Sensors and Actuators B 213 (2015) 92–101

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

A facile formation of silver dendrites on indium tin oxide surfaces using electrodeposition and amperometric sensing of hydrazine

R. Sivasubramanian, M.V. Sangaranarayanan*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

ARTICLE INFO

Article history:
Received 19 September 2014
Received in revised form 12 February 2015
Accepted 13 February 2015
Available online 21 February 2015

Keywords:
Silver dendrites
Indium tin oxide
Electrodeposition
Hydrazine
Electrocatalysis
Amperometry

ABSTRACT

Silver dendritic structures have been prepared using constant potential deposition on indium tin oxide (ITO) electrodes from an aqueous solution of $AgNO_3$ and KNO_3 without any surfactants or structure directing agents. The applied potential is shown to be a crucial factor in the formation of dendrites. Depending upon the magnitude of the applied potentials, morphologies vary from polygons to dendrites. The shape evolution of the silver dendrites has been investigated by varying the deposition time and metal precursors. The mechanism of formation of dendrites is interpreted using the diffusion limited aggregation (DLA) model. The fractal dimensions of the dendrites calculated using the box counting algorithm are in agreement with those predicted by the DLA model. The Ag dendrites coated ITO electrodes exhibit excellent electrocatalytic activity toward oxidation of hydrazine in alkaline medium. The sensing of hydrazine is carried out with amperometry, where from the limit of detection and linear calibration range is deduced as 0.5 μM and 100–1700 μM respectively. The effect of ascorbic acid, urea, ethanol, glucose, K^+, Cl^-, Br^- and I^- ions as possible interfering agents in the detection of hydrazine is analyzed.

1. Introduction

The analysis of materials with dendritic structures constitutes a fascinating area of research on account of their diverse applications and non-equilibrium growth patterns [1]. The dendritic structures are often referred to as fractals and are characterized by open, random and chain-like structures which exhibit scale invariance and have no natural length scales [2]. These structures provide a framework for the study of disordered systems while possessing morphology-dependent properties [3]. In particular, the dendritic structures pertaining to Au [4] and Pt [5] are known as an excellent electrocatalysts. Further, dendritic silver nanostructures have received increasing attention due to their applicability in surface enhanced Raman scattering (SERS) [6], superhydrophobicity [7] and in electroanalysis [8]. Of various synthetic strategies for the preparation of dendrites, electrodeposition offers a simple, versatile and facile technique since the structures are devoid of any impurities while their rigid adherence on the electrode surface ensures stability. It has been demonstrated that increase in the driving force of crystallization results in structures with diverse morphologies ranging from polygons to dendrites [9]. While the synthesis of silver dendrites using electrochemical techniques is known [10–13], the factors governing their formation have not been systematically explored. Recently, it was demonstrated that low concentrations of the supporting electrolyte (KNO_3) have significant influence on the morphology of silver dendrites [14]. Analogously, the optimum current density and concentration of polyvinyl pyrolidone (PVP), can also yield dendritic rods, sheets and flower like structures [15]. Further, silver deposited on Au [16] and Ni electroplated on Cu [17] electrodes constitute simple prototypes for dendritic nanostructures.

A major interest in the study of the dendrites covered surfaces lies in the molecular recognition. The feasibility of Ag dendrites in the oxidation of hydrazine and formaldehyde [14,18] as well as in the reduction of oxygen [19] has been demonstrated earlier. Hydrazine is used in fuel cells on account of its high energy density [20]. Further, it is commonly employed in the synthesis of pesticides as well as pharmaceutical products. It is also used as scavengers for oxygen in high pressure boilers and as rocket fuels [21]; hence it acts as contaminants of ground water. The U.S. Environmental protection agency has estimated the level of inhalation risk of hydrazine as 4.9×10^{-3} $\mu g/m^3$ in air [22]. In this context, the development of improved devices for the sensing of hydrazine is of utmost importance. Several methods employing spectrophotometric [23], fluorimetric [24], chemiluminescence [25] and chromatographic [26] techniques have also been reported. However, these methods are usually expensive, time consuming and often require elaborate pretreatments. On the other

---

* Corresponding author. Tel.: +91 44 22574209; fax: +91 44 22570545.
E-mail address: sangara@iitm.ac.in (M.V. Sangaranarayanan).

http://dx.doi.org/10.1016/j.snb.2015.02.065
0925-4005/© 2015 Elsevier B.V. All rights reserved.

hand, electrochemical methods have satisfactory features such as ease of analysis, cost effectiveness and re-usability [27]. The real time monitoring of hydrazine using electroanalytical methods is required in various food preservatives and in environmental analysis. Hydrazine is also employed in fuel cells and hence its quantitative estimation is essential [28].

There have been various studies on the electrochemical detection of hydrazine and in particular, nanoporous gold [29], palladium coated boron doped diamond electrode [30] and gold nanoparticles decorated on activated carbon modified glassy carbon electrode [31] have been investigated with the satisfactory detection limits. However, the preparation of modified electrodes is often cumbersome and requires stringent experimental conditions. Hence a facile and robust method is preferable for the detection of hydrazine. Since Ag dendrites possess high surface area on account of the open structures, these are anticipated to provide a low limit of detection and higher sensitivity. Herein, we report a facile electrochemical technique for obtaining silver dendrites on indium tin oxide (ITO) surfaces and illustrate the influence of various control parameters. The efficient sensing of hydrazine by the Ag-dendrites covered ITO surface is also demonstrated using amperometry.

2. Experimental

2.1. Reagents

KNO_3 (>98%), KCl (>98%), KBr (>98%), KI (>98%) and $NH_2NH_2{\cdot}H_2O$ (99%), from Merck (USA), $AgNO_3$ (>99%) from Finar reagents, AgF (>98%) from Alfa Aesar, CH_3COOAg (>99%) from SRL Ltd. India, and NaOH (>98%) from Fischer reagents were employed as received. The triply distilled water was employed for preparing all the solutions.

2.2. Electrochemical measurements

Cyclic voltammetric and chronoamperometric experiments were carried out using IVIUM compact stat (the Netherlands) with a conventional three electrode assembly. The ITO ($R_s \sim 15\,\Omega$) was employed as the working electrode while platinum wire and Ag/AgCl (3 M KCl) served as the counter and reference electrode respectively. All the working, reference and counter electrodes were procured from CH Instruments USA. The temperature was maintained at 25 ± 1 °C throughout. All the potentials are reported with respect to Ag/AgCl electrode.

2.3. Electrodeposition of Ag on ITO

Prior to the deposition of Ag, the ITO electrode was cleaned by ultrasonication in water and acetone followed by drying. The constant potential deposition of Ag was carried out on ITO from a solution of 0.1 M KNO_3 and 5 mM of $AgNO_3$. The deposition was performed at various potentials (−0.20 V, −0.50 V and −0.80 V) and also at different deposition times (60 s, 180 s, 300 s and 600 s).

2.4. Characterization studies

The morphologies of the silver deposits were recorded using Scanning Electron Microscope (SEM) (Hitachi S4800) equipped with energy dispersive X-ray spectroscopy analyzer and Transmission Electron Microscope (TEM) from Philips CM12 operating at 200 kV acceleration. For TEM images, the deposits were removed from the ITO substrate by ultrasonication in water for 5 min. A small amount of the dispersed suspension is deposited on the carbon coated Cu grid. The XRD patterns of the deposits were obtained using Bruckner D8 advanced X-ray diffractometer equipped with Cu Kα radiation.

2.5. Cyclic voltammetry

The electrocatalytic oxidation of hydrazine was carried out using cyclic voltammetry from a solution of 1 M NaOH and 5 mM hydrazine on the Ag coated ITO prepared at various potentials (−0.20 V, −0.50 V and −0.80 V).

2.6. Electrochemical sensing of hydrazine

The amperometric sensing of hydrazine was carried out from 1 M NaOH solution at an applied potential of −0.05 V. The experiment was carried out in a stirred solution at a speed of 900 rotations per minute. The working electrode was the Ag dendrites coated ITO with a geometrical area of 1 cm^2 dipped into NaOH solution. The counter and reference electrodes were each placed at a distance of 0.1 mm from the working electrode. A stock solution of 10 mM hydrazine was prepared and various aliquots were then added to the alkaline solution and the steady state current response was recorded for every 50 s.

3. Results and discussion

The ITO electrode was subjected to deposition at a constant potential of −0.80 V for 600 s. The dependence of the morphologies on various experimental parameters viz. deposition potential, time of deposition and the concentration of precursor is analyzed.

3.1. Morphological characterization of silver dendrites

3.1.1. SEM and TEM analysis

Fig. 1a depicts the SEM image of Ag deposited at a potential of −0.80 V for 600 s. The dendritic structures are noticed with a long main trunk and short side branches decorated by small leaf-like structures. The length of the main trunk is about 4 μm while that of the side branches is ~2 μm. The main and side branches are present in the common plane on the surface of ITO. The side trunk of each branch is almost parallel to each other and they make an angle of about 60° with the main trunk indicating that the growth of dendrites occurs in a preferential orientation. The TEM studies also confirm the dendrite-like structures as shown in Fig. 1b. The main trunk of the dendrite is found to be ~2 μm and the side branches are found to be ~500 nm in length. The selected area electron diffraction (SAED) reveals spot patterns (Fig. 1d) which are characteristic of the crystalline nature of silver dendrites. The distance between the lattice planes is 0.204 nm which is in agreement with *d* spacing of (2 0 0) lattice plane of face centered cubic (FCC) silver are consistent with the JCPDS reference ID 04-0783. The presence of Ag is confirmed by energy dispersive X-ray spectroscopy (EDX) measurements with a weight percentage of ~24 as shown in Fig. 1c.

3.1.2. XRD studies

Fig. 2 depicts the XRD pattern of silver deposited on ITO at a potential of −0.80 V. The XRD studies reveal the crystalline nature of silver, while the peaks at 38.3°, 44.3°, 64.4°, 77.5° correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) plane respectively. These values are consistent with JCPDS reference ID 04-0783 confirming the presence of face centered cubic pattern of electrodeposited silver. The peak at 38.3° corresponding to (1 1 1) plane is found to be of high intensity when compared to other planes. Although not perfectly single crystalline, Ag preferentially grows along the (1 1 1) plane and the presence of other planes are noted to a minor extent. This is attributed to the low surface energy of (1 1 1) plane estimated from the density functional theory [32] according to which the surface energy of single crystals follows the trend $\gamma_{111}(1.12\,J/m^2) < \gamma_{100}(1.20\,J/m^2) < \gamma_{110}(1.29\,J/m^2)$.