

Poly (N, N-dimethylaniline)-SDS/Ag composite as an electrocatalyst for oxidation of formaldehyde

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Abstract: In this work, electropolymerization of N,N-dimethylaniline (DMA) onto a carbon paste electrode (CPE) has been done in the presence of sodium dodecyl sulfate (SDS) in an acidic solution. It was a novel matrix for the deposition of silver (Ag) particles. Then, the electrochemical oxidation of formaldehyde (CH₂O) is studied at the surface of this modified electrode in an alkaline solution. The electrochemical behavior and electrocatalytic activity of the electrode were studied using cyclic voltammetry studies. Several parameters such as the number of potential cycles for preparation of the polymeric film, and variables such as Ag⁺ concentration, accumulation time of Ag⁺ ions, and CH₂O concentration were also investigated for obtaining optimal conditions. Under these conditions, the peak current response increased linearly with CH₂O concentration over the range of 0.05–0.8 mM.

Keywords: Electropolymerization, Electrooxidation, Ag, SDS, CH₂O

Introduction

CH₂O is a small organic molecule. It is the simplest aldehyde. It is soluble in water and acetone. CH₂O can be oxidized to HCOOH and can be reduced to CH₃OH. CH₂O can be used in the production of urea-CH₂O and phenol-CH₂O resins. It can be applied as a disinfectant, fungicide, fumigant, and preservative in agriculture and medicine. It is also used to inactivate viruses and detoxify bacterial toxins in the production of some vaccines [1, 2].

On the other hand, CH₂O is important for various applications including fuel cells and electrochemical detection. Therefore, the electrochemical oxidation of CH₂O at various electrodes is of interest. Many studies have used modified electrodes for the electrochemical oxidation of CH₂O because of its slow kinetic at the bare electrodes. They act as a catalyst for oxidation of CH₂O and reduce overvoltage [3-5].

Conducting polymer (CP) matrices have been employed as catalyst support materials for the oxidation of small organic molecules. Also, incorporating metallic particles into the porous matrixes is to increase the specific area of these materials. Among the CPs, poly (Aniline)-based systems are explored much, undoubtedly because of their ease of synthesis and unique redox characteristics [6-8]. Using some metallic catalysts (Pt, Au, Pd) for the CH₂O oxidation is not economical for practical and industrial applications because of the high cost and short supply of these metals. Thus, a great deal of interest has been focused on an alternative metal (non-noble metal) while maintaining high catalytic activity and less expensive materials as anodes for CH₂O oxidation [9-11]. Silver (Ag) is cheaper and unique due to its high conductivity, catalytic activity, non-toxicity, and ease of synthesis [12]. The electrocatalytic activity of Ag particles and its application potential toward the sensitive determination of biologically relevant molecules like dopamine, H₂O₂, and glucose are well recognized in the literature [13-15].

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Previously, we combined the advantageous features of polymer modification, dispersion of metallic particles into an organic polymer and carbon paste technology by construction of modified CPEs with different polymers for electrocatalytic oxidation of some analytes [16-18]. Herein, we prepared poly (N, N-dimethylaniline) or (PDMA) films by electropolymerization at the surface of the CPE in the presence of SDS. Then, Ag^+ ions were incorporated into the polymeric matrix by immersion of the polymeric-modified electrode in an AgNO_3 solution. Properties of PDMA-SDS/Ag were investigated toward the electrocatalytic oxidation of CH_2O in an alkaline medium at ambient temperature. Our studies showed that this polymeric-modified electrode can be a good candidate for oxidation of CH_2O .

Results and Discussions

Synthesis of polymeric film

Electropolymerization was applied for the fabrication of PDMA at the surface of CPE through consecutive cyclic voltammetry. Figure 1 shows cyclic voltammograms of CPE in 0.1 M H_2SO_4 solution containing 1 mM DMA and 1 mM SDS for 10 cycles at $\nu=50 \text{ mV s}^{-1}$. Based on this figure, oxidation of monomer (DMA) occurs at about 0.82 and 1.0 V (a, b) in the first cycle. A pair of reduction peaks appear at the potentials about 0.5 and 0.3 V (c', d') related to the polymer formed, in the reverse scan. In the second cycle, also two new oxidation peaks (c, d) related to the polymer can be observed. In the higher cycles, the peak height of polymer growth increased, but the peak height related to the oxidation of monomer decreases.

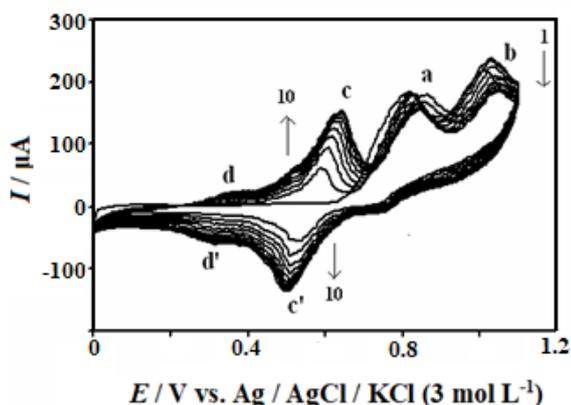


Figure 1: Cyclic voltammograms of CPE during consecutive potential cycles (10 cycles) between 0 and 1.1 V in 0.1 M H_2SO_4 solution containing 1 mM DMA and 1 mM SDS, $\nu=50 \text{ mV s}^{-1}$.

The redox behavior of the polymeric film was investigated in an electrolyte solution containing 0.1 M H_2SO_4 . As can be seen in

Figure 2, the obtained polymeric film at the surface of CPE shows a well-defined redox behavior in an acidic solution. While for the CPE, no clear peak is seen. It confirms the formation of PDMA at the surface of CPE.

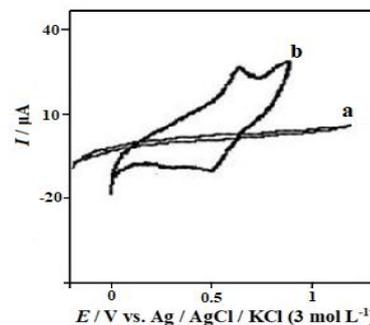


Figure 2: Cyclic voltammograms of CPE (a) and PDMA-SDS/CPE in 0.1 M H_2SO_4 solution $\nu=50 \text{ mV s}^{-1}$

In order to incorporate Ag^+ ions into the PDMA-SDS film, PDMA-SDS/CPE was placed at an open circuit in a well-stirred aqueous solution of 0.1 M NaOH containing 0.1 M AgNO_3 . Accumulation of Ag^+ ions was carried out by complex formation between ions with amine group sites in the polymer backbone, for a given period of time (20 min).

Electrochemical behavior of CH_2O at the surface of PDMA-SDS/Ag/CPE

Figure 3 shows the cyclic voltammograms of PDMA-SDS /CPE and PDMA-SDS/Ag/CPE in 0.1 M NaOH solution in the absence and presence of 1 mM CH_2O at 20 mV s^{-1} . It is clear that PDMA-SDS/CPE exhibits no activity toward the oxidation of CH_2O . The electrochemical response of a PDMA-SDS/Ag/CPE upon CH_2O addition showed an increase in the anodic peak current and a decrease in the cathodic peak current. This indicates that CH_2O is oxidized by active Ag moiety via a cyclic mediation redox process. Ag species are immobilized on the electrode surface, and the one with a higher valence oxidizes CH_2O via a chemical reaction followed by the generation of low-valence Ag.

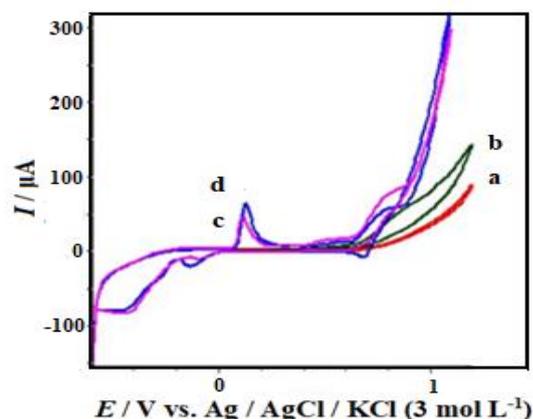


Figure 3: Cyclic voltammograms of PDMA-SDS/CPE in 0.1 M NaOH solution in the absence (a) and the presence of 1 mM CH₂O (b) at $\nu = 20 \text{ mV s}^{-1}$. (c) and (d) as same as curve a and curve b, but only for PDMA-SDS/Ag/CPE.

The observations can explain clearly the role of the PDMA-SDS in the enhancement of the electrocatalytic oxidation currents of CH₂O. Indeed, this film is a good and proper bed for the immobilization of Ag⁺ ions. It seems that the main and plausible reason for such an enhancement is the formation of a polymer film backbone at the surface of CPE that provides the facile arrival of CH₂O on silver catalytic centers.

Optimization of variables affecting electrode response in the presence of CH₂O:

In order to optimize of electrode and variables for the efficient performance of PDMA-SDS/Ag/CPE towards CH₂O oxidation, we investigated the variation of currents for oxidation in the presence and absence of 1mMCH₂O (ΔI) for different number cycles of polymerization, concentrations of Ag⁺ ions, and various times for Ag accumulation.

Effect of cycles number through preparation of polymer:

One of the main advantages of electropolymerization is the control of polymer thickness, which can be achieved by changing the number of cycles during its preparation. The influence of cycle numbers for preparation of the PDMA-SDS films on the electrocatalytic oxidation of CH₂O was investigated and the corresponding results are shown in Figure 4A. Under the constant accumulation time of Ag⁺ ions, the anodic peak current rises progressively for cycle numbers up to 10 cycles and drops afterward. This implies that the electrocatalysis

of CH₂O oxidation is sensitive to the thickness of the polymer film. Increasing the anodic peak current for cycle numbers up to 10 cycles may be due to the occupation of Ag particles in the pores of polymers with the real sizes. Decreasing in anodic peak current for CH₂O oxidation beyond 10 cycles may be due to the lessening of the real surface area of Ag particles by the excessive presence of polymers on the electrode surface.

Also, the value of ΔI increased gradually with increasing the concentration of monomer. The maximum value was about 20 mM and then leveled off, so this concentration was chosen as the optimum value (Figure 4B).

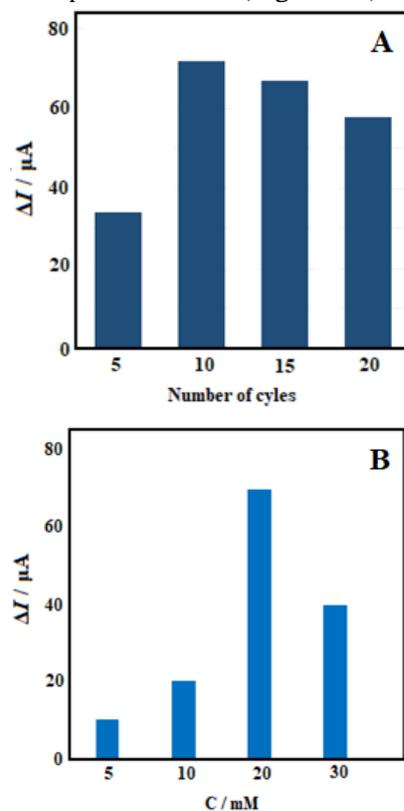


Figure 4:(A) Variation of ΔI with number of cycles and (B) Variation of ΔI with concentration of monomer

Effect of AgNO₃ solution concentration

The effect of the amount of Ag⁺ was studied by varying the concentration of AgNO₃ (0.05, 0.1, 0.5, and 1 M) in the deposition bath. It was observed that as the concentration of Ag⁺ in the bath increased, the CH₂O oxidation currents also increased up to 0.1 M; after which, it remained almost constant (Figure 5). This may be due to the fact that probably surface activesites of modified electrodes get saturated at this concentration hindering further deposition of Ag⁺.

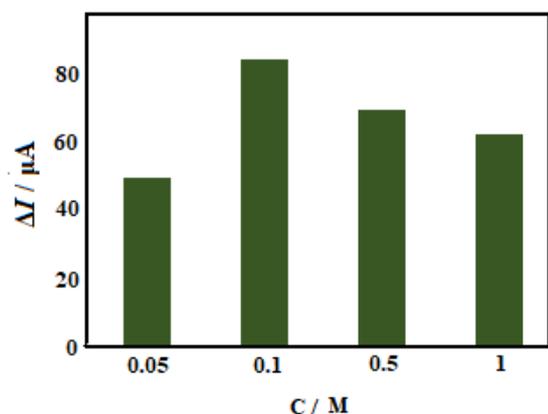


Figure 5: Variation of ΔI with concentration of Ag^+

Effect of accumulation time

The effect of the accumulation time was studied by varying the exposure times of PDMA-SDS/CPE in the deposition bath containing 0.1 M AgNO_3 . The value of ΔI increased gradually with increasing accumulation times (10, 20, and 30 min). The maximum value was got at 20 min and then leveled off, so this value was chosen as the optimal time (Figure 6).

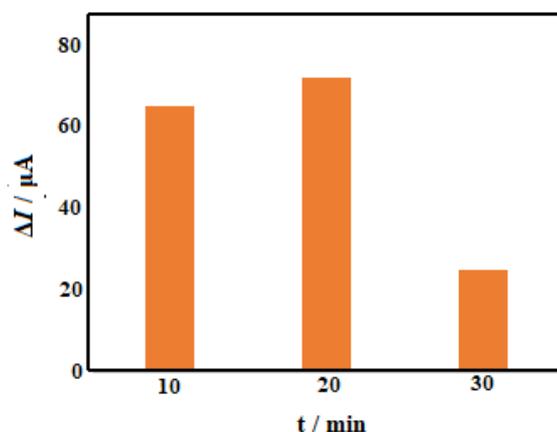


Figure 6: Variation of ΔI with concentration of Ag^+

Effect of CH_2O concentration

A set of experiments was carried out to study the effect of CH_2O concentration. Cyclic voltammetric curves at a scan rate of 20 mV s^{-1} for CH_2O concentrations in 0.1 M NaOH were recorded in Figure 7. Peak heights increase with the increase of CH_2O concentrations. The current density of the anodic peak increases significantly while the cathodic peak current decreases. This indicates an electrocatalytic oxidation of CH_2O . The characteristic shape of CV in this potential region indicates that the signal is due to the oxidation of CH_2O . The

catalytic peak current is proportional to the concentration of CH_2O in the range of 0.05 to 0.8 mM. The linear regression equation is $I (\mu\text{A}) = 2.2 C (\text{mM}) + 58 (R^2 = 0.981)$. The detection limit calculated from the calibration graph was 0.03 mM when the signal-to-noise ratio was 3.

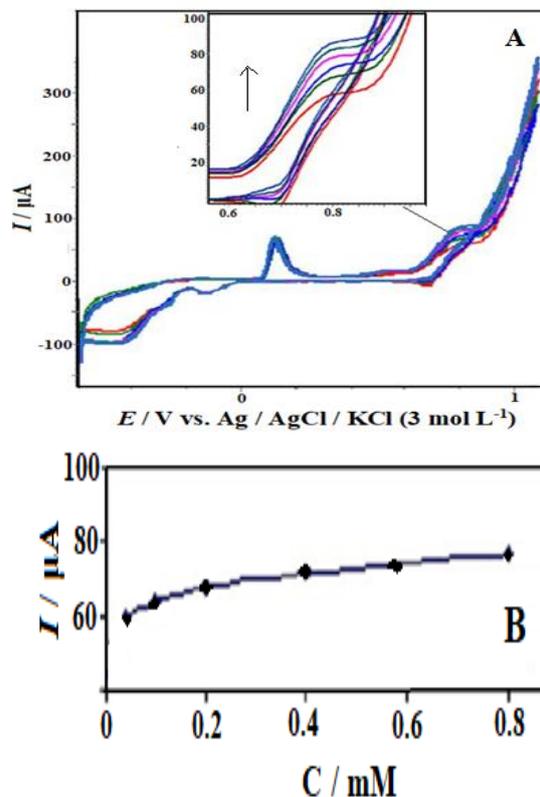


Figure 7. (A) Cyclic voltammograms of PDMA-SDS/Ag/CPE in 0.1 M NaOH containing different concentrations of CH_2O and (B) Variation of I vs. CH_2O concentration

Conclusion

In this work, Ag^+ ions loaded into a PDMA-SDS/CPE through immersion of the polymeric modified carbon paste electrode in AgNO_3 solution. This modified electrode was found to be capable of catalyzing the electrooxidation of CH_2O very efficiently. Electrocatalysis of CH_2O oxidation is sensitive to various parameters such as thickness of the polymer film, Ag^+ concentration, accumulation time and CH_2O concentration. Simplicity, low cost, and renewable surface are the advantages of this sensor for the determination of CH_2O .

Experimental

Reagents and materials

The solvent used in this work was twice distilled water. Sulfuric acid from Fluka was used as the supporting electrolyte. DMA,

NaOH, AgNO₃ and SDS from Merck were used as received. 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 = 0.10 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

Instrumentation

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP 2063-C Electrochemical Analysis System, Behpajoo, Iran) coupled with a Pentium IV personal computer. Voltammetry method was conducted using a three-electrode cell. Modified CPEs (PDMA-SDS/CPE and PDMA-SDS/Ag/CPE), a platinum electrode, and Ag|AgCl|KCl (3 M) were used as the working electrode, a counter electrode and a reference electrode, respectively.

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