

Short Communication

Electrochemical Polymerization of Methylene Blue on Glassy Carbon Electrode

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Electrochemical polymerization of methylene blue on a glassy carbon electrode was performed in Na₂SO₄ solution at pH=2.0. The electrochemical properties of the as prepared polymers modified electrodes were studied by cyclic voltammetry. The result shows that the polymers have high electroactivity and fast charge transfer ability. The morphology of the polymers was investigated by scanning electron microscopy and the structural properties of the polymers were obtained by infrared spectrum.

Keywords: Methylene blue; Electrochemical polymerization; Polymers

1. INTRODUCTION

Modifications of the electrode surface could alter the electrochemical properties of the electrode. It has been widely used in the field of electroanalysis, electrocatalysis and electrochemical energy conversion and storage [1–7]. The modification methods including adsorption, bonding and deposition[8]. Polymers modified electrodes have some advantages such as good reproducibility and homogeneity than those other modified electrodes. Recently, modified electrodes with conducting polymers have many applications in the electrochemical fields owing to their simple synthesis, good conductivity and high electroactivity[9–12]. For the preparation of conducting polymers modified electrodes, electropolymerization is widely used because this method can directly prepare stable, uniform and compact polymer film on the electrode surface[13].

Methylene blue, also named methylthioninium chloride, is a derivative of thionine. As thionine can be electropolymerized in aqueous solution to prepare conducting polymer [14–16], methylene blue

could also be electropolymerized to prepare new polymers with unique functionalities and electrochemical properties.

In this work, the electrochemical polymerization of methylene blue in Na_2SO_4 solution (pH=2.0) on a glassy carbon electrode was studied. The electrochemical properties of the polymers modified electrodes were studied by cyclic voltammetry. The morphology of the polymers was investigated by scanning electron microscopy and the structural properties of the polymers were obtained by infrared spectrum.

2. EXPERIMENTAL SECTION

2.1 Reagents and instrumentation

Methylene blue and other chemicals were purchased from Sinopharm Chemical Reagent Inc. (Beijing, China). Double-distilled water was used to prepare the solutions. 0.02 M methylene blue solution was prepared as stock solution and 0.1 M H_2SO_4 solution was used to adjust pH.

All electrochemical polymerization and other voltammetric experiments were carried out on a CS350 Electrochemical Workstation (Wuhan Corrtest Instruments CO., LTD, Wuhan, China). A traditional three-electrode system was used for the electrochemical experiments. Three-electrode system including a glassy carbon electrode (working electrode), a saturated calomel electrode (reference electrode) and a platinum wire electrode (counter electrode).

2.2 Preparation of polymers

Before to use, the glassy carbon electrode (GCE) was polished with a leather containing 0.05 μm Al_2O_3 slurry, then, the GCE was cleaned ultrasonically in ethanol and double-distilled water.

For the preparation of polymer/GCE, the GCE was immersed in a electrochemical cell containing 10 mL of 0.2 M Na_2SO_4 solution (pH=2) and 2.0 mM methylene blue. The electropolymerization was carried out using the cyclic voltammetry (CV) method at scan rate of 50 mVs^{-1} between -0.2 and $+1.2$ V for 25 cycles. Then, the polymers modified electrode was washed with water and dried for further use.

2.3 Polymer properties study

Cyclic voltammetry was used to study the electrochemical properties of the polymers modified electrode, the scanning potential range was from $+0.7$ V to -0.5 V at a scan rate of 100 mV/s . The surface morphology of the polymers was investigated by scanning electron microscopy (Nova NanoSEM 450, USA) and the structural properties of the polymers was obtained by infrared spectrum (NEXUS-670, USA).

3. RESULTS AND DISCUSSION

3.1. Electrochemical polymerization of methylene blue

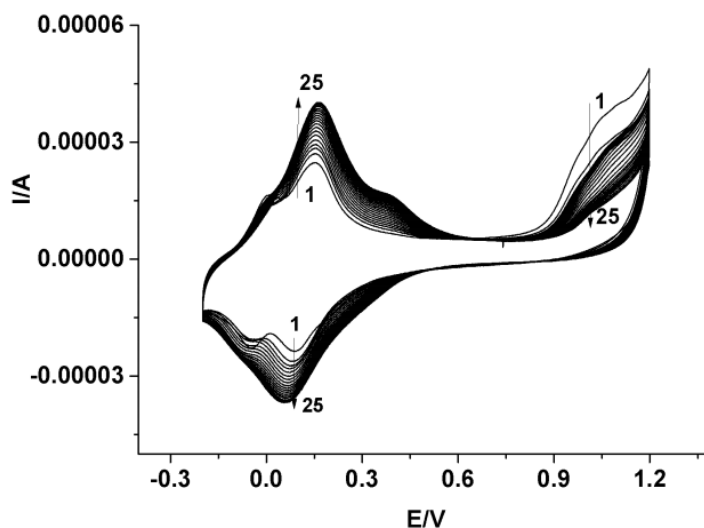


Figure 1. Cyclic voltammograms of electro-polymerization of methylene blue in a 0.2 M Na_2SO_4 solution (pH=2) and 2.0 mM methylene blue. Scan rate: 50 mVs^{-1} .

Figure 1 shows the cyclic voltammograms of electro-polymerization of methylene blue in a 0.2 M Na_2SO_4 solution (pH=2) and 2.0 mM methylene blue. From the first scan, an anodic peak (+ 0.15 V) and a cathodic peak (+0.09 V) were observed, they are belong to the redox peak of the methylene blue monomer[17]. This phenomena could be considered that initial adsorption of methylene blue monomer occurred on the GCE surface[18]. As also can be seen in the first scan, the anodic current at about +0.89 V increase quickly, and a broad anodic peak appears at 1.02 V, which is ascribed to the formation of the polymer. It was reported that cation-radical species are formed at about +0.8 V for the electropolymerization of phenoxazines or phenothiazines if the parent monomer has primary amino group as ring substituents [19]. The electropolymerization reaction started at fairly high potential values where active cation-radical species are formed[20]. With increasing the scan cycles, the anodic and cathodic peak current increased gradually, and the corresponding potentials shift to more positive and negative values. The results indicated that the formation of the polymer film on the electrode surface, and the film thickness gradually increases with increasing scan cycles. It is similar to the electro-polymerization of thionine[21] and azure B[22] which have analogous chemical structure to methylene blue.

3.2. Electrochemical properties of the polymers

Figure 2 shows the cyclic voltammogram of the polymers modified electrode in a 0.2 M Na_2SO_4 solution (pH=2). As can be seen, an anodic peak (+ 0.15 V) and a cathodic peak (+0.05V) were observed, indicating the as-prepared polymers have an electroactivity in the solution.

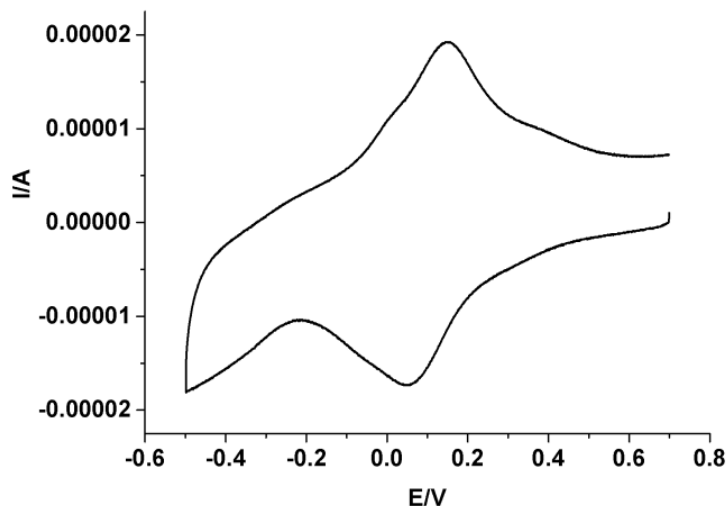


Figure 2. Cyclic voltammogram of the polymers modified electrode in a 0.2 M Na_2SO_4 solution (pH=2) . Scan rate: 100 mVs^{-1} .

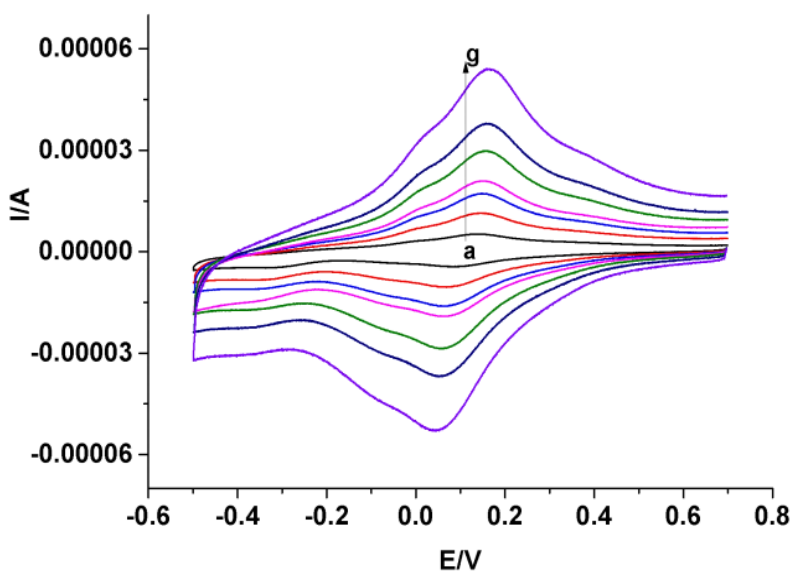


Figure 3. Cyclic voltammograms of the polymers modified electrode in a 0.2 M Na_2SO_4 solution (pH=2) with different scan rates. From a-g: 20; 50; 80; 100; 150; 200; 300 mV/s .

The effect of the scan rate on the cyclic voltammograms of the polymers modified electrode was studied. Figure 3 shows the cyclic voltammograms of the polymers modified electrode in a 0.2 M Na_2SO_4 solution (pH=2) with different scan rates. As shown in Figure 3, with increasing the scan rates, the anodic and cathodic peak current increased gradually, and the corresponding potentials shift to more positive and negative values. Moreover, even at high scan rate of 300 mV/s , well-defined redox peak still obtained, suggesting a high electroactivity and a fast charge transfer ability of the polymers.

Figure 4 shows the plots of the anodic and cathodic peak currents versus the square root of the scan rate for the polymers modified electrode in a 0.2 M Na_2SO_4 solution. As shown in figure 4, the

anodic and cathodic peak currents are linearly with $v^{1/2}$ in the scan rate range of 20 - 300 mV/s, which suggesting an diffusion controlled process for the the polymers modified electrode in a0.2 M Na_2SO_4 solution.

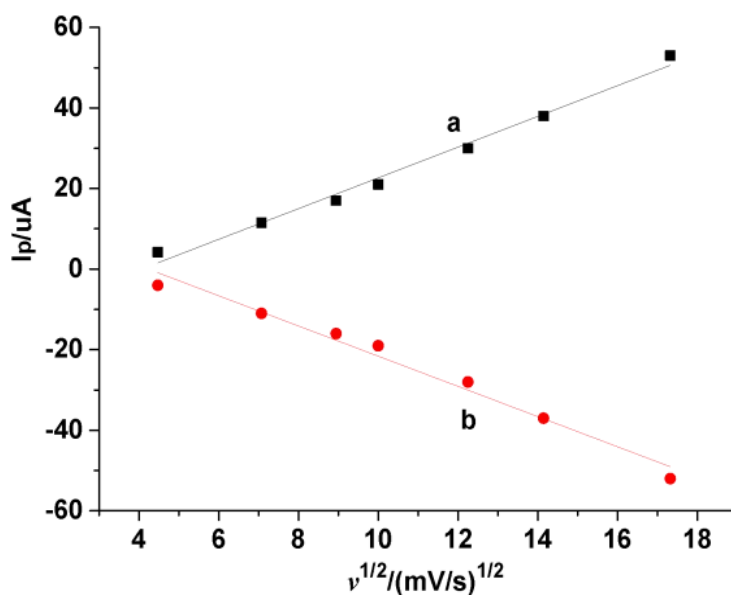
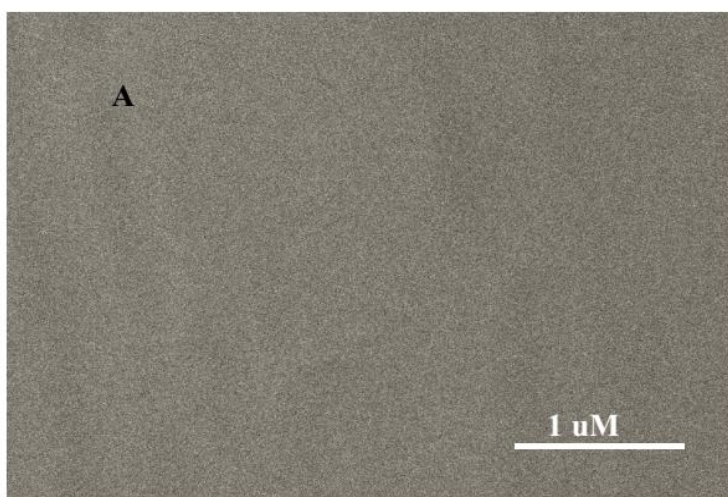


Figure 4. Plots of the anodic(a) and cathodic(b) peak currents versus the square root of the scan rates.

3.3. Surface morphology of the polymer

Scanning electron microscopy(SEM) was used to characterize the surface morphology of the prepared polymers. Figure 5 shows the surface morphology of cleaned GCE and electropolymerized polymers on GCE. As can be seen from Figure 5A, the cleaned GCE has a very smooth surface. After polymerization, a rough surface was observed, suggesting the formation of polymers. The rough surface is made up of many aggregated nanostructured particles, and the size of the particles is about 100nm, which indicates that the prepared polymer has a large surface area. Thus, it can facilitate the electron transfer of the polymer modified electrode.



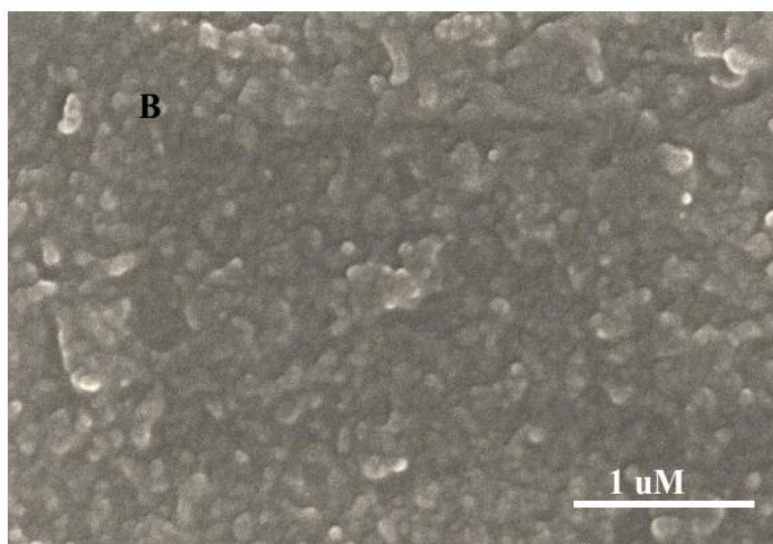


Figure 5. The surface morphology of cleaned GCE(A) and electropolymerized polymers on GCE(B).

3.4. Infrared spectrum of the polymers

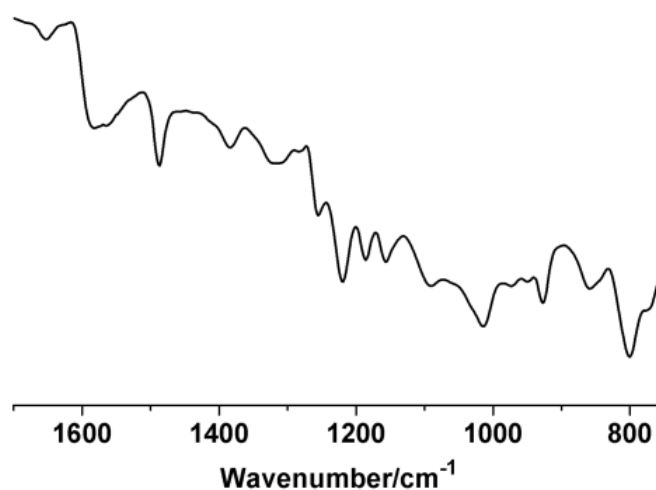


Figure 6. The infrared spectrum of the prepared polymers.

Figure 6 shows the infrared spectrum of the prepared polymers. Many peaks were found in the curve. A peak at 1654 cm^{-1} is belong to the stretching vibrations of C=O bond. Two peaks at 1582 , 1487 cm^{-1} is belong to the phenyl ring stretching vibrations and C=N stretching vibrations. A peak at 1381 cm^{-1} is belong to the symmetric bending vibrations of C-H bond. A peak at 1316 cm^{-1} is belong to the vibrations of C-N bond. Five peaks at 1258 , 1219 , 1182 , 1155 and 1014 cm^{-1} is belong to the vibrations of the heterocycle skeleton. Three peaks at 926 , 858 and 800 cm^{-1} is belong to out-of plane C-H bending vibrations. All the above peaks indicated the structures of the prepared polymer.

4. CONCLUSION

Electrochemical polymerization of methylene blue on a glassy carbon electrode was carried out in this work. The surface morphology, the structural properties and the electrochemical properties of the polymers were investigated. The high electroactivity and fast charge transfer ability of the polymer make it a potential material in the electrochemistry field.

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