



Direct current electrodeposition of Co-ITO nanoflakes modified steel electrode for highly selective non enzymatic detection of catechol

S. Premlatha ^{a, b, *}, G.N.K. Ramesh Babu ^b

^a CSIR-Academy of Scientific and Innovative Research, India

^b Electroplating and Metal Finishing Technology Division, CSIR-Central Electrochemical Research Institute, Karaikudi, 630003, Tamilnadu, India



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ABSTRACT

Dihydroxy benzenes are considered as toxic pollutants that had harmful impact on environment. The present study is focused on the fabrication of an electrochemical sensor based on Co-ITO nanoflakes electrode on mild steel surface for highly sensitive and selective detection of catechol, prepared using simple electrodeposition route without any binders. The surface morphology, elemental composition and the crystal structure were confirmed from SEM, EDX XPS and XRD analyses respectively. The electrochemical characterization was done using cyclic voltammetry and chronoamperometric techniques. The electrocatalytic oxidation of catechol at Co and Co-ITO modified electrode was studied in 0.1 M NaOH vs Ag/AgCl at 50 mVs⁻¹ scan rate. When catechol was added, the anodic oxidation peaks got increased with the decrease in the cathodic reduction current which revealed the electrocatalytic activity of Co-ITO nanoflakes electrode. Chronoamperometric experiments were performed to get the linear range, sensitivity and detection limit. For each and every addition of catechol, a stepwise increment of current was observed. The interference test and real sample analysis were also performed which revealed good selectivity and recovery. The above results demonstrated that Co-ITO nanoflakes electrode could be a promising electrode for catechol sensing in real situations.

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1. Introduction

Catechol is one of the isomer of dihydroxy benzene, used as a raw material for the preparation of pesticides, drugs, cosmetics, and many synthetic chemicals [1,2]. It is a toxic poly phenolic compound highly responsible for water pollution due to their discharge from industries, hospitals and house hold wastes that can cause severe damage to the eco system [3,4]. These compounds are also responsible for the problems associated with lungs, liver, kidneys, and genitor urinary tract in humans and animals through their absorption via skin and mucous membranes and even cause cancer and damage to DNA [5–7]. Environmental Protection Agency (EPA) and European Union (EU) have included catechol in the list of primary pollutants due to its high toxicity and low degradability in the environment. It is also identified as human carcinogen by the International Agency for Research on Cancer [8,9]. Since it is ubiquitous, the rapid and sensitive detection of catechol is

significant in human health and environmental viewpoints. Many methods have been reported for the quantification of catechol such as spectrophotometry [10], high performance liquid chromatography [11,12], flow injection analysis [13], chemiluminescence [14], gas chromatography-mass spectrometry [15] etc. But, these methods requires tedious procedures, highly skilled operators and sample pre-treatments [16]. In contrast, electrochemical methods had triggered great deal of interest in catechol detection because of its simplicity, portability, robustness, high sensitivity, low cost and ease of miniaturization [6,17]. It is well known that the direct detection of catechol at bare electrodes needs high overpotential and the electrode kinetics is rather slow and often suffers from fouling effect. To circumvent these problems, chemical modification is an effective way to enhance the sensitivity and minimize the overpotential [18]. Recently, different types of modifiers have been employed in detection of catechol. Some of them are noble metal composites [19], carbon composites [20,21], conducting polymer based composites [22], etc. However, the high cost and complex procedures impedes their practical utilization. Tyrosinase and lactate based enzymatic sensors are recently demonstrated for catechol sensing [13]. These kind of enzymatic sensors are suffered

* Corresponding author. CSIR-Academy of Scientific and Innovative Research, India.

E-mail address: spremlatha87@gmail.com (S. Premlatha).

from tedious immobilization procedures, high cost and instability of the enzymes [5]. Hence, the non enzymatic catechol sensors are garnered enormous attention among sensor community.

Nanocomposites have aroused enormous attention owing to their rational nanostructures and fine-tuned morphology may promote the rate of the reaction and reduces the overpotential. Nanocomposites can be prepared by incorporating particles, polymers, fibers, nanotubes etc with a metal matrix [23,24]. Transition metals/metal oxide nanostructures have been reported as a better electrocatalyst in sensing applications and possess wide range of electronic, physical and chemical properties [25,26]. Especially, cobalt based compounds has received increasing attraction in electrocatalysis, and electrochemical sensors fabrication due to its intrinsic electrocatalytic activity, good conductivity, high surface area, low cost, and natural abundance [27–29]. It was found that, composites made with cobalt are proven to be a better electrocatalyst in electrocatalytic applications. However, catalyst support is always needed to improve the electrochemical sensitivity and utilization of active sites. In this aspect, metal oxide nanoparticles are widely used due to its key properties such as high surface area and good conductivity. The substrate also plays a vital role in surface modification. Conventionally, glassy carbon electrode was used as substrate for immobilization of active materials. In addition to that, the sensing material was entrapped with nafion and drop casted on the glassy carbon surface but for large scale applications, alternative substrate material is needed. This motivated the authors to develop a binder free modified steel electrode for catechol determination. S. Cui et al. fabricated mesoporous cobalto-cobaltic oxide modified glassy carbon electrode for simultaneous detection of hydroquinone and catechol [27]. N. Lavanya [30] et al. fabricated Co-SnO₂ as a highly sensitive electrochemical sensor for simultaneous determination of phenolic compounds catechol and hydroquinone with detection limit of 0.09 μM. Y. Jiang [31] et al. developed an electrochemical sensor for catechol detection using In-ZnO nanosheets modified carbon nanotubes-polyimide film and obtained a detection limit of 0.39 μM. In this work, Co-ITO nanoflakes were electrodeposited on mild steel substrate and directly applied as an electrocatalyst for sensitive detection of catechol. Though, cobalt based catechol sensor was well studied, electrodeposition of Co-ITO nanoflakes on steel substrate is a novel approach in electrochemical sensor fabrication. To the best of author's knowledge, there is no such report dealt for catechol sensor. The facile and cost effective Co-ITO nanoflakes modified electrode could be a promising candidate in catechol sensing applications.

2. Experimental

2.1. Materials and methods

All the chemicals were of analytical grade and are used without further purification. Cobalt (IV) acetate, catechol and hydroquinone were bought from Merck. Boric acid, Phenol, Nitrophenol, Resorcinol were bought from Nice chemicals. ITO nanopowder (>100 nm) was purchased from Sigma Aldrich. The electrolyte solutions were freshly made up of Millipore water.

The electrochemical characterization was studied from cyclic voltammetry and chronoamperometric methods using SP-150 Biological science instrument (France make) Potentiostat/galvanostat. Three electrode cell configuration containing Co-ITO modified mild steel of 1 cm² geometrical area was used as working electrode, the same area of platinum foil as counter and Ag/AgCl as reference electrode respectively. The SEM images and EDX spectrum were taken from Hitachi, (model 3000H) electron microscope. The predominant orientation and the crystal structure were acquired from X-ray diffractometry (Bruker) using Cu K_α radiation having the

wavelength of 1.5406 Å. XPS spectrum of the prepared composite was analyzed from Multilab 2000 spectrometer. The TEM images of Co and Co-ITO composite were taken from Tecnai 20 G2 (FEI make) microscope.

2.2. Preparation of Co and Co-ITO nanoflakes modified electrode

The Co and Co-ITO nanoflakes modified electrode was prepared using simple and scalable electrodeposition strategy in a two electrode cell configuration under galvanostatic mode. To prepare the cobalt electrolyte, initially, 40 g/L of boric acid was dissolved in 200 ml of millipore water. And then 100 g/L of cobalt (IV) acetate, 0.1 g/L of sodium lauryl sulphate and 4 g/L of commercial ITO nanoparticles were added one by one and the resultant solution was ultrasonicated for 15 minutes. Boric acid maintains the bath pH during electrodeposition process. Cobalt acetate was used as metal ion supplier and SLS as antipitting agent. The electrolyte was continuously agitated with the aid of mechanical stirrer for eight hours to get the homogenous suspension. Cobalt metal and mild steel plates of dimensions 7 cm × 1 cm × 0.5 mm were placed in the electrolyte as anode and cathode respectively. Prior to electrodeposition, the mild steel panel was polished manually with different grade emery sheets, degreased with trichloroethylene, alkaline electrocleaning in NaOH and Na₂CO₃ solution, finally acid pickling in 10 % sulphuric acid to get mirror finish surface. The non plated surface was covered with lacquer. The electrodeposition parameters such as current density, pH, and concentration of the nanoparticles are previously optimized by performing consecutive experiments. The electrolyte composition and the optimized parameters are given in Table 1. The electrodeposition was carried out for 15 minutes and the obtained thin film was washed in running water, dried and stored in a desiccator for further use. The thickness of the electrodeposited thin film was measured by the weight difference before and after electrodeposition.

3. Results and discussion

3.1. Morphological studies

SEM images were used to investigate the morphological details of Co and Co-ITO nanoflakes modified electrode. As seen in Fig. 1a, the morphology observations of Co was revealed as interconnected thick nanoflakes arrays uniformly distributed all over the substrate but, the thickness of the nanoflakes is not uniform in some sites. The surface of the each nanoflake is having dendrite like features which oriented themselves perpendicularly to mild steel surface and is interlinked with open up network. This existed surface morphology is well agreed with the literature [32]. The cobalt crystal growth can be controlled by adjusting the electrodeposition parameters particularly current density and time. When the current density and time increases, the surface morphology becomes very

Table 1
Bath composition and operating parameters for Co-ITO electrodeposition.

| Bath constituents | Concentration |
|-----------------------------------|----------------------------|
| Cobalt (IV) acetate tetra hydrate | 100 g/L |
| Boric acid | 40 g/L |
| Sodium lauryl sulphate | 0.1 g/L |
| ITO nanoparticles | 4 g/L |
| Temperature (C°) | 30 |
| pH | 4 |
| Current density | 4 A/dm ² |
| Agitation | 600 rpm (Magnetic stirrer) |
| Anode | Cobalt (Alfa Aesar) |
| Cathode | Pre-treated mild steel |

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