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# Electrocatalytic reduction of *ortho* nitrobenzaldehyde using modified aluminum electrode and its determination

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ABSTRACT

A simple, cost effective and rapid electrochemical method has been developed for the determination of micro level *ortho* nitrobenzaldehyde (ONB) based on outstanding properties of modified aluminum electrode tin nanorods/anodic aluminum oxide/aluminum (SnNR/AAO/Al) for the first time. The SnNR/AAO/Al electrode was fabricated by a second step anodization, followed by electrodeposition and its electrochemical behavior was investigated in detail. The cyclic voltammetry results indicated that the SnNR/AAO/Al electrode exhibited efficient electrocatalytic activity toward reduction of ONB in the acidic solution. It provides an appreciable improvement of reduction peak for ONB at −0.721 V. Furthermore, various kinetic parameters such as transfer electron number, transfer proton number and standard heterogeneous rate constant were calculated from the scan rates. The electrocatalytic behavior was further exploited as a sensitive detection scheme for the ONB determination by differential pulse voltammetry. Under the optimized conditions, the concentration range and detection limit are 0.1–100 μmol/L and 0.05 μmol/L, respectively, for ONB. The analytical performance of this modified sensor has been evaluated for detection of real sample such as river water and recovery of ONB was achieved all-out up to 102.3% under standard addition method.



## Introduction

The analysis of aromatic nitrocompounds such as nitrobenzene, nitrobenzaldehyde and nitrophenols in natural waters and its effluents has a major reputation for environmental control due to their appearance from a wide range of activities (Mulchandani et al., 2005). These compounds have toxic effect on humans, animals and plants and they give a detrimental taste and odor to drinking water, even at a very low concentration (Niaz et al., 2009). For these reasons, many aromatic nitrocompounds have been included in the environmental legislation. Among these compounds, *ortho* nitrobenzaldehyde (ONB) is also one of the hazardous materials (Yu et al., 2008), because of its toxic and recalcitrant nature. ONB is used as an important intermediate for the synthesis of a number of chemicals such as nifedipine (Adalat, Procardia), dyes, agrochemicals and other organic compounds. At least 730,000 tons of ONB is produced annually in the southeast of China (Yu et al., 2010). Further, a vast quantity of ONB contaminated wastewaters are generated during the manufacturing process. For these reasons, it has great significance to develop a fast reliable and inexpensive method for treating such wastewater prior to its discharge even though no acceptable limit of ONB has been specifically set.

Many sensitive, reliable, precise, common analytical techniques, such as gas chromatography and biotreatment (Cathum et al., 2009; Liu et al., 2012) methods have been developed for the determination of ONB. However, these methods require expensive instrumentation, complicated pretreatment procedure and professional operators, which limit their application for real-time detection of these compounds. But electrochemical

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determination of organic pollutants has attracted a great deal of awareness due to its analytical performances, such as low detection limits, wide linear response range, good stability and reproducibility. The use of bare electrodes has revealed some drawbacks because of the electrode surface fouling with insulating of polymer films or by-products consequential from compound oxidation or reduction.

Aluminum is the cheapest metal possessing unique properties such as excellent thermal and electrical conductivity, low density, light weight etc. By modifying the surface of aluminum, a variety of novel sensors can be fabricated which can compete with even carbon nanotube modified electrodes. Electrochemically synthesized nano-porous aluminum oxide (AAO) is one of the most attractive candidates to use as a multifunctional nanostructured surface matrix. This ceramic membrane is a self-ordered nano-porous array, which is suitable for many technical applications. The rapidly growing interest in the use of the AAO for electronics and nano-material synthesis is due to its self-assembled and well controllable pore structure, high throughput and low fabrication cost compared to conventional lithographic (electron beam, focused ion beam, X-ray, scanning tunneling microscopy (STM)/atomic force microscopy (AFM), etc.) techniques. AAO has served as a template in manufacturing of nanowires and nanoarrays (Moghimi and Rajabi-Siahboomi, 1993; Sulka et al., 2011). Since nano AAO membranes can be easily fabricated, they offer a promising platform for development of microarray sensors (Song et al., 2011) and electrochemical sensors (Calavia et al., 2010; Pournaghi-Azar et al., 2010a, 2010b; Song et al., 2010; Cheng et al., 2008).

This article describes the mechanistic studies on the electrocatalytic reduction of ONB with a simply prepared tin nanorods SnNR/AAO modified aluminum electrode. The probable analytical application of the modified electrode was assessed, and it has been used for voltammetric detection of ONB in the low level concentration range. The present study enlarges the application range of tin nanorods into detection of important organic pollutant in real water samples using an electrochemical method.

## 1. Experimental

### 1.1. Chemicals

ONB was procured from Sigma Aldrich (USA) and used without further purification. All other chemicals and reagents were of analytical grade purchased from Merck India Ltd., Mumbai, India. For the electrochemical experiments, sodium phosphate buffer (0.25 mol/L $Na_2HPO_4/NaH_2PO_4$) was used as supporting electrolyte and the pH was adjusted with an acid or base solution. All solutions were prepared with triply distilled water.

### 1.2. Preparation of SnNR/AAO/Al modified electrode

Tin nanorods (SnNR) modified aluminum electrode was prepared in two steps: the first step involved electrochemical synthesis of ordered AAO by anodization, then the SnNR were fabricated on AAO template by electrochemical deposition method.

An aluminum sheet (purity 99.99%, thickness 0.3 mm) was used as substrate for the preparation of AAO template. Before anodization, the aluminum was annealed at 450°C for 30 min and degreased with acetone. The Al electrode was electrochemically polished in a mixture of concentrated sulfuric and phosphoric acids. To obtain highly ordered nano pore arrays on AAO, a two-step anodization process was employed. The primary step anodization was carried out by DC power supply at 40 V in 0.3 mol/L $H_2C_2O_4$ at room temperature for 2 hr using Al as anode and graphite as cathode. Then the produced alumina layer was eroded by immersing in a solution of phosphoric acid (6.0 wt.%) and chromic acid (1.8 wt.%) at 60°C. The secondary step anodization was carried out to obtain a regular array of AAO at below 5°C keeping other conditions similar to that used for the primary step anodization. In order to ensure the electrochemical deposition, the thickness of barrier layer reduced by decreasing the anodizing voltage systematically with 2.0 V/min intervals after the anodization was finished (Routkevitch et al., 1996). After anodization, the pores in AAO were then widened by etching in 5.0 wt.% phosphoric acid for 30 min and then washed with de-ionized water.

Fabrication of the tin nanostructures was carried out by DC electrodeposition in a simple two-electrode electrochemical cell consisting of the AAO template as cathode and lead plate as the anode using an electrolyte containing 7.0 g/L $SnCl_2$ and 25.0 g/L $C_6H_{17}N_3O_7$. The current density was adjusted to 0.5 mA/cm$^2$ and to facilitate the mass transfer, a magnetic stirrer was used to agitate the electrolyte. The schematic diagram of the entire process of formation of the modified electrode was represented in **Fig. 1**.

### 1.3. Characterization of SnNR/AAO/Al modified electrode

#### 1.3.1. Surface characterization

The surface of the porous alumina template and Sn deposition on alumina were observed by AFM (NT-MDT model solver Pro M and Veeco, Santa Barbara, USA). The element composition of the modified electrode was studied by energy dispersive X-ray spectroscopy (EDAX). The nanostructure and the crystalline nature of the tin nanorods array were characterized by X-ray diffraction (XRD, Model PW 1710, Philips Co. Ltd., Japan).

#### 1.3.2. Electrochemical characterization of SnNR

Cyclic voltammetry, electrochemical impedance spectroscopy and differential pulse voltammetry (DPV) were performed using CHI 760c (CH Instrument Inc., USA) electrochemical workstation. A conventional three-electrode system was used with platinum disk act as a counter electrode, calomel as the reference electrode and modified aluminum as the working electrode. During electrochemical measurements, electrons travel from the Al/alumina–Sn/solution interface and through the alumina to the Sn nanorods that are electrically connected to the aluminum plate. For cyclic voltammetry experiments, the potential was scanned between −1.6 and −0.2 V at a scan rate of 100 mV/sec in 0.25 mol/L phosphate buffer. The electrochemical impedance spectroscopy (EIS) experiment performed in the presence of 5.0 mmol/L $K_3[Fe(CN)_6]$ as a redox probe prepared in 0.1 mol/L KCl. The impedance was measured in the frequency range from 100 MHz to 100 kHz at an open circuit potential of −0.3 V vs. calomel reference electrode with a voltage amplitude of 5 mV and the respective semicircle diameter corresponds to charge-transfer resistance ($R_{ct}$). DPV experiments were performed in the potential range from −1 to −0.3 V for the selective determination of ONB at the pulse amplitude of 50 mV and a scan