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Highly improved electrooxidation of formaldehyde on nickel/poly (o-toluidine)/Triton X-100 film modified carbon nanotube paste electrode

Jahan-Bakhsh Raouf*, Reza Ojani, Samaneh Abdi, Sayed Reza Hosseini

Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran, 3rd Kilometer of Air Force Road, Postal Code: 47416-95447, Babolsar, Iran

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ABSTRACT

In present work, o-toluidine (OT) monomer is electropolymerized in the presence of an aqueous acidic solution containing Triton X-100 (TX-100) non-ionic surfactant onto multi-walled carbon nanotube paste electrode (CNTPE). The as-prepared substrate is used as a porous matrix for dispersion of Ni (II) ions by immersing the modified electrode in a nickel (II) sulfate solution. The modified electrodes are characterized by field emission scanning electron microscopy (FE-SEM) and electrochemical methods. The electrochemical characterization of the nickel/poly (o-toluidine)/Triton X-100 film modified carbon nanotube paste electrode (Ni/POT (TX-100)/MCNTPE) exhibits redox behavior of Ni(III)/Ni(II) couple in alkaline medium. It has been shown that POT/TX-100 film at surface of the CNTPE improves efficiency of the catalyst toward formaldehyde electrooxidation. Moreover, the effects of various parameters such as TX-100 concentration, formaldehyde concentration, OT concentration, film thickness and accumulation time on the electrooxidation of formaldehyde as well as long-term stability of the Ni/POT (TX-100)/MCNTPE have also been investigated.

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1. Introduction

Knowledge of the reactivity of formaldehyde (HCHO) in an electrochemical environment is important for various applications including fuel cells and electrochemical detection. Therefore, electrochemical oxidation of HCHO at various electrodes has been receiving much attention. Pt and Pt alloys [1–8], copper and copper alloys [9–11], polycrystalline palladium [12], gold [13], palladium nanoparticles electrodeposited on carbon ionic liquid composite electrode [14] and palladium nanoparticles on functional multi-walled carbon nanotubes [15,16] have been studied as anode catalysts for the HCHO

oxidation. However, one of the limiting factors is that precious metals (Pt, Pd, Au, etc.) are readily poisoned by adsorbed intermediates, which blocks the metal active sites. Besides, the high cost and short supply of these metals are not economical for practical and industrial application [17]. Thus, a great deal of interest has, recently, been focused on an alternative metal (non-noble metal) while maintaining the high catalytic activity and less expensive materials as anodes for HCHO oxidation. On the other hand, nickel is a low cost, relatively abundant material that is used extensively in numerous industrial applications. It is well established that Ni can be used as a catalyst due to its surface oxidation

* Corresponding author. Tel.: +98 112 5342392; fax: +98 112 5342350.

E-mail address: j.raouf@umz.ac.ir (J.-B. Raouf).

properties [18]. Ni has demonstrated long-term stability in alkaline solutions [19,20], hence, it is a useful catalyst for the electrooxidation of methanol and HCHO in alkaline medium [18,21–26].

Recent researches have demonstrated that coating the electrode surface with conducting polymers (CPs) is an attractive approach for enhancing the power and scope of electrochemically modified electrodes [27–29]. CP matrices have been employed as catalyst support materials for the oxidation of small organic molecules in place of conventional supports, because when catalyst is dispersed in carbon black, a part of the active sites remains inaccessible to the reactant molecules. The reason for incorporating metallic particles into the porous matrixes is to increase the specific area of these materials and thereby improve catalytic efficiency. Another reason is the higher tolerance of the metal particles to poisoning due to the adsorption of CO species, in comparison with the serious problem of bulk metal electrodes poisoning.

Carbon nanotubes (CNTs) are considered as a novel nano-sized material playing a vital role in the field of nanotechnology. They are widely used in materials sciences, electronic and physical fields for various applications in the form of novel nanodevices, tips for scanning probe microscopy, quantum wires, sensors and catalyst supports, etc. [30–34]. One of the main potent properties of carbon nanotubes is that it can enhance the electron transfer between the electroactive species and the electrodes. The CNT electrodes display superior performance than other electrodes in terms of promoting electron-transfer, improving reversibility of electrochemical reaction, enhancing signal/noise ratio, high accessible surface area and high stability [35,36].

Recently, we have combined the advantageous features of polymer modification, dispersion of metallic ions on CPs coated carbon paste electrode by construction of Ni/P-1,5-DAN/MCPE [37], Ni/P(NMA)/MCPE [38], which can successfully catalyze the oxidation of HCHO in alkaline medium. Our literature survey indicates that, there is no report as yet on the usage of nickel/poly (*o*-toluidine)/TX-100 film modified carbon nanotube paste electrode (Ni/POT (TX-100)/MCNTPE) for HCHO electrooxidation. Thus, in this paper, with respect to advantages of carbon nanotubes, carbon paste and non-ionic surfactants such as TX-100 [39], we have decided to investigate the electrocatalysis and parameters affecting the electrocatalytic oxidation of HCHO. The results show that TX-100 significantly enhances the catalytic efficiency of nickel for electrooxidation of HCHO in 0.1 M NaOH solution.

2. Experimental

2.1. Chemicals

The solvent used in this work was double distilled water. Sulfuric acid (from Merck) and sodium hydroxide (from Merck) were used as the supporting electrolytes. The NiSO₄·6H₂O (from Fluka), OT monomer (from Fluka), Formaldehyde (from Merck) and Triton X-100 (from Merck) were used as received. High viscosity paraffin (density: 0.88 g cm⁻³) (from Fluka) was used as a pasting liquid for the CNTPE. Graphite powder (particle diameter: 0.10 mm, from Merck) and multi-walled

carbon nanotube (with purity >95%, outer diameter 5–20 nm, inner diameter 2–6 nm, length 1–10 μm, number of walls 3–15, apparent density 0.15–0.35 g cm⁻³ from Nanostar Tech. Co., Tehran, Iran) were used as the working electrode substrates. The as-received multi-walled carbon nanotubes were treated with concentrated acids (H₂SO₄/HNO₃: 3/1) for purification of MWCNTs.

2.2. Instrumentation

The electrochemical experiments were performed using potentiostat/galvanostat (BHP 2061-C-Electrochemical Analysis System, Behpajoo, Iran) coupled with a Pentium IV personal computer. The utilized three-electrode system was composed of Ag|AgCl|KCl (3 M) as reference electrode, a platinum wire as auxiliary electrode, unmodified carbon paste and modified carbon nanotube paste as working electrode substrate. The surface morphology of the deposits was evaluated by field emission scanning electron microscope (FE-SEM) Hitachi, S-4160. All experiments were carried out at ambient temperature.

2.3. The electrode modification

A mixture of graphite powder (0.50 g) plus multi-walled carbon nanotubes (0.24 g) were blended by hand mixing with a mortar and pestle. Using a syringe, 0.85 g paraffin was added to the mixture and mixed well until a uniformly wetted paste was obtained. The resulting paste was then inserted in the bottom of a glass tube (internal radius: 1.7 mm). The electrical connection was implemented by a copper wire lead fitted into the glass tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste out of the tube and smoothing the resulting surface on white paper until a smooth shiny surface was observed. The unmodified carbon paste electrode was prepared in the same way without adding carbon nanotubes to the mixture to be used for comparison purposes. Later modifications of the mentioned electrodes were performed in three steps:

- Electropolymerization of OT monomer at the surface of CNTPE by using potential cycling (15 cycles at potential scan rate, $v = 50 \text{ mV s}^{-1}$) between 0.0 and 1.2 V vs. Ag|AgCl|KCl (3 M) in an aqueous solution containing 2.0 mM OT, 0.5 M H₂SO₄ and 6.0 mM TX-100 for construction of POT (TX-100)/MCNTPE.
- Incorporation of Ni (II) ions (as inexpensive metallic ions) to the POT (TX-100) films by immersing the freshly POT (TX-100)/MCNTPE in a well-stirred aqueous 0.1 M NiSO₄ solution for accumulation time of 7.0 min.
- After nickel ions incorporation, the electrode was rinsed with twice distilled water. At beginning of experiment, the Ni/POT (TX-100)/MCNTPE was immersed in 0.1 M NaOH solution and the potentials were cycled between 0.1 and 0.8 V vs. Ag|AgCl|KCl (3 M) at $v = 50 \text{ mV s}^{-1}$ until a reproducible cyclic voltammogram (CV) were attained. The procedure of construction the modified electrode was schematically shown in Scheme 1.

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