cary Eclipse). The electrical properties of the films have been performed by Ecopia HMS 3000 van der Pauw Hall effect measurement system at room temperature. Electrochemical experiments were accomplished using a CHI 609D electrochemical workstation (CHI, USA) with a standard three-electrode cell. An indium tin oxide (ITO) substrate was used as the working electrode (working area of $1 \times 1 \text{ cm}^2$), a Pt wire as a counter electrode and Ag/AgCl as a reference electrode.

2.3. Low energy ion beam implantation on WO_3 thin films

The WO_3 NPs obtained from the previous procedure [16] were dispersed in de-ionized water solution (5 mg/ml) and sonicated for 1 h. Subsequently, the homogeneous suspension was coated on ITO substrate. A simple droplet technique was adopted to make WO_3/ITO electrode, where 100 μl of this spreading solution was dispensed onto the ITO electrode and a standard spinner (Spin NXG-P1) was employed to spin the electrode at different speeds ranging from 100 to 1000 rpm for 200 s. The resulting thin films were dried at 60 °C for 1 h. The WO_3 thin films on ITO electrode have been implanted with nitrogen ion using the low-energy ion beam facility (LEIBF) at Inter University Accelerator Centre, New Delhi. The ion energy and beam current of nitrogen ion beams were set to 100 keV and 1 μA , respectively and implanted with the optimized fluence of 1×10^{15} ions/ cm^2 . Ion beam was allowed to incident on the scanned area of $1 \times 1 \text{ cm}^2$.

2.4. Sensing system

The activation of modified electrodes were performed by shifting the prepared electrodes to the electrolyte (0.1 M KOH), and subjecting it to 100 cyclic voltammetry (CV) cycles across the potential range –0.3 to 0.9 V (vs. Ag/AgCl), at a scan rate of 50 mV/s. CV measurements were recorded for 500 μM of ACh at the scan rate of 50 mV/s and the response current was documented. Amperometric measurements were conducted for the quantification of ACh by the nitrogen ion implanted WO_3/ITO at +0.595 V (vs. Ag/AgCl) in 10 mL of stirred alkaline solution at the rotation rate of 400 rpm. The geometric surface area of the thin film is 0.4325 cm^2 .

3. Results and discussion

3.1. Physical characterization of nitrogen ion implanted WO_3 thin films

The XRD patterns of WO_3 thin films coated on ITO electrodes before and after nitrogen ion implantation are shown in Fig. 1A. The pristine WO_3 displays low intensity diffraction peaks suggesting that the film is of poor crystalline quality. Upon nitrogen ion implantation, the peak intensity increases and the peak widths get tapered indicating that the induced grain growth occurred due to localized heat generation which melt the particle surface through ion-matter interactions. The diffraction peaks of both pristine and implanted WO_3 could be well-indexed to intrinsic monoclinic structure of WO_3 (JCPDS No. 72–0677). However, there exists trivial change in the lattice parameters of the implanted WO_3/ITO , implying a slight lattice distortion in the W-O framework after nitrogen ion implantation. The average crystallite size of pristine WO_3 and the implanted WO_3 were found to be 35 nm and 53 nm, respectively. The significant increase in crystallite size confirms the grain growth during ion implantation.

Fig. 1B illustrates the room temperature photoluminescence (PL) spectra of pristine and nitrogen ion implanted WO_3 thin films. The high intensity peaks at 420 nm and 488 nm are associated with oxygen vacancies and defect concentration, respectively [24]. Compared to pristine, increment in peak intensity occurs at nitrogen ion implanted WO_3 thin films which could be attributed to the fast nucleation growth of the WO_3 octahedral group with high crystallinity and higher recombination rate.

Surface morphology of the implanted WO_3 thin films were examined using FESEM. The pristine WO_3 film shows agglomerated clusters with near spherical shapes (Fig. 1C). After the exposure of nitrogen ion implantation, the spherical WO_3 crystallites were converted into bean-like morphology as shown in Fig. 1D. It is worthy

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