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Article

Silver nanoparticle decorated poly(2-aminodiphenylamine) modified carbon paste electrode as a simple and efficient electrocatalyst for oxidation of formaldehyde

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ABSTRACT

This work describes the promising activity of silver nanoparticles on the surface of a poly(2-amino diphenylamine) modified carbon paste electrode (CPE) towards formaldehyde oxidation. Electrodeposition of the conducting polymer film on the CPE was carried out using consecutive cyclic voltammetry in an aqueous solution of 2-aminodiphenylamine and HCl. Nitrogen groups in the polymer backbone had a Ag ion accumulating effect, allowing Ag nanoparticles to be electrochemically deposited on the surface of the electrode. The electrochemical and morphological characteristics of the modified electrode were investigated. The electro-oxidation of formaldehyde on the surface of electrode was studied using cyclic voltammetry and chronoamperometry in aqueous solution of 0.1 mol/L NaOH. The electro-oxidation onset potential was found to be around −0.4 V, which is unique in the literature. The effect of different concentrations of formaldehyde on the electrocatalytic activity of the modified electrode was investigated. Finally, the diffusion coefficient of formaldehyde in alkaline media was calculated to be 0.47×10^{-6} cm^2/s using chronoamperometry.

1. Introduction

The development of efficient electrocatalysts for oxidation of small organic molecules (such as CH_3OH, HCOOH, and HCHO) has received considerable attention owing to their great potential as fuels in clean and high-efficiency energy conversion devices [1–4]. Although HCHO is of less importance than methanol, the study of its electro-oxidation has attracted much attention mainly because of two aspects. First, HCHO is one of the intermediate products of methanol oxidation, so the study of its electrochemical oxidation is important for full understanding of methanol oxidation. The second aspect is the toxicity of HCHO, which is one of the major hazardous substances emitted from widely used construction and decorative materials. It also is widely used in the chemical, wood processing, paper, and textile industries, and in technologically important processes such as electroless copper plating. Long periods of exposure to levels of HCHO that exceed safe concentrations may cause adverse effects to human health [5]. The World Health Organization also identified HCHO as “Carcinogenic to humans” [6]. Among the various approaches that have been explored to conquer these challenges, one of the most important is the oxidation of HCHO to less harmful materials such as formic acid or CO_2.

In recent years, many reports have been published on the oxidation of HCHO under a wide range of conditions and on various electrodes, although most have been carried out on Pt electrodes [7–16]. However, although Pt is one of the most efficient metal catalysts for oxidation of HCHO, it is easily poisoned

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by the CO-like intermediate produced from incomplete oxidation of the fuel. Another problem intrinsic to Pt is its high cost. One approach to solving these problems is the development of a cheaper, non-poisonable catalyst while maintaining high activity for the oxidation process. In this approach several reports have already been published on the surfaces of catalysts such as Cu [7], Ni [13,14], and Ag [17]. In the present work, we report the strong activity and high stability of Ag nanoparticles on the surface of poly(2-aminodiphenylamine) as a new, simple, and low cost electrocatalyst. HCHO oxidation at the surface of this electrocatalyst exhibits a very low over-potential in comparison with those of commonly used electrocatalysts such as Pt and Pd.

2. Experimental

2.1. Reagent and materials

The solvent used in this study was distilled water. Silver nitrate, sodium hydroxide, 2-aminodiphenylamine (2ADPA), and formaldehyde, all of analytical grade, were obtained from Merck and used without further purification. Hydrochloric acid (1 mol/L) prepared from the concentrated acid (Fluka) was used as the supporting electrolyte for electropolymerization. High viscosity paraffin (density: 0.88 g/cm^3) from Fluka was used as the pasting liquid for the carbon paste electrode (CPE). Graphite powder (particle diameter = 0.1 mm) from Merck was used as the working electrode material.

2.2. Instrumentation

Cyclic voltammetry and chronoamperometry experiments were carried out using a potentiostat/galvanostat (Sama 500-C Electrochemical Analysis System, Sama, Iran) coupled with a Pentium IV personal computer for data acquisition. The electrochemical cell was assembled as a conventional three-electrode system with the nano-Ag/P(2ADPA)/CPE (3.4-mm diameter) as the working electrode, Ag/AgCl/KCl (3 mol/L) as the reference electrode (Metrohm), and platinum wire as the counter electrode.

2.3. Preparation of CPE and P(2ADPA)/CPE electrodes

A CPE was prepared by hand mixing 0.3 mL of paraffin oil and 1.0 g of graphite powder with a mortar and pestle until a uniformly wetted paste was obtained. A portion of the homogeneous paste was packed firmly into the bottom of a glass tube (internal radius = 1.7 mm), and electrical contact was provided by a copper wire fitted into the glass tube. The surface of the electrode was smoothed on white paper and rinsed with distilled water prior to each experiment.

A P(2ADPA)/CPE electrode was fabricated using an electropolymerization technique according to our previous work [18]. In brief, a carbon paste electrode was immersed into a cell containing an aqueous solution of 1.0 mol/L HCl and 5 mmol/L 2ADPA. Poly(2ADPA) was electrochemically deposited on the surface of the CPE by applying consecutive cyclic voltammetry between −0.2 and 0.9 V at a scan rate of 100 mV/s.

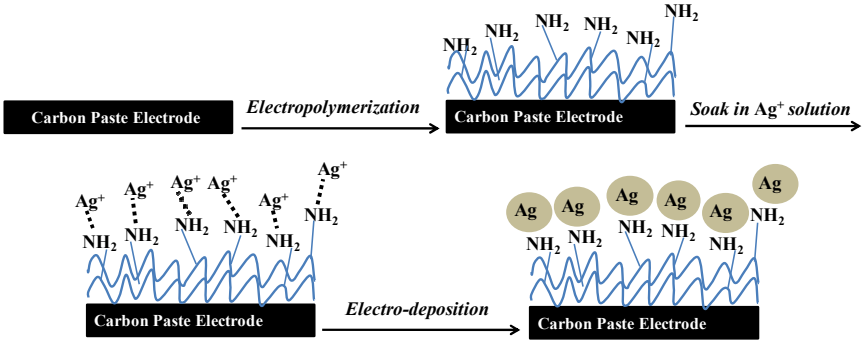
3. Results and discussion

3.1. Preparation and characterization of nano-Ag/P(2ADPA)/CPE

To deposit Ag nanoparticles onto the polymeric film, the freshly prepared P(2ADPA)/CPE was soaked in a well stirred 1.0 mmol/L $AgNO_3$ solution at open circuit for 10 min. Accumulation of Ag^+ ions occurred by complex formation between Ag^+ and amine sites of the polymer backbone on the CPE. The electrode was then rinsed with distilled water and transferred into a cell containing 0.1 mol/L NaOH solution. The Ag nanoparticles were fixed on the surface of the electrode by applying consecutive potential cycling between −0.5 to 1.0 V at a scan rate of 100 mV/s until steady state voltammograms were obtained. Scheme 1 illustrates the overall modification process used to prepare the nano-Ag/P(2ADPA)/CPE.

The distribution of Ag nanoparticles over the electrode surface was observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The white particles in Fig. 1(a) clearly show the deposited Ag nanoparticles, which were less than 150 nm in diameter. This coating of Ag at the surface of electrode was further confirmed by EDX analysis. As shown in Fig. 1(b), energy peaks at around 3.0 and 3.2 keV were ascribed to characteristic peaks of Ag. These results indicate the successful preparation of the Ag/P(2ADPA)/CPE electrode.

Figure 2(a) shows the electrochemical behavior of the Ag nanoparticles at the surface of P(2ADPA)/CPE in 0.1 mol/L



Scheme 1. Schematic of fabrication route to Ag/P(2ADPA)/CPE.