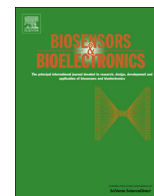




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Tantalum oxide honeycomb architectures for the development of a non-enzymatic glucose sensor with wide detection range

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ABSTRACT

Tantalum oxide honeycomb nanostructures (THNS) were fabricated by electrochemical anodisation of tantalum in H₂SO₄–HF medium. XRD analysis showed that annealing of THNS at 400 °C improves the crystallinity. HRSEM and AFM results illustrated that nanopores with an average diameter of 30 nm were uniformly distributed and the pore size reduced to 24 nm and 18 nm during subsequent electrodeposition of Pt and CuO. Electrodeposited Pt and CuO exhibited face centered cubic (fcc) and monoclinic crystal structure respectively. Cyclic voltammetric studies revealed that, on the hybrid material electrooxidation of glucose occurs at a lower potential (0.45 V). The sensor exhibited linear response to glucose up to 31 mM, fast response time (< 3 s) and a low detection limit of 1 μM (S/N=3). The sensor is free of interference from ascorbic acid, uric acid, dopamine and acetaminophen. Sensor was used to analyze glucose in blood serum samples.

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1. Introduction

Glucose is the primary source of energy for living cells but its excess concentration in human blood causes diabetes mellitus, a chronic disease affecting an estimated 200 million people worldwide, a number that is expected to double in the next 20 years (Yang et al., 2010). This necessitates the development of a fast, reliable, sensitive and a selective method for its determination. The blood glucose concentration in a healthy individual varies between 4 mM and 8 mM, whereas in diabetic patients the range is wider, 2–30 mM (Li et al., 2009). Many methods have been developed for the estimation of blood glucose including spectrophotometry (Lee and Karim, 2006; Shi et al., 1997; Vasilarou and Georgiou, 2000), chromatography (Bauer and Younathan, 1980; Wilson et al., 1981), electrochemistry (Wang, 2007) and Raman spectroscopy (Stuart et al., 2005), some of which are available commercially (Newman and Turner, 2005). Amongst these, glucose determination by electrochemical methods has received immense interest because of its high reliability, sensitivity, selectivity, requirement of simple instrumentation and low manufacturing cost (Craig and O'Neill, 2003; Nie et al., 2011).

Traditional electrochemical glucose sensors are based on the determination of H₂O₂ produced or O₂ consumed during biochemical oxidation of glucose in the presence of enzymes (Wang, 2007). Though a great amount of work has been devoted for improving the sensitivity and selectivity of these enzyme based glucose sensors, their stability to changes in pH, temperature, humidity and toxic chemicals is still a challenge (Singh et al., 2010). In order to overcome these shortcomings enzyme free detection involving direct electrocatalytic oxidation of glucose on a metal or metal-oxide modified electrode surfaces has been widely studied (Park et al., 2006). Variety of metals, alloys and oxides of Pt, Au, Pd, Cu, Ni and Co have been widely explored for the catalytic oxidation of glucose (Bo et al., 2011; Ding et al., 2011; Guo et al., 2011). Among these, direct electrooxidation of glucose on nanostructured platinum electrodes has been well studied and is found to involve adsorption, followed by kinetically controlled oxidation which helps improve selectivity towards glucose. Thus nanostructured platinum helps improve the selectivity towards glucose. Copper and nickel based materials are found to be excellent catalyst for the direct electrooxidation of carbohydrates in an alkaline medium. This is attributed to the formation of thermodynamically less stable redox mediator Cu (III) and Ni (III) (Babu and Ramachandran, 2010; Lu et al., 2009). Various kinds of CuO nanostructures such as nanowires (Zhang et al., 2008), nanorods (Batchelor-McAuley et al., 2008) and nanoflowers (Umar et al., 2009) have been utilized for sensitive and selective amperometric detection of glucose (Wang et al., 2010b).

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Nanoporous and nanotubular structures of oxides of metals such as Zr (Tsuchiya et al., 2005), Ti (Paulose et al., 2006), W (Hahn et al., 2007), Nb (Wei et al., 2012), Al (Lee et al., 2008) and Ta (El-Sayed and Birss, 2009) possess enhanced surface area and high aspect ratio resulting in enhanced electrocatalysis. These nanoporous/nanotubular structures act as a template for the deposition of nanomaterials that helps improve the selectivity and sensitivity of the sensor (Babu et al., 2010; Kang et al., 2007; Luo et al., 2011; Rong et al., 2007; Wang et al., 2010a; Zhu et al., 2009). Titanium and tantalum oxide nanotube arrays have been investigated for their biosensing capabilities due to their high dielectric strength, wide band gap and excellent biocompatibility. Electrochemical anodization is one of the most commonly employed methods for the synthesis of these metal oxide nanotube arrays. Various electrolytes have been employed for the fabrication of tantalum oxide nanotubes which includes glycerol-NH₄F, H₂SO₄-HF and glycerol-phosphate combinations (Allam et al., 2008; Barton et al., 2009a; Lee and Schmuki, 2011a) of which Ta₂O₅ nanotubes fabricated from electrolytes containing HF are found to be less ordered (Allam et al., 2008).

The present study focuses on the development of a non-enzymatic, amperometric glucose biosensor that exhibits excellent sensitivity, selectivity and wide range of detection. THNS were fabricated by a single step anodization and modified with platinum and CuO nanoparticles. The response of the sensor towards blood glucose concentration was evaluated in alkaline medium and found to be very satisfactory.

2. Experimental

2.1. Reagents and Materials

D-Glucose (ACS reagent), L-ascorbic acid (reagent grade), uric acid (≥99%), *p*-acetaminophenol (analytical standard), chloroplatinic acid (ACS reagent) and tantalum foil (0.25 mm, ≥99.9% trace metals basis) were obtained from Sigma-Aldrich. All other chemicals used in this study were of analytical grade and used as received. 0.1 M NaOH was used as the supporting electrolyte for glucose estimation. Deionized water (15 MΩ) was used for all the experiments.

2.2. Instrumentation

All electrochemical experiments were performed using CHI 660C electrochemical workstation (CH Instruments, Texas, USA) and the electrochemical anodization experiments were performed using a DC power supply (20 V, 1A). A three electrode cell with THNS or modified THNS as working electrode, platinum wire as auxiliary electrode and saturated calomel electrode (SCE) as reference were used for electrochemical measurements. FEI Quanta FEG 200 high resolution scanning electron microscope (HRSEM) coupled with energy dispersive spectrophotometer (EDS), FEI Nova NanoSEM and Park XE-70 atomic force microscope were used for morphological study of the modified electrodes. Centrifuge (5810R, Eppendorf, Germany) was used for the separation of serum. Deionized water was obtained from Millipore Elix-10 system (Millipore, Germany).

2.3. Fabrication of tantalum oxide nanopores on tantalum electrode

THNS were fabricated by the electrochemical anodization of tantalum foil in an electrolyte containing 16.4 M sulfuric acid and 2.5 M hydrofluoric acid as reported (El-Sayed and Birss, 2009). Prior to the anodization, the tantalum foil was polished with 0.05 μm alumina, washed with deionized water, ultrasonicated in

acetone and distilled water respectively for 15 min each. The tantalum foil was masked with teflon to expose an area of only 4 mm². This electrode was then placed between two platinum cathodes which are separated by a distance of 1 cm. A positive potential of 15 V was applied for 120 s under constant stirring. The electrode was washed with deionized water, dried and annealed at 400 °C for 2 h. The annealed electrode named as THNS.

2.4. Platinum/copper oxide modification of THNS

Platinum was electrodeposited on THNS electrode from an electrolyte containing 5 mM chloroplatinic acid using the three electrode electrolytic cell. The electrodeposition was performed by cycling the potential between 0.5 and -0.8 V at a scan rate of 100 mV/s for three cycles. The electrode was named as Pt/THNS. Metallic copper was deposited onto Pt/THNS electrode at -0.4 V from an electrolyte consisting of 50 mM CuSO₄ in 1 M H₂SO₄ for 220 s. The deposited copper was further oxidized to copper oxide by cycling the potential between -0.2 and 0.8 V for three cycles in 0.1 M NaOH at a scan rate of 100 mV/s. The obtained electrode is referred to as CuO/Pt/THNS.

2.5. Real sample analysis

1.5 mL of blood was collected from volunteers in a micro centrifuge tube containing EDTA, centrifuged at 12000 rpm for 40 min. The clear serum was collected and 50 μL of this serum was injected to the testing solution containing 4 mL of 0.1M NaOH.

3. Results and discussions

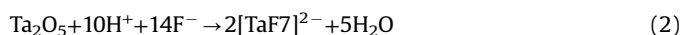
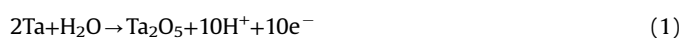
3.1. Morphological characterization

The pores are highly ordered with a uniform pore diameter of 30 ± 2 nm and are evenly distributed all over the surface (Fig. 1A) which is supported by the AFM image Fig. 1B. Electrodeposition of platinum on the THNS resulted in the partial filling up of the nanopores as shown in Fig. 1C&D and the presence of Pt in the pores was confirmed from EDS. It is evident from the AFM image that the pore diameter has been reduced to 24 nm after Pt deposition. Fig. 1E represents the HRSEM image of CuO/Pt/THNS electrode after 220 s of electrodeposition of Cu on the Pt/THNS electrode resulting in further decrease of pore diameter to 18 nm as indicated by AFM image (Fig. 1F). The presence of copper and oxygen in the form of CuO on the surface was established using EDS analysis.

3.2. Formation of THNS

The mechanism of oxidation of Ta in acidic fluoride medium is not well understood. The most accepted principle is similar to that of the formation of TiO₂ nanotube arrays. The anodization of tantalum normally yields thick oxide layer which is soluble in strong HF solution as tantalum fluoride (Barton et al., 2009a). Strong acidic medium of H₂SO₄ and HF supported the formation of highly oriented nanodimples (Barton et al., 2009b). Ta₂O₅ nanopore formation by electrochemical oxidation of Ta in glycerol and sulfuric acid medium has been recently reported by various authors (Allam et al., 2008; Wei et al., 2008).

The mechanism of formation and growth of Ta₂O₅ nanopore arrays in a medium containing concentrated H₂SO₄ and HF can be depicted as follows (El-Sayed and Birss, 2009).



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