Materials Science and Engineering C 58 (2016) 782–789

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Pulse electrodeposited nickel-indium tin oxide nanocomposite as an electrocatalyst for non-enzymatic glucose sensing

P. Sivasakthi, G.N.K. Ramesh Bapu *, Maruthai Chandrasekaran

Electroplating and Metal Finishing Technology Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630006, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form 4 September 2015
Accepted 7 September 2015
Available online 14 September 2015

Keywords:
Pulse electrodeposition
Nanocomposites
Glucose sensor
Electrocatalyst
Real sample analysis

ABSTRACT

Nickel and nickel-ITO nanocomposite on mild steel substrate were prepared by pulse electrodeposition method from nickel sulphamate electrolyte and were examined as electrocatalysts for non-enzymatic glucose sensing. The surface morphology, chemical composition, preferred orientation and oxidation states of the nickel metal ion in the deposits were characterized by SEM, EDAX, XRD and XPS. Electrochemical sensing of glucose was studied by cyclic voltammetry and amperometry. The modified Ni-ITO nanocomposite electrode showed higher electrocatalytic activity for the oxidation of glucose in alkaline medium and exhibited a linear range from 0.02 to 3.00 mM with a limit of detection 3.74 μM at a signal-to-noise ratio of 3. The higher selectivity, longer stability and better reproducibility of this electrode compared to nickel in the sensing of glucose are pointers for exploitation in practical clinical applications.

1. Introduction

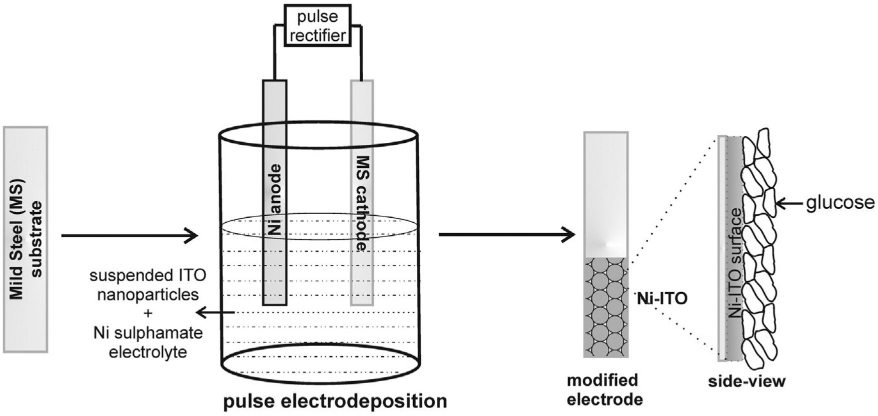
In recent years, nanocomposite electrodes have found widespread application in sensors and biosensors for electro-oxidation of carbohydrates [1], aliphatic alcohols [2], sugars [3], hydrogen peroxide [4–7] and other compounds due to their high surface-to-volume ratio and excellent chemical stability [8]. Nanocomposites can be generated by methods such as electrodeposition, thermal spray, physical vapour deposition, chemical vapour deposition and electroless deposition. However, electrodeposition is reported to be a better method due to its convenience and economy [9]. In electrodeposition, three modes of current can be used: direct current (DC), pulse current (PC) and pulse reverse current (PRC). Pulse current deposits have a unique deposit composition and microstructure as compared to direct current deposits [10]. Wang et al. [11], who pulse electrodeposited Ni-ZrO_2 nanocomposite coatings, showed that the composites exhibited higher hardness and better wear resistance than those prepared by direct current. Another study reported that pulse deposition was a suitable method for Fe–Ni–Cr alloys with controlled composition [12]. Effects of DC and PC codeposition of nickel-nanodiamond powder were investigated by Lee et al. [13], who found that microhardness of the coatings obtained by PC deposition was higher than those by the DC method, both with and without diamond powder incorporation.

Electrocatalytic oxidation of glucose has relevance not only in blood glucose sensing, but also in other fields such as food industry [14], fuel cells and batteries [15]. Non-enzymatic routes for glucose sensing present advantages such as high sensitivity, low cost, short response time and high reliability as compared to enzymatic routes [16]. Nickel-based nanocomposites have only rarely been investigated for electro-oxidation of glucose, glycine [17], carbohydrates [18] and methanol [19]. Recently, Subramanian et al. [20] reported the use of electrophoretically deposited reduced graphene oxide-$Ni(OH)_2$ composites for non-enzymatic glucose sensing. Lu et al. [21] demonstrated the use of Ni(II)-based metal–organic coordination polymer nanoparticle/reduced graphene oxide nanocomposites for highly sensitive and selective non-enzymatic glucose sensing. Multi-walled carbon nanotubes decorated with palladium nanoparticles as a novel platform for electrocatalytic sensing applications [22]. Glucose sensing on a glassy carbon electrode modified with glucose oxidase and a magnetic polymeric nanocomposite was reported [23]. Other studies reported assembly of $Ni(OH)_2$ nanoplates on reduced graphene oxide nanocomposite for enzyme-free glucose sensing [24] and nanoparticles of $Ni(OH)_2$ embedded chitosan membrane as electrocatalyst for non-enzymatic oxidation of glucose [25]. We believe that Ni-ITO (indium tin oxide) nanocomposite could be a new sensing material for electro-oxidation of glucose due to factors including ITO's mechanical characteristics, low cost, high electrical conductivity, wide electrochemical working window, stability and amenability for nanometric high surface area depositions [26]. Although very few reports have appeared on Ni-ITO as an electrocatalyst for certain analytes, there has hitherto been no report on the pulse electrodeposited Ni-ITO nanocomposites for the electro-oxidation of glucose. The electrochemical method of sensing is advantages compared to other methods. Various electrodes and modified materials were repeated in the literature for the sensing of bio-molecules and pollutants in

---

* Corresponding author.
E-mail addresses: rameshbapugnk@cecri.res.in, bapu2657@yahoo.com (G.N.K. Ramesh Bapu).

http://dx.doi.org/10.1016/j.msec.2015.09.036
0928-4931/© 2015 Elsevier B.V. All rights reserved.



Scheme 1. Schematic illustration of the preparation of pulse electrodeposited Ni-ITO nanocomposite for glucose sensing.

environmental studies. The modified carbon paste electrodes were widely used for the sensing of bio-molecules and organic pollutants [27–35]. In this report, we present our results on the non-enzymatic glucose sensing behaviour of pulse deposited Ni-ITO nanocomposites, as shown in Scheme 1.

2. Experimental

2.1. Preparation of Ni-ITO nanocomposite electrode

All chemicals were of analytical grade and the plating solutions were prepared in double distilled water. The bath composition was as follows: 300 g l^{-1} of $Ni(SO_3NH_2)_2$ (Nice Chemicals), 40 g l^{-1} of H_3BO_3 (Nice Chemicals), 5 g l^{-1} of $NiCl_2 \cdot 6H_2O$ (Nice Chemicals), 0.05 g l^{-1} of sodium lauryl sulphate (Nice Chemicals) and 2.5 g l^{-1} of ITO nanoparticles (average particle size: 50 nm, Sigma-Aldrich). The required amount of ITO was added to the bath solution and agitated with a mechanical stirrer for 8 h to obtain uniform suspensions. The plating was done at a stirring rate of 600 rpm and *p*H 3 at an average current density of 4 A dm^{-2} for 30 min at 50 °C. The deposition was carried out in a two-electrode cell, with electrolytic grade pure Ni as the anode and mild steel substrate (2.5 cm × 5 cm) as the cathode. Prior to deposition, the substrate was polished sequentially with grades 4, 5 and 6 emery papers and degreased with trichloroethylene and then electro-cleaned at 6 A dm^{-2} in a cleaning solution containing 25 g l^{-1} of Na_2CO_3 and 35 g l^{-1} of NaOH at 70 °C, followed by activation in 5% H_2SO_4 solution for 20 s. A Micro Star pulse power supply (DPR 20-10-30, USA) was used with pulse currents at 10% duty cycle and 10 Hz frequency.

2.2. Characterization of Ni and Ni-ITO nanocomposite electrode

The morphological features and chemical composition of the Ni and Ni-ITO nanocomposite deposits were analysed by a Hitachi S-3000H (Japan) scanning electron microscope and energy dispersive X-ray spectrometer. The grain sizes of the deposits were examined by a Bruker X-ray diffractometer (Netherlands) between (2θ) values of 20° and 100° at a scan rate of 2° per min using Cu-K_α ($\lambda = 1.5405$ Å) radiation. The oxidation states of the constituent elements were determined by MULTILAB 2000 X-ray photoelectron spectrophotometer (Thermo Scientific).

2.3. Electro-oxidation of glucose on Ni and Ni-ITO nanocomposite electrodes

The electro-oxidation of glucose in 0.1 M NaOH was investigated by cyclic voltammetry and amperometry in a conventional three-electrode glass cell with an area of 0.25 cm^2 of the deposited Ni and Ni-ITO nanocomposite exposed on one side as working electrode, a platinum foil as counter electrode and an Ag/AgCl as reference electrode at 25 ± 1 °C and run on an Biologic SP-150 galvanostat/potentiosat.

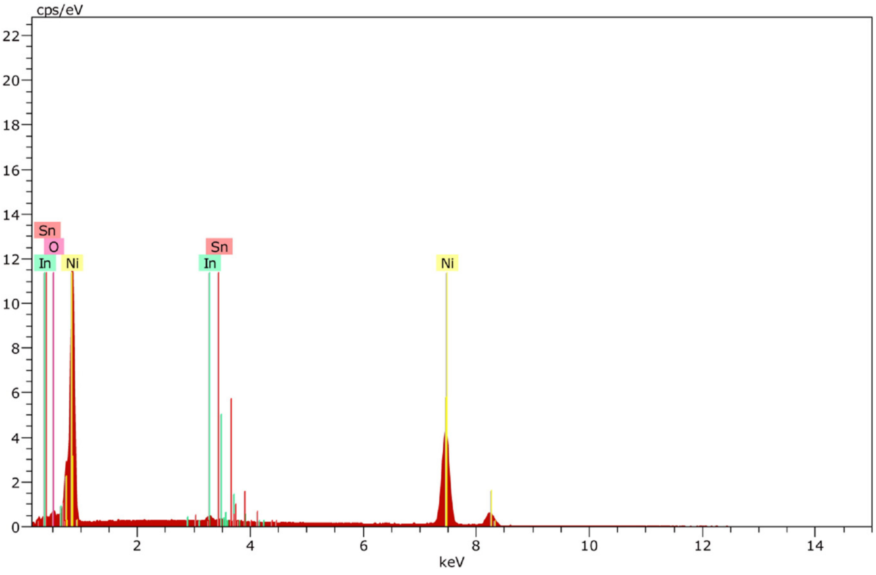


Fig. 1. EDAX analysis of the Ni-ITO nanocomposite containing 2.5 g l^{-1} of ITO nanoparticles.