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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-aminodiphenylamine) 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} cm²/s using chronoamperometry.

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1. Introduction

The development of efficient electrocatalysts for oxidation of small organic molecules (such as CH₃OH, 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 CO₂.

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/cm³) 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 AgNO₃ 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.

Fig. 1. SEM image (a) and EDX analysis (b) of Ag/P(2ADPA)/CPE.

NaOH solution at a scan rate of 20 mV/s. The anodic and cathodic transitions observed in the voltammogram are in good agreement with those reported in the literature [19–24]. From the cyclic voltammogram depicted in Fig. 2(a) and those in the literature, a schematic pathway for the transitions occurring during the potential cycling can be presented as follows:

Anodic transitions:

Cathodic transitions:

The first small anodic peak (A_I), which appeared as a shoulder at around 0.2 V, is related to the initial oxidation of Ag to $\text{Ag}(\text{OH})_2^-$ through adsorption of OH^- and desorption of the soluble species $\text{Ag}(\text{OH})_2^-$, which diffuses away from the electrode surface [25].

The second small peak (A_{II}) centered at about 0.25 V is attributed to the formation and precipitation of a monolayer of Ag_2O from the supersaturated solution of $\text{Ag}(\text{OH})_2^-$, which progressively blocked off the dissolution reaction of Ag to $\text{Ag}(\text{OH})_2^-$ [25].

The two major anodic peaks, A_{III} and A_{IV} , located at about 0.32 and 0.73 V are related to the formation of multilayers of Ag_2O and AgO , respectively, according to the following equations [19]:

Conversely, during the cathodic sweep before the appearance of the first reduction peak, another anodic peak (A_V) was observed. This could be attributed to continuous nucleation and growth of Ag_2O film as a result of the direct electro-oxidation of Ag metal [23,26]. The two cathodic peaks, C_{IV} and C_{III} , observed during the reverse scan are attributed to the electro-reduction of AgO to Ag_2O and Ag_2O to Ag metal, respectively.

The electrochemical behavior of P(2ADPA)/CPE was investigated to fully confirm the origins of the above oxidation and reduction peaks. As shown in Fig. 2(b), no observable anodic or cathodic peaks occurred for P(2ADPA)/CPE in alkaline medium. This fully proves that all redox peaks observed on Ag/P(2ADPA)/CPE are attributable to oxidation and reduction of deposited Ag nanoparticles according to the reactions described above. To clarify the effect of the poly(2-aminodiphenylamine) on the Ag deposition, the electrochemical behavior of Ag/CPE was investigated in 0.1 mol/L NaOH solution (Fig. 2(b), curve (2)). It is obvious that the peak current of Ag/CPE was much lower than that of Ag/P(2ADPA)/CPE, which confirms that the $-\text{NH}$ and $-\text{NH}_2$ functional groups of the polymer had an adsorptive effect on the Ag species.

3.2. HCHO oxidation

As we have previously reported, HCHO oxidation at P(2ADPA)/CPE in 0.1 mol/L NaOH solution is very poor, and it is not possible to obtain oxidation before the discharge of the supporting electrolyte [18]. However, Ag nanoparticles at the surface of P(2ADPA)/CPE act as a catalyst for HCHO oxidation.

Fig. 2. (a) Typical cyclic voltammogram of Ag/P(2ADPA)/CPE in 0.1 mol/L NaOH solution (scan rate of 20 mV/s); (b) Electrochemical behavior of P(2ADPA)/CPE (1) and Ag/CPE (2).

Fig. 3. Cyclic voltammograms of Ag/P(2ADPA)/CPE in 0.1 mol/L NaOH solution containing (1) 0.0, (2) 0.013, (3) 0.027, (4) 0.04, (5) 0.067, (6) 0.094, and (7) 0.17 mol/L of formaldehyde. Scan rate of 20 mV/s.

Figure 3 presents the electrochemical behavior of nano-Ag/P(2ADPA)/CPE in the absence and presence of different concentrations of HCHO at -0.5 to 0.2 V. In this potential range the predominant species was metallic Ag and, as can be seen, the modified electrode did not display any anodic or cathodic peaks in the absence of HCHO. In the presence of HCHO, the oxidation process is well evidenced by the broad peak centered at around -0.02 V and an onset potential of about -0.4 V. Increase in the concentration of HCHO caused a proportional enhancement in the anodic current, and the oxidation of HCHO continued during the cathodic half cycle, probably owing to oxidation of partially oxidized surface residues. It should be noted that in this potential range, HCHO oxidation takes place on pure metallic Ag nanoparticles, not on its oxidized species.

Table 1 shows a comparison of the nano-Ag/P(2ADPA)/CPE with other reported HCHO oxidation catalysts. The overpotential of HCHO oxidation over Ag is significantly lower than those reported in the literature for other metals, which shows that the Ag nanoparticles on the surface of P(2ADPA) had significantly higher electrocatalytic activity towards HCHO oxidation.

3.3. Chronoamperometry studies

Chronoamperometry offers more information about the electro-oxidation of HCHO at the surface of the modified electrode. Figure 4 shows typical current-time curves obtained in

Fig. 4. Chronoamperograms obtained at Ag/P(2ADPA)/CPE in the absence (1) and the presence of 0.013 (2), 0.027 (3), 0.04 (4), 0.067 (5), and 0.094 mol/L (6) formaldehyde. Electrode potential was 0.0 V vs. Ag|AgCl|KCl (3 mol/L).

the absence and presence of different concentrations of HCHO at a set working electrode potential of 0.0 V vs. Ag|AgCl|KCl (3 mol/L). As can be seen, the chronoamperograms are in good agreement with the cyclic voltammograms. No current was obtained in the absence of HCHO, while in the presence of HCHO, an increase in the concentration of HCHO was followed by an increase in the oxidation current of the electrode. These results indicate the ability of the modified electrode to oxidize HCHO in alkaline media.

Chronoamperometry was also used to estimate the diffusion coefficient of HCHO. For an electroactive material with diffusion coefficient D , the current response under diffusion control is described by the Cottrell equation [29]:

$$I = nFAD^{1/2}C\pi^{-1/2}t^{-1/2} \quad (9)$$

Plotting the current as a function of the inverse square root of time gives a linear relationship (Fig. 5), indicating a diffusion controlled process. Using the slope of this straight line, the mean value for the diffusion coefficient of HCHO was found to be $0.47 \times 10^{-6} \text{ cm}^2/\text{s}$.

3.4. Stability of electrode

To evaluate the stability of the Ag/P(2ADPA)/CPE, a chronoamperometric experiment was carried out for a large time window (1500 s) in the presence of HCHO. Figure 6 shows that after applying a potential step of 0.0 V, a rapid drop in anodic

Table 1

Comparison of the efficiency of Ag/P(2ADPA)/CPE for HCHO oxidation with those of previously reported electrodes.

Electrocatalyst	Electrolyte	Potential (V)	Reference
Pt/PAANI/MWNTs/GCE	0.5 mol/L H ₂ SO ₄	0.414	[8]
Pt-Pd/PPy-CNT	0.5 mol/L H ₂ SO ₄	0.64	[12]
Pt-Pd/CNT	0.5 mol/L H ₂ SO ₄	0.63	[27]
Pd-fMWNT	0.1 mol/L NaOH	0.71	[11]
Pd-MWNT/GCE	0.1 mol/L NaOH	0.42	[1]
Pd-CILE	0.1 mol/L NaOH	0.15	[9]
Au(111)	0.5 mol/L H ₂ SO ₄	0.65	[28]
Ru/Au(111)	0.5 mol/L H ₂ SO ₄	0.43	[28]
Ni(OH) ₂ /POT(TX-100)/MCNTPE	0.1 mol/L NaOH	0.70	[13]
Nano-Ag/P(2ADPA)/CPE	0.1 mol/L NaOH	-0.02	this work

Fig. 5. Plot of I versus $t^{-1/2}$ derived from the chronoamperogram data of Fig. 4. Formaldehyde concentration (mol/L): (1) 0.013; (2) 0.027; (3) 0.04; (4) 0.067; (5) 0.094.

Fig. 6. Long-period chronoamperogram of the Ag/P(2ADPA)/CPE electrode in 0.04 mol/L HCHO + 0.1 mol/L NaOH for period of 1500 s. The electrode potential was 0.0 V vs. Ag|AgCl|KCl (3 mol/L).

current was obtained for about the initial 100 s. This initial decrease was followed by a much slower decline such that the current after 1500 s was about 83% of that observed at 100 s.

These results obviously indicate that the prepared catalyst had good stability toward HCHO.

4. Conclusions

We have investigated Ag nanoparticles on the surface of poly (2-amino diphenylamine) modified carbon paste electrode as an efficient and low cost electrocatalyst for oxidation of HCHO. In alkaline solution, the Ag nanoparticles exhibited a number of anodic and cathodic peaks corresponding to the Ag/Ag(I) and Ag(I)/Ag(II) redox couples. HCHO oxidation commences on pure metallic Ag nanoparticles at potentials of around -0.4 V. The effect of different concentrations of HCHO on the electrocatalytic activity of this modified electrode was investigated and the proposed electrode exhibited an efficient electrocatalytic activity up to a HCHO concentration of 0.17 mol/L. Chronoamperometric experiments indicated that the prepared catalyst had good stability toward HCHO oxidation under the investigated conditions.

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Graphical Abstract

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Ag nanoparticles were incorporated on poly-2ADPA modified carbon paste electrode and their electrochemical behavior in alkaline media was investigated. The Ag nanoparticles exhibited promising electrocatalytic activity for formaldehyde oxidation.

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